

STATIC AND DYNAMIC SIMULATIONS OF PHOTOPROCESSES IN ORGANIC
PHOSPHORESCENT AND THERMALLY ACTIVATED DELAYED FLUORESCENT
MATERIALS

by

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ABSTRACT

STATIC AND DYNAMIC SIMULATIONS OF PHOTOPROCESSES IN ORGANIC PHOSPHORESCENT AND THERMALLY ACTIVATED DELAYED FLUORESCENT MATERIALS

The development of organic phosphorescent and thermally activated delayed fluorescence (TADF) emitters have emerged as potential candidates for high efficiency organic light-emitting diodes (OLEDs). The common design strategy of both organic phosphorescent and thermally activated emitters is their purely organic structures which provides an opportunity to develop environmentally friendly, low-cost devices with high device efficiencies. Investigation of working mechanisms and design strategies of all electronic devices is important to develop high efficiency technologies. In organic phosphorescent materials, device efficiencies have been increased with the radiative decay observed from the T_1 to S_0 state. On the other hand, efficiency of TADF materials is mainly controlled by the reverse intersystem crossing (RISC) between T_1 and S_1 states which leads to the harvesting of generated triplet excitons.

In this thesis, experimentally synthesized TADF and room temperature organic phosphorescence materials (oRTP) with various structural properties were modeled to investigate the photophysical processes in their working mechanisms. In the first part, a general benchmark study has been performed on a wide range of TADF emitters with various structural properties. The purpose of this general study was exploring the well performing computational protocol for further, more specific theoretical analyses. In the second and third part of this thesis, boron-based and sulfone-based TADF emitters were analyzed in detail and the role of boron and sulfone containing acceptor moieties on RISC efficiency have been explored. These studies provide a unique perspective on the underlying mechanism of photoprocesses in TADF devices.

ÖZET

ORGANİK FOSFORESANS VE TERMAL AKTİF GECİKMELİ FLORESANS MALZEMELERİN FOTOOLAYLARININ STATİK VE DİNAMİK SİMÜLASYONLARI

Organik fosforesans ve termal aktif gecikmeli floresans malzemeleri OLED teknolojisi için oldukça önemli gelişmeler olarak ortaya çıkmışlardır. Bu malzemelerin en önemli ortak özelliği, her iki grubun da tamamen organik yapıda olmasından ötürü çevre dostu teknolojilere olanak sağlamaları ve yüksek verimli cihazların elde edilmesine fırsat yaratmalarıdır.

Bütün elektronik cihazların çalışma prensiplerinin ve dizayn stratejilerinin leşfedilmesi, yüksek verimli ve düşük maliyetli ürünler yaratmak için son derece önemlidir. Organik fosforesan materyallerinde cihaz verimleri, birinci uyarılmış triplet seviyesinden temel seviyeye gerçekleşen ışık yayımlı sönümlenme ile artırılmıştır. Öte yandan TADF materyalleri ise T_1 ve S_1 seviyeleri arasında gerçekleşen geri sistemler arası geçiş sayesinde triplet ekzitonlarının yeniden S_1 seviyesine toplanması ve ışık yayımlı rahatlaması sistemiyle çalışmaktadır.

Bu tez çalışmasında, deneysel olarak sentezlenmiş ve aktiviteleri kanıtlanmış TADF ve fosforesans malzemelerin teorik olarak modellemeleri yapılmıştır. Tezin birinci çalışmasında, farklı yapılarda moleküller içeren genel bir metodoloji çalışması yapılmış ve planlanan daha ileri analizler için en iyi metodolojik protokol raporlanmıştır. İkinci ve üçüncü çalışmalarda ise bor ve sülfon temelli elektron kabul edici gruplar içeren TADF malzemeleri ele alınarak bu grupların fotofiziksel özelliklere etkileri incelenmiştir. Tezin ilk üç çalışmasında statik hesaplar yardımıyla analizler gerçekleştirilirken, üçüncü ve son çalışmada dinamik modelleme gerçekleştirilmiştir. Dinamik simulasyonlar, benzofenon türevi olan bir organik fosforesans malzeme üzerinde gerçekleştirilmiş ve bu malzemelerin fotofiziksel olayları ayrıntılı bir şekilde ele alınmıştır.

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LIST OF SYMBOLS

E_{xc}	Exchange-correlation Functional
$\hat{H}$	Hamiltonian Operator
$H(r)$	Energy Density
k^a	Local Stretching Force Constant
k_B	Boltzmann's Constant
k_{RISC}	Reverse Intersystem Crossing Rate Constant
S_n	Singlet Excited States
$T_{ext[n(r)]}$	Interaction between Electron and the External Potential
T_n	Triplet Excited States
$T_{[n(r)]}$	Kinetic Energy
$V_{xc[n(r)]}$	Non-classical Exchange-correlation Energy
Γ	Detachment Density Matrix
Λ	Attachment Density Matrix
ΔE_{ST}	Singlet-Triplet Energy Gap
Φ_S	Quantitative Topological Descriptor
χ	(R)ISC Possibility
π	Bridge
$\rho(r)$	Electron Density
Ψ	Wavefunction
ψ_i	Kohn-Sham Orbitals
θ	Dihedral Angle

LIST OF ACRONYMS/ABBREVIATIONS

A	Acceptor
B3LYP	Becke-3-parameter Lee-Yang-Parr Functional
BLYP	Becke-Lee-Yang-Parr Functional
C-PCM	Conductor-like Polarizable Continuum Model
CT	Charge Transfer
Cz	Carbazole
D	Donor
DMAC	Dimethylacridine
DFT	Density Functional Theory
DPA	Diphenylamine
DPS	Diphenylsulfone
EQE	External Quantum Efficiency
GGA	General Gradient Approximation
GTO	Gaussian Type Orbitals
HOMO	Highest Occupied Molecular Orbital
IEF-PCM	Integral Equation Formalism Polarizable Continuum Model
IQE	Internal Quantum Efficiency
ISC	Intersystem Crossing
LCAO	Linear Combination of Atomic Orbitals
LDA	Local Density Approximation
LE	Local Excited
LUMO	Lowest Unoccupied Molecular Orbital
M062X	Hybrid Meta Exchange-Correlation Functional
NTO	Natural Transition Orbital
OLEDs	Organic Light-Emitting Diodes
PBE0	Perdew–Burke–Ernzerhof Hybrid Functional
PCM	Polarizable Continuum Model
PXZ	Phenoxazine

PTZ	Phenothiazine
RISC	Reverse Intersytem Crossing
SOC	Spin-Orbit Coupling
STO	Slater Type Orbitals
TADF	Thermally Activated Delayed Fluorescence
TD-DFT	Time-Dependent Density Functional Theory

1. GENERAL INTRODUCTION

This thesis focuses on employing computational methodologies to investigate the intersystem crossing (ISC), reverse intersystem crossing (RISC) processes and the role of excited state descriptors on these photoprocesses. ISC and RISC transitions are the two main steps of Phosphorescence and Thermally Activated Delayed Fluorescence activity of Organic Light Emitting Diodes. Chapter 4 contains the results from the Density Functional Theory Functional Study of a series of TADF emitters. Chapter 5 contains the results obtained from photophysical analyses of a series of Boron Based TADF Emitters. Chapter 6 contains the ISC and RISC mechanisms of a series of Sulfone Based TADF Emitters. Finally, Chapter 7 contains the dynamic Surface Hopping (SH) Between The Excited States simulations of a model Room Temperature Phosphorescent (RTP) emitter.

1.1. Fluorescence

Generation of luminescence through excitation of molecules by ultraviolet or visible light photons are known as photoluminescence [7]. Photoluminescence can be divided into two categories which are Fluorescence and Phosphorescence. Fluorescence was first described by George Gabriel Stokes in 1852, and, it is a member of luminescence processes in which emission takes place between the states of the same multiplicity, within the 10^{-9} and 10^{-6} s range [8]. Moreover, Fluorescence, is a property of atoms or molecules to absorb light at a particular wavelength and, to emit light at a longer wavelength which is known as the Stokes shift [9]. Stokes shift is a situation arising from energy loss during the emission process [10].

Fluorescence emission which occurs between first excited singlet state and ground state is a radiative deactivation without spin changes, thus, it is a theoretically allowed transition [11, 12]. Though they have important drawbacks, first generation fluorescent materials, which are also known as organic light emitting diodes (OLEDs) offer several advantages such as flexible device structures, reduced power consumption and high brightness [13, 14]. On the other hand, despite possessing useful properties, their drawbacks such as insufficient device

efficiencies and high driving voltage limit their applications [4]. To overcome the device efficiency problem, scientist improved second generation OLED materials which are known as Phosphorescent emitters (PhOLEDs).

1.2. Phosphorescence

According to the International Union of Pure and Applied Chemistry (IUPAC) definition, Phosphorescence is a radiative transition between states of different electronic spin multiplicities [15]. Phosphorescence can be observed by light absorption, electric current and, by a chemical reaction. Light induced phosphorescence has great importance for the photo physics and photochemistry of molecules and also for the electronic structure theory in organic chemistry. Phosphorescent materials have attracted great attention due their potential applications in display, optical storage, and sensor technologies [16]. There are two critical photophysical processes in Phosphorescence, which are, 1) spin flipping from an excited singlet state to a triplet state (ISC) and, 2) radiative decay from an excited triplet state to the ground state (see Figure 1.1) [17].

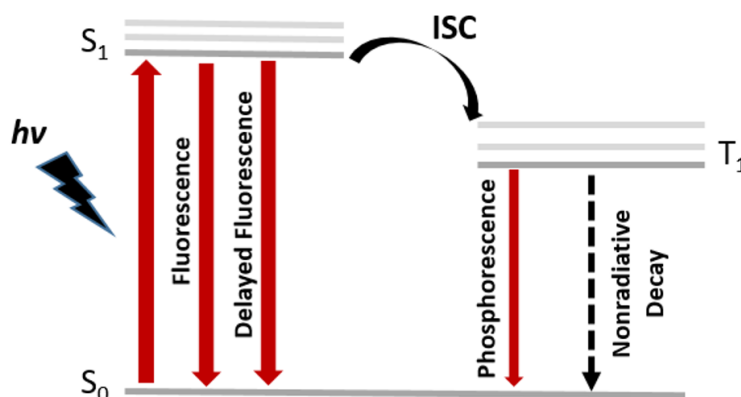


Figure 1.1. Illustration of the photophysical processes involved in Phosphorescence process.

It has been reported that luminophores with phosphorescent emission can potentially utilize 75% of generated excitons and they function to eliminate short lived autofluorescence [18]. Therefore, opening alternative emission channel through the population of triplet states became an important improvement in preventing the loss of triplet excitons via non-radiative decay processes. PhOLED is an important innovation in display technology because the cause

of low device efficiencies in OLED mechanism is the ground of phosphorescence emission. Moreover, phosphorescent materials have a wide application area such as in electronics, optics, and biological areas [16, 19–23]. On the other hand, phosphorescent luminophores still have an important drawback which is their sensitivity towards temperature and oxygen.

Phosphorescence is very sensitive to the access of oxygen, temperature and molecular aggregation. Correspondingly, these obstacles prevent their applications in medicine, photobiology and optoelectronics [24]. Until recent time, highly expensive, toxic and environmentally unfriendly materials such as metal sulfides, oxides, and organometallic luminophores with Ir (III) and Pt (II) have been used as Phosphorescent emitters [16]. These kind of structures are efficient phosphors because both spin flipping and radiative decay processes are promoted by spin - orbit coupling (SOC) which is a parameter increasing with the presence of metals and heteroatoms [25]. Moreover, since the phosphorescence activity of the luminophores is normally observed under inert conditions, their usage in high technology applications has been restricted. Correspondingly, materials with efficient room-temperature phosphorescence (RTP) which brings an important solution to the efficiency problem of phosphorescent emitters has drawn great attention [26, 27].

Room temperature phosphorescence is known as the depopulation of lowest lying triplet state (T_1) to the singlet ground state with a lifetime of more than 100 ms [28]. According to the quantum mechanics, population of triplet states occur via non-radiative intersystem crossing process (ISC) between singlet and triplet states which is a process controlled by various factors such as the energy gap between the involved singlet and triplet states, and the spin orbit coupling between the relevant states [29]. According to the heavy atom effect, the SOC is proportional to the fourth power of nuclear charge, therefore, introducing non-metal atoms is a widely used strategy to enhance spin orbit coupling via the heavy atom effect [30]. For instance, inclusion of halogen atoms (Cl, Br, I etc.) and, introduction of the carbonyl moiety of heteroatoms having a lone pair of electrons (O, S, N, P, Se, etc.) strategies have been used to enhance SOC values, thus, the rate of ISC process [30]. Therefore, most effective room temperature phosphorescence emitters with strong ISC are metal containing inorganic or organometallic compounds, which have the drawbacks of

high cost and toxicity, low processability, low flexibility and stability [31]. In contrast to these drawbacks, organic RTP materials have the advantages of good biocompatibility [32], stability and good processability [33–35]. Moreover, RTP materials have attracted tremendous attention due to their applications in the field of intelligence security [27], optical detecting [36] and biochemical imaging [37]. On the other hand, unfortunately, organic RTP can be only observed in particular organic molecules. There are two key factors for the construction of efficient organic RTP molecules which are; the inclusion of both singlet to triplet intersystem crossing and the suppression of the nonradiative quenching processes from triplet states [35].

1.3. Thermally Activated Delayed Fluorescence

Thermally Activated Delayed Fluorescence (TADF), a photophysical process which first rationalised by Perrin in 1929, is also known as E-type delayed fluorescence (DF) [38]. Later in 1941, it has been described by Lewis in fluorescein solutions. In 1961, TADF in eosin and benzyl have been reported by Parker and Hatchard [39]. The progress of TADF investigation was recently reinvigorated by Adachi and co-workers, and, it has been described as a way of harvesting non-emissive triplet excited states in Organic Light Emitting Diodes (OLEDs) [38].

TADF emitters have emerged as most promising organic emissive materials owing to their 100% internal quantum efficiencies (IQE) [40], metal-free characteristic, low production cost, and high thermal stability in their devices [1, 41, 42]. According to spin statistics, while the 25% of electronically generated excitons are singlets, a large proportion, which is 75%, are triplets [43]. Thus, the distribution of excitons to singlet and triplet states leads to decrease in fluorescence efficiency, which is occurred by the transition from first excited singlet state (S_1) to the ground state (S_0). Recently, organic materials with TADF characteristics, which can utilize triplet excitons via reverse intersystem crossing (RISC) from triplet excited states (T_n) to (S_1) have become a hot research topic in display technology (see Figure 1.2) [44].

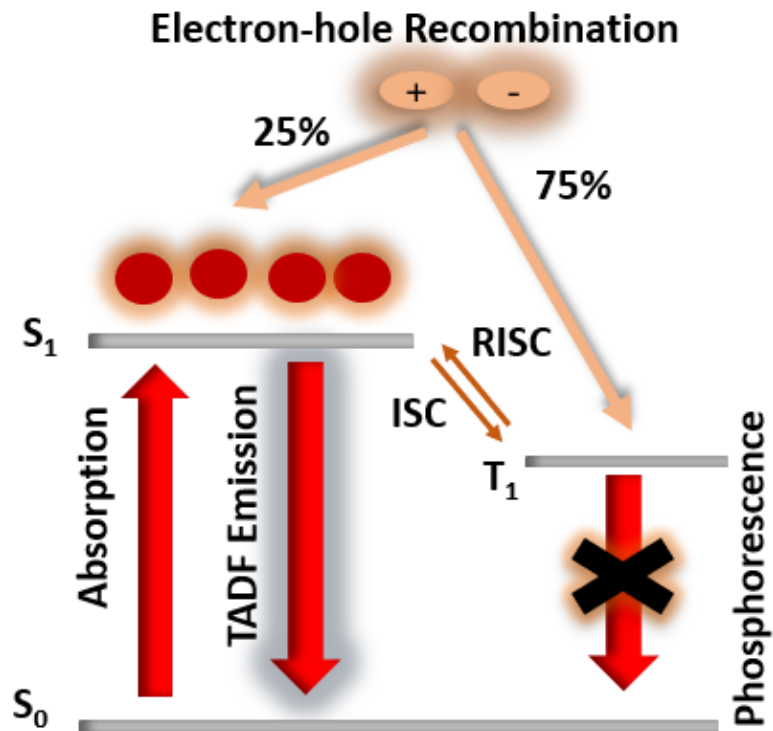


Figure 1.2. Representation of TADF emission in Jablonski diagram.

Utilization of triplet excitons is largely influenced by the competition between phosphorescence and RISC processes, which is controlled by the energy gap (ΔE_{ST}) and spin-orbit coupling between the involved states. Therefore, the key point in the design of TADF molecules is to obtain small (ΔE_{ST}) and strong SOC to promote the up-conversion of excitons in triplet states to singlet state under thermal activation. As stated in Fermi's Golden Rule,

$$k_{RISC} = \frac{2\pi}{\hbar} |V_{SOC}|^2 \times \rho_{FCWD} \quad (1.1)$$

$$\rho_{FCWD}^{CMT} = \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{(\Delta E_{ST} + \lambda)^2}{4\lambda k_B T}\right), \quad (1.2)$$

reverse intersystem crossing rate constant (k_{RISC}) which is the rate-determining factor of TADF activity depends on spin orbit coupling matrix element (V_{SOC}^2) and thermokinetic barrier (ρ), which depends on reorganization energy (λ), temperature (T), Boltzmann constant (k_B) and ΔE_{ST} [42]. To date, several efforts have been performed to achieve small energy gaps which requires efficient separation of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs). The reason behind this strategy is because the

main electronic configurations describing the states involved in RISC process correspond to the HOMO-LUMO transition [45]. To meet this strategy, TADF emitters generally adopt D-A, D-A-D, D- π -A, A-D-A, D- π -A- π -D type (D = electron donor, A = electron acceptor) structures [46, 47]. On this basis, various donors such as phenoxazine [4], dimethylacridine [48], phenothiazine, carbazole, diphenylamine, thianthrene, dihydrophenazine as well as acceptors including dimesitylboryl units [49, 50], sulphonyl groups [51], aromatic ketones [52] and many aromatic nitrogen heterocyclic units [53] have been employed to develop high efficiency TADF emitters. The connectivity between the D and A units also has a profound effect on the singlet - triplet energy gap. Twisted geometries with near orthogonality around the D-A bond are highly favorable to obtain small ΔE_{ST} values [38]. Moreover, the strength of donating and accepting abilities of D and A groups also affect the degree of HOMO and LUMO localisation, i.e. weak donors and acceptors induce less significant HOMO and LUMO localisation, which leads to larger ΔE_{ST} values and smaller TADF contribution [51].

As represented in Equation (1.1), another important parameter in RISC rate constant is the spin orbit coupling matrix element. It is generally known that heavy metals such as Ir, Pt, and halogens have large SOC due to their relativistic effects, hence favoring RISC [54]. For pure organic molecules SOC are much smaller, however they can be increased when the triplet and singlet have a different electronic (diabatic) nature. According to the El Sayed Rule, large SOC are observed between a singlet state with $^1(n, \pi^*)$ or $^1(\pi, \pi^*)$ nature and a triplet state with $^3(\pi, \pi^*)$ or $^3(n, \pi^*)$ nature. On the contrary, transition from $^1(\pi, \pi^*)$ to $^3(\pi, \pi^*)$ and from $^1(n, \pi^*)$ to $^3(n, \pi^*)$ are unfavorable [55].

1.4. Photophysics and Photochemistry

Interaction between light and matter has been discovered since the very early stages of humanity. A wide variety of concepts ranging from the nature of light to the excited - state phenomena have attracted great attention in scientific community. Nowadays, various technological developments and theoretical knowledge have boosted the understanding the photo-processes observed with the interaction of light with matter. In general terms, pho-

tophysics describes the study of photo-induced processes where the initial structure of the system is recovered after the deactivation of excited state [56]. On the other hand, photochemistry describes the characterization studies of photoproducts that occurred after the interaction between light [56].

1.4.1. Light Absorption

Photoinduced processes start with the absorption of a photon used to excite the molecule to a higher energy level. Changes observed upon light absorption, such as; rotational, vibrational, and/or electronic structure depend on the photon energy. Systems in dark are assumed to be in the ground state which describes the most stable arrangement of molecules. After the absorption of UV-Vis radiation, the system is transferred to the excited state in which the electronic structure is not the most stable one. There are two factors that determine which excited state(s) are populated. The first factor is the photon energy, which is the energy difference between the ground and excited state (ΔE) which can be stated as:

$$\Delta E = hv. \quad (1.3)$$

The second parameter comes from the Fermi's Golden Rule which relates the probability of the transition to the transition dipole moment (TDM) formed by the electric field of the molecule during light absorption [57] is given as:

$$TDM_{n \rightarrow m} = \sum_{\alpha=x,y,z} \langle \psi_m | \hat{\mu}_\alpha | \psi_n \rangle. \quad (1.4)$$

The n and m are the ground and excited states respectively, and $\hat{\mu}_\alpha$ is the dipole moment operator for the component alpha. According to the Equation (1.5), when TDM is zero, the transition is forbidden and will not be observed upon the photoexcitation. Conversely, when n to m transition has a large TDM , molecules will be excited. Absorptions observed upon photoexcitation can be represented with photon energies giving the absorption spectrum of the molecule and the area of the band is directly proportional to the probability of the transition. Oscillator strength (f) which includes the terms ΔE and TDM can be calculated by the equation:

$$f_{n \rightarrow m} = \frac{2}{3} \Delta E_{nm} |TDM_{n \rightarrow m}|^2. \quad (1.5)$$

While the excited states reported with large f are reported as the bright states, forbidden or dark states are reported with f values close to zero [58].

1.4.2. Potential Energy Landscapes

Potential energy landscape determines the structure, dynamics and thermodynamics within a particular electronic state.

1.4.3. Adiabatic Processes

After initial excitations of the molecules, the system relaxes towards the lower energy region of the excited state. This is an ultrafast process which takes place in the femtosecond or picosecond scale, and happens independently from the nature of the system under study. As the molecule reaches minimum energy point of the state, the excess energy of the electronic state can be removed by the emission of photon with the energy which is equal to the energy difference between the excited and ground state energies. If excited state is a singlet state, which has the same spin with the ground state, the emission process is called fluorescence and occurs within the 10^{-9} - 10^{-6} s range [58].

1.4.4. Non-Adiabatic Processes, Internal Conversions and Intersystem Crossings

In some specific arrangements of the nuclei, two or more electronic states may have the same energies. Points with the same energies lead to the high probability of non-adiabatic jumps opening the alternative pathways that do not yield light emission. In some cases, crossings are observed between the different spin states which lead to the population transfer as ISC [59]. The population transfer between the different spin states requires strong spin orbit coupling which is defined as the interaction between the magnetic moment of the electrons and the magnetic field caused by their motion (see Equation (1.6)). The SOC parameter can be states as:

$$\text{SoC}_{ij} = \sqrt{\sum_u |\langle T_{i,u} | \hat{H}_{SO} | S_j \rangle|^2}; \quad u = x, y, z, \quad (1.6)$$

where $\hat{H}_{SO}$ stands for the SOC Hamiltonian, S_j and T_i refer to the singlet and the triplet states, respectively. SOC is not the only parameter affecting the ISC probability, however, ΔE_{ji} , which is the energy gap between the states j and i , also plays an important role.

The ISC, which leads to the population transfer towards the triplet states opens an alternative emission pathway which is known as the Phosphorescence. Phosphorescence emission occurs as a transition from T_1 to S_0 state and is observed in the 10^{-3} - 10^2 s range [15].

2. OBJECTIVE AND SCOPE

The present thesis is devoted to the study of parameters underlying TADF and phosphorescence mechanisms, in particular, ISC and RISC processes, using adequate computational tools. The first main goal tackled in this thesis is providing an exhaustive comparison between different methodologies and proposing the most appropriate level of theory which describes the parameters effective in ISC and RISC processes. Following the methodology study, investigating the roles of various descriptors which are nature of states, singlet - triplet energy gap and the SOC on photophysical properties of TADF and phosphorescent emitters was our next purpose.

After understanding the role of methodology and descriptors, the next purpose was assessing the relationship between molecular structure and photophysical properties for a range of boron-based and sulfone-based TADF molecules, to understand the behavior of boron and sulfone in different acceptor moieties.

Following the static calculations, simulating the surface hopping mechanism, in other words, the ISC, by dynamic simulations and understanding the kinetic models together with competitive photoprocesses in organic luminescent materials became our last scope to model the complete picture of photoprocesses in these emitters.

3. THEORETICAL BACKGROUND

3.1. Quantum Chemistry. A Historical Perspective

3.1.1. The Birth of Quantum Chemistry

Quantum chemistry, which is defined as the application of quantum mechanics to the study of chemical processes, has been associated by the Austrian physicist Erwin Schrödinger's publication in December, 1926 with the time-dependent Schrödinger equation [60] as follows:

$$i\hbar \frac{\partial}{\partial t} \Psi(r, R, t) = \hat{H}_t \Psi(r, R, t), \quad (3.1)$$

where i is the imaginary unit, $\hbar$ stands for the Planck constant divided by 2π is the time-dependent Hamiltonian operator and $\Psi(r, R, t)$ refers to the wave function which depends on the nuclear (R) and electronic (r) coordinates and time t . According to the Equation (3.1), stationary wave $\Psi(r, R)$ that do not depend on time can be determined and called as time-independent Schrödinger equation [61] and given as:

$$\hat{H}_s \Psi(r, R) = E \Psi(r, R), \quad (3.2)$$

where $\hat{H}_s$ is the time-independent (static) Hamiltonian and E refers to the energy of the system described by $\Psi(r, R)$. $\hat{H}_s$ contains all electron-electron, nucleus-nucleus, and electron-nucleus interactions present in the system. In non-relativistic quantum chemistry, $\hat{H}_s$ has the form shown as:

$$\begin{aligned} \hat{H}_s = & - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \\ & + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}, \end{aligned} \quad (3.3)$$

where i and j are the coordinates of two electrons, N and M state for the total number of electrons and nuclei, respectively, A and B refer to the coordinates of two nuclei, ∇^2 is the Laplacian operator, Z_A is the atomic number of a nucleus A , Z_B is the atomic number of a nucleus B , r_{ij} states for the distance between the i th and j th electrons, r_{iA} refers to the distance between the i th electron and the A th nucleus, and R_{AB} stands for the distance between the A th and B th nuclei. Thus, the five terms of Equation (3.3) corresponds to: i) kinetic energy of the electrons, ii) kinetic energy of the nuclei, iii) Coulomb attraction between the electrons and

the nuclei, iv) electronic repulsion, and v) nuclear repulsion.

3.1.2. Quantum Chemistry As A Research Tool In Chemistry

For medium- and large-size molecular systems, solving the eigenvalue problem in Equation (3.2) would be impossible and, this impossibility after the discovery of the Schrödinger equation, became the origin of various methodologies. In 1927, Max Born and J. Robert Oppenheimer proposed Born-Oppenheimer approximation, which states that the movement of electrons can be treated independently from the nuclei, because the electrons are much lighter than the nuclei, breaking down the wave function Ψ into its nuclear and electronic parts [62] as:

$$\Psi(r, R) = \psi_{nuclear}(R) \chi \psi_{elec}(r). \quad (3.4)$$

With the help of approximation in Equation (3.4), the second term of Equation (3.3) equals to zero, and the fifth term becomes a constant. Consequently, $\psi_{elec}(R)$ describes the electrons moving in the field of the motionless nuclei. In this way, the electronic problem can be solved as:

$$\hat{H}_{elec} \psi_{elec} = E_{elec} \psi_{elec}, \quad (3.5)$$

where $\hat{H}_{elec}$ states for the electronic Hamiltonian operator.

Due to the multivariable dependencies of the electron repulsion term $1/r_{ij}$, following the approximations stated until this part is still insufficient to solve the many-electron equations. For the purpose of simplifying the resolution, Douglas R. Hartree and Vladimir Fock proposed Hartree-Fock (HF) method in 1930 in which the electronic repulsion term of the Hamiltonian is substituted by an average potential caused by the rest of the electrons. Within the HF approximation, the multi-electron operator $\hat{H}_{elec}$ can be separated in effective one-electron operators f_i or just Fock operators (see Equation (3.6)) [63] and represented as:

$$f(i) = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + v^{HF}(i). \quad (3.6)$$

In Equation (3.6), $v^{HF}(i)$ represents the average potential seen by the i^{th} electron caused by the other electrons. In this way, the complex many-electron problem is converted into simpler one-electron problems in which the electron-electron interactions are treated in an average way as [63]:

$$f(i)\chi(x_i) = E\chi(x_i), \quad (3.7)$$

being χ the spin-orbitals which describe a given electron i with coordinates x_i , including both spatial and spin coordinates. The Equation (3.7) has to be solved through a procedure called self-consistent field (SCF) procedure which was formulated at the beginning of the 1930s decade. However, until some empirical values were used in the calculations, its application to even small molecules was impossible and it could be used only for light atoms like helium. In SCF strategy, some wave functions have been constructed to the Fock operator and then it is iterated by using the output functions as new input functions or with more sophisticated methods until the input and output functions are the same.

Despite the fact that HF method is a fast procedure, its well known inaccuracies in the study of several molecular properties such as molecular geometries, excited states and ionization energies boosted the development of post-HF methods, such as the density functional theory (DFT) and many others which have been described in Section 3.2.

3.2. Molecular Quantum Mechanics

It is known that electrons as charged particles cause Coulomb repulsion and the motion of one electron influences the motion of the others. Description of this dynamic correlation which is arised by the instantenous mutual repulsion of electrons is the stem of HF theory. Other methods such as Configuration Interaction (CI), Møller-Plesset Perturbation Theory and Coupled Cluster are also based on the wave function calculation, however, they are computationally very expensive. On the other hand, Density functional methods with a lower computational cost can offer accurate results [64].

3.3. Semi-Empirical Methods

In order to simplify the Hartree–Fock (HF) method, Semi-empirical (SE) methods use parameters derived from experimental data and theoretical approximations. The distinct approximations of semi-empirical methods to the Hamiltonian are neglecting many integrals, especially two electron integrals, in order to speed up the calculations and reduce the com-

putational cost. For these purposes, semi-empirical methods consider only the valence shell electrons and use a minimal basis. Various semi-empirical methods have been parametrized with different approximations and the most commonly used one is Zero Differential Overlap approximation (ZDO) which can also be grouped to one and two electron integrals.

Zero Differential Overlap approximation neglects the overlap between different basis functions centered on different atoms. While the complete neglect of differential overlap (CNDO) [65] uses zero-differential overlap (ZDO) for the two-electron integrals, intermediate neglect of differential overlap model (INDO) [66] covers the one-center two electron integrals which are over the orbitals centred on the same atom. There are many modern semi-empirical methods and the mostly used methods are the neglect of diatomic differential overlap model (NDDO) [65] which includes the MNDO, AM1, PM3, PM6, and PM7 methods.

Modified neglect of diatomic overlap (MNDO) method, introduced by Thiel and Dewar, overestimates the repulsions between atoms which are separated by their van der Waals distances [67]. In Austin Model 1 (AM1) [68], hydrogen bondings are treated better than MNDO, but they are still misrepresented. On the other hand, equations and formalism of parametrized model number 3 (PM3) [69] are same with the AM1 method, however, PM3 uses different number of parameters for each element. Improved models of PM3 are the parametrized model 6 (PM6) and parametrized model 7 (PM7). While core-core interactions and new parameters for transition metal systems are included in PM6, PM7 adds explicit terms to describe non-covalent interactions (NCIs) [70].

3.4. Density Functional Theory

In 1964, Hohenburg-Kohn proposed that the density of a system determines all its ground-state properties which is the stem of Density Functional Theory [71]. Density Functional Theory is one of the most popularly used method for quantum mechanical calculations of many-body systems. Opposite to Hartree-Fock Theory which deals with the wave function, DFT is based on the electron density.

3.4.1. Electron Density

Solution of the time-independent Schrödinger equation is not the only strategy to solve the many-electron problem. As an alternative approach, electron density $\rho(r)$ can be used as a descriptor of the electronic structure of the system. Since the $\rho(r)$ is a measurable parameter, employing it to a given system appear physically more intuitive than a wave function based approach. Electron density is defined as [71]:

$$\rho(r) = N \int \dots \int |\varphi(r_1, r_2, \dots, r_N)|^2 ds_1 dr_2 \dots dr_N, \quad (3.8)$$

where $\rho(r)$ stands for the probability to find any of the N electrons within the volume element dr_N with arbitrary spin while the $N - 1$ electrons have arbitrary positions and a spin represented by φ .

3.4.2. The Hohenberg and Kohn Theorems

The first Hohenberg-Kohn (HK) theorem states that every observable of a system can be calculated from the ground-state $\rho(r)$, thus, the observables can be written as a functional of the ground-state $\rho(r)$. According to the HK theorem which can be expressed as:

$$E_T[\rho(r)] = F[\rho(r)] + V_{\text{ext}}[\rho(r)], \quad (3.9)$$

the total energy of the system can be determined by the sum of the universal functional $F[\rho(r)]$ and an external potential $V_{\text{ext}}[\rho(r)]$ [72]:

$$F[\rho] = T_0[\rho] + J[\rho] + T_u[\rho] + V_q[\rho]. \quad (3.10)$$

As represented in Equation (3.9), functional depends on the $\rho(r)$ and since the ground state energy is determined by the electron density, now it is important to find the $\rho(r)$ that minimizes the energy.

3.4.3. The Kohn Sham Procedure

In 1965, Kohn and Sham developed an orbital-based scheme in which the total kinetic energy T is separated into the kinetic energy of non-interacting N -electrons (T_0), with the same density that the real interacting system, and a part which specifically accounts for the interactions (T_u). Additionally, the electron-electron repulsion is divided into the a non-

classical contribution (V_q) and classical Coulomb interaction (J). Consequently, the $F[\rho(r)]$ term of the Kohn-Sham approximation, can be expressed as [73]:

$$F[\rho] = T_0[\rho] + J[\rho] + T_u[\rho] + V_q[\rho]. \quad (3.11)$$

The unknown part of the kinetic energy (T_u) and the non-classical electron-electron interaction energy given by (V_q) can be combined to form the exchange-correlation functional $E_{xc}[\rho]$. Accordingly, we can represent the total energy as:

$$E_T[\rho] = T_0[\rho] + J[\rho] + V_{\text{ext}}[\rho] + E_{XC}[\rho]. \quad (3.12)$$

While the first three terms can be calculated explicitly, the exchange-correlation term $E_{xc}[\rho]$ includes all unknown contributions to the energy arising from the non-classical effect of self-interaction correction, exchange and correlation.

Over the last decades, various approximations have been reported, however, various functionals arised not only from the methods used for the exchange energy, but also from the precentage of HF exchange.

3.5. Density Functional Theory Functionals

According to the Local Density Approximation (LDA), electron density is uniform in everywhere and can be stated as:

$$E_{XC}^{LDA}[\rho(r)] = E_X^{LDA}[\rho(r)] + E_C^{LDA}[\rho(r)] = \int \rho(r) \epsilon_X^{LDA} \rho(r) dr + \int \rho(r) \epsilon_C^{LDA} \rho(r) dr, \quad (3.13)$$

$$E_X^{LDA}[\rho(r)] = C_X \int \rho(r)^{4/3} dr, \quad (3.14)$$

and ϵ_X^{LDA} referring the exchange energy per electron as:

$$\epsilon_X^{LDA} = C_X \rho^{1/3}, \quad (3.15)$$

with C_X a constant, which is equal to 0.7386 [74, 75]. On the other hand, Local Spin Density Approximation (LSDA) accounts for spin dependence into the methods and allows the presence of different spins for different orbitals of the electrons in the spin polarized systems. $E_{XC}^{LSDA}[\rho(r)]$ is expressed as [76]:

$$E_{XC}^{LSDA}[\rho(r)] = E_{XC}^{LSDA}[\rho_\alpha(r), \rho_\beta(r)] = E_X^{LSDA}[\rho_\alpha(r), \rho_\beta(r)] + E_C^{LSDA}[\rho_\alpha(r), \rho_\beta(r)], \quad (3.16)$$

where α and β refers to spin up and down densities, respectively. $E_X^{LSDA}[\rho_\alpha(r), \rho_\beta(r)]$ is defined as:

$$E_X^{LSDA}[\rho_\alpha(r), \rho_\beta(r)] = -2^{1/3} C_X \int [\rho_\alpha^{4/3}(r) + \rho_\beta^{4/3}(r)] dr, \quad (3.17)$$

and exchange energy per electron ϵ_X^{LSDA} is described as:

$$\epsilon_X^{LSDA} = -2^{1/3} C_X [\rho_\alpha^{1/3} + \rho_\beta^{1/3}]. \quad (3.18)$$

The second generation of density functionals is the generalized gradient approximation (GGA). Differently from LDA methods, GGA assumes that the electron density is not homogeneous and includes both the density and gradients ($\Delta\rho(r)$) for the variation of ρ with position which can be expressed as:

$$E_{XC}^{GGA}[\rho_\alpha(r), \rho_\beta(r)] = \int f(\rho_\alpha(r), \rho_\beta(r), \Delta\rho_\alpha, \Delta\rho_\beta), \quad (3.19)$$

where f is a function of ρ_α and ρ_β , and their gradients. As stated in Equation (3.19), E_{XC}^{GGA} is divided into exchange and correlation parts and each part is modelled independently.

While Meta-GGA (M-GGA) version of the GGA depends on the kinetic energy density or higher order density gradients, Hybrid density functional (H-GGA) methods join non-local Hartree-Fock exchange (HFX) with local/semi-local conventional GGA exchange in the E_{XC} term obtained from KS orbitals. E_{XC} term can be expressed as:

$$E_{XC}[\rho(r)] = a_0 E_X^{HFX}[\{\psi_i\}] + (1 - a_0) E_X^{DFT}[\rho(r)] + E_C^{DFT}[\rho(r)], \quad (3.20)$$

where a_0 coefficient refers to the fraction of HFX.

Another GGA version is the Hybrid-meta GGA (HM-GGA) which depends on the HF exchange, the electron density and its gradient, and the kinetic energy density.

Lastly, the functionals used in this thesis are Hybrid M06-2X, Becke Three-Parameter Hybrid functional B3LYP, Becke One-Parameter Hybrid functional BLYP, PBE correlation including PBE1PBE and, Long-Range Corrected CAM-B3LYP and ω B97XD functionals.

3.5.1. The M06-2X Functional

The M06-2X hybrid functional belong to a series of approximations to the $E_{xc}[\rho]$ term developed by Truhlar and coworkers. In M06-2X method, the total exchange-correlation energy (E_{XC}^{M06-2X}) is computed through contributions of both DFT (E_X^{M06-2X}) and HF (E_X^{HF}) exchange energies [77] as:

$$E_{XC}^{M06-2X} = \frac{X}{100} E_X^{HF} + \left(1 - \frac{X}{100}\right) E_X^{M06-2X} + E_C^{M06-2X}. \quad (3.21)$$

In Equation (3.21), X equals to 54 and determines the percentage of Hartree Fock exchange. The M06-2X functional is based on the mGGA, in which several corrections in the calculation of the gradients of the electron density are introduced to palliate discontinuities of the density faced for many systems [78]. Only three functionals, namely B3LYP and PBE0, which are commonly used in TADF literature and M06-2X, which has been proved that it best represent the photophysical properties reported in this thesis, shall be briefly described in the following.

3.5.2. The B3LYP Functional

B3LYP scheme is one of the most commonly used DFT functionals in which $E_{xc}[\rho]$ is approximated as:

$$E_{XC}^{B3LYP} = (1 - a)E_X^{LSDA} + aE_{XC}^{HF} + bE_X^{B88} + cE_C^{LYP} + (1 - c)E_C^{VWN}, \quad (3.22)$$

where the X , C and XC subscripts refers to the exchange, correlation, and exchange-correlation, respectively, and the *LSDA* refers to the local spin-density approximation method [72]. The *B88* states for the Becke exchange functional [79], *LYP* is the gradient-corrected correlation developed by Lee, Yang and Parr, and *VWN* stands for the exact exchange energy of an uniform electron gas defined by Vosko, Wilk, and Nusair in the framework of the LSDA approximation [76]. The a , b , and c are the parameters fitted to optimally reproduce the electron affinities (EAs), some total energies of a collection of small systems, atomization and ionization energies [72].

3.5.3. The PBE0 Functional

Perdew, Burke and Ernzerhof have introduced a GGA functional referred to as PBE in which all the parameters are fundamental constants [80]. They obtained this using the Perdew–Wang (PW) correlation functional, and a new exchange contribution which can be expressed as:

$$E_x^{PBE} = \frac{bx^2}{1 + ax^2} \quad (3.23)$$

where $b=50.00336$, $a=50.00449$ and x and ρ are the electron density and its gradient respectively. PBE0 is the parameter free density functional approach using the PBE functional and HF exchange with predefined coefficients.

3.5.4. The Advantages and Drawbacks of DFT-Based Methods

The low computational cost of DFT-based methods is their most important advantage. Therefore, calculation of geometries, energies, frequencies and other molecular properties of small and medium-sized systems can be done in acceptable times. However, there are important drawbacks which arise from the parameter adjustment performed in the design of the functional. In other words, a DFT functional can provide good results for a specific type of systems whereas can fail in the description of other type systems [81]. Thus, it is always necessary to calibrate the DFT data toward accurate ab initio methods or, alternatively, experimental recordings.

3.6. Basis Sets

The mathematical expression used to define the orbitals of a system and which is based on linear combination of atomic orbitals (LCAO-MO) approximation is known as the Basis Set and can be expressed as [82]:

$$\psi_i = \sum_{\mu=1}^n \phi_{\mu} c_{\mu i}, \quad (3.24)$$

where ψ is the i^{th} molecular orbital, ϕ_{μ} denotes the μ^{th} atomic orbital, $c_{\mu i}$ molecular orbital coefficients, and n is the number of atomic orbitals. There are two types of basis sets, namely Slater-Type Orbitals (STO's) [83], Gaussian-Type Orbitals (GTO's) [84]. STO's have exponential dependence to the distance between the nuclei and electrons change. These are more efficient and accurate at representing molecular orbitals. On the other hands, GTO's have exponential dependence to the quadratic distance between nuclei and electrons. Though GTO's provide a worse description of the molecular orbitals, they present a better computational evaluation of the two-electron integrals and are widely used in the calculations of electronic structures.

Several different types of basis sets have been developed over the years, such as, minimal, double zeta (DZ), triple zeta (TZ), quadruple-zeta (QZ), and so on. The concept of minimal basis set suggests that only the minimum number of basis functions per atom is used in the description of the occupied atomic orbitals. In DZ basis set, the number of basis functions are duplicated and this can be used for the first row elements. From a chemical standpoint, it is known that the most important electrons are valence electrons, therefore, DZ basis set has been simplified to duplicate only the valence basis functions valence double zeta (VDZ) basis set have been developed. While doubling the number of basis functions, same procedure leads to the TZ and valence triple zeta (VTZ) basis sets. In some cases, the increase in the number of s and p functions for each atom is not enough to well describe the properties within the study, and functions with higher angular momentum, such as p functions for hydrogen and d functions for heavier atoms, can be required. In such cases, these functions are called polarization functions, and they give rise to the DZP and TZP basis sets.

Over the years, Pople et. al introduced split-valence basis sets to split and treat valence and core orbitals separately. These basis sets use only one basis function for each core atomic orbital, and a larger basis for the valence atomic orbitals, thus decrease the computational cost. Most commonly used Pople basis sets are 3-21G, 6-21G, 6-31G(d), 6-311G(d,p) and 6-31++G(d,p). In diffuse function, a plus sign (+) refers to the addition of diffuse functions to heavy atoms and, two plus signs (++) show the addition of diffuse function to light atoms [85].

3.7. Solvation Models

Solvation models account for solvent environments of molecular systems and mimic experimental environments to obtain more accurate results. The solvent models can be categorized into two groups which are explicit and implicit solvent models. Explicit models are more realistic than the implicit models, however, they are computationally more expensive. While all solvent molecules are included in the explicit solvent model, and free energy of solvation is calculated by considering interactions between solvent-solute, implicit solvent model, which is also known as continuum solvation model presents the solvent as a continuous medium and provides uniform polarizability by employing static dielectric constant. The

equation represented as:

$$\Delta G_{solvation} = \Delta G_{cavity} + \Delta G_{dispersion} + \Delta G_{electrostatic} + \Delta G_{repulsion}, \quad (3.25)$$

shows the relation for the calculation of total free energy of solvation, where ΔG_{cavity} refers to the free energy required to form the solute cavity, $\Delta G_{dispersion}$ refers to the interactions between solute and solvent, $\Delta G_{electrostatic}$ is the electrostatic energy and $\Delta G_{repulsion}$ is the energy caused by the exchange solute-solvent interactions.

Various implicit solvation models have been developed, such as conductor-like polarizable continuum model (CPCM) [86], integral equation formalism polarizable continuum model (IEF-PCM) [87], solute model based on density (SMD) [88], and COSMO [89], etc. Tomassi and coworkers developed one of the commonly used implicit solvent model which is Polarizable Continuum Model (PCM) [90, 91].

PCM defines the cavity surface through spheres defined by Van der Waals (VDW) radii centered at each atom. On the other hand, Conductor-like PCM (CPCM) treats the conductor-like screening solvation boundary condition. Cancès and Menucci developed another commonly used continuum solvation model named as IEFPCM. IEFPCM uses a set of overlapping spheres to model the solute, with radii of the spheres similar to solute atoms [87].

3.8. Wigner Distribution Function

In 1932, Eugene Wigner introduced Wigner quasi-probability distribution or Wigner-Ville distribution which is a quantum mechanical approach for relating wave function to probability distribution in phase space [92]. Wigner distribution function has a wide range of applications, including amplitude and phase retrieval, signal processing, optical devices, and phase space coupling coefficient computation. There are two ways of generating Wigner distribution, which are from the coordinate-space or momentum-space wave functions. The Wigner transform using the coordinate-space function can be stated as:

$$W(x, p) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \psi^* \left(x + \frac{s}{2} \right) \psi \left(x - \frac{s}{2} \right) e^{ips} ds, \quad (3.26)$$

where ψ denotes the wave function, p represents momentum, and x indicates location. The

term $\psi^* \left(x + \frac{s}{2}\right)$ can be stated as:

$$\psi^* \left(x + \frac{s}{2}\right) = \left\langle \psi \left| x + \frac{s}{2} \right. \right\rangle, \quad (3.27)$$

and the term $\psi \left(x - \frac{s}{2}\right)$ in Equation (3.26) can be expressed as:

$$\psi \left(x - \frac{s}{2}\right) = \left\langle x - \frac{s}{2} \left| \psi \right. \right\rangle. \quad (3.28)$$

3.9. Surface Hopping Dynamics

Surface hopping dynamics is an extension of classical molecular dynamics (MD) to excited states. The term “hops” comes from the events where a trajectory switches from one potential energy surface (PES) to another [93]. In PES of a particular state, the nuclei are treated classically and move according to Newton’s equations and an electronic wavefunction is propagated using the time-dependent electronic Schrödinger equation, which incorporates non-adiabatic couplings (NACs) between the electronic states and these NACs determines the time that a hop will occur. NAC is not the only coupling that affects the hops, but there are two more types of couplings which are spin-orbit couplings (SOCs) and laser-dipole couplings (LDCs).

In this thesis, ISC, IC and RISC processes are nonadiabatic electronic transitions and there are more than one PESs which should be considered. In 2011, Prof. Dr. Letizia Gonzalez and her research group developed a software package known as Surface-hopping-in-adiabatic-representation including-arbitrary-couplings (SHARC) which is the software used in the dynamic ISC and IC simulations of this thesis. Compared to other methodologies, surface hopping provides a number of advantages such as being a user friendly method because the classical mechanics ansatz for the nuclear motion makes the method conceptually simple and easy to implement. Additionally, the trajectories need only local information such as energies and couplings on the electronic states and each trajectory is independent from the rest of the ensemble.

The widespread use of SH method arises from its applicability to large systems because all degrees of freedom can be included in the simulation. In MD, the nuclear motion is approximated with classical mechanics. Therefore, the nuclear equation of motion is given by

Newton's second law [94]:

$$m_A \frac{d^2}{dt^2} \mathbf{R}_A(t) = -\nabla_A E_\beta(\mathbf{R}(t)), \quad (3.29)$$

where R_A is the nuclear position of atom A, m_A is the mass of atom A and $-\nabla_A E_\beta(R(t))$ is the gradient of the energy of the electronic state β with respect to the position of atom. In the standard formulation of MD, Integration from time to time Δ_t $t + \Delta_t$ can be done with the velocity-Verlet algorithm expressed by the following equations [95]:

$$\mathbf{a}_A(t) = -\frac{1}{m_A} \nabla_A E_\beta(\mathbf{R}(t)), \quad (3.30)$$

$$\mathbf{R}_A(t + \Delta t) = \mathbf{R}_A(t) + \mathbf{v}_A(t) \Delta t + \frac{1}{2} \mathbf{a}_A(t) \Delta t^2, \quad (3.31)$$

$$\mathbf{a}_A(t + \Delta t) = -\frac{1}{m_A} \nabla_A E_\beta(\mathbf{R}(t + \Delta t)), \quad (3.32)$$

$$\mathbf{v}_A(t + \Delta t) = \mathbf{v}_A(t) + \frac{1}{2} [\mathbf{a}_A(t) + \mathbf{a}_A(t + \Delta t)] \Delta t, \quad (3.33)$$

a_A being the acceleration of atom A and v_A being the velocity of atom A. To include the nonadiabatic effects for surface hopping scheme, a prescription for the choice of the correct active state β at each time step is required and the choice of correct active state is based on the evolution of an electronic wavefunction along the nuclear trajectory.

4. COMPUTATIONAL DESCRIPTOR ANALYSIS ON EXCITED STATE BEHAVIORS OF A SERIES OF TADF AND NON-TADF COMPOUNDS

4.1. Overview

The thermally activated delayed fluorescence (TADF) behaviours of seventeen organic TADF emitters and two non-TADF chromophores bearing various donor and acceptor moieties were investigated, focusing on their torsion angles, singlet–triplet gap (ΔE_{ST}), spin orbit couplings (SOC) and topological Φ_S index. Electronic structure calculations were performed in the framework of the Tamm–Dancoff approximation (TDA) allowing the possible reverse intersystem crossing (RISC) pathways to be characterized. The electronic density reorganization of the excited states was checked also with respect to the different exchange–correlation functional and absorption spectra were obtained by considering vibrational and dynamical effects through Wigner sampling of the ground state equilibrium regions. Examining all the parameters obtained in our computational study, we rationalized the influence of electron-donating and electron-accepting groups and the effects of geometrical factors, especially torsion angles, on a wide class of diverse compounds ultimately providing an easy and computationally effective protocol to assess TADF efficiencies.

4.2. Introduction

Since the original proposal of organic light-emitting diodes (OLEDs) by Tang and Van Slyke in 1987 [96], significant progresses have been achieved in their development and application in different technologies, including display apparatus. OLEDs represent an important innovation in lighting markets, providing improved image quality, high brightness, low fabrication costs, low power consumption and high durability [97, 98]. They operate based on the physical phenomenon known as electroluminescence (EL), i.e. the conversion of electrical energy into light [99]. In OLEDs, EL is achieved by fluorescent materials, which undergo a two-step process, an initial absorption leading to the population of an electronically

excited state and a subsequent radiative decay to the electronic ground state, which is known as prompt fluorescence [34].

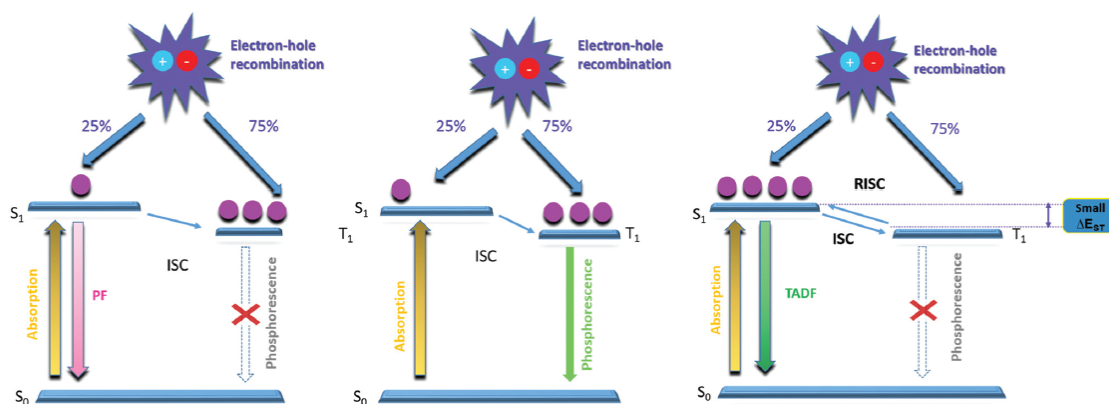


Figure 4.1. Jablonski diagram for OLED, PHOLED and TADF materials, respectively.

However, despite possessing useful properties, several drawbacks still limit the development of OLEDs, notably related to technical issues, such as high-power consumption, insufficient device efficiency, and high driving voltage. Insufficient device efficiencies in OLEDs have led to the use of high quantum yield phosphorescent materials utilizing alternative routes to achieve radiative decay. These are based on intersystem crossing (ISC) and hence the population of triplet states, leading to phosphorescence [100]. The exploitation of both singlet and triplet excited states has led to an increase in internal quantum efficiencies (IQE) up to 100%. Although the use of phosphorescent materials significantly increased quantum efficiencies in OLEDs, the use of heavy metals, such as Ir or Pt, limited their application due to increased device costs, environmental pollution, and toxicity. Moreover, the lack of stability is an additional drawback of phosphorescent OLEDs (PhOLEDs). Indeed, chemical degradation leading to charge traps, non-radiative recombination sites, and luminance loss, are serious issues affecting PhOLEDs [100].

In the quest to increase OLED efficiencies, thermally activated delayed fluorescence (TADF) materials have attracted great attention as they lead to the population of both singlet and triplet states without using any heavy metals (see Figure (4.1)) [101–106]. Soon after the first organic TADF emitter was reported in 2011, studies related to TADF based OLEDs gained momentum and nowadays, external quantum efficiencies (EQE) reaching up to 30% together with internal quantum efficiencies (IQE) of 100% have been reported. In addition to

their applications in OLEDs, TADF materials also have applications in fluorescence lifetime imaging [107], and oxygen sensing [108–112]. TADF materials also possess the critical advantage of serving as host materials in emission layers [111], and enabling different color emission [5, 40, 110, 112–123].

Emission, which may span from blue to red, is mainly controlled by the degree of intramolecular charge transfer (ICT) of the involved excited states [121]. Since ICT is one of the most important parameters in TADF activity, numerous design strategies were attempted to enhance this fundamental process. One strategy involves the use of donor–acceptor (D–A), D– π –A, D– π –A– π –D molecular frameworks, in which the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbital (LUMO) are localized on donor and acceptor units, respectively, hence leading to spatially separated frontier orbitals [122].

Various donor and acceptor groups were designed to enhance charge transfer in TADF luminophores. The most frequently used donor moieties are diphenylamine [34, 123, 124], carbazole [5, 125–133], acridine [45, 110], and phenoxazine derivatives [46, 134, 135], while the most common acceptor units include boron [50, 118, 124, 136–140], sulfone [5, 116, 130], and benzophenone derivatives (Fig. 2) [31, 110, 141, 142]. However, TADF systems are not limited to these building blocks, as other interesting frameworks were designed such as cyanobenzenes [142], triazines [143], oxadiazoles [142], sulfones [144], and spiro derivatives [125, 145].

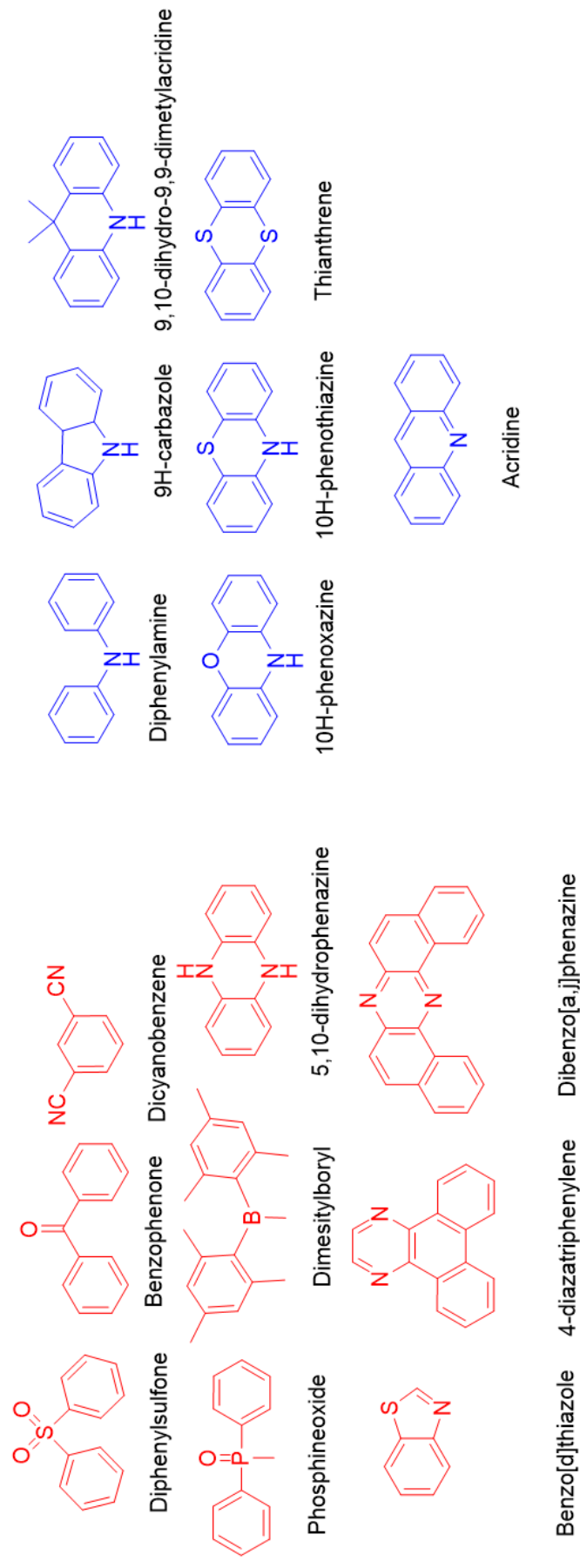


Figure 4.2. Commonly used acceptor (red) and donor (blue) moieties in TADF molecules.

From a photophysical point of view, TADF is based on the up conversion from the triplet (T_1) to the singlet (S_1) state, which is only possible if ΔE_{ST} is sufficiently small, i.e. less than 0.1 eV. This energetic alignment facilitates the reverse intersystem crossing process (RISC), which is also known as the up-intersystem crossing process (UISC) [146]. Although TADF compounds with ΔE_{ST} values smaller than 0.1 eV show the best performances, some fluorophores with ΔE_{ST} values close to 0.5 eV exhibit TADF emission. However, though the TADF mechanism usually involves RISC between T_1 and S_1 states, an alternative possible pathway driven by higher excited triplet states is also observed. Indeed, in some circumstances more than one triplet state is present below the S_1 state, allowing reverse internal conversion (RIC) between T_1 and the upper lying triplet states. This is followed by a RISC between T_n , i.e. the triplet state closest to the first excited singlet state and S_1 [147]. Furthermore, rigid molecular architectures are usually preferred over flexible ones for high performance TADF devices, since they minimize non-radiative decay due to vibrational and rotational motions [148].

In addition to a small ΔE_{ST} gap, the electronic coupling between charge transfer singlet ^1CT and local triplet (^3LE) states strongly influences TADF efficiency [47]. Indeed, the magnitude of spin orbit coupling (SOC) is crucial to determine RISC efficiency and ultimately delayed fluorescence [149]. The rate of RISC (k_{RISC}) is usually expressed by combining Fermi's golden rule with Marcus' theory [150], as:

$$k_{RISC} = \frac{2\pi}{\hbar} |H_{SO}|^2 (4\pi\lambda k_B T)^{-\frac{1}{2}} \exp\left(\frac{-E_A}{k_B T}\right), \quad (4.1)$$

$$E_A = \frac{(\Delta E_{ST} + \lambda)^2}{4\lambda}. \quad (4.2)$$

The key parameters being the reorganization energy λ , the SOC expressed by H_{SO} , and E_A which is related to the ΔE_{ST} energy gap through Equation (4.2). More topological descriptors of the electronic density reorganization such as the amount of CT (^qCT) and the effective CT distance (^dCT) for ground and excited states have also been used to computationally preview TADF performance [151]. The CT character of T_1 states has also been analyzed through the excited state dipole moments [152].

Furthermore, environmental factors are also important in dictating the overall TADF efficiency, in particular the ISC rates, as shown by their sensitivity to solvent polarity [146]. In addition, as Yu-Zhong Xie and co-workers pointed out, minimum energy crossing points (MECP) between S_1 and T_1 states are crucial, since they represent funneling regions, allowing the non-adiabatic transition between different electronic states [153].

In our previous study, we investigated a series of benzophenone based TADF emitters and non-TADF chromophores by quantum chemical calculations. Our main goal in that contribution was to understand the photophysical properties of benzophenone emitters and their derivatives in terms of absorption spectra, charge separations in the excited states, ΔE_{ST} gaps and SOC magnitude [154]. Here, on the other hand, we plan to extend the objectives of the previous study investigating TADF emitters with various acceptor moieties and propose a new, more general, computational strategy applicable to a large variety of TADF emitters. For this purpose, we analyzed the relationship between molecular structures and photophysical properties of a wide range of emitters by means of ab initio calculations. To understand the correlation between the molecular structure and TADF properties, a comparative study is performed along molecules that possess TADF features and compounds known to be poor TADF emitters (henceforth, they will be referred to as non-TADF molecules).

Indeed, a systematic study on the relationship between structural, electronic properties, and the TADF efficiency of different classes of compounds is somehow missing. We plan to bridge this gap by using molecular modelling and simulation to provide a unified description of the different parameters related to TADF performance. For this purpose, ground state structural properties, such as the torsional angles, are explored and related to the optical properties and the singlet–triplet gap. Our analysis of different excited state descriptors, including singlet–triplet gap, SOC magnitude, and the amount of charge transfer provides a useful and computationally effective protocol to rationalize TADF efficiency. Although the RISC probability decreases with the increase in ΔE_{ST} , H_{SO} which competes with ΔE_{ST} , albeit being usually overlooked, may play a significant role and hence, should be properly accounted for to sketch useful design rules for TADF compounds.

4.3. Computational Methodology

Prior to the evaluation of all optical and photophysical properties, conformational analysis was performed using the Gaussian 16 software package [155] to characterize all possible conformers of the chosen TADF and non-TADF molecules. Density Functional Theory (DFT) calculations with the M06-2X [77, 105] meta-hybrid functional and the 6-31+G(d,p) [154] basis set have been carried out to optimize the ground state conformers and the corresponding S_1 and T_1 geometries. However, all conformers are expected to share the same TDA behavior since the latter is mainly dictated by the twisting angle between donor and acceptor moieties or between the donor and bridge moieties, which are highly conserved in the conformational space. While for ground state equilibrium geometries we have checked that no imaginary vibrational frequencies are present, this was not performed for S_1 and T_1 equilibrium geometries due to the lack of analytical Hessians. The choice of M06-2X functional is justified by its good performance in reproducing the geometries of aromatic compounds [156].

In our previous study, the excited state properties obtained by taking into account all the possible conformers of TADF molecules have been proven identical to the ones of the lowest energy conformer [154]. Thus, we continue our analysis considering the lowest energy conformers of each molecule only.

The energy and nature of excited states are assessed at the B3LYP [157]/6-31+G(d,p), M06-2X/6-31+G(d,p), CAM-B3LYP [158]/6-31+G(d,p), and ω B97XD [159]/6-31+G(d,p) levels of theory, and 6-311++G(3df,3pd) [160] and 6-311++G(2d,2p) [161] basis sets were used, in all calculations, for sulfur and phosphorus atoms, respectively. A series of benchmark calculations with Becke's hybrid B3LYP functional and 6-31+G(d,p) and 6-311+G(d,p) basis sets are also performed. From this test, it is clearly observed that increasing the basis set does not induce any noticeable change in the calculated absorption spectra.

Integral equation formalism polarizable continuum model (IEF-PCM) is used in all calculations [162], to implicitly model the solvent environment. Optimized geometries were rendered with the CYLview software package [163].

Tamm Dancoff Approximation (TDA) was employed for all the excited state calculations. This choice is due to the fact that the TDA method provides a more balanced description of both triplet and singlet excited states, and compared to Time- Dependent DFT (TD-DFT) is free from triplet instability issues [164]. All excited state calculations have been carried out with the Gaussian 16 software package.

Absorption spectra were modeled as vertical transitions from the S_0 equilibrium geometry. Subsequently, to include dynamic and vibrational effects, 30 conformations, sampling the vicinity of the Frack– Condon region, were generated through a Wigner distribution [92] as implemented in the Newton-X [165] software package. Vertical transitions from each S_n snapshot were convoluted using Gaussian functions of full-width at half length (FWHL) of 0.15 eV. Absorption spectra calculations via the Wigner distribution method have been performed with the B3LYP, PBE0, M062X, BLYP [166] and TPSSh [167] functionals using the 6-31+G(d,p) basis set.

The nature of the excited states is evaluated using Natural Transition Orbitals (NTOs), obtained with the Nancy-EX code [168, 168] and visualized with the Avogadro [169] software package. In addition, Φ_S values, defining the overlap between the attachment and the detachment densities, were calculated.

Spin–orbit couplings (SOC) between S_1 and T_1 states have been calculated at the TDA level by using the Amsterdam Density Functional (ADF) code [170, 171] at the B3LYP/DZP [172] and M06-2X/DZP levels of theory. DZP was used since Pople basis sets are not available in ADF.

4.4. Results and Discussion

Herein, a series of different TADF emitters with various donor and acceptor groups were selected from the literature and were investigated by TDA-DFT methods (see Figure 4.4). In an attempt to identify the presence of TADF characteristics in the selected emitters, several descriptors were assessed, such as the twisting angle between donor and acceptor units, ΔE_{ST} ,

NTO densities along with the charge transfer topology indices (Φ_S) [173], and SOC values between the S_1 and T_n states involved in the RISC process.

We selected TADF compounds containing different acceptor groups, such as phosphine oxides, phenazines, anthraquinones, phenanthrenes, diphenylsulfones and benzophenones. Specifically, we consider the phosphine oxide (PX-ZPO, DPXZPO and TPX-ZPO [174]), dibenzo[a,j] phenazine (MeODP-DBPHZ, POZ-DBPHZ) [175], anthraquinone-based compounds (AQ-DMAC, AQ-DPA) [34], phenanthrene containing compounds (m-ATP-PXZ [176], TPA-DCPP [133]) diphenylsulfone-based compounds (DMAC-DPS, PPZ-DPS) [34] and benzophenone containing compounds (m-PX2BBP and Cz2BP) [142]. Additionally, we studied PXZ-PXB bearing a 10H-phenoxaboryl electron acceptor group [135], DMAC-TRZ with a 2,4,6-triphenyl-1,3,5-triazine (TRZ) acceptor moiety [177], and 2CzPN with a dicyanobenzene group [98]. Furthermore, and as a comparison, we also considered two non-TADF molecules namely, pCBP and PhCz [178].

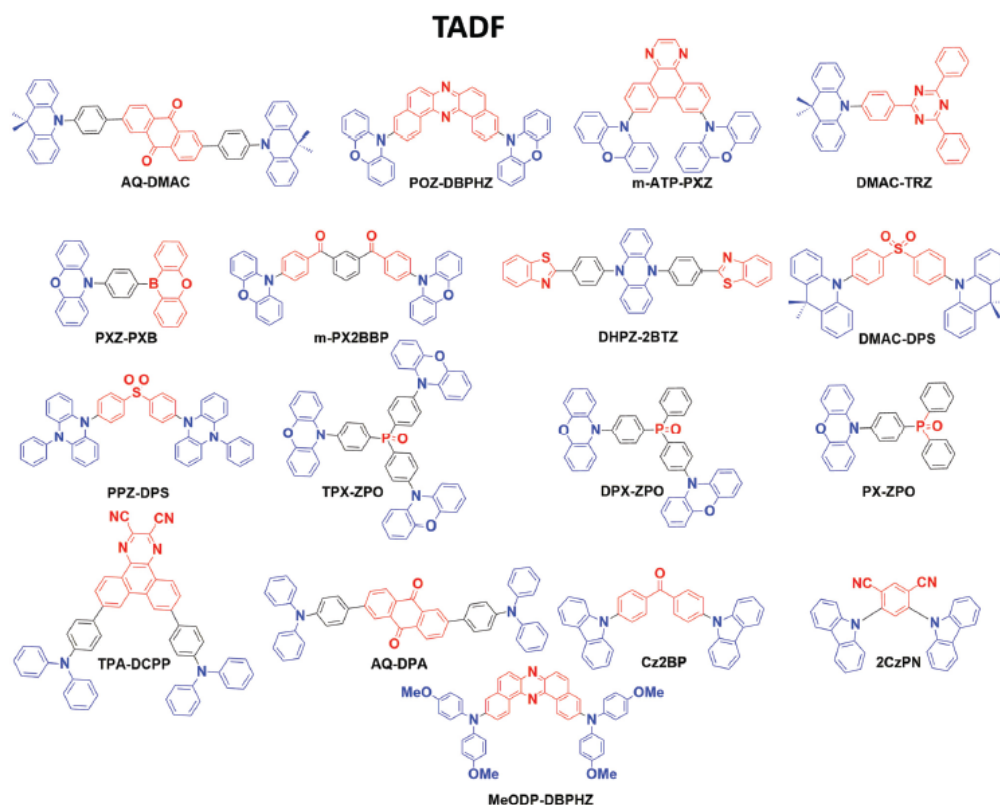


Figure 4.3. TADF molecules investigated in this study. Blue: donor; red: acceptor; black: π -bridge.

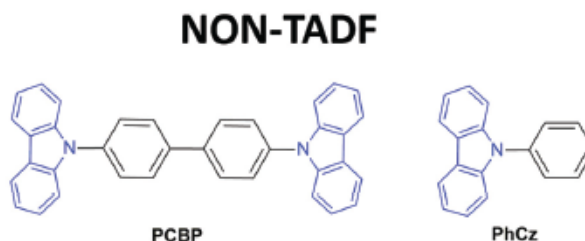


Figure 4.4. Non-TADF molecules investigated in this study. Blue: donor; red: acceptor; black: π -bridge.

4.4.1. Twist angle between donor (D), acceptor (A) and bridge (B) moieties

The torsion angle between donor/acceptor units and the bridge moieties is a straightforward descriptor allowing one to rationalize the TADF activity, and the calculated values are reported in Figure 4.5. As a matter of fact, twisting angles of 90 will constitute the perfect arrangement to break conjugation, thus leading to small ΔE_{ST} values and, hence, enhance TADF. However, while minimizing ΔE_{ST} values, perfectly orthogonal geometries lead to an important disadvantage for luminescence, since the oscillator strength, which is one of the key parameters for light emission, is then strongly reduced. Among seven different donor units we show that the best performing group is clearly DMAC with its $\approx 90^\circ$ twisting, while the PXZ moiety with $\approx 80^\circ$ twist angle is the second most efficient donor group. As expected, the favorable value of the twist angle is reflected in PXZ-containing compounds which present small ΔE_{ST} values, as seen both experimentally and theoretically. PPZ and DHPZ display a twisting of $\approx 100^\circ$ between the adjacent neighboring groups. These structural features also correlate with ideal ΔE_{ST} values (≈ 0.1 eV) and well separated frontier orbitals.

On the contrary, TPA-DCPP, AQ-DPA and MeODP display relatively lower TADF activity due to their small twist angle, which is close to 30° . The small twisting can be attributed to the freely rotating phenyl rings, which cause a general planarization of the compounds. The last donor unit, Cz, induces a torsion angle of around 50° – 60° . The relatively low torsion angle of the carbazole moiety can be attributed to a smaller steric repulsion due to the five-membered ring in the donor group.

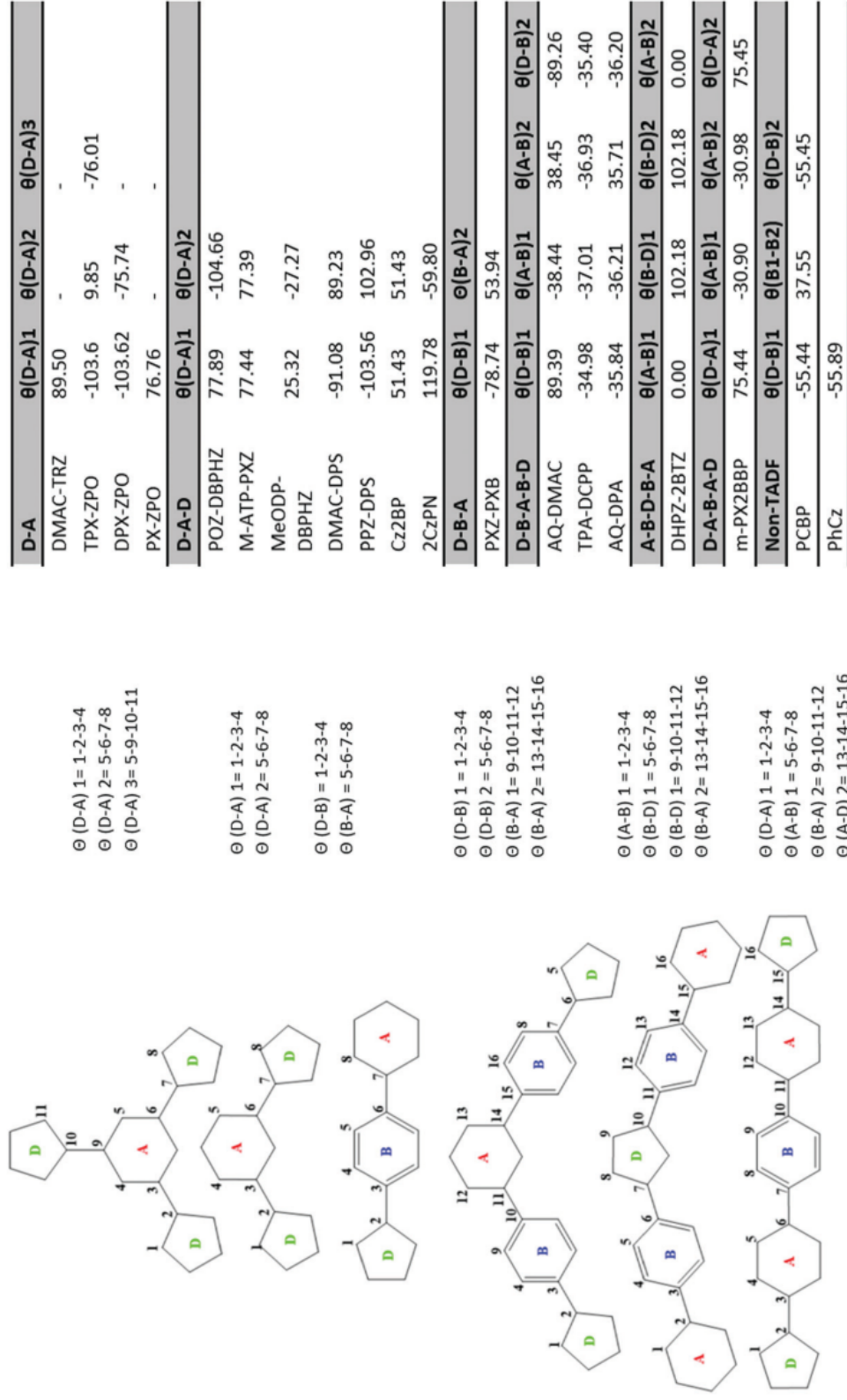


Figure 4.5. Ground state twist angles of TADF and non-TADF molecules. D: donor unit, A: acceptor unit, B: bridge unit.

In addition to the torsion angles between the donor and adjacent moieties, we also examined the twisting angles between acceptor units and their adjacent donor or bridge moieties (Figure 4.5). While the triphenyl triazine acceptor induces a twisting angle of 90° , DBPHZ and m-ATP units reach approximately 80° . On the other hand, the DPS moiety leads to an ideal 90° twisting with DMAC and 100° angle with the PPZ group. Instead, relatively low performance TADF emitters, such as Cz2BP and 2CzPN, assume a butterfly shape. Benzophenone-containing TADF emitters presenting a D–A–D scaffold, reach twist angles of $\approx 52^\circ$ and $\approx 120^\circ$ thus leading to a non-orthogonal geometry. Indeed, also due to its efficient ISC, benzophenone was previously explored as an OLED emitter.

Table 4.1. Differences between the torsion angles of S_0 and T_1 states computed at M06-2X/6-31+G(d,p) level of theory.

S_0/T_1 Geometries Torsion Angles				
	$\theta(\text{D-A})1$	$\theta(\text{D-A})2$		
1	89.5/63.62			
	$\theta(\text{D-A})1$	$\theta(\text{D-A})2$		
2	77.89/-69.93	-104.7/-103.4		
3	77.44/75.74	77.39/66.03		
4	25.32/29.27	-27.27/-30.34		
5	-91.08/71.68	89.23/71.68		
6	-103.56/-101.8	102.96/95.49		
7	119.78/-56.63	-59.8/-56.63		
	$\theta(\text{D-B})1$	$\theta(\text{D-B})2$		
8	-78.74/69.19	53.94/37.06		
	$\theta(\text{D-B})1$	$\theta(\text{A-B})1$	$\theta(\text{A-B})2$	$\theta(\text{D-B})2$
9	-34.98/-29.33	-37.01/-27.72	-36.93/-27.72	-35.4/-29.33
10	-35.84/-41.52	-36.21/35.79	35.71/-15.04	-36.2/-24.47
	$\theta(\text{A-B})1$	$\theta(\text{B-D})1$	$\theta(\text{B-D})2$	$\theta(\text{A-B})2$
11	0/0	102.18/-90.34	102.18/90.24	0

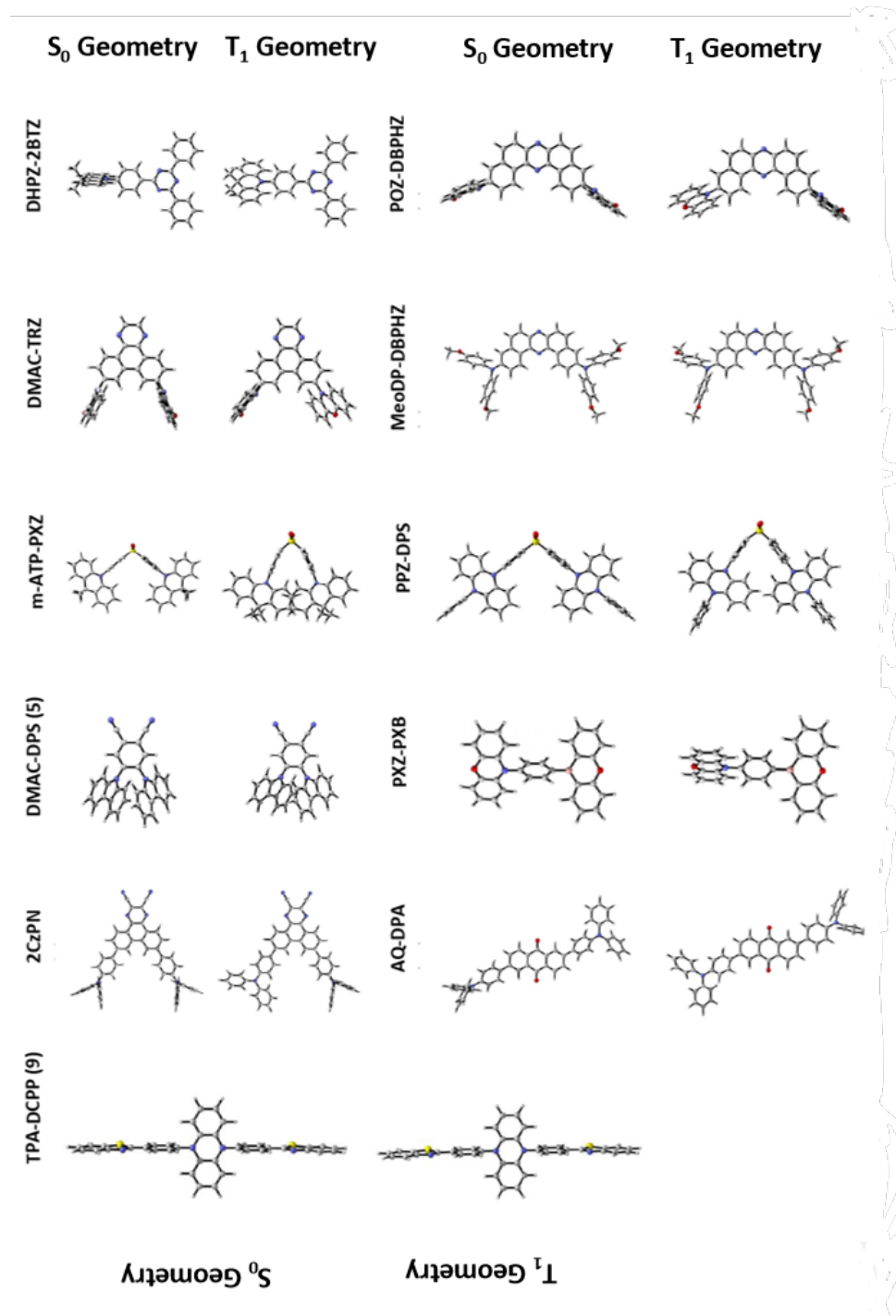


Figure 4.6. 3D representations of S_0 and T_1 geometries of some compounds with different ground state and excited state geometries.

In addition to the Franck–Condon region, the torsion angles at the equilibrium T_1 geometries were also examined, and, as reported in Figure 4.6, only slight changes can be observed except for compound 7. Moreover, torsion angles at the S_1 equilibrium geometries were also obtained for AQ-DMAC, POZ-DBPHZ, DHPZ-2BTZ, PPZ-DPS, Cz2BP, TPA-DCPP, AQ-DPA and MeODPDBPHZ. It has been observed that equilibrium geometries for the first excited singlet state are very close to those of the ground state. Therefore, to reduce computational costs, further analyses have been performed in the Franck–Condon region, only. Thus, geometry relaxation is important only for the T_1 state, leading to a decrease in orthogonality, and consequently to the increase of the HOMO–LUMO overlap and ΔE_{ST} . Indeed, excited state twisting is recognized as a key feature of TADF molecules. To sum up, DMAC, PXZ and DHPZ units appear as the most appropriate donors to establish the desired orthogonality leading to twisting angles around 80° and 100° . On the other hand, DPA derivatives have smaller twisting angles ($\approx 40^\circ$), which lead to an increased HOMO–LUMO overlap Table 4.2 and ΔE_{ST} . Moreover, when considering acceptor moieties, anthraquinone and diphenylsulfone groups provide almost ideal orthogonal arrangements. It should be pointed out, however, that the term ideal here refers to geometrical properties and twisting angle only and not to the device performance.

4.4.2. Electronic density reorganization and effect of the functional

The reorganization of the electronic density due to the excited state population has been analyzed by examining the behavior of the corresponding NTOs. Furthermore, we compare the natures of S_1 and T_1 states obtained using M06-2X, CAMB3LYP and ω B97XD to assess the influence of the exchange–correlation functional in the topology of the electron density reorganization (see Table 4.3), and hence, in providing the correct diabatic description of the most relevant states. In this respect, the B3LYP functional was excluded, since TADF compounds rely heavily on CT, exasperating the known deficiencies of hybrid functionals, especially for bridged compounds leading to spatially long-range CT states. Since the molecular set under investigation is composed of mostly donor– π –acceptor charge transfer molecules, we did a benchmark study with medium-range separated M06-2X and long range separated CAM-B3LYP and ω B97XD functionals.

Though slightly unsatisfactory performances of CAM-B3LYP and ω B97XD have been reported for some donor–acceptor systems [43], their behavior was not tested for the set of molecules under investigation, which are typical donor– π –acceptor systems.

Table 4.2. Phi-S values of S_1 states computed at different levels of theory and the 6-31+G(d,p) basis set.

Phi-S Values	M062X	ω B97XD	CAMB3LYP
AQ-DMAC	0.310	0.511	0.479
POZ-DBPHZ	0.094	0.841	0.099
M-ATP-PXZ	0.144	0.176	0.134
PXZ-PXB	0.064	0.487	0.511
DMAC-TRZ	0.213	0.503	0.519
m-PX2BBP	0.247	0.525	0.549
DHPZ-2BTZ	0.085	0.733	0.746
PPZ-DPS	0.160	0.612	0.591
DMAC-DPS	0.201	0.550	0.564
TPX-ZPO	0.252	0.601	0.254
DPX-ZPO	0.252	0.647	0.26
PX-ZPO	0.212	0.525	0.235
TPA-DCPP	0.728	0.588	0.612
AQ-DPA	0.610	0.517	0.642
Cz2BP	0.410	0.579	0.633
2CzPN	0.599	0.567	0.584
MeODP-DBPHZ	0.739	0.483	0.514
pCBP	0.782	0.497	0.587
PhCz	0.847	0.862	0.863

High Φ_S values indicate a large overlap between electron and hole densities, thus, LE character. On the other hand, small Φ_S values indicate that the degree of overlap between electron and hole densities is small, and thus the presence of a CT excited state. S_1 states computed with the M06-2X functional mostly present a noticeable CT character, which is known to favor TADF efficiency. Conversely, CAM-B3LYP and ω B97XD functionals preview a locally excited S_1 state for some TADF compounds. Also taking into account the orthogonal arrangement, which should indeed favor charge separation, it appears that the LE character should be regarded as an artifact as opposed to the more reliable M062X results. Hence, M062X will be consistently used hereafter.

Table 4.3. Natures of S_1 and T_1 states computed at different functionals and 6-31+G(d,p) basis set.

Compounds	M062X		CAM-B3LYP		B3LYP		ω B97XD	
	S_1	T_1	S_1	T_1	S_1	T_1	S_1	T_1
AQ-DMAC	CT	LE	LE	LE	CT	CT	CT+LE	CT+LE
POZ-DBPHZ	CT	LE	CT	LE	CT	CT	LE	LE
M-ATP-PXZ	CT	LE	CT	LE	CT	CT+LE	CT	LE
PXZ-PXB	CT	LE	LE	LE	CT	LE	LE	LE
DMAC-TRZ	CT	CT	CT	CT	CT	LE	CT	LE
m-PX2BBP	CT	LE	LE	CT+LE	CT	CT+LE	LE	CT+LE
DHPZ-2BTZ	CT	CT+LE	CT	LE	CT	CT+LE	CT+LE	LE
PPZ-DPS	CT	CT+LE	CT+LE	CT+LE	CT	CT	CT+LE	CT+LE
DMAC-DPS	CT	CT	CT+LE	CT+LE	CT	CT	CT+LE	CT+LE
TPX-ZPO	CT	LE	CT+LE	LE	CT	CT	CT+LE	CT+LE
DPX-ZPO	CT	LE	CT	LE	CT	CT	CT+LE	CT+LE
PX-ZPO	CT	LE	CT	LE	CT	CT	CT+LE	LE
TPA-DCPP	CT	CT+LE	LE	LE	CT	CT+LE	LE	LE
AQ-DPA	CT+LE	CT+LE	CT+LE	CT+LE	CT	CT+LE	LE	CT+LE
Cz2BP	LE	LE	LE	LE	CT	LE	LE	LE
2CzPN	CT	CT+LE	CT	CT+LE	CT	CT+LE	LE	LE
MeODP-DBPHZ	CT+LE	LE	CT+LE	CT+LE	CT+LE	CT+LE	CT+LE	CT+LE

Table 4.4. Torsion angles and natures of S_1 states with different functionals.

Compounds	Torsion Angle	M062X	CAM-B3LYP	wB97XD
		S_1	S_1	S_1
AQ-DMAC	89.39	CT	LE	CT+LE
PXZ-PXB	78.74	CT	LE	LE
DMAC-TRZ	89.5	CT	CT	CT
PPZ-DPS	103.56	CT	CT+LE	CT+LE
DMAC-DPS	91.08	CT	CT+LE	CT+LE
TPX-ZPO	103.6	CT	CT+LE	CT+LE
DPX-ZPO	103.62	CT	CT	CT+LE

Table 4.5. Torsion angles and oscillator strengths computed at M062X/6-31+G(d,p) level of theory.

Compound	Torsion Angle	f	f
	D- π or D-A	$S_0 \rightarrow S_1$	$S_0 \rightarrow S_2$
AQ-DMAC	89.39	0	0.0001
POZ-DBPHZ	77.89	0.0001	0.0004
M-ATP-PXZ	75.96	0.0015	0.0001
PXZ-PXB	78.74	0.0042	0.026
DMAC-TRZ	89.5	0.0001	0.0001
m-PX2BBP	104.53	0.0005	0.0005
DHPZ-2BTZ	0	0	0.0016
PPZ-DPS	103.56	0.0005	0.0016
DMAC-DPS	91.08	0.0001	0.0003
TPX-ZPO	103.6	0.0021	0.0023
DPX-ZPO	103.62	0.0026	0.0025
PX-ZPO	77.45	0.0028	0.0059
TPA-DCPP	143.99	0.5431	1.0986
AQ-DPA	144.51	0.0019	0.9761
Cz2BP	52.67	0.0158	0.768
2CzPN	131.64	0.1434	0.2731
MeODP-DBPHZ	153.54	1.1566	0.0418

Figure 4.7 reports the correlation between the change in the degree of overlap between S_1 and T_n states and the energy gap between the relevant states. We may observe that when the nature of S_1 and T_1 changes the energy gap increases. Though a linear relationship with $R^2 = 0.99$ could not be observed, a direct correlation with a positive slope has been observed. However, these should not be necessarily considered as a drawback to the RISC mechanism, since due to the El Sayed rule the SOC between states of different character should increase.

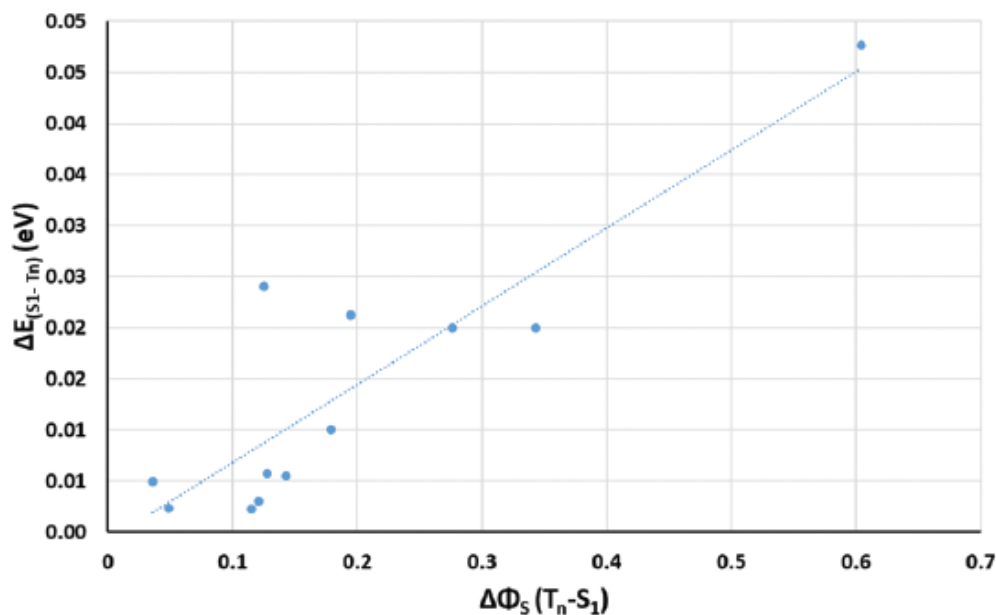


Figure 4.7. Correlation between ΔE_{ST} and the change in electronic density reorganization computed at M062X/6-31+G(d,p) level of theory.

4.4.3. Correlation between $\Delta E_{S_1-T_1}$ and RISC efficiency

According to Kasha's Rule [153], the population of high lying singlet states is followed by ultrafast internal conversion (IC) to S_1 , and eventually ISC leading to the population of the triplet manifold. IC is also active on the triplet manifold, hence leading to the T_1 population. Thus, RISC from T_1 to S_1 is not the only possible pathway, indeed reverse internal conversion (RIC) between T_1 and upper lying T_n states may be possible if the former are quasi-degenerate, which in turn will open a channel for RISC between excited T_n and S_1 states [147, 179].

Globally, however, RISC will be mainly determined by the energy order of singlet and triplet states, together with their efficient couplings. Bredas et al. have shown that the separation of frontier molecular orbitals alone is not sufficient to assure TADF efficiency and highlighted the fact that other factors, including the possibility of mixed CT- T_1 states with a small ΔE_{ST} gap, are crucial [179]. The electron donating character of the donor moiety may also have a noticeable effect on ΔE_{ST} , with the increase of electron donation leading to its decrease. Additionally, using donor and acceptor moieties with appropriate ionization potentials and electron affinities is another key parameter in minimizing the ΔE_{ST} gap [152].

As shown in Figure 4.8, the energy levels of singlet and triplet states indicate that for many compounds, more than one triplet state is lying below the S_1 level. Additionally, in some instances T_1 and T_2 states were found to be almost energetically degenerate.

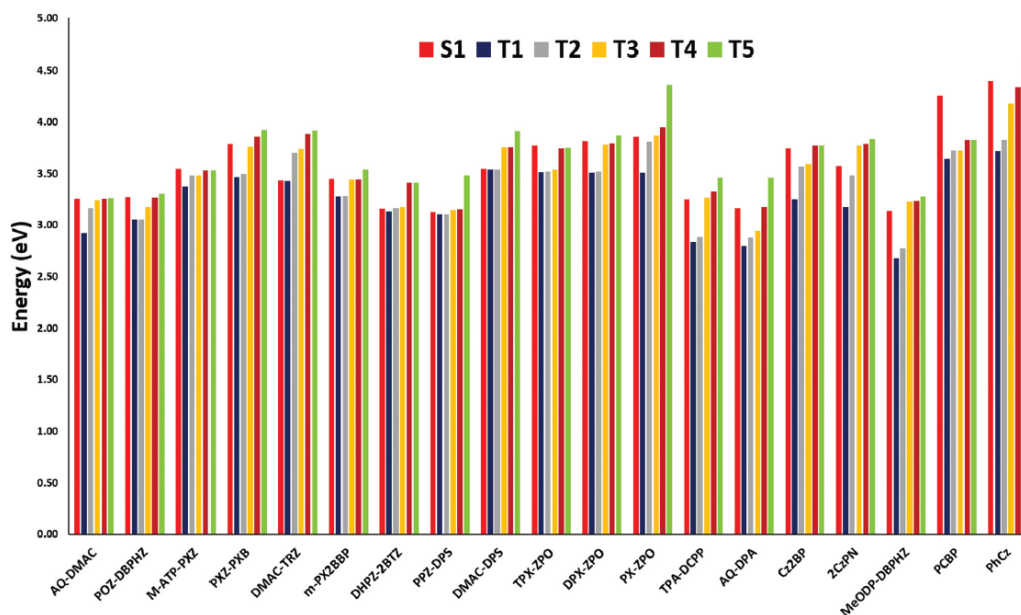


Figure 4.8. Energies of S_1 and T_1 – T_5 levels computed at the M062X/6-31+G(d,p) level of theory.

For some compounds, such as DHPZ-2BTZ and PPZ-DPS, a three-state degeneracy involving S_1 , T_1 and T_2 is observed. Globally, all these facts may point to the fact that higher triplet states may, indeed, contribute to the RISC process. Therefore, to identify the states responsible for RISC, the specific value of SOC should be analysed together with the energetic gaps.

4.4.4. Correlation between SOC and RISC efficiency

Besides the ΔE_{ST} descriptor, we also determined the effects of structural modifications on the SOC between S_1 and T_1 states. Indeed, despite giving rise to low lying CT with negligible electron–hole overlap, orthogonal arrangement of donor and acceptor moieties may have a negative effect on SOC, hence influencing in a more subtle way the ultimate RISC rate. Although TADF compounds are generally known to have low SOC values, it is found that RISC occurs on a timescale shorter than 100 ns at 300 K [179]. Furthermore, LE triplet states

may be involved in increasing the possibility of RISC due to the El Sayed's rule [180, 181]. In this context, Penfold and Monkman suggested a RISC mechanism which involves a three state degeneracy between S_{CT} , T_{CT} and T_{LE} [182]. Herein, we computed the SOC between S_1 and the first five triplet states (see Figure 4.9). As represented in Figure 4.9, striking differences in SOC between S_1 and different triplet states are observed. It should be pointed out that since the SOC value enters the Marcus's formula directly, couplings between the states involved in RISC are highly important.

Detailed analysis of Figure 4.9 shows that the energy gap between the singlet and triplet states with the largest SOC are very close to the experimental energy gaps. In other words, we observed that the experimental ΔE_{ST} values are very close to the calculated gaps between strongly-coupled singlet and triplet states. For instance, for AQ-DMAC, m-ATP-PXZ, DHPZ-2BTZ, and AQ-DPA, the SOC between S_1 and T_3 are larger compared to all the other states, and the absolute deviations of the computed S_1-T_3 energy gaps with the experimental values are smaller than 0.05 eV. For POZ-DBPHZ, PXZ-PXB and TPX-ZPO, S_1 and T_4 have the largest SOC and their gaps deviate by less than 0.1 eV compared to the experiment.

On the other hand, for DMAC-TRZ, DPX-ZPO, PX-ZPO and 2CzPN, the SOC between S_1 and T_1 states are the highest, moreover, their corresponding energy gaps deviate by approximately 0.1 eV from the experiment, suggesting a more classic scenario involving only the lowest triplet state. For the DMAC-TRZ emitter, it should be pointed out that the SOC between S_1-T_2 states is larger than for S_1-T_1 . However, while the T_2 state is higher, and hence shows a large energy gap, T_1 is almost degenerate with S_1 . Thus, when compared with the experiment, the gap between S_1 and T_1 states is approximately 0.006 eV. As a matter of fact, SOC appears as a more promising, and crucial descriptor in determining the states involved in the RISC process. It should also be pointed out that various TADF groups are represented in our set, and in all the cases SOC was able to reliably describe the experimental efficiency, even in the presence of wide and diverse donor and acceptor groups, and in general different functional moieties.

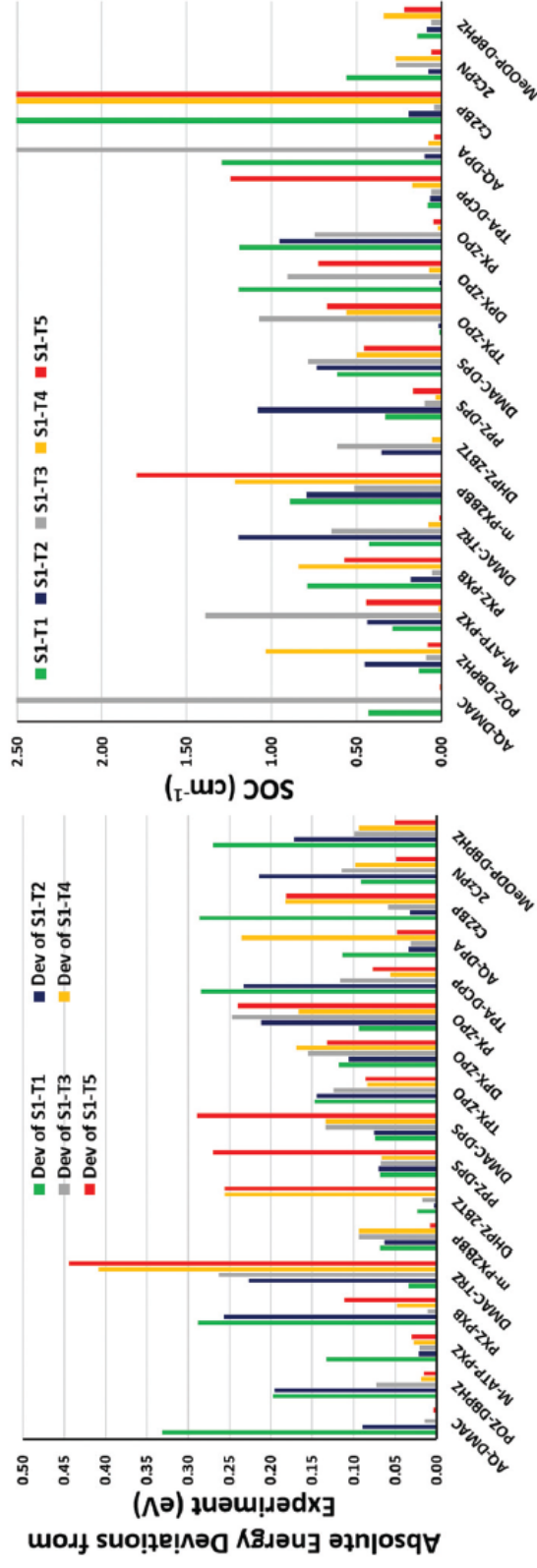


Figure 4.9. Absolute deviations of S – T gaps from the experiment and the SOC values computed at the M062X/6-31+G(d,p) level of theory.

As a general rule, good TADF efficiency requires either moderate SOC and very small $\Delta E(S_1 - T_1)$ or moderate $\Delta E(S_1 - T_1)$ and very high SOC. Thus, almost perfectly orthogonal scaffolds including strong D and A moieties, which will result in very small $\Delta E(S_1 - T_1)$ and SOC values, will be less efficient than moderate strength D and A groups if they still present torsion angles leading to acceptable $\Delta E(S_1 - T_1)$ and strong SOC. Another important role of SOC is its deterministic behaviour in competition between the direct transition from S_1 to S_0 and ISC/RISC. According to Hund's rule transition dipole for the $S_1 - S_0$ transition, causing a slow radiative rate of fluorescence, hence, excited state dynamics favour the ISC to triplet states [183].

For the molecule set under investigation, ΔE_{ST} and SOC descriptors support the preference of ISC over fluorescence emission. As reported in Figure 4.9 and Table 4.6, TADF emitters under investigation exhibit strong SOC values, thus strong ISC to the triplet states. Moreover, Table 4.3 reports that these emitters exhibit CT character S_1 states, with localized HOMO and LUMO orbitals, thus, they are expected to have small transition dipole moments for the radiative decay between S_1 and S_0 states. Moreover, due to the very small energy gaps between the relevant states, the ΔE_{ST} descriptor also favors ISC over fluorescence emission.

4.4.5. Topological Φ_S index

The Φ_S index measures the degree of overlap between particle and hole densities, and the smaller its value the larger the charge separation in the excited states. Hence, the Φ_S index can be used as an indicator for TADF efficiencies. As represented in Figure 4.10, going from TADF to non-TADF compounds, Φ_S indices definitely increase. This situation is also coherent with the decrease of orthogonality and increase of ΔE_{ST} .

The compounds with the smallest twisting angles between donor and acceptor units, such as Cz2BP, MeODP-DBPHZ, TPA-DCPP and AQ-DPA, or the non-TADF pCBP and PhCz present higher Φ_S indices, because of the highly delocalized π electrons, which result in hole and particle density overlap and increased LE character.

Table 4.6. Spin orbit coupling values computed at M062X/6-31+G(d,p) level of theory at ground state geometry.

Compounds	S_1-T_1	S_1-T_2	S_1-T_3	S_1-T_4	S_1-T_5
AQ-DMAC	0.433	0	3.792	0.001	0.008
POZ-DBPHZ	0.132	0.45	0.092	1.036	0.079
M-ATP-PXZ	0.29	0.435	1.394	0.016	0.441
PXZ-PXB	0.792	0.182	0.058	0.845	0.572
DMAC-TRZ	0.428	1.195	0.649	0.075	0.013
m-PX2BBP	0.889	0.797	0.514	1.216	1.798
DHPZ-2BTZ	0.000	0.353	0.616	0.057	0.000
PPZ-DPS	0.332	1.082	0.099	0.034	0.167
DMAC-DPS	0.616	0.735	0.787	0.498	0.456
TPX-ZPO	0.015	0.017	1.077	0.561	0.67
DPX-ZPO	1.195	0.015	0.906	0.069	0.724
PX-ZPO	1.192	0.954	0.749	0.024	0.047
TPA-DCPP	0.082	0.065	0.059	0.17	1.244
AQ-DPA	1.295	0.098	3.312	0.077	0.042
Cz2BP	8.934	0.194	0.042	3.119	8.831
2CzPN	0.56	0.074	0.267	0.272	0.061
MeODP-DBPHZ	0.143	0.086	0.063	0.342	0.217

4.4.6. Topological Φ_S index

On the other hand, compounds with higher twisting angles and lower ΔE_{ST} values exhibit lower Φ_S indices, which indicates an increased CT character [184]. As shown in Figure 4.10 and Figure 4.11, while most of the TADF compounds have Φ_S values for S_1 smaller than 0.3, non-TADF compounds have Φ_S values close to unity. Namely this is the case for TADF active MeODP, Cz2BP, TPA-DCPP, AQ-DPA and non-TADF pCBP, PhCz. The latter also presents torsion angles far from 90° and the hole and particle densities are delocalized over the conjugated bridges, thus justifying the high Φ_S values (see Table 4.3). On the contrary, for compounds which have orthogonal D–A geometries, such as DMAC-TRZ, DMAC-DPS and AQ-DMAC, hole densities are distributed on the donor moieties while particle densities are almost perfectly localized on the acceptor groups.

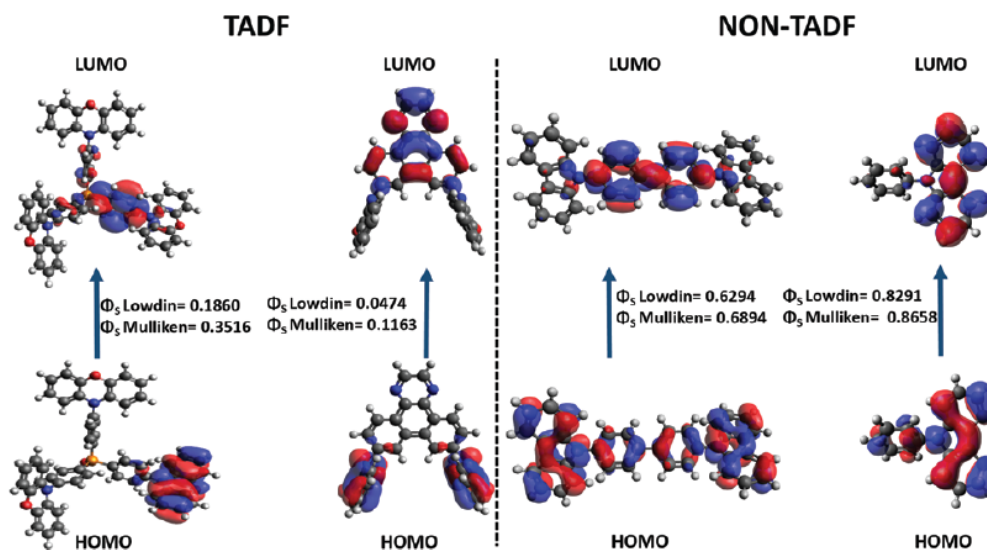


Figure 4.10. Φ_S indices of S_1 states and frontier molecular orbital overlap differences of TADF TPX-ZPO, m-ATPPXZ and non-TADF pCBP, PhCz molecules, respectively.

In Figure 4.11, Φ_S indices for S_1 , T_1 , T_2 , T_3 , T_4 and T_5 states have been reported. It is obvious that while S_1 generally has a CT character with small Φ_S indices, triplet states have larger Φ_S indices, thus indicating an increased LE character.

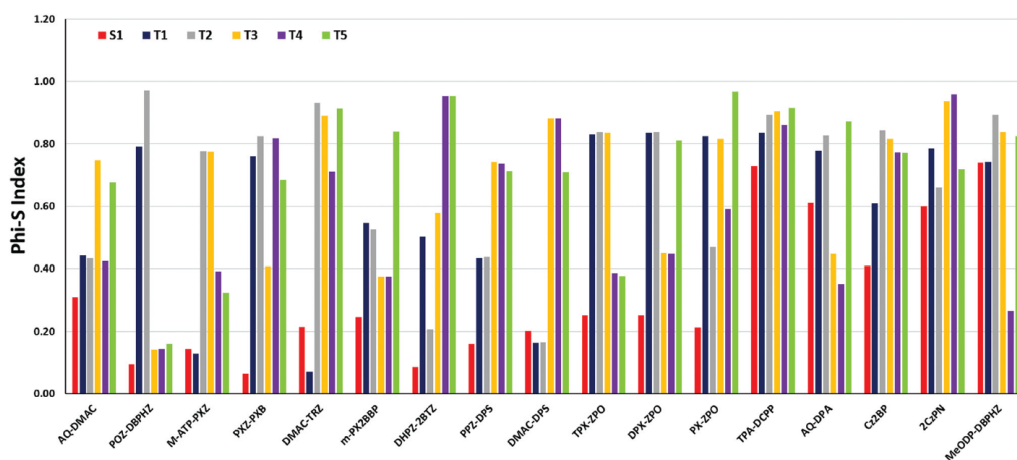


Figure 4.11. Φ_S indices of S_1 , T_1 , T_2 , T_3 and T_4 states computed at the M062X/6-31+G(d,p) level of theory.

Since the change in the nature of the states is favorable to enhance SOC, this feature should be considered as beneficial for TADF efficiency. Moreover, when compared to Figure 4.8, it has been observed that energetically degenerate states such as T_3 and T_4 in AQ-DMAC have remarkable differences in their Φ_S indices, which leads to differences in

their SOC values with the S_1 state. This situation is a way of obtaining strong RISC between the singlet and isoenergetic, mixed triplet states.

In summary, five main descriptors: torsion angle, nature of states, ΔE_{ST} , Phi-S index and SOC, were investigated for a series of TADF emitters, including benchmark calculations via TDA approximation. Here are the main findings from the benchmark study: For the nature of states analyses, PBE0, B3LYP, M06-2X, CAM-B3LYP and ω B97XD functionals with the 6-31+G(d,p) basis set were used. In our calculations, we observed the deficiency of hybrid functionals for modelling CT emitters. On the other hand, CAM-B3LYP and ω B97XD were found to represent LE singlet states, which is not consistent with the structural properties of the TADF emitters.

Our calculations on the nature of excited states indicate that the M06-2X is the only functional which well reproduces the nature of excited states for the TADF emitters under investigation. To further check the degree of overlap between electron and hole orbitals, we reported Φ_S indices computed at the M06-2X/6-31+G(d,p), CAM-B3LYP/6-31+G(d,p) and ω B97XD/6-31+G(d,p) levels of theory. Our findings indicate that the M06-2X/6-31+G(d,p) level of theory provides the correct degree of separation between electron and hole orbitals.

Based on the results from the nature of states analysis, we further modelled the ΔE_{ST} and SOC parameters with the M06-2X functional and observed that it nicely reproduces the experimental ΔE_{ST} data obtained from the literature and it represents reliable SOC values consistent with RISC processes. Based on the findings from five descriptor analyses, we theoretically proposed a comprehensive methodological approach for TADF design strategies. Moreover, via considering the effects of five descriptors, we conclude that the SOC parameter has a determinative role in TADF efficiency. Thus, the primary target in designing and synthesizing new TADF emitters should be optimizing the SOC involved in the RISC process. Furthermore, we highlighted the role of intermediate triplet states on TADF performance, which should be taken into consideration when modelling the photophysical properties of TADF emitters.

4.5. Conclusion

Through a systematic study of a large panel of potential TADF chromophores we have elucidated the reasons behind the performance of the different descriptors, which may be used to forecast RISC probability. Singlet/triplet gap, ΔE_{ST} , is usually associated with twisting angles and the presence of strong electron donating and withdrawing groups. The results obtained with M06-2X are reliable and consistent with experimental data.

Additionally, we also observed a significant deviation in the twisting angles of TADF molecules between ground and triplet excited state equilibrium geometries. The identification of ΔE_{ST} values for the states presenting the larger SOC, allows us to identify RIC accessible channels and further supports the role of SOC as the most reliable descriptor of TADF performance. Indeed, for most of the studied cases, SOC is the determinant factor in determining the probability of RISC. Furthermore, as the electronic density reorganization seems fundamental to assure TADF, Φ_S indices have been explicitly considered. A good correlation has been observed with structural parameters, such as the twisting angles, or electronic properties, including ΔE_{ST} values, also coherently with previously reported trends.

Oscillator strength may also be regarded as highly important, especially dictating luminescence efficiency and is strongly correlated with the geometric properties. Our results show that while designing new TADF emitters with favourable properties such as small ΔE_{ST} values and strong SOC, the geometrical features of the constituents should be carefully adjusted vanishing oscillator strengths. Therefore, instead of perfect orthogonal geometries, smaller torsions with moderate ΔE_{ST} values, strong SOC and strong oscillator strengths, will lead to more efficient TADF devices. To sum up, our calculations successfully explain the TADF performance of a wide range of donor and acceptor groups and their characteristic structural behavior, also highlighting useful and computationally efficient indicators. We also further analyzed the possible RISC paths and showed that RIC involving the highest excited triplet states may play an important role in mediating RISC when leading to high SOC. Hence, ΔE_{ST} , oscillator strength, and SOC descriptors should be combined when performing computational screening and rational molecular design.

5. PHOTOPHYSICAL PROPERTIES OF BORON-BASED CHROMOPHORES AS EFFECTIVE MOIETIES IN TADF DEVICES: A COMPUTATIONAL STUDY

5.1. Overview

Thermally activated delayed fluorescence (TADF) materials have shown great potential in the design of organic metal-free optoelectronic devices and materials and, therefore, are the subject of intense investigations. This contribution presents the effects of various parameters on the photophysical properties of a series of Boron-based TADF emitters. These include torsion angle, the changes in the electronic density, energy gap between the first excited singlet (S_1) and the first excited triplet states (T_1), oscillator strength (f) and spin-orbit coupling (SOC). Through a comprehensive structural analysis, we firstly show the most favorable conformation of the ground state of donor (D) and acceptor (A) moieties that are popular in TADF emitters. Further, the properties of the excited state manifolds are obtained with Tamm-Dancoff Approximation (TDA), thus rationalizing their optical and photophysical properties. Globally, our results settle the basis for the rationalization of the effects of different parameters on reverse intersystem crossing (RISC) probabilities, which is the rate-limiting step for TADF, thus favoring the rational design of novel highly efficient TADF materials with strong triplet exciton harvesting.

5.2. Introduction

Although organic light emitting diodes (OLEDs) are some of the most promising devices in displays and lighting technology, they still suffer from important drawbacks. Indeed, the overall device efficiency, which is fundamental in applications, is one of the weakest points of OLED technology. Due to the intrinsic limitations of spin-statistics, only 25% of the excitons produced by the applied electric potential are generated as singlets while the remaining 75% are in triplet states [185]. However, while organic materials may usually be fluorescent their

phosphorescence quantum yield is generally low, resulting in the loss of the majority of the excitons and in low electroluminescence [55]. Furthermore, OLED efficiency is also limited by other non-radiative relaxation pathways of the singlet or triplet excitons [186]. To cope with such phenomena and hence with the challenges of electron–light conversion, other strategies, in addition to the optimization of fluorescence quantum yield, have been proposed including triplet-triplet annihilation (TTA) [187], singlet fission (SF) [42], phosphorescence emission, and thermally activated delayed fluorescence (TADF) (see Figure 5.1) [146].

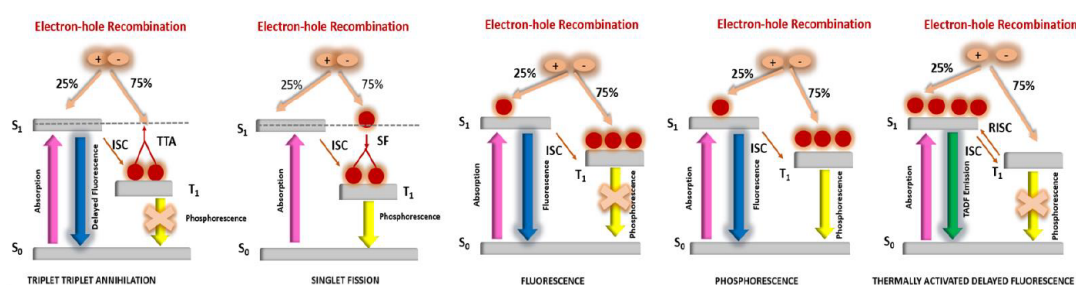


Figure 5.1. Photophysical processes observed in electronic excitations of optoelectronic materials.

In TTA, one singlet excited state is originated from two low-lying triplet states leading to the increase of the external quantum efficiencies (EQE) compared to OLED materials [188]. On the other hand, in SF, a molecule converts a singlet excited state into two triplet states, with spin densities localized on adjacent moieties, leading to a theoretical EQE of 200%, which can be highly attractive for solar cell applications [186].

Phosphorescence emission is achieved with the second generation OLED devices, whose components include heavy metals, such as iridium and platinum, characterized by a high efficient triplet state radiative decay due to the increased spinorbit coupling (SOC) [21]. Although, second generation emitters provide high efficiency devices, they also suffer from the need to include rare metals, which are plagued by undesirable environmental and economic shortcomings. Thus, the development of alternative approaches to harvest both singlet and triplet states is still highly attractive. In this respect, TADF materials have been recently proposed since they are capable of exploiting triplet excited states. This is achieved via reverse intersystem crossing (RISC) in which lowlying triplets (T_1) are converted back to the singlet manifold (S_1).

TADF materials are highly promising emitters in display technology and thus, have become a hot research topic [189]. They are also referred to as ‘third generation’ OLEDs and show important advantages such as high efficiency [190], low fabrication costs, and wide emission color range [191]. Furthermore, it has been shown that TADF emitters may also be used as high-performance metal-free photosensitizers (PSs) with remarkable photosensitizing ability, including in the domain of photodynamic therapy. As an example, in 2019, mitochondria-targeting nanoparticles with TADF ability have been successfully used against cancer cells [192].

From a photophysical point of view, in TADF materials, the population ratio between singlet and triplet states is largely controlled by the competition between RISC and phosphorescence [193]. In particular, thermally activated RISC, which drives the population accumulation in the triplet states, should be maximized. Fortunately, tuning RISC efficiency should also lead to the concomitant minimization of competitive nonradiative decay. It is generally recognized that to attain an efficient RISC the energy gap between S_1 and T_1 states (ΔE_{ST}) should be sufficiently small to allow the population transfer between the two manifolds via thermal activation [146]. However, the spin conversion between S_1 and T_1 is also influenced by the magnitude of the spinorbit coupling (SOC), which should be high. ΔE_{ST} in TADF materials can be minimized by adopting a donor (D) – acceptor (A) molecular design, where the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are spatially separated, thus reducing the exchange integral between S_1 and T_1 states and consequently closing the gap between the states [194, 195]. On the other hand, as stated by El Sayed’s rule, high SOC necessitates a large variation in the electronic density of the excited states, which can also be achieved by n-orbital participation [150].

Several studies aiming at simulating the spinforbidden non-radiative transition between S_1 and T_1 states have been reported. It is generally known that heavy metals such as Ir, Pt, and halogens have large SOC due to their relativistic effects, hence favoring (R)ISC. For pure organic molecules SOC are much smaller, however they can be increased when the triplet and singlet have a different electronic (diabatic) nature. Generally, large SOC are observed between a singlet state with $^1(n, \pi^*)$ or $^1(\pi, \pi^*)$ nature and a triplet state with $^3(\pi, \pi^*)$ or

$^3(n, \pi^*)$ nature. On the contrary, transition from $^1(\pi, \pi^*)$ to $^3(\pi, \pi^*)$ and from $^1(n, \pi^*)$ to $^3(n, \pi^*)$ are unfavorable. Many molecular modeling studies have been devoted to the problem of ISC in organic materials. In 2012, Marian summarized the theoretical principles and calculation methods of SOC [25]. In 2017, Bredas discussed how ΔE_{ST} and SOC influence the RISC rate constants [179]. In 2016, Peng et al. defined a parameter, n-orbital composition, describing the effects of heteroatoms on SOC matrix elements and the states involved in ISC and RISC [6].

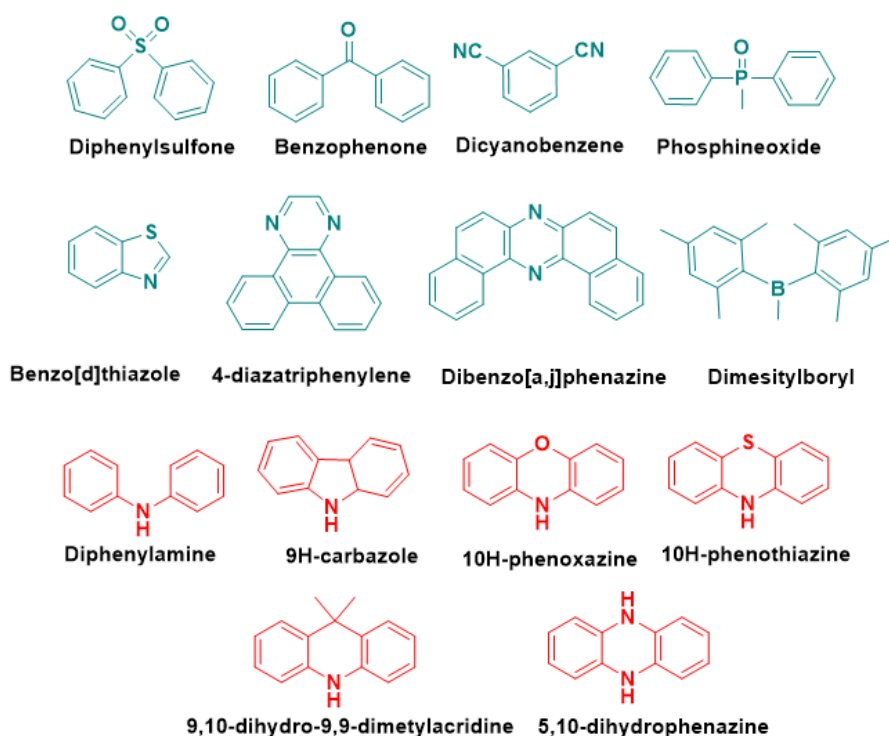


Figure 5.2. Acceptor (blue) and donor (red) moieties in TADF literature.

It should also be noted that in RISC, in coherence with thermal activation, the rate constant depends also on the Boltzmann constant (k_B) and the temperature. As reported in literature, D-A structures are not the only possible molecular arrangements for TADF materials, other designs, such as, D- π -A, D- π -A- π -D may be envisaged. In all these cases HOMOs and LUMOs are spatially separated leading to small ΔE_{ST} gaps, high SOC and blue color emission. The main aim of incorporating donor and acceptor groups is enhancing charge-transfer (CT) character leading to high efficiency emitters. The most commonly used donor moieties in TADF emitters are dimethylacridine (DMAC), phenoxazine (PXZ), carbazole

(Cz), diphenylamine (DPA), spiroacridan, phenothiazine (PTZ) and dihydrophenazine. On the other hand, the most frequently used acceptor groups involve diphenyl sulfone (DPS), benzophenone (BP), boron derivatives, cyano-substituted aromatics, triazine and pyrimidine (see Figure 5.2).

In the various molecular modeling works published to date, TADF and RISC processes have been analyzed with the help of various parameters. The most frequently used descriptors are frontier molecular orbital (FMO) distributions, ΔE_{ST} , SOC, and reorganization energy, λ . Moreover, parameters related to the topological description of the changes in the electronic density in the excited states have also been proposed and their correlation with RISC has been reported [150]. In addition to these electronic based descriptors, there have been studies focusing on the correlation between geometric parameters and the evolution of the excited state [194]. Furthermore, the probability of radiative decay from S_1 to S_0 has also been taken into account via the calculation of the corresponding oscillator strength, because a good OLED candidate should show good intrinsic luminescence via either prompt or delayed fluorescence [151].

In a previous contribution, we further investigated the effects of various descriptors to determine RISC efficiency and concluded that SOC plays an important role in shaping RISC pathways between triplet and singlet states [196]. We have also investigated the behavior of different descriptors for benzophenone based TADF emitters and performed a functional benchmark study for the molecular set under investigation [154]. In the present contribution, we assess the relationship between molecular structure and photophysical properties for a range of boron-based TADF molecules (see Figure 5.3 - 5.7).

Boron, participates in π -conjugation via its available p_z orbital, and thus enhances charge transport, and, therefore, represents an attractive choice for optoelectronic materials [197]. In 2015, Adachi and coworkers reported the first boron-based TADF emitters consisting of 10H-phenoxaborin as acceptor and N-heterocyclic donor groups [198]. In 2016, a new approach termed ‘multiresonance (MR) HOMO-LUMO separation’ has been proposed by Hatakeyama and colleagues.

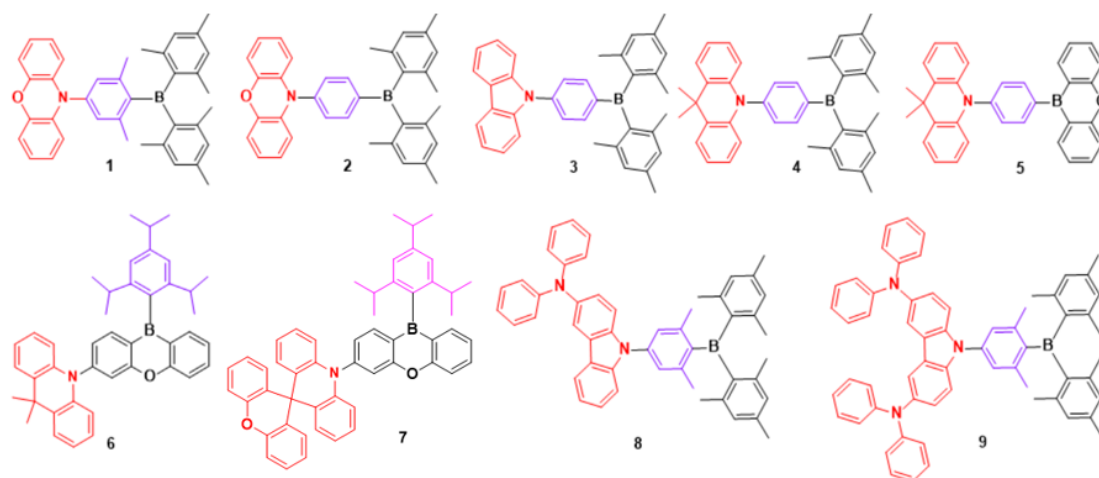


Figure 5.3. Para Substitution to $-BMe_2$ and to Boron Atom in 10H-Phenoxaboranyl Moiety.

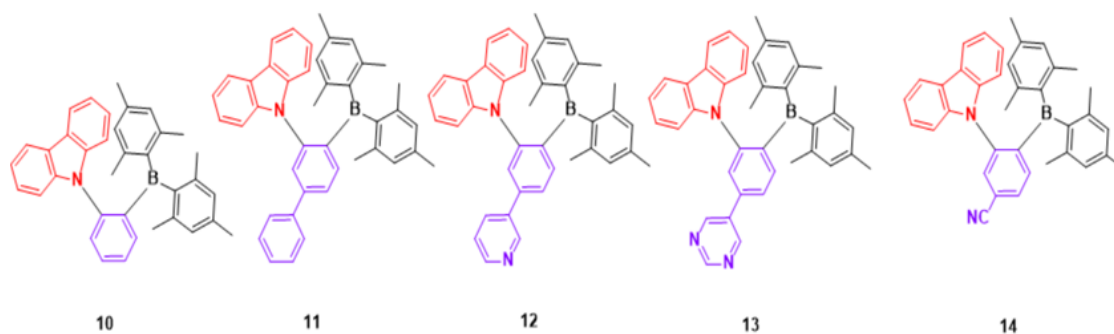


Figure 5.4. Ortho Substitution to $-BMe_2$ Acceptor Moiety.

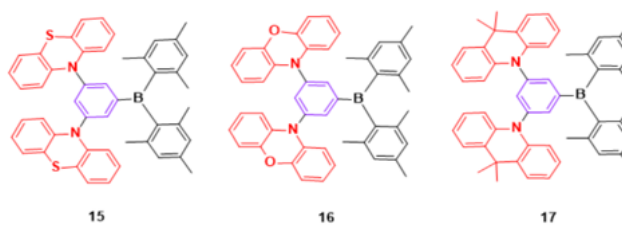


Figure 5.5. Meta Substitution to $-BMe_2$ Acceptor Moiety.

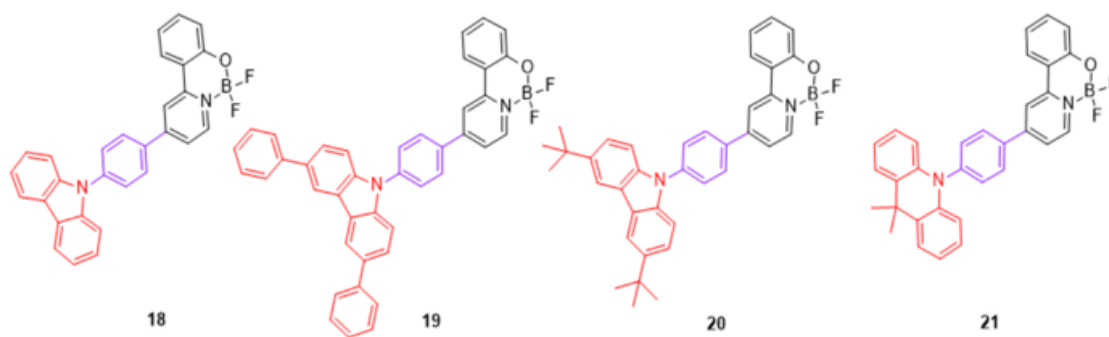


Figure 5.6. Para Substitution to $-BF_2$ Acceptor Moiety.

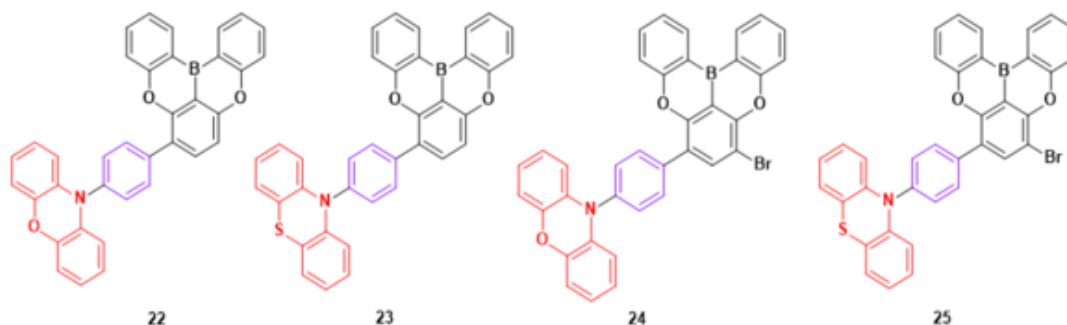


Figure 5.7. Para Substitution to OBA Acceptor Moiety.

MR is mainly observed in boron emitters in which the atom in para position with respect to Boron is substituted with nitrogen, thus enhancing the resonance effect and leading to remarkable HOMO and LUMO spatial separation [197–199]. Furthermore, it has also been observed that MR-type blue TADF emitters have high device efficiencies, and narrow emission bands with high color purity [200]. High color purity with very narrow emission bands is an important property of MR-TADF emitters, however, this feature is also accompanied by important drawbacks, such as, slower RISC rate compared to other TADF emitters [201].

One of the main strategies which can be used to accelerate RISC rate is to provide a high density of close lying ^3CT states, which can be achieved through peripheral substitution [202]. Alternatively the inclusion of heavy main group atoms such as S or Se to the molecular skeleton can be considered [203]. Finally, the inclusion of heavy metals is a suitable strategy

to increase SOC values and improve RISC rates in MR-emitters, although this reduces the economic and ecological sustainability of the devices [204]. On the other hand, it has been reported that increasing the molecular rigidity and suppressing large excited state structural changes represents an efficient approach to achieve high color purity [203]. Therefore, design strategies focused on rigidity of the scaffold have been implemented. As an alternative to fused π systems, ortho-substituted D-A structures that suppresses excited state structural changes can also be used to obtain devices with high color purity. Design strategies of boron based TADF emitters are not limited to these systems and other chromophores with various kinds of boron acceptors such as, dimesitylboryl (Mes₂B), 9,10-dihydro-9,10-diboraanthracene (DBA) [205], phenoxaboryl [206], B,N-doped analogues [207], have been proposed.

Herein, we mainly focused on the effects of various donors and boron-based acceptors on the character of the most relevant excited states. We also consider the relation between their donor acceptor strength and the emission colors as well as their influence in affecting RISC efficiencies. Moreover, we also analyze the possible electronic excitation pathways to understand the exact mechanism leading to the excited state relaxation while presenting a comprehensive comparison between the different emitting groups.

5.3. Computational Methodology

All the geometry optimizations were performed using Gaussian 16 [155] program package to model all the possible conformers of boron-based TADF emitters. Ground state geometries were optimized with Density Functional Theory (DFT) calculations; the corresponding S_1 and T_1 equilibrium geometries have been obtained at TDA level. For geometry optimizations, a series of benchmark calculations with TPSSh [53] /6-31+G(d,p), ω B97XD [208] /6-31+G(d,p) and M06-2X [156] /6-31+G(d,p) levels of theory were used and meta-hybrid M06-2X functional was chosen. This choice is also justified since it is well known that this functional performs well in reproducing electronic energies, and equilibrium geometries of compounds bearing aromatic moieties [156]. To increase the accuracy, 6-311++G(3df,3pd) [209] basis set was used, in all calculations, for sulfur atom. For selected

model compounds, the energy order of the different conformers was checked using a series of single point calculations with B3LYP [157] and TPSSh [210] on top of M06-2X optimized geometries confirming that the lowest energy conformer does not depend on the choice of the functionals.

Following the assessment of the structural parameters, a comprehensive benchmark study on the excited state properties has been conducted using Tamm Dancoff Approximation (TDA) with LC- ω PBE, M06-2X, CAM-B3LYP [158] and ω B97XD functionals. Excited state energies and oscillator strengths are the two main parameters used to judge the properties of the functionals; we observed that except for LC- ω PBE, the other three functionals behave similarly in both oscillator strength and excited state energies.

In our previous study, which has been mainly focused on the effects of functionals on descriptor analyses, we investigated the performance of M06- 2X, CAM-B3LYP and ω B97XD functionals in detail and we observed that the nature of excited state calculations with M06- 2X and ω B97XD functionals yield more reliable results compared to the CAM-B3LYP functional [196]. Figure S9 reports absolute deviations from experimental data and it is observed that except for some outliers such as; Spiroacridan-Phenoxaboryl-TIPP, DACMES3B, NOBF2-Cz [211] and NOBF2-DPCz [211], calculations with M06-2X/6-31+G(d,p) gave deviations smaller than 0.05 eV. Moreover, absolute deviations from calculations with ω B97XD /6-31+G(d,p) also yielded small values, however, it has been observed that ω B97XD could not reproduce some of the most remarkable molecules such as PXZMES3B, 10H-Phenoxaboryl-Phenyl-DMAC, DACMES3B, 2DACMES3B, B-2PTZ and B- 2DMAC. Overall, both M06-2X and ω B97XD are good performing functionals for energy gap calculations, however, compared to ω B97XD , calculations with M06-2X have smaller number of outliers.

Furthermore, the effects of the basis were assessed taking into account 6-31G(d) [124], 6-31G(d,p) [212], 6-31+G(d) [213], and 6-31+G(d,p) [124] sets. It was clearly observed that increasing the basis set does not induce any significant change on the excited state energies and the corresponding oscillator strengths. The choice of TDA over Time-Dependent DFT (TDDFT) is due to its better performance in describing both singlet and triplet excited states,

since it is not plagued with triplet instability issues [164].

The effects of conformational variability on the excited state properties was also checked concluding that when the change in equilibrium geometries do not involve the angles close to the donor moieties, their effect on excited state energies is negligible. Moreover, it has also been observed that ground state conformational changes do not occur in the donor moieties, and instead involve the acceptor fragments.

All calculations were performed taking into account solvent effects, in accordance with experiments, by using the polarizable continuum model in the integral equation formalism (IEF-PCM) [162].

The absorption spectra have been computed by generating 40 conformers through a Wigner distribution [92] based on the calculation of the harmonic vibrational frequencies as implemented in the Newton-X [165] software package. The final spectrum is obtained by the convolution of all the vertical transitions and the corresponding oscillator strengths. Absorption spectra were modeled using B3LYP, BLYP [53], PBE0 [214,215], M06-2X and ω B97XD functionals and 6-31+G(d,p) basis set. To reproduce the band shape the vertical transitions from each snapshot were convoluted using Gaussian functions of full-width at half-length (FWHL) of 0.15 eV.

The nature of excited states was assessed using Natural Transition Orbitals (NTOs) and Φ_S indices, defining the overlap between the attachment and the detachment densities that is, the electron density removed/rearranged during the excitation. NTOs and Φ_S were obtained with the Nancy-EX code [168,216] and visualized with the Avogadro [169] software package. Other parameters describing the degree of overlap between HOMO and LUMO orbitals, such as D-index, S-index and t-index were computed using the Multiwfn [217] software package. SOC elements between S_1 , and T_n states involved in RISC mechanism were calculated with Amsterdam Density Functional Code (ADF) [170], at the M06-2X/DZP [172] level of theory. Since Pople basis sets are not available in ADF, the Slater type DZP was chosen.

5.4. Results and Discussion

We report the behavior of a series of D- π -A type TADF emitters bearing boron containing acceptor moieties and different donor groups such as PXZ, PTZ, DMAC, Spiroacridan, Cz, Diphenylamino carbazole (DAC) and bis(diphenylamino) carbazole (2DAC) which are introduced to the para- (1-9, 18-25 (in Figure 5.3) or ortho- (10-17 in Figure 5.4 - 5.5) position relative to the acceptor groups. Four important and widely used acceptors, namely Dimesitylboryl (Mes2B), 10H-Phenoxaboryl, Difloroboron ($-\text{BF}_2$), and 5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (OBA) are selected to understand their effects on the electronic properties. Indeed, Mes2B unit has strong electron accepting ability coupled with p- π^* conjugation and is one of the most popular acceptor groups in TADF literature [148]. 10H-Phenoxaboryl is important due to its rigid structure, which is highly efficient in assuring orthogonal arrangements, hence favoring small singlet-triplet gaps [135]. On the other hand, the $-\text{BF}_2$ unit, thanks to its strong electron withdrawing capability provides low LUMO levels leading to an increase in intramolecular charge-transfer (ICT) character [218]. The last acceptor unit OBA is usually described as providing large torsion angle making it an efficient acceptor group in blue emitting TADF materials [52].

5.4.1. Benchmark Analyses

To make sure that the methodology that we determined in our first article is appropriate for the boron-based emitters, we performed a comprehensive functional benchmark analysis. As reported in Figure 5.8, we observed that increasing the basis set does not change the energies of excited states and the oscillator strengths. On the other hand, a series of widely used DFT functionals such as, LC- ω PBE, M062X, CAMB3LYP and ω B97XD have been used for the same excited state properties; excited state energies and oscillator strengths. In our analyses, we observed that except LC- ω PBE, other three functionals behave similarly in both oscillator strength values and excited state energies.

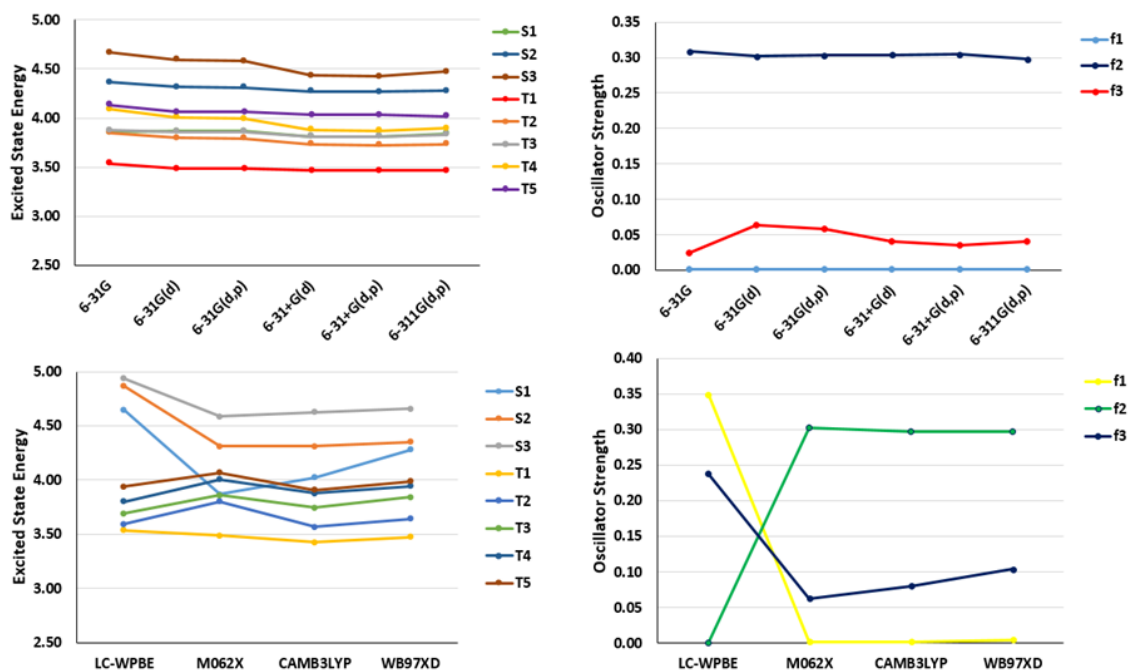


Figure 5.8. Basis set and functional benchmark of compound 10H-Phenoxaboryl-Ph-DMAC. Basis set benchmark has been calculated with M06-2X functional, and functional benchmark has been calculated with 6-31G(d) basis set.

5.4.2. Torsion Angle Analyses

A comprehensive conformational analysis was firstly performed to investigate the geometrical features of TADF molecules. As reported in literature, orthogonality, which results in decreased Electron-Hole overlap and small ΔE_{ST} values is one of the key features for TADF performance [219]. Table 5.1 reports the torsion angles between donor groups and phenyl linkers in the boronbased TADF emitters (see also the schematic representation in Figure 5.9). As shown in Table 5.1, dimethylacridine and spiroacridan stand out with their perfectly orthogonal geometry (compounds 4-7), followed by phenoxazine and phenothiazine with torsion angle close to 80°. On the other hand, carbazole, which is known for its poor TADF activity has a torsion angle of 50° (para position) most probably since its five-membered central ring has smaller steric hindrance compared to the other donors presenting sixmembered rings.

Table 5.1. Torsion angles of the donor units modeled in this study and the representation of torsion angle in model NOBF2-DMAC [46] emitter.

Donor Moiety	Torsion Angle (D - π linker)
Phenoxazine (PXZ)	~ 80
Carbazole (Cz) – in para position	~ 50
Carbazole (Cz) – in ortho position	~ 75
Dimethylacridine (DMAC)	~ 90
Spiroacridan	~ 90
Diphenylamino carbazole (DAC)	~ 50
Bis(Diphenylamino carbazole) (2DAC)	~ 50
Phenothiazine (PTZ)	~ 80

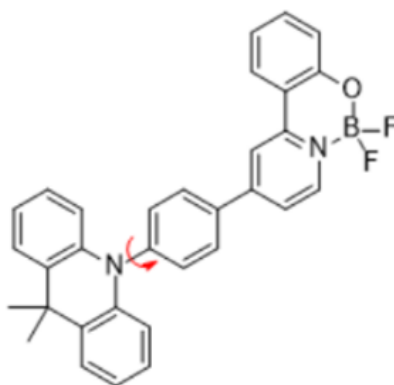


Figure 5.9. Representation of torsion angle in model NOBF2-DMAC [46] emitter.

This fact is also partially justified by the observation that replacing the substituent to the ortho position increases orthogonality and leads to an acceptable torsion of about 75° as shown for Cz-o-B (10), [66] Cz-Ph-o-B (11) [220], Cz-Pyridine-o-B (12) [221], Cz-Pyrimidine-o-B (13) and Cz-CN-o-B (14) [221].

In light of these results, it can be stressed that changing the location of carbazole from para to ortho position appears as an effective strategy to increase steric hindrance and induce orthogonality, thus, decreasing ΔE_{ST} . In other carbazole containing donor moieties, namely DAC and 2DAC, it was observed that the addition of phenyl rings on carbazole does not change steric hindrance, keeping the torsion angles close to 50° .

Thus, while DMAC, PXZ, Spiroacridan, and PTZ donors have favorable orthogonal

geometrical arrangements, carbazole geometry may be tuned by changing its regioisomery and increasing its steric hindrance. The torsion angles of the acceptor moieties were also studied to infer the degree of separation between π - linkers and acceptor moieties, and hence the possible disruption of conjugation leads to the separation of electron and hole orbitals.

The acceptor groups discussed in this study have a torsion angle of $\approx 50^\circ$ and thus their effect on TADF efficiency seems more limited. This structural feature further suggests that the modifications in donor moiety should lead to a greater change in ICT. This assumption will be examined in more detail in the following sections. To assess the excited state properties of the emitters we also optimized S_1 and T_1 geometries and in particular we evidenced the appearance of ‘Excited State Twisting’ as pictorially represented in Figure 5.10.

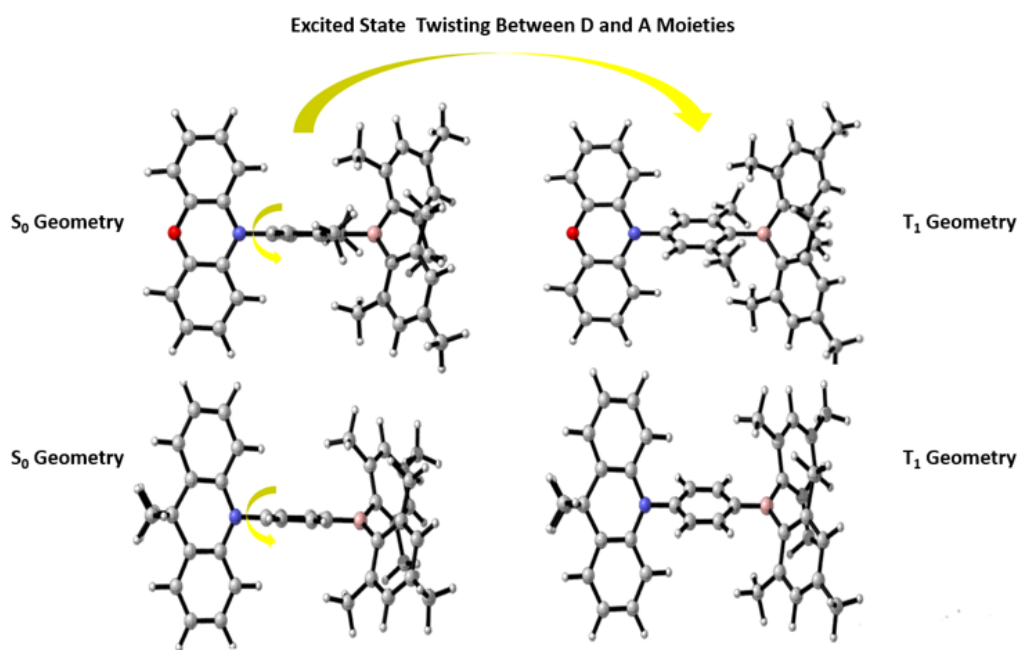


Figure 5.10. Excited state twisting observed in T_1 geometries.

Indeed, the orthogonality between donor and acceptor moieties decreases in the case of the lowest triplet states. The twisted geometry partially reinstates conjugation and will favor more local excited states.

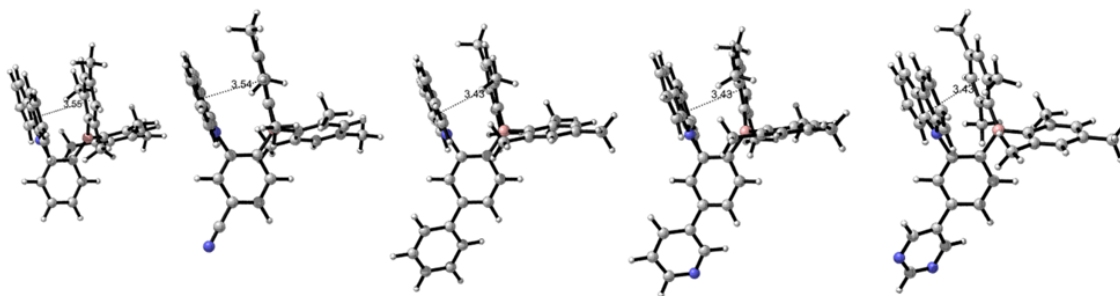


Figure 5.11. Distances (Angstrom) between the centroids of aromatic rings computed at M06-2X/6-31+G(d,p) level of theory.

Moreover, the optimized structures reported in Figure 5.11 show that the ortho substituted TADF emitters exhibit intramolecular $\pi - \pi$ interactions between the carbazole unit and the mesityl group of acceptor moiety, the two interacting unit being at about 3.43- 3.55 Å distance. Within the whole set, intramolecular $\pi - \pi$ interactions were observed only in emitters where D/A groups are in close proximity and showing face-to-face arrangement. Similarly, this kind of intramolecular interaction is expected to induce an increased rigidity via the suppression of rotation around C-C bond between the central phenyl group and donor moiety or the mesityl group of the acceptor. This feature is expected to affect not only the TADF descriptors reported in our study such as Electron/Hole separation and ΔE_{ST} , but also the photoluminescence quantum yield (PLQY) of these kinds of emitters, reducing occurrence of competitive non-radiative decays [222].

Thus, ortho- substitution can lead to favorable device properties, such as, high PLQY and faster RISC which can be observed via the smaller Electron/Hole overlap and ΔE_{ST} values. Moreover, SOC for these kind of emitters are larger than for the para- substituted ones, such as Cz-Ph-Mes2B. The larger SOC values of ortho- substituted emitters can be attributed to the hybridization of charge transfer and local excitation states, which is a behavior observed in molecules exhibiting intramolecular $\pi - \pi$ interactions between cofacially packed donor and acceptor moieties [223].

5.4.3. Oscillator Strength

To unravel the photoexcitation mechanisms, we further analyzed the magnitudes of oscillator strengths and reported these values in Table 5.2. As a consequence of spatial separation between HOMO and LUMO orbitals, excitations usually feature strong CT character, a behavior which leads to very small oscillator strengths, and is not compatible with intense emission requirements. Therefore, separation between FMOs should be optimized to both minimize ΔE_{ST} while maintaining sufficient oscillator strength to make light emission possible. Herein, firstly oscillator strengths for $S_0 \rightarrow S_1$ transitions are determined and data from this analysis are used to observe the effects of geometric parameters on excitation to the first excited singlet state.

As represented in Table 5.2, a large group of compounds exhibit vanishing oscillator strengths which are caused by large twist angle between donor and their adjacent moieties, which result in poor overlap between electron and holes. On the contrary, emitters with small twist angles such as Cz-Ph-Mes2B, DACMES3B, 2DACMES3B, NOBF2-Cz, NOBF2-DPCz, and NOBF2-DTCz exhibit larger oscillator strengths compared to other emitters. In addition to this expected trend, we have also observed that despite having large twist angles, NOBF2- and OBA-based compounds exhibit large oscillator strengths ($f \sim 0.3-0.4$). This indicates that the $S_0 \rightarrow S_1$ transitions for these compounds are dominant in their absorption spectra. Indeed, large oscillator strength of NOBF2- and OBA- based emitters are consistent with their LE character in S_1 states.

Table 5.2. Torsion angles between donor and π bridges of S_0 geometries and oscillator strengths corresponding to $S_0 \rightarrow S_1$ transitions computed at M06-2X/6-31+G(d,p) level of theory.

Oscillator Strengths		
COMPOUNDS	$S_0 \rightarrow S_1$	Torsion Angle (GS)
PXZ-Mes2B	0.0013	104.01
PXZ-Ph-Mes2B	0.0028	101.76
Cz-Ph-Mes2B	0.581	52.44
DMAC-Ph-Mes2B	0.0019	90.41
10H-Phenoxaboryl-Phenyl-DMAC	0.0016	90.64
DMAC-Phenoxaboryl-TIPP	0.0001	88.39
Spiroacridan-Phenoxaboryl-TIPP	0.0026	82.55
DACMES3B	0.4013	53.76
2DACMES3B	0.4544	52.48
Cz-o-B	0.0148	75.25
Cz-Ph-o-B	0.0231	75.71
Cz-Pyridine-o-B	0.0201	77.91
Cz-Pyrimidine-o-B	0.0158	77.95
Cz-CN-o-B	0.0105	75.59
B-2DMAC	0.0016	3.96
B-2PTZ	0.0019	102.26
B-2PXZ	0.0012	101.69
NOBF2-Cz	1.4944	52.3
NOBF2-DPCz	0.976	51.78
NOBF2-DTCz	0.844	50.07
NOBF2-DMAC	0.5853	89.52
OBA-O	0.3246	78.4
OBA-S	0.3266	101.12
OBA-Br-O	0.3485	77.72
OBA-Br-S	0.3477	101.79

5.4.4. Energy Splitting Between S_1 and T_n States (ΔE_{ST})

Although, usually TADF compounds should have ΔE_{ST} values smaller than 0.1 eV, some TADF emitters with singlet–triplet energy splitting larger than this threshold have been reported [39].

For the set of molecules under investigation, the energy gaps between S_1 and the first five triplet states have been computed at M06-2X/6-31+G(d,p) and ω B97XD /6-31+G(d,p)

levels of theory (see Table 5.3 and Table 5.4). The calculated energy gaps were compared with experimental data and, as reported in Table 5.3, we found that the experimental energy gaps involved in RISC are, globally, well reproduced when considering the gaps between S_1 and the closest triplet states.

It should also be underlined that some energy gaps represented in Table 5.3 have negative signs, which indicate that the relevant triplet state is higher than the S_1 state. This includes different kind of compounds such as PXZMES3B, 10H-Phenoxaboryl-Phenyl-DMAC 2DACMES3B, Cz-Pyridine-o-B, Cz-Pyrimidine-o-B, Cz-CN-o-B, B-2PXZ, B- 2DMAC, NOBF2-DTCz,[46] NOBF2-DMAC, OBA-O, OBA-S, OBABr- O, OBA-Br-S. Thus, possible reverse internal conversion R(IC) pathways between T_1 and T_n levels [147] cannot be excluded for these compounds.

In addition to ISC/RISC analyses based on ΔE_{ST} values, we also examined the relation between torsion angles and the ΔE_{ST} values. As we discussed previously, the analyses of torsion angles show that PXZ, DMAC, Spiroacridan and PTZ moieties lead to orthogonal structures. On the other hand, Cz based emitters have 50o torsion angles which are far from orthogonality. In light of this structural analysis, ΔE_{ST} values of PXZ, DMAC, Spiroacridan and PTZ containing emitters are expected to be smaller than the Cz containing emitters. As shown in Table 5.3, the calculated ΔE_{ST} values sufficiently reproduces the expected correlation. For instance, while PXZ-Ph- Mes2B, DMAC-Ph-Mes2B and Spiroacridan-Phenoxaboryl-TIPP have ΔE_{ST} smaller than 0.1 eV; Cz-Ph-Mes2B, Cz-o-B and NOBF2-Cz emitters have ΔE_{ST} larger than 0.1 eV.

Table 5.3. Energy splitting (in eV) between S_1 and first five triplet levels computed at M06-2X/6-31+G(d,p) level of theory.

Compounds	$\Delta E(S_1-T_1)$	$\Delta E(S_1-T_2)$	$\Delta E(S_1-T_3)$	$\Delta E(S_1-T_4)$	$\Delta E(S_1-T_5)$	Experiment
PXZMES3B (1)	0.231	0.185	0.156	0.008	-0.063	0.008
PXZ-Ph-Mes2B (2)	0.03	-0.006	-0.059	-0.116	-0.351	0.033
Cz-Ph-Mes2B (3)	0.463	0.319	0.248	0.177	0.085	0.46
DMAC-Ph-Mes2B (4)	0.01	-0.047	-0.103	-0.198	-0.342	0.041
10H-Phenoxaboryl-Phenyl-DMAC (5)	0.341	0.085	0.005	-0.062	-0.223	0.013
DMAC-Phenoxaboryl-TIPP (6)	0.014	-0.022	-0.22	-0.358	-0.573	0.06
Spiroacridan-Phenoxaboryl-TIPP (7)	0.933	0.476	-0.065	-0.222	-0.39	0.01
DACMES3B (8)	0.413	0.348	-0.212	-0.456	-0.543	0.019
2DACMES3B (9)	0.476	0.304	0.173	0.144	0.058	0.021
Cz-o-B (10)	0.24	0.127	0.056	-0.106	-0.133	0.15
Cz-Ph-o-B (11)	0.234	0.056	0.027	-0.055	-0.141	0.18
Cz-Pyridine-o-B (12)	0.215	0.053	0.007	-0.085	-0.165	0.13
Cz-Pyrimidine-o-B (13)	0.192	0.036	-0.02	-0.146	-0.209	0.08
Cz-CN-o-B (14)	0.156	-0.005	-0.087	-0.311	-0.342	0.05
B-2PTZ (15)	0.18	0.166	0.059	-0.021	-0.049	0.03
B-2PXZ (16)	0.083	0.021	-0.109	-0.139	-0.161	0.039
B-2DMAC (17)	0.367	0.066	-0.101	-0.124	-0.188	0.03
NOBF2-Cz (18)	0.571	0.433	0.044	-0.006	-0.051	0.2
NOBF2-DPCz (19)	0.361	0.163	-0.331	-0.368	-0.429	0.08
NOBF2-DTCz (20)	0.664	0.416	0.335	0.276	0.167	0.22
NOBF2-DMAC (21)	0.583	0.392	0.329	0.2	0.087	0.2
OBA-O (22)	0.606	0.386	0.075	0.024	-0.011	0.09
OBA-S (23)	0.606	0.418	0.078	0.024	-0.061	0.09
OBA-Br-O (24)	0.608	0.327	0.052	-0.034	-0.059	0.04
OBA-Br-S (25)	0.608	0.357	0.054	-0.036	-0.101	0.07

Table 5.4. Energy splitting between S_1 and first five triplet levels computed at ω B97XD/6-31+G(d,p) level of theory.

Compounds	$\Delta E(S_1-T_1)$	$\Delta E(S_1-T_2)$	$\Delta E(S_1-T_3)$	$\Delta E(S_1-T_4)$	$\Delta E(S_1-T_5)$	Experiment
PXZMES3B	0.687	0.645	0.57	0.407	0.227	0.008
Dimesitylboryl-Phenyl-Phenoxazine	0.499	0.353	0.314	0.1	0.055	0.033
Dimesitylboryl-Phenyl-Carbazole	0.679	0.589	0.528	0.5	0.464	0.46
Dimesitylboryl-Phenyl-DMAC	0.366	0.334	0.3	0.135	0.049	0.041
10H-Phenoxaboryl-Phenyl-DMAC	0.759	0.619	0.389	0.368	0.192	0.013
DMAC-Phenoxaboryl-TIPP	0.316	0.23	0.022	0.015	-0.028	0.06
Spiroacridan-Phenoxaboryl-TIPP	0.441	0.354	0.149	0.09	0.034	0.01
DACMES3B	0.614	0.531	0.501	0.426	0.413	0.019
2DACMES3B	0.623	0.417	0.378	0.354	0.302	0.021
Cz-o-B	0.398	0.332	0.26	0.248	0.118	0.15
Cz-Ph-o-B	0.462	0.279	0.253	0.237	0.19	0.18
Cz-Pyridine-o-B	0.426	0.27	0.231	0.209	0.171	0.13
Cz-Pyrimidine-o-B	0.38	0.246	0.19	0.169	0.128	0.08
Cz-CN-o-B	0.282	0.15	0.074	0.019	-0.051	0.05
B-2PTZ	0.544	0.529	0.382	0.303	0.116	0.03
B-2PXZ	0.382	0.36	0.243	0.196	0.066	0.039
B-2DMAC	0.714	0.322	0.298	0.295	0.149	0.03
NOBF2-Cz	0.731	0.624	0.391	0.206	0.177	0.2
NOBF2-DPCz	0.558	0.189	0.111	0.015	0.013	0.08
NOBF2-DTCz	0.736	0.555	0.49	0.449	0.198	0.22
NOBF2-DMAC	0.701	0.57	0.423	0.319	0.163	0.2
OBA-O	0.675	0.584	0.325	0.12	0.1	0.09
OBA-S	0.675	0.584	0.328	0.158	0.103	0.09
OBA-Br-O	0.678	0.536	0.311	0.073	0.07	0.04
OBA-Br-S	0.678	0.534	0.313	0.111	0.071	0.07

5.4.5. Singlet Triplet Alignment

As represented in Figure 5.12, the Jablonski diagrams obtained at GS, S_1 and T_1 equilibrium geometries show different trends in both the energy and the nature of the involved states. In particular, large differences in the state alignment depending on the equilibrium geometry are present. This in turn limits considerably the possibility to rationalize TADF from considerations drawn at Franck-Condon, without considering the excited state relaxation. Indeed, for the compounds represented in Figure 5.12, at Franck-Condon geometry, S_1 is in close proximity to a manifold of triplet states, which could possibly lead to thermally activated ISC towards different states. However, this quasi-degeneracy in the triplet manifold is lifted at both S_1 and T_1 equilibrium geometry, where only the lowest triplet state remains accessible. Furthermore, we also observed that the natures of S_1 and T_1 states depends on the geometry.

Indeed, at the S_1 equilibrium geometry both states have CT character, which in turn should lead to small SOC and low ISC probability. Conversely, at T_1 equilibrium geometries the two states are respectively local and charge-transfer, hence the SOC increases, favoring RISC, despite the slight increase of the energy gap.

5.4.6. Nature of States

In our previous studies, we have stressed the importance of Natural Transition Orbitals (NTOs) in analyzing the changes of the electronic density in the S_1 and T_1 states [154]. Herein, we characterize such changes with different parameters such as: the density based descriptor D-index, which is the distance between electron and hole centroids, the Sm index, defining the overlap between electrons and holes, the t-index, which measures the degree of separation between frontier molecular orbitals, and finally, the Φ_S index which can be defined as the overlap between attachment (electron) and detachment (hole) densities [168].

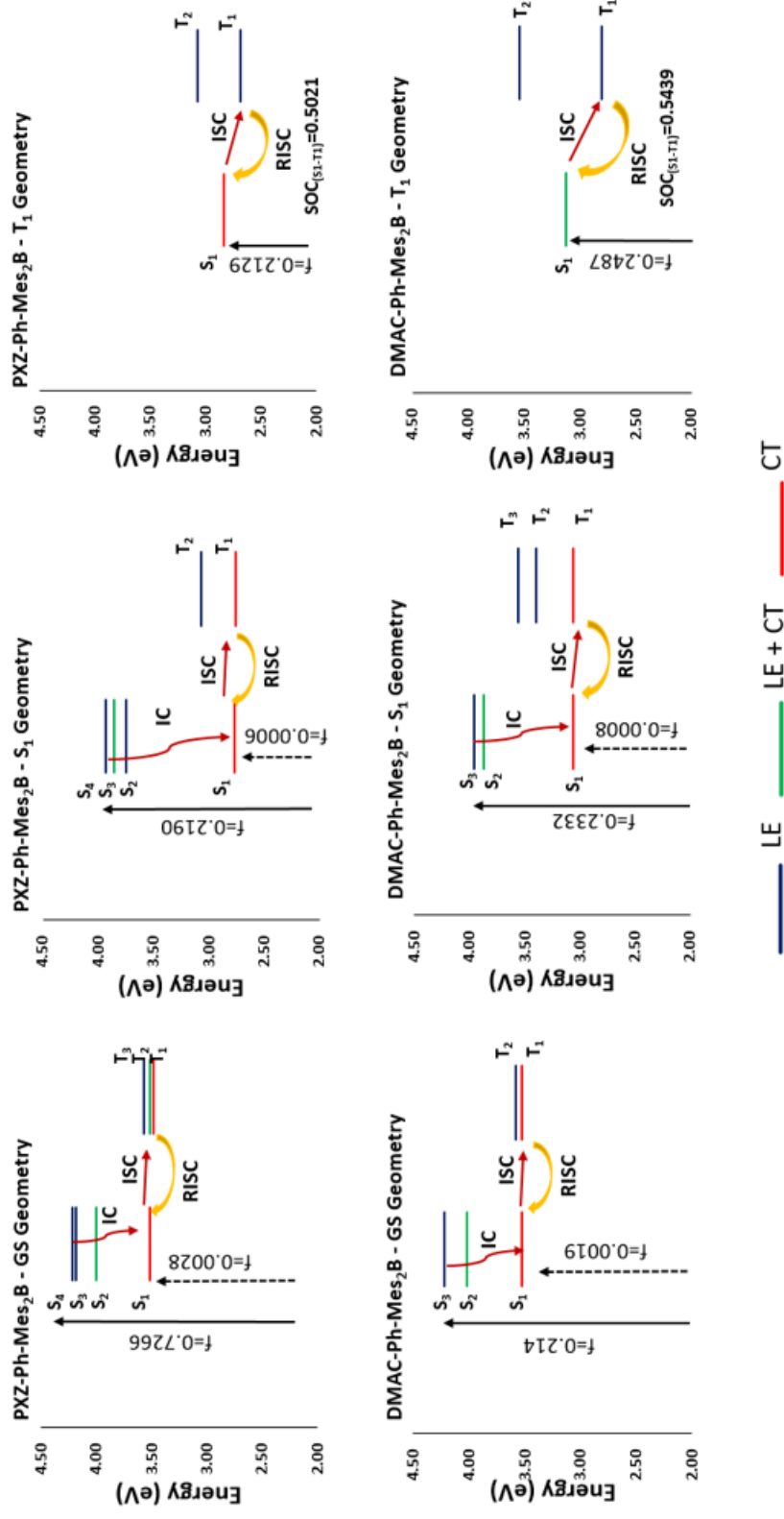


Figure 5.12. Jablonski diagrams for GS (S_0), S_1 and T_1 geometries of PXZ-Ph-Mes₂B and DMAC-Ph-Mes₂B computed at M06-2X/6-31+G(d,p) level of theory. Blue, green and red lines correspond to LE, LE+CT mixed and CT states respectively.

The most important structural reorganizations are observed for the T_1 states and our calculations predict that the corresponding planarization is enhancing the LE nature of the state. This effect can also be witnessed by the change in the topological descriptors computed at T_1 or Franck-Condon geometries, suggesting a different diabatic nature for this state. As shown in Table 5.5, the nature of S_1 and T_1 states are different at S_0 and T_1 equilibrium geometries. The reason behind this behavior may be traced to the large structural reorganization, which is observed upon excitation.

As we stated previously, the decrease in orthogonality, which is observed in T_1 state geometries, leads to higher LE character. Due to the time-scales of TADF-involved processes, the systems have enough time to equilibrate along the T_1 potential energy surface. Thus, since we are mostly interested in RISC starting from T_1 state, we mainly focused on the descriptors obtained from the optimized T_1 geometries. As can be seen from Table 5.6, the D indices of the T_1 states are systematically smaller than the corresponding indices for the S_1 states, again pointing to a larger LE character of the former. Moreover, we observe that the D indices of S_1 are generally larger than 3 Å clearly identifying these states as charge-transfer. However, D indices of the S_1 states for the OBA-S, and OBA-Br-S, are found to be smaller than 1 Å, which can indicate that LE character is here dominant. The same behavior is also confirmed by the other complementary descriptors including Φ_S . However, a sharp separation between LE (close to 1.0) and CT (close to 0.0) value is observed for this descriptor while smoother transitions were observed for the D index. Thus, Φ_S index appears, at least to this respect, as a more reliable indicator for precisely assigning the natures of these states.

Indeed, as shown in Table 5.6, for the S_1 state Φ_S , especially for PXZ and DMAC containing molecules, is mostly around 0.5 indicating mixed CT-LE character, while Cz-containing molecules exhibit dominant LE character with high Φ_S values around 0.7. On the other hand, Φ_S for the T_1 state are generally found to lie close to 0.8, indicating dominant LE natures.

Table 5.5. Natures of S_1 and T_1 states computed from S_0 and T_1 geometries at M062X/6-31+G(d,p) level of theory.

Compounds	S_0 Geometry		T_1 Geometry		Torsion Angle Between D and A Groups or D and π Bridges	
	S_1	T_1	S_1	T_1	S_0 Geometry	T_1 Geometry
PXZMES3B (1)	CT	LE	LE+CT	LE+CT	-101.01	-64.63
PXZ-Ph-Mes2B (2)	CT	LE+CT	LE+CT	LE+CT	-101.76	68.34
Cz-Ph-Mes2B (3)	CT+LE	LE	LE+CT	LE+CT	-52.44	42.46
DMAC-Ph-Mes2B (4)	CT	CT	LE+CT	LE+CT	-90.41	-63.6
10H-Phenoxaboryl-Phenyl-DMAC (5)	CT	LE	CT	LE+CT	90.64	64.85
DMAC-Phenoxaboryl-TIPP (6)	CT	CT	CT	CT	88.39	69.92
Spiroacridan-Phenoxaboryl-TIPP (7)	CT	LE	CT	CT	-82.55	-66.18
DACMES3B (8)	LE+CT	LE+CT	LE+CT	LE+CT	-53.76	49.88
2DACMES3B (9)	CT	LE+CT	LE+CT	LE+CT	-52.43	48.9
Cz-o-B (10)	LE+CT	LE	LE+CT	LE+CT	75.25	49.1
Cz-Ph-o-B (11)	CT	LE	LE+CT	LE+CT	75.71	-47.58
Cz-Pyridine-o-B (12)	CT	LE	LE+CT	LE+CT	-77.91	-47.94
Cz-Pyrimidine-o-B (13)	CT	LE	LE+CT	LE+CT	75.75	-77.96
Cz-CN-o-B (14)	CT	LE+CT	LE+CT	LE+CT	78.3	50.82
B-2PTZ (15)	CT	LE	CT	LE+CT	-102.26	81.05
B-2PXZ (16)	CT	LE+CT	CT	CT	101.69	82.38
B-2DMAC (17)	CT	LE	CT	LE+CT	11.88	-80.48
NOBF2-Cz (18)	LE+CT	LE+CT	LE+CT	LE+CT	-52.3	-50.48
NOBF2-DPCz (19)	LE+CT	LE+CT	CT	LE+CT	51.78	43.08
NOBF2-DTCz (20)	LE+CT	LE	LE+CT	LE+CT	50.07	42.49
NOBF2-DMAC (21)	LE+CT	LE	LE+CT	LE+CT	-89.52	68.96
OBA-O (22)	LE	LE	LE+CT	LE	78.4	112.63
OBA-S (23)	LE	LE	LE	LE	101.13	91.69
OBA-Br-O (24)	LE	LE	CT	LE	-77.72	73.94
OBA-Br-S (25)	LE	LE	LE	LE	-101.79	-91.56

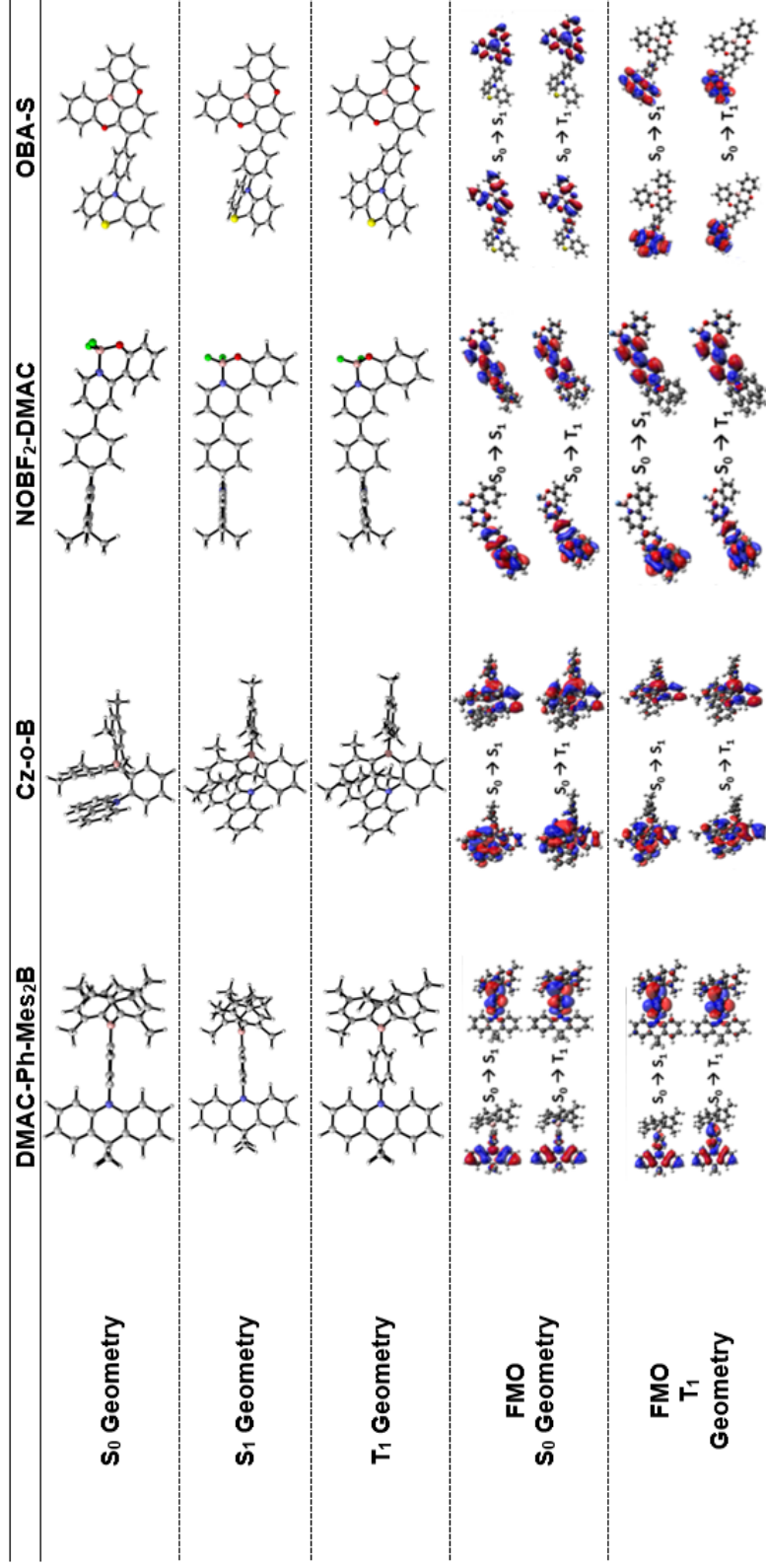


Figure 5.13. Geometric relaxations in excited states and NTO distributions computed at S_0 and T_1 geometries at M062X/6-31+G(d,p) level of theory.

Figure 5.13 summarizes the main geometry changes observed in the excited states of DMAC-Ph-Mes2B, Cz-o-B, NOBF2-DMAC and OBA-S together with the HOMO and LUMO orbitals computed at S_0 and T_1 geometries. The main geometrical changes involve the degree of orthogonality, or in some compounds such as OBA-S, the planarization of donor moieties. It is clear that the decreased orthogonality in T_1 states leads to an increased LE character in FMO. Besides this, FMO analysis of OBA-S compound shows that the donor groups, which are folded in the ground state, can stay planar in the excited state. As reported in Table S49 and Table S50, unlike previous groups with CT/ S_1 and LE/ T_1 states, OBA- and NOBF2- groups exhibit LE character in both singlet and triplet states. However, these compounds may still be characterized by small singlet triplet energy gap and large SOC, thus leading to efficient RISC. Moreover, as reported in Figure 5.14 and Table S60, our calculations show that in addition to T_1 other higher triplet states, whose population could be thermally allowed, lay below S_1 . Hence, a competition between RISC-assisted TADF (involving higher lying triplet states) and direct RISC from T_1 to S_1 can be expected.

To check, more generally the involvement of higher triplet states in our set, the energy differences between T_1 and T_2 states has been considered and close triplet states were analyzed. In Figure 5.14 we report the energy of the first two singlet and five triplet states, and we observe that generally, compounds with dimethylboryl acceptor moiety and PXZ, DMAC donor groups, (PXZMES3B, PXZ-Ph-Mes2B [49], DMAC-Ph-Mes2B [206], DACMES2B, B-2PXZ and B-2DMAC [50]), have closer T_1 and T_2 . Since T_2 levels are very close to S_1 and T_1 a possible RISC from T_2 to S_1 can be envisaged. To analyze the effects of these close lying T_2 states, their nature has been determined (see Table 5.7) and SOC between T_2 and S_1 states have been obtained.

Furthermore, in all the cases reported in Figure 5.14 the low energy triplet states are found below S_1 . Therefore, RISC from multiple triplet states may represent a possible deactivation pathway affecting the excited state dynamics and life-times.

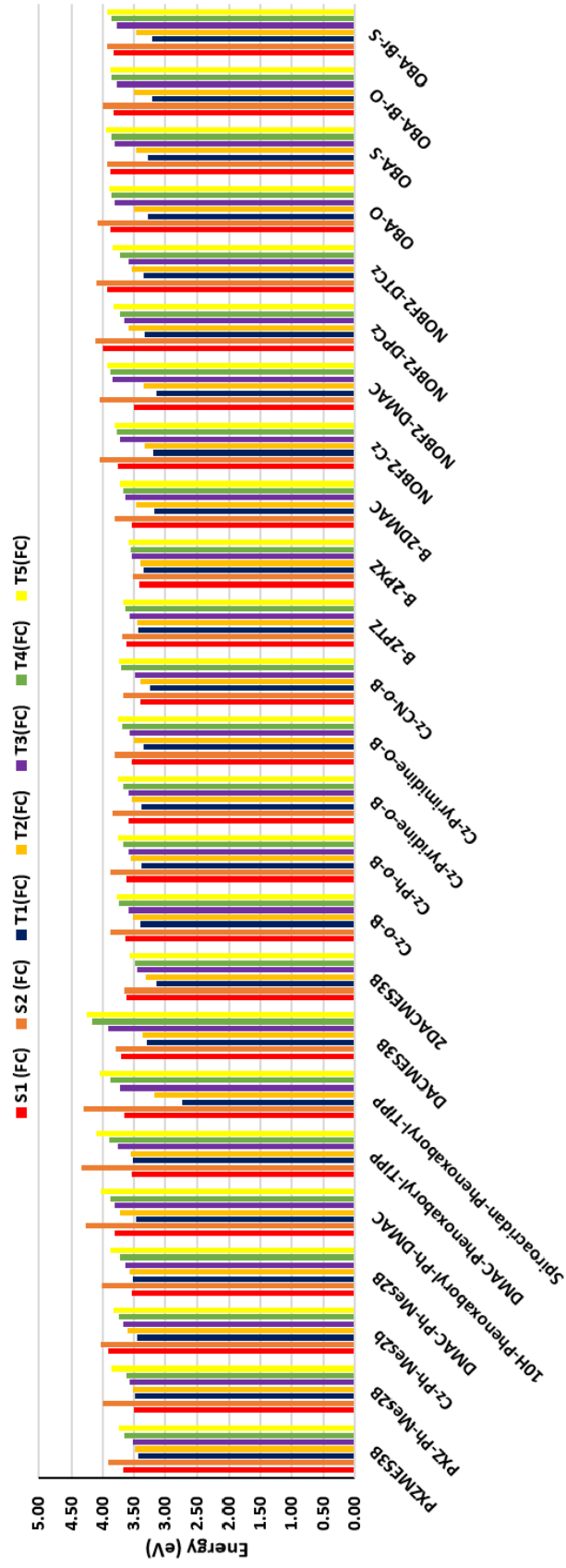


Figure 5.14. Energies of S_1 , S_2 and first five triplet states computed at M062X/6-31+G(d,p) level of theory. FC refers to the Franck Condon, i.e. the ground state equilibrium geometry.

Table 5.7. Natures of S_1 , T_1 and T_2 states computed from S_0 geometries at M062X/6-31+G(d,p) level of theory.

Emitters	S_0 Geometry		
	S_1	T_1	T_2
PXZMES3B	CT	LE	LE
PXZ-Ph-Mes3B	CT	LE+CT	LE+CT
Cz-Ph-Mes3B	CT+LE	LE	LE
DMAC-Ph-Mes3B	CT	CT	LE
10H-Phenoxaboryl-Phenyl-DMAC	CT	LE	LE
DMAC-Phenoxaboryl-TIPP	CT	CT	LE
Spiroacridan-Phenoxaboryl-TIPP	CT	LE	CT
DACMES3B	LE+CT	LE+CT	LE
2DACMES3B	CT	LE+CT	LE+CT
Cz-o-B	LE+CT	LE	LE+CT
Cz-Ph-o-B	CT	LE	LE+CT
Cz-Pyridine-o-B	CT	LE	LE+CT
Cz-Pyrimidine-o-B	CT	LE	LE+CT
Cz-CN-o-B	CT	LE+CT	LE+CT
B-2DMAC	CT	LE	CT
B-2PTZ	CT	LE	LE+CT
B-2PXZ	CT	LE+CT	LE+CT
NOBF2-Cz	LE+CT	LE+CT	LE
NOBF2-DMAC	LE+CT	LE+CT	LE
NOBF2-DPCz	LE+CT	LE	LE
NOBF2-DTCz	LE+CT	LE	LE
OBA-O	LE	LE	LE
OBA-S	LE	LE	LE
OBA-Br-O	LE	LE	LE
OBA-Br-S	LE	LE	LE

5.4.7. Spin-Orbit Coupling (SOC)

SOC which arises from the one-electron Dirac equation is responsible for mixing orbital and spin degrees of freedom, and thus allows the coupling of electronic states of different multiplicities [147]. As reported in literature [98,224,225], reducing ΔE_{ST} should be accompanied by the optimization of SOC, which in organic TADF molecules is challenging. As reported in Table 5.8, for compounds 1, 2, 3, 4, 6 and 7, the SOC values between S_1-T_2 are larger than the ones between S_1-T_1 . Moreover, SOC from upper triplet states are generally

lower than the SOC's between S_1 – T_2 , which suggests that the upper triplet states may undergo internal conversion to T_2 and T_1 followed by RISC through $T_1 \rightarrow S_1$ and $T_2 \rightarrow S_1$ channels.

The role of higher triplet states, in providing a potential pathway for RISC, has been extensively discussed in the previous studies. As reported in the literature, this has been observed in anthracene derivatives, organic dyes, and excited state intramolecular proton transfer (ESIPT) materials [226]. For anthracene, as reported by Kobayashi et al., RISC from T_2 to S_1 state can be observed when the T_1 states further excited to higher triplet states [226]. On the other hand, the origin of RISC from upper triplet states can also be attributed to the large T_2 – T_1 energy gap or the presence of heavy atom substitutions. It has been observed that the RISC from highly triplet exciton (hot exciton process) is an effective way of increasing device efficiencies and is mainly controlled by the energy level alignment of the excited states [227].

Mainly, based on the magnitude of SOC, we tried to compare our theoretical data to experimental external quantum efficiencies (see Table 5.9). Our results show that the computed SOC's are sufficient to fully reproduce the experimental results. Yet, care should be taken when analyzing the experimental efficiencies, since the conditions of the preparation of the device may be important in dictating the overall performance. Yet, even if the selected molecules have been studied under different conditions some valuable tendencies can be extracted. Indeed, compounds with SOC above 0.4 cm^{-1} usually exhibit efficiencies between 14.0 % and 23.0 %. Conversely, SOC below the 0.4 cm^{-1} threshold correlates with efficiency lower than 14.0 %, with two exceptions which are DACMes3B, 2DACMes3B and, PXZ-Mes3B, whose efficiency is high despite the small SOC. However, the high efficiencies of these emitters can be attributed to their extremely small ΔE_{ST} less 0.04 eV, which can thus favor RISC from an energetical point of view.

Table 5.8. Spin – orbit coupling values computed at M06-2X/DZP level of theory.

COMPOUNDS	SOC(S_1-T_1)	SOC(S_1-T_2)
PXZ-Mes3B	0.393	0.835
PXZ-Ph-Mes3B	0.502	1.436
Cz-Ph-Mes3B	0.213	0.733
DMAC-Ph-Mes3B	0.544	0.702
10H-Phenoxaboryl-Phenyl-DMAC	0.619	0.565
DMAC-Phenoxaboryl-TIPP	0.554	1.031
Spiroacridan-Phenoxaboryl-TIPP	0.542	1.093
DACMES3B	0.215	0.227
2DACMES3B	0.21	0.04
Cz-o-B	0.301	1.265
Cz-Ph-o-B	0.207	0.491
Cz-Pyridine-o-B	0.222	0.483
Cz-Pyrimidine-o-B	0.305	1.001
Cz-CN-o-B	0.495	1.124
B-2DMAC	0.406	0.411
B-2PTZ	0.369	0.202
B-2PXZ	0.077	1.153
NOBF2-Cz	0.425	0.169
NOBF2-DMAC	0.35	0.246
NOBF2-DPCz	0.18	0.307
NOBF2-DTCz	0.184	0.308
OBA-O	0.782	0.367
OBA-S	0.009	0.008
OBA-Br-O	0.865	0.351
OBA-Br-S	0.012	0.021

Table 5.9. Experimental device efficiencies and theoretical SOC values of the investigated TADF emitters.

Emitters	η EQE (%)	SOC (S_1-T_1)
PXZ-MES3B	22.8	0.393
PXZ-Ph-Mes2B	17.3	0.502
DMAC-Ph-Mes2B	16	0.544
10H-Phenoxaboryl-Ph-DMAC	14.6	0.619
DMAC-Phenoxaboryl-TIPP	21.7	0.554
Spiroacridan-Phenoxaboryl-TIPP	20.1	0.542
DACMES3B	14	0.215
2DACMES3B	21.6	0.21
Cz-o-B	24.1	0.301
B-2PTZ	7.6	0.369
B-2PXZ	10.1	0.077
B-2DMAC	19.3	0.406
NOBF2-Cz	11	0.425
NOBF2-DMAC	13.2	0.35
NOBF2-DPCz	13.4	0.18
NOBF2-DTCz	12.7	0.184
OBA-O	17.8	0.782
OBA-S	4.4	0.009
OBA-Br-O	22.5	0.865
OBA-Br-S	9.2	0.012

Figure 5.15 represents the Jablonski diagrams of compounds Cz- Ph-Mes2B and Cz-o-B computed at M06-2X/6-31+G(d,p) level of theory. Due to the lack of orthogonality between the donor and π - bridge, Cz-Ph-Mes2B was found to have large overlap in electron and hole orbitals which lead to high ΔE_{ST} value ($\Delta E_{ST} = 0.463$ eV). In the case of ortho- substituted Cz-o-B emitter with the same donor and acceptor moieties but different isomerism, a larger separation between S_1 and T_2 states, and larger SOC (0.3008 cm^{-1}) between S_1 and T_1 states are observed. This result is attributed to the change in the nature of S_1 states in more sterically hindered ortho Cz-o-B. Indeed, this regioisomery causes a mixed CT + LE character with the increase in torsion angle with π bridge (75°), which leads to an increase in SOC value with both T_1 and T_2 states. Overall, though larger SOC values are obtained between states of different character, these values are still very small, which is a known consequence of charge transfer contribution in TADF emitters [39].

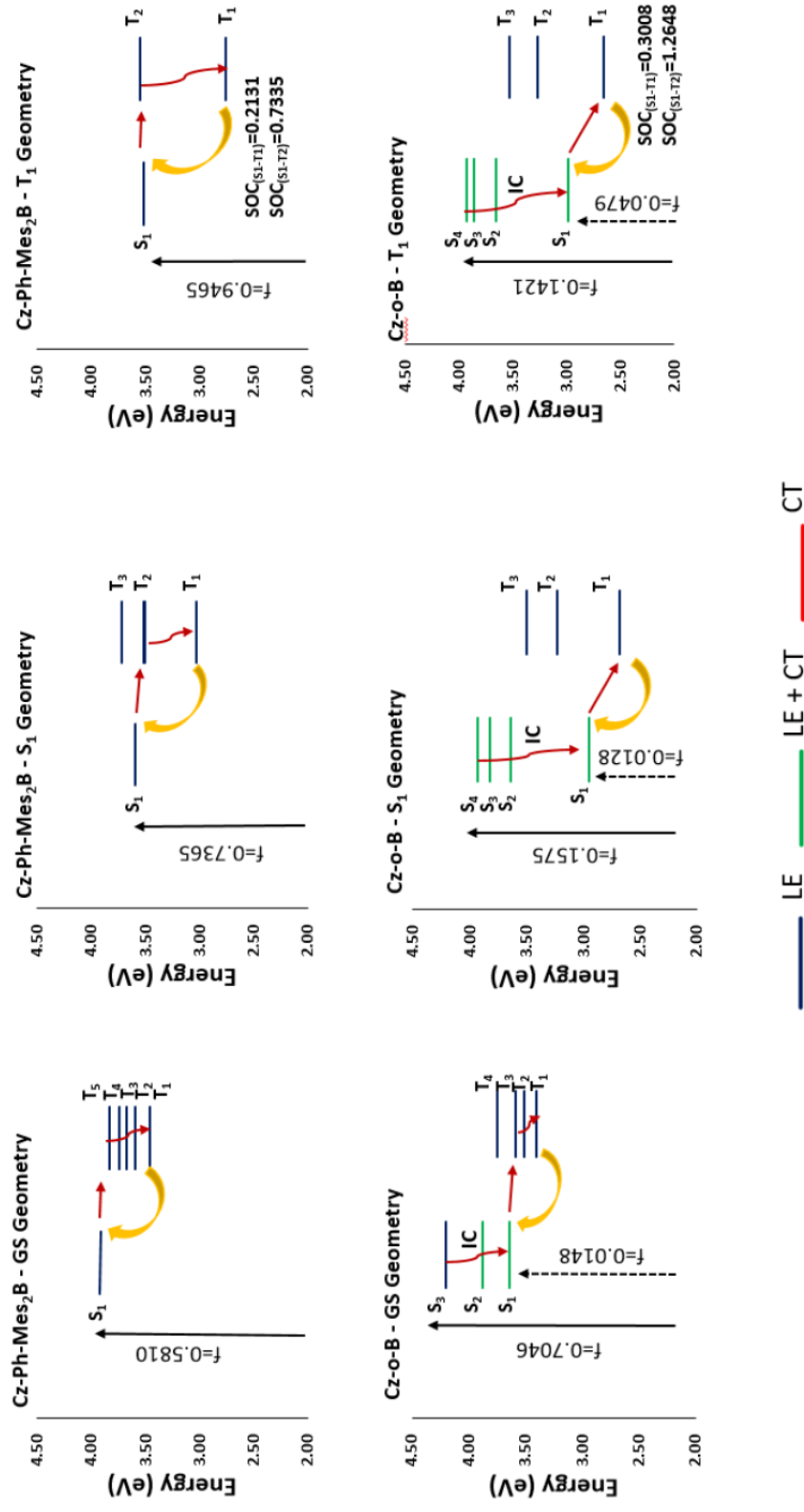


Figure 5.15. Energy level diagrams for GS, S₁ and T₁ geometries of Cz-Ph-Mes₂B and Cz-o-B emitters computed at M06-2X/6-31+G(d,p) level of theory.

5.4.8. Donor – Acceptor Strengths

Herein, we focused our attention on two important points, the desired geometries of selected donor and acceptor moieties, and the relative strengths of these units. As reported in literature, one of the crucial strategies in designing high efficiency TADF molecules is achieving a structure with spatially separated HOMO and LUMO orbitals and using strong donor and acceptor moieties is a way of having localized and separated frontier molecular orbitals. The spatial separation between HOMO and LUMO orbitals decreases the energy gap between S_1 and T_1 states, which leads to enhanced RISC processes [55]. This implies that as the strength of donating and accepting moieties increases, leading to more effective π electron transfer in conjugated systems, the HOMO–LUMO gaps (E_g) decreases [191,228,229]. Thus, reducing ΔE_{ST} is achieved by using strong donor and acceptor units [230,231].

Furthermore, the electron donating and accepting ability of D and A groups do not only affect ΔE_{ST} , but they also have an important role in tuning the emission color of TADF emitters [232]. The experimental emission wavelengths show that the molecules cover efficiently the blue and green portion of the electromagnetic spectrum. In our molecular set, we benefited from the electron accepting ability of the boron atom and we have analyzed its effect on LUMO orbitals. In general, acceptor moieties affect LUMO orbitals by reducing their energies and for boron-based emitters this behavior is globally reproduced. However, we observed that for NOBF2- based compounds, the boron atoms do not contribute to the LUMO orbitals, differently from other molecules. Indeed, while for NOBF2-Cz, NOBF2-DTCz, NOBF2-DPCz and NOBF2-DMAC boron has 1.061 %, 1.279 %, 1.274 % and 1.184 % contribution to the LUMO, respectively, in Cz-Ph-Mes2B, and DMAC-Ph-Mes2B boron achieves 25.431 % and 26.150 % contributions. This behavior indicates that the electron accepting ability of NOBF2- moiety is mainly controlled by the nitrogen atom in NOBF2-unit and the carbon atom in pyridine ring. On the other hand, in Cz-Ph-Mes2B and DMAC-Ph-Mes2B emitters with dimesitylboryl acceptor moiety, boron has a more pronounced effect on the LUMO.

It is known that as HOMO energy increases, electron donating ability increases, and as LUMO energy decreases, electron accepting ability increases, hence tuning the HOMO-LUMO gap. In Figure 5.16, HOMO-LUMO energies and ΔE_{ST} values computed at M06-2X/6-31+G(d,p) level of theory were reported. We may observe that the donor strength order is as: 2DAC > DAC > PXZ > DMAC > Spiroacridan > Cz (HOMO energies of related compounds are; -6.0765 eV, -6.1808 eV, -6.3349 eV, -6.4135 eV, -6.6450 eV, -6.8956 eV for compounds 2DACMes3B, DACMes3B, PXZ-Ph-Mes2B, DMAC-Ph-Mes2B, Spiroacridan-Phenoxaboryl- TIPP and Cz-Ph-Mes2B respectively).

On the other hand, with the help of LUMO energies, the acceptor strength order may be sketched as: 10H-Phenoxaboryl > Mes2B. Moreover, as reported in Figure 5.16 the relation between ΔE_{ST} and E_g values is consistent with the expected behavior correlating the decrease of E_g with ΔE_{ST} . This observation once again proves that the strong electron accepting and donating abilities of donor and acceptor moieties are highly beneficial for achieving small singlet–triplet energy gaps.

The electron accepting and donating strength can also be considered via the simulated absorption spectra (see Figure 5.17, 5.18, 5.19, 5.20, 5.21 and 5.22). Although, the presence of multiple absorption bands, arising from different $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, leads to a rather complicated absorption spectrum, a trend of the absorption wavelength can be easily observed, especially for the brighter $\pi \rightarrow \pi^*$ band. As shown in Figure 5.17, the lowest energy absorption band of 2DAC-Mes3B (9) takes place at longer wavelength than DAC-Mes3B (8), which is followed by PXZ-Ph-Mes2B (2), DMACPh- Mes2B (5), Cz-Ph-Mes2B (3) and 10H-Phenoxaboryl-Ph- DMAC (5) respectively. On the other hand, no significant change in the absorption spectra between 6 and 7 is observed.

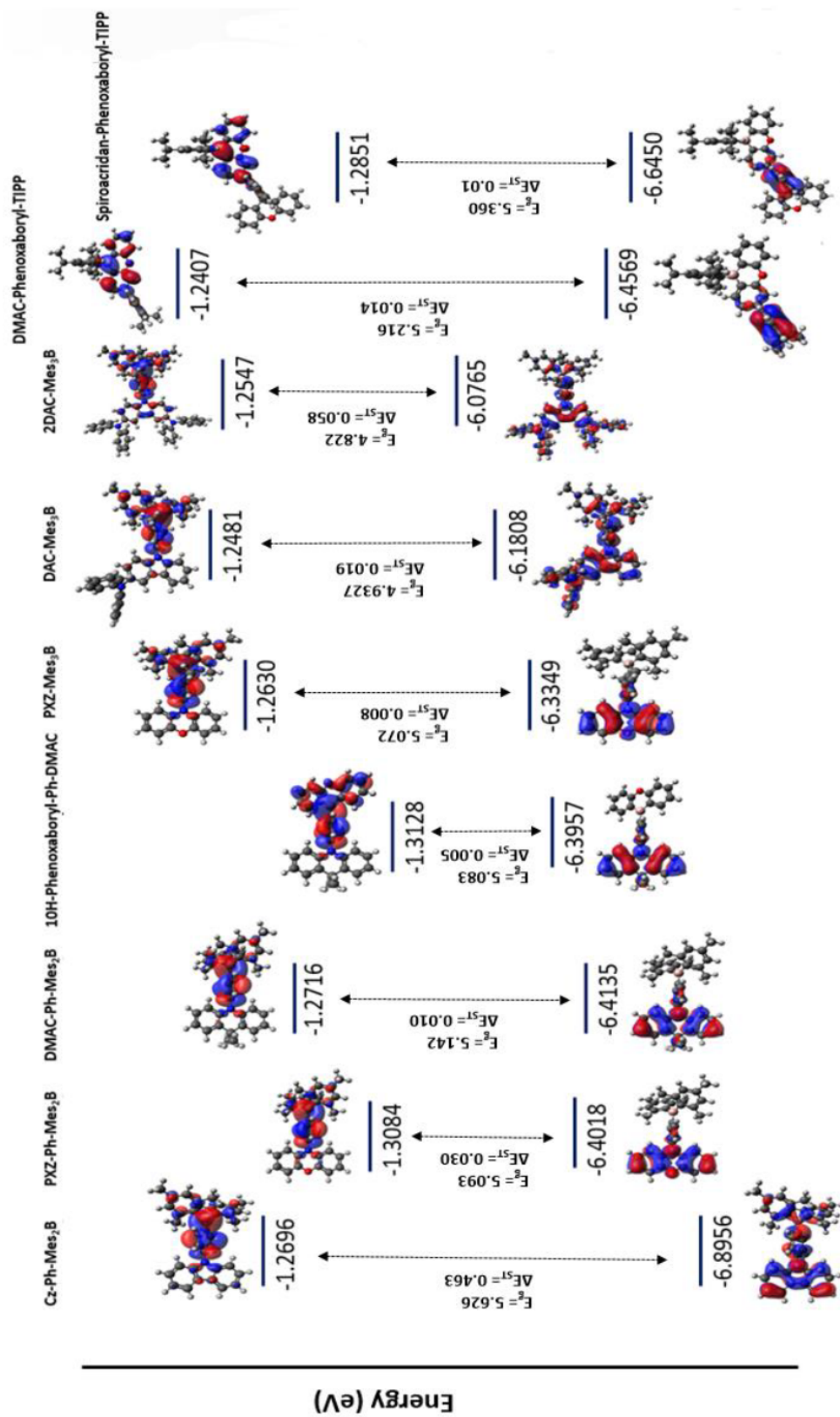


Figure 5.16. HOMO and LUMO energies of first nine compounds and frontier molecular orbital distributions computed at M06-2X/6-31+G(d,p) level of theory.

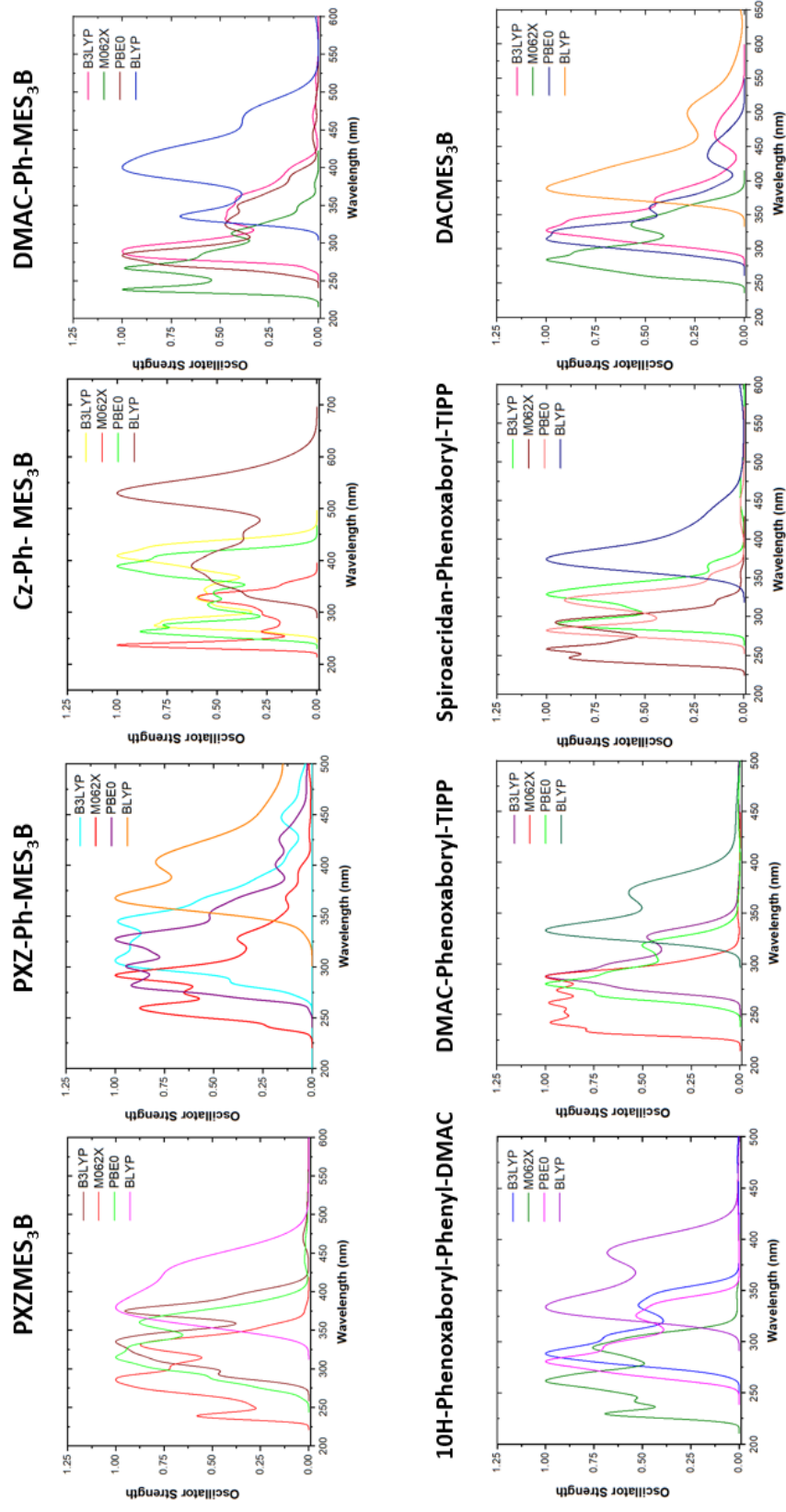


Figure 5.17. Absorption spectra of Group 1 emitters computed with different functionals.

2DACMES₃B

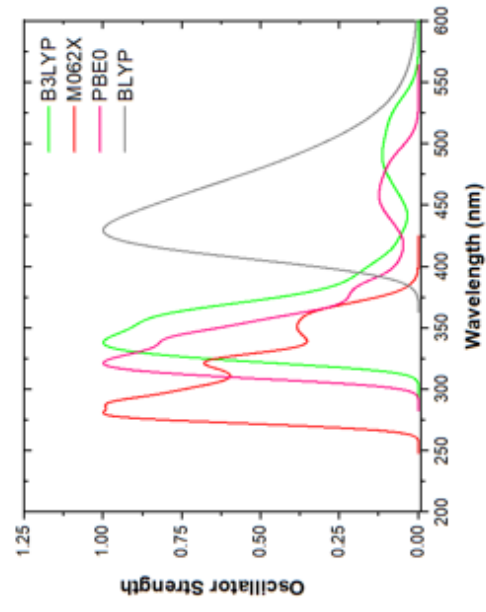


Figure 5.18. Absorption spectra of Group 1 emitters computed with different functionals.

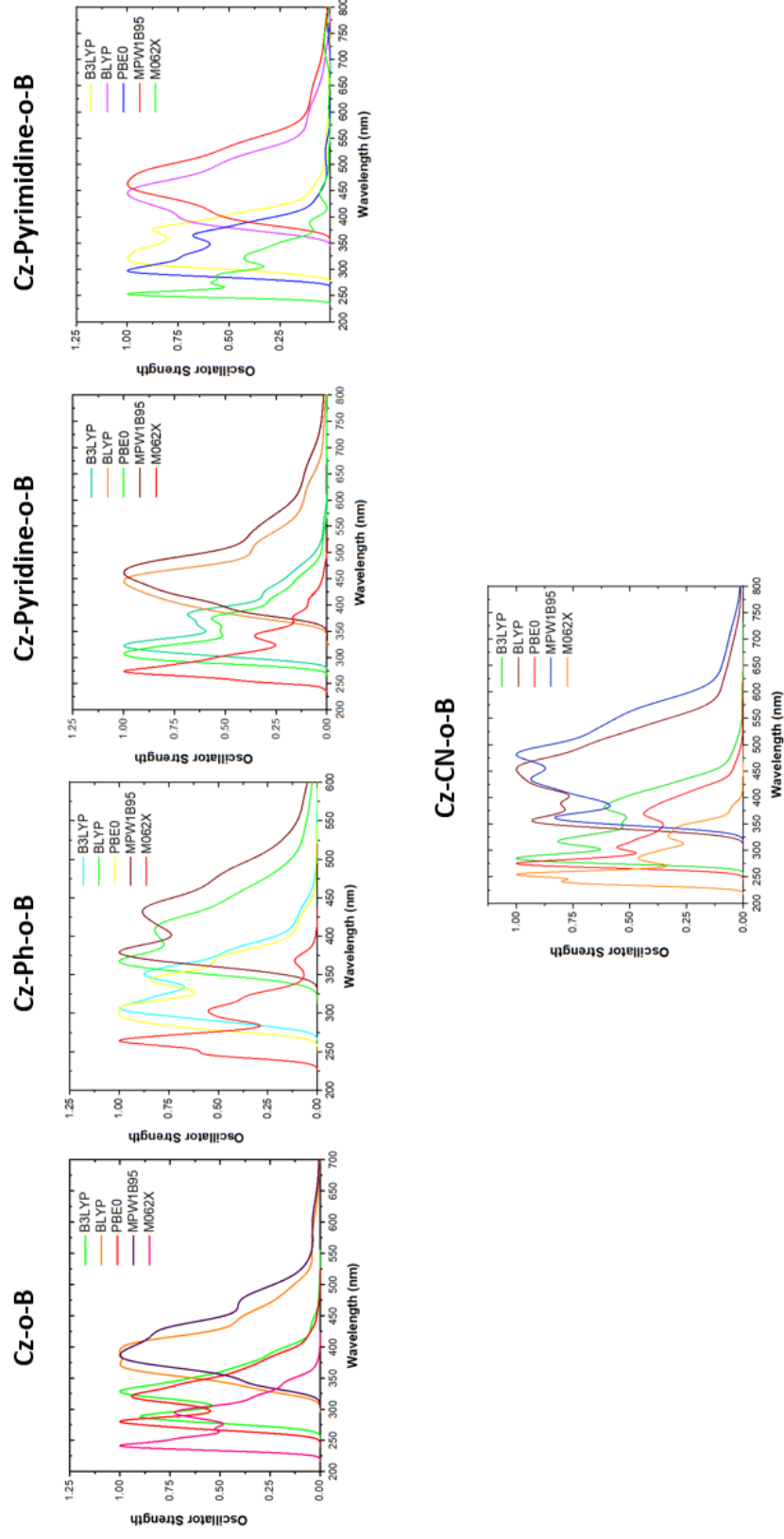


Figure 5.19. Absorption spectra of ortho substituted emitters computed with different functionals.

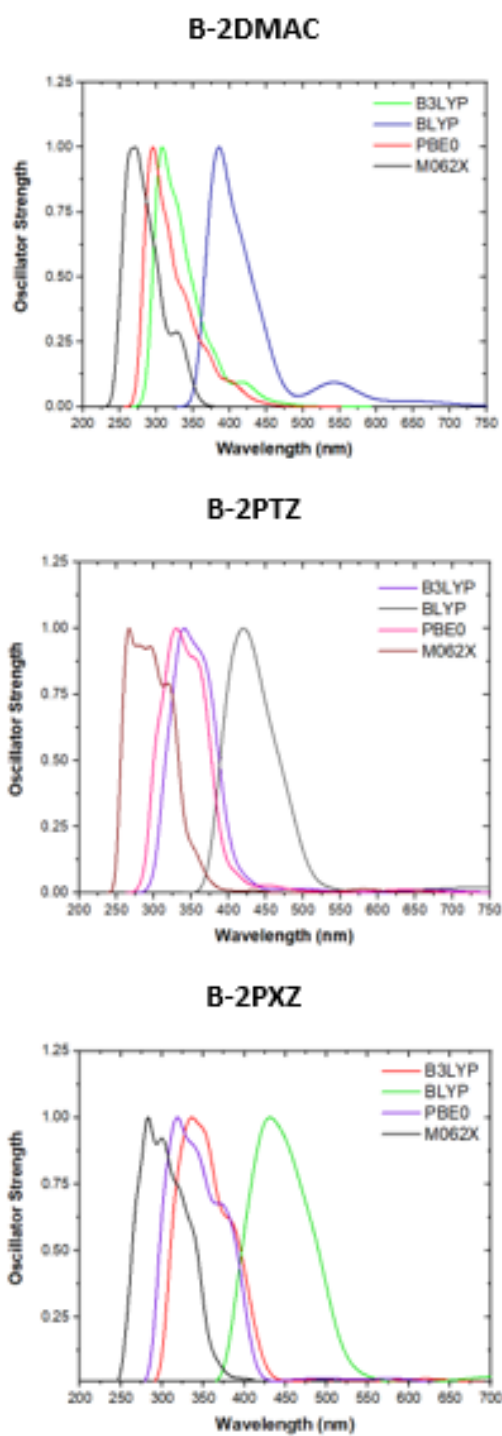


Figure 5.20. Absorption spectra of meta substituted emitters computed with different functionals.

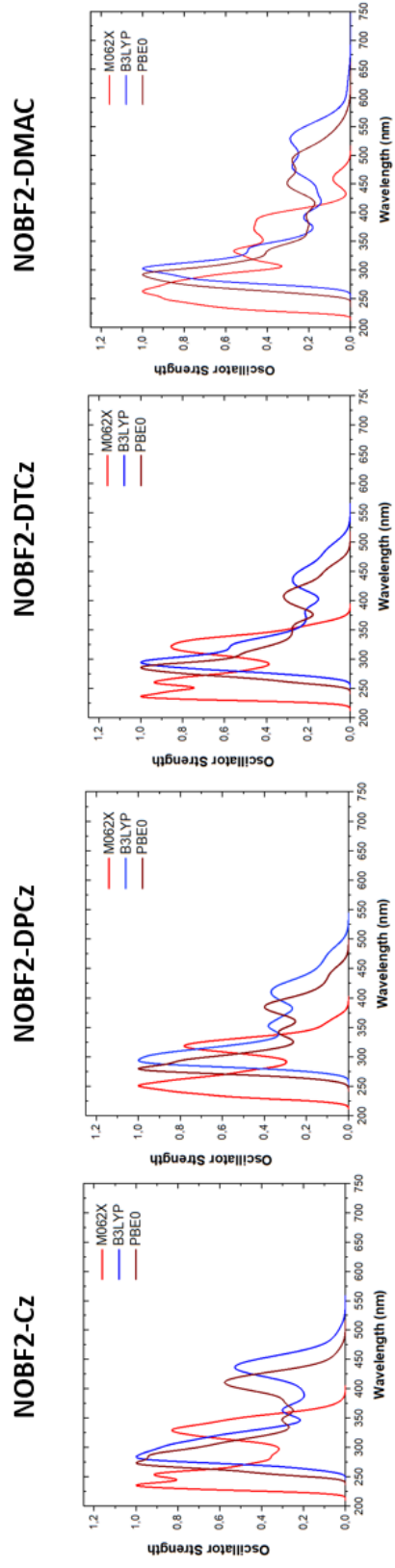


Figure 5.21. Absorption spectra of BF₂ containing emitters computed with different functionals

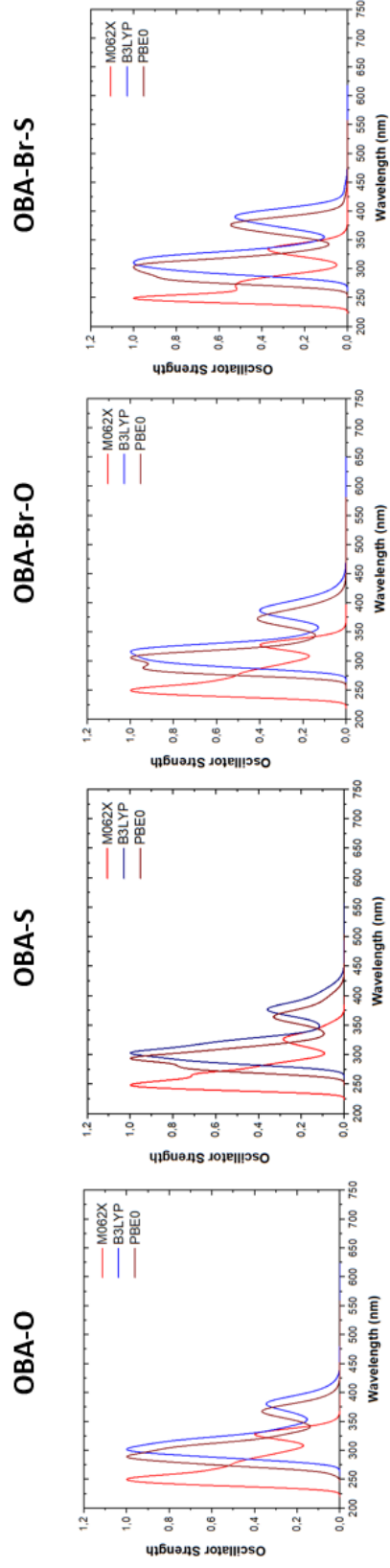


Figure 5.22. Absorption spectra of OBA containing emitters computed with different functionals

5.5. Conclusion

Herein, a series of tri-coordinated and tetra-coordinated boronbased TADF emitters, which are widely used in display technology have been systematically investigated to understand their RISC pathways and efficiencies. Indeed, due to their contribution to π -conjugation through the empty p_z orbital, coordinated boron-based emitters show high photoluminescence quantum yield. Moreover, due to their low electron withdrawing ability, they usually exhibit blue emission, it is possible, however, by various design strategies, to obtain different color emissions.

Globally, our systematic investigation has shown several important aspects: 1) creating highly orthogonal structures with sterically hindered donor moieties helps to reduce singlet–triplet energy gaps, however, this strategy leads to a decrease of oscillator strength, inherent emission probability, and SOC; 2) boron-based acceptor moieties used in this study usually induce a 50° torsion angle, 3) the ground state geometries are very similar to S_1 equilibrium geometries, however, more pronounced geometry changes are observed at T_1 equilibrium geometries, 4) the geometry changes in T_1 lead to a corresponding change in the nature of the excited states, thus increasing RISC efficiency; 5) while S_1 states generally have CT character, T_1 can be characterized as LE or mixed CT-LE; 6) unlike other TADF emitters, NOBF2- and OBA- based compounds have LE- S_1 states and LE- T_1 states, 7) the efficiency of the carbazole moiety can be increased by forcing appropriate geometrical arrangements, for instance via ortho- or para- regioisomery 8) the presence of quasidegenerate T_1 and T_2 states opens alternative efficient channels for RISC, 9) up-conversion from higher triplet states to S_1 has been identified as a possible pathway for RISC 10) unexpectedly, NOBF2- and OBA-based emitters, despite the same nature of S_1 and T_1 states, have high SOC.

In light of all these findings, we highlight the importance of selecting the correct connectivity between donor and acceptor moieties. Our results and observations reported in this manuscript strongly suggest that possible alternative pathways may be operative for RISC. In turn, this would require a careful selection of donor and acceptor moieties to achieve

the desired electron exchange energy, HOMO-LUMO gap, strong oscillator strength and high SOC.

Finally, we observed that boron emitters can be used in different architectures either as tri-coordinated or tetracoordinated; boron atom may or may not contribute to LUMOs and they can achieve small ΔE_{ST} and strong enough SOC to allow efficient RISC.

6. PHOTOPHYSICAL PROPERTIES OF SULFONE-BASED TADF EMITTERS IN RELATION TO THEIR STRUCTURAL PROPERTIES

6.1. Overview

In this work, Thermally Activated Delayed Fluorescence (TADF) of a series of emitters with sulfone-based acceptor moieties were studied by Density Functional Theory (DFT) methods. Sulfone derivatives were shown to be high performing TADF emitters over recent years. When discussing the TADF efficiency, various properties, such as, singlet–triplet energy gap (ΔE_{ST}), spin–orbit coupling (SOC) and, nature of states stand out due to their roles in reverse intersystem crossing (RISC). Here, we mainly focused on three important structural parameters that affect the intersystem crossing (ISC) and RISC pathways and their efficiencies. These three parameters are: 1) effect of meta- and para- conjugation, 2) effect of rigid acceptor moieties and 3) effect of phenyl bridge on photophysical properties.

6.2. Introduction

In recent years, Thermally Activated Delayed Fluorescence (TADF) materials have attracted considerable attention due to their 100% exciton harvesting abilities and high device efficiencies [233]. For traditional fluorescent materials, known as organic light emitting diodes (OLEDs), only 25% of excitons lead to luminescence, and the remaining 75% are triplets that are deactivated by nonradiative transitions [234–236]. To overcome low device efficiencies of fluorescent emitters, phosphorescent materials (PhOLEDs) containing heavy metals were developed and due to their emission from triplet state to ground state, the loss of triplet excitons was prevented [148, 197]. Although the loss of excitons were prevented, the heavy metals in their structure led to undesirable consequences, such as, high cost and environmental pollution [154]. In 2012, Adachi and co-workers developed TADF materials as a promising technology, which provides high efficiency, cost saving and environmentally friendly applications (see Figure 6.1) [215, 234, 237, 238].

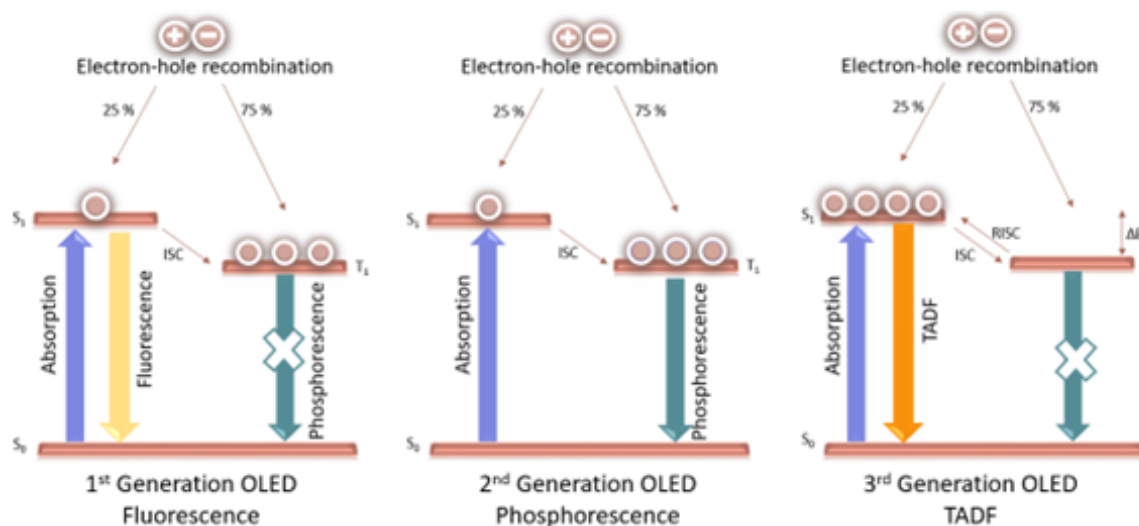


Figure 6.1. OLED, PhOLED and TADF mechanism.

Due to the efficient harvesting of triplet excitons, TADF materials offer advanced applications in electroluminescence [128], sensors [113], bioimaging [113,238], and organic lasers [214]. Metal free TADF emitters can achieve 100% internal quantum efficiencies by harvesting triplet excitons via the RISC process from the first excited triplet state (T_1) to the first excited singlet state (S_1) under thermal activation [150,228,239,240]. Many TADF materials usually adopt a twisted donor (D)–acceptor (A) geometry to minimize the overlap between highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO), which lead to small S_1 – T_1 energy gap (ΔE_{ST}) [224]. ΔE_{ST} parameter can be represented as:

$$\Delta E_{ST} = 2 \iint \Phi_L(1)\Phi_H(2) \frac{e^2}{r_1 - r_2} \Phi_L(2)\Phi_H(1) dr_1 dr_2, \quad (6.1)$$

decreasing the exchange interaction integral of the HOMO and the LUMO wavefunctions is an efficient way to minimize the ΔE_{ST} . Recent studies reported that in a cofacial configuration of D and A moieties, emitters have the possibility to exhibit Through-Space Charge-Transfer (TSCT) which leads to separation between the HOMO and LUMO, thus, leading to small ΔE_{ST} values. However, compared to the Through-Bond Charge-Transfer (TBCT) systems, TSCT systems have relatively lower electronic interactions between D and A moieties, which lead to increased rotations between D and A groups and strong non-radiative decays [241]. To sum up, there are two possible ways of separating frontier molecular orbitals, which is, rationally designing TBCT and TSCT systems.

Furthermore, TADF efficiency is not only dependent on ΔE_{ST} , but also highly related to the spin-orbit coupling (SOC), that is, effective RISC relies on both small ΔE_{ST} and large SOC [113, 128, 150, 231, 242]. For many TADF emitters, due to their purely organic structures, SOC values were found to be intrinsically weak, which makes it difficult to obtain efficient RISC in TADF and ISC in phosphorescence. To enhance SOC values in TADF emitters, the heavy-atom effect was used; since SOC is proportional to the fourth power of the nuclear charge, the most common strategy for improving SOC is introducing non-metal atoms to the molecular structure, such as halogens [224, 243].

In this work, we demonstrate photophysical and structural behaviors of a series of sulfone-based TADF emitters using computational methods. As listed in Figure 6.2, the set of molecules under investigation has various sulfone-based acceptor moieties such as; diphenyl-sulfone (DPS), dibenzo- thiophene-S, S,-dioxide (DBTO2), 9,9-dimethyl-9H-thioxanthene 10,10-dioxide (TXO2), and thianthrene 5,5,10,10-tetraoxide (TTR).

The acceptor moieties depicted in this molecule set (see Figure 6.2) are reported in our previous studies as well as in recent TADF literature [154, 196]. In our previous reports, we theoretically investigated the characteristics of dimethylacridine (DMAC), carbazole (Cz), phenoxazine (PXZ), phenothiazine (PTZ) and diphenylamine (DPA) as donor moieties [244]. By simulating a wide molecule set with different donor and acceptor moieties, we study the effects and significance of the sulfur atom in various structures. As reported in literature, DPS is a multi-talented acceptor moiety, with strong electron withdrawing ability due to the highly electronegative oxygen atoms and provides excellent TADF activity due to its central twist [48, 245]. Moreover, since it has tetrahedral geometry, it is known to restrict the π -conjugation of the emitters leading to CT compounds. While the DBTO2 and TXO2 acceptor moieties were used to understand the influence of acceptor rigidity on descriptors; the TTR group was selected to predict the effects of two iso-energetic low energy conformers –SO2 unit on conjugation between D-A units and on conjugation between D-A units and on energy levels.

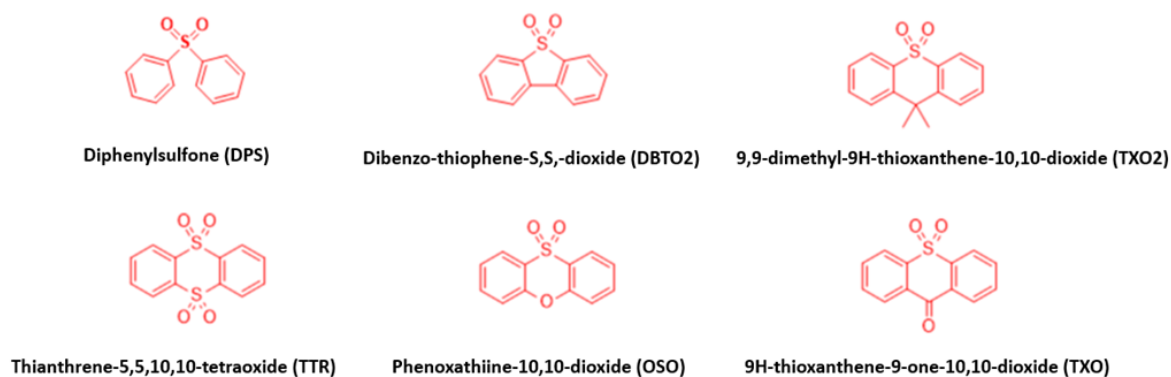


Figure 6.2. Sulfone based acceptor moieties investigated in this study.

6.3. Computational Methodology

To better understand the structural and photophysical properties of the emitters discussed in this study, a computational analysis was conducted using the Gaussian16 [155] and Amsterdam Density Functional (ADF) [170] software packages. Geometries in the ground and excited S_1 and T_1 states were optimized at the M062X [77]/6-31+G(d,p) [246] level of theory. Tamn Dancoff Approximation (TDA) [152] calculations for the $S_0 \rightarrow S_n$ and $S_0 \rightarrow T_n$ transitions using the M062X/6-31+G(d,p) and ω B97XD [208]/6-31+G(d,p) levels were performed with respect to the optimized S_0 state geometries. In our previous contribution, we modeled the excited state behaviors of a series of TADF emitters with various functionals such as M062X, ω B97XD and CAMB3LYP and the results obtained with M062X were found to be reliable and consistent with experimental data [196]. The reliability of data obtained with M062X functional was tested with the nature of state and ΔE_{ST} analyses.

In light of our previous findings from methodological study, we chosed to model sulfone based emitters with M062X functional and, ω B97XD has been used only for benchmark purpose. TDA choice is due to the fact that the TDA method provides a more balanced description of both triplet and singlet excited states, and compared to Time-Dependent DFT (TD-DFT), it is free from triplet instability issues [164]. 6-311++G(3df,3pd) [247] extra basis set was used for the sulfur atom in all calculations. From the theoretical calculations, it can be observed that different acceptor and donor moieties exhibit characteristic torsions.

Moreover, some compounds exhibit two different iso-energetic low energy conformers presenting TADF as well as non-TADF activities. While near orthogonal geometries resulted in very small ΔE_{ST} values making the RISC process viable, planar conformers were shown to yield larger ΔE_{ST} values representing non-TADF behavior.

In order to better analyze electron processes at excited states, including internal conversion (IC), ISC and RISC processes, we report the lowest 10 states for singlet and triplet excitations. Surprisingly, energy differences between excited states show the possibility of high-energy hot exciton pathways in ISC processes. Moreover, the nature of the excited singlet and triplet states is evaluated using Natural Transition Orbitals (NTOs), obtained with the Nancy-EX code [168] and visualized with the Avogadro [169] software package. Additionally, Φ_S values, defining the overlap between the attachment and the detachment densities were calculated. In other words, it measures the degree of overlap between particle and hole densities and while the smaller its value shows the larger charge transfer character, the larger its value represents larger local excitation character.

In consideration of the first-order perturbation theory, SOC values between excited singlet and triplet geometries were computed at S_1 and T_1 geometries using the ADF software package at M062X/DZP [172] level of theory. The choice of M062X functional for SOC calculations is based on the analyses of the nature of states that we performed in our previous contribution [196]. In our previous contribution, we modeled a TADF active molecule set consisting various structures and aimed to investigate the best functional which well reproduces the nature of excited states. In light of our data, we observed and reported that S_1 states that we modeled via M062X functional mostly present a noticeable CT character, which is known to favor TADF efficiency. On the other hand, ω B97XD presents locally excited S_1 states for most of the TADF emitters. Moreover, due to the structural properties of TADF emitters, they should favor CT character, therefore, LE states observed by the ω B97XD functional should be regarded as an artifact compared to the reliable performance of M062X. According to the El Sayed rule, the nature of excited states plays an important role on SOC, therefore, the functional which best reproduces the nature of states will be the

most appropriate functional for the SOC calculations. The excited state energies, oscillator strengths and, Phi-S indices, obtained from excited state calculations were calculated using two different functionals, ω B97XD and M062X. Herein, M062X was chosen for further SOC analyses, which is highly important for (R)ISC processes and controlled by nature of states. ω B97XD has been used only for benchmark purposes.

The ultraviolet-visible (UV-Vis) absorption spectra of the investigated emitters were modeled by generating 30 conformers through a Wigner distribution as implemented in the Newton-X software package [92]. Vertical transitions from each snapshot were convoluted using Gaussian functions of full-width at half length (FWHL) of 0.15 eV. Integral equation formalism polarizable continuum model (IEF-PCM) was used in all calculations, to implicitly model the solvent environment [46, 213, 248]. Toluene is used for all emitters except DBTO-PXZ and Cz-TTR, which have been modelled in dichloromethane and ethyl ethanoate, respectively. Optimized geometries were rendered with the CYLview software package [249].

6.4. Results and Discussion

6.4.1. Effects of meta- and para- Conjugation on Photophysical Properties

Although sulfone-based TADF emitters have been reported by several research groups, the majority of these studies focus on para-substituted materials. Comparatively, we theoretically investigated both meta- and para-substituted sulfone based emitters to clarify the effects of different positions of the donor moieties on photophysical properties. As depicted in Figure 6.3, we modeled five meta- and five para-substituted molecules with the DPS donor moiety and various donor groups, such as, Cz, PTZ, PXZ, DMAC and DPA.

It is well-known that photophysical properties of organic compounds are highly affected by geometric parameters. The majority of the studies in literature focus exclusively on symmetric emitters with D-A-D skeletons [250]. However, a few studies have been reported to clarify the effects of asymmetric emitters in TADF efficiencies [250].

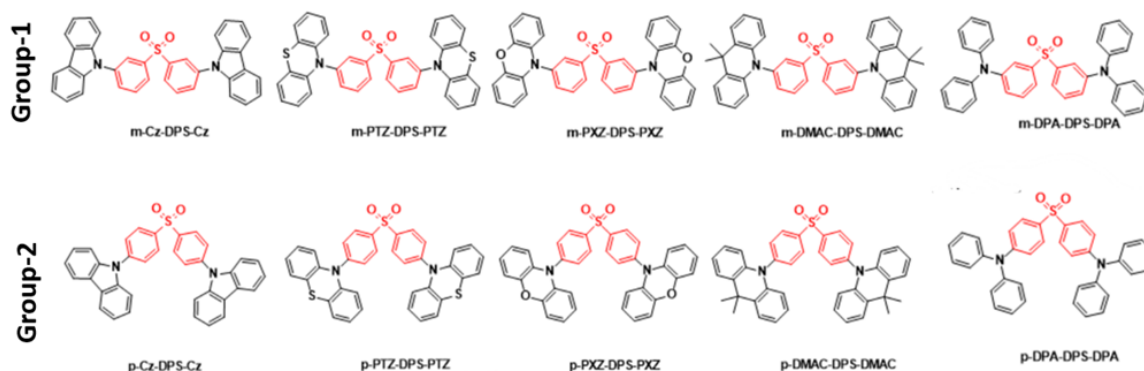


Figure 6.3. Meta- (Group 1) and para-substituted (Group 2) TADF emitters with DPS acceptor moiety.

Optimized geometries of meta- and para-substituted TADF emitters show that for S_0 state structures, the tetrahedral geometry of DPS moiety do not change, however, significant changes were observed in the bending of donor moieties. As reported in Table 6.1 and 6.2, while para-substituted DPS containing TADF emitters yield highly symmetrical structures, their meta-substituted analogues have asymmetric geometries.

Table 6.1. Torsion angles of the Group 1 emitters computed at M06-2X/6-31+G(d,p) level of theory.

Compounds	$\theta(\text{D-A})_1 S_0/S_1/T_1$	$\theta(\text{D-A})_2 S_0/S_1/T_1$
m-Cz-DPS-Cz	52.45/59.74/55.72	53.17/60.72/44.73
m-PTZ-DPS-PTZ	-99.76/-88.74/-89.89	-75.03/-77.68/-78.82
m-PXZ-DPS-PXZ	73.63/88.17/84.75	73.63/87.71/84.75
m-DMAC-DPS-DMAC	-92.38/-89.71/-104.21	108.04/106.61/113.13
m-DPA-DPS-DPA	-25.20/-41.88/-22.79	41.79/53.01/53.02

Table 6.2. Torsion angles of the Group 2 emitters computed at M06-2X/6-31+G(d,p) level of theory.

Compounds	$\theta(\text{D-A})_1 S_0/S_1/T_1$	$\theta(\text{D-A})_2 S_0/S_1/T_1$
p-Cz-DPS-Cz	-51.39/-53.88/-45.78	51.40/63.11/46.54
p-PTZ-DPS-PTZ	-74.86/-74.47/-71.45	71.11/88.05/96.55
p-PXZ-DPS-PXZ	-104.20/-105.73/-106.21	102.17/89.53/69.12
p-DMAC-DPS-DMAC	-91.08/-92.03/-105.44	89.23/89.55/72.95
p-DPA-DPS-DPA	-30.48/-43.11/-34.82	-0.0216159

Herein, a comprehensive analysis on the effects of symmetric and asymmetric geometries as well as the bends in donor groups was performed. Bent conformations in ground state are known to avoid molecular aggregation and the formation of intermolecular excimers [251]. Therefore, emitters with bent donor moieties are expected to be favorable in preventing molecular aggregation, which leads to non-emissive decays [251]. Following the geometry analyses, we further modeled the energy alignments of singlet and triplet states and aimed to investigate the differences between meta- and para-substituted emitters.

Figure 6.4 demonstrates that except for the DPA-derivative, para-substituted emitters yield lower energy triplet levels compared to their meta- counterparts; and low-lying singlet state energies decreased in para-substituted emitters. Moreover, we also observed that many compounds in the first two groups exhibit iso-energetic S_1 and S_2 states, which may cause multiple emission bands with identical or different natures. On the other hand, lower energy triplet states in para-emitters create greater number of possible pathways for RISC process, which also leads to greater amount of exciton harvesting from iso-energetic triplet states below the S_1 level.

In absorption spectra analyses, para-substituted emitters yield lower energy bands compared to the meta-substituted compounds. This behavior of para-substitution suggests that geometries with smaller distortion cause stronger electron conjugation in the excited state. It should also be noted that theoretical absorption spectra of both meta- and para-emitters exhibit dominant high intensity bands in higher energies, indicating that while $S_0 \rightarrow S_1$ absorptions are almost negligible, strong excitations to upper singlet states are highly dominant in both Group 1 and 2 (Table 6.3). Comparisons between meta- and para-substituted emitters showed that para-substituted compounds have larger oscillator strengths, which is an important parameter in understanding excited state transitions.

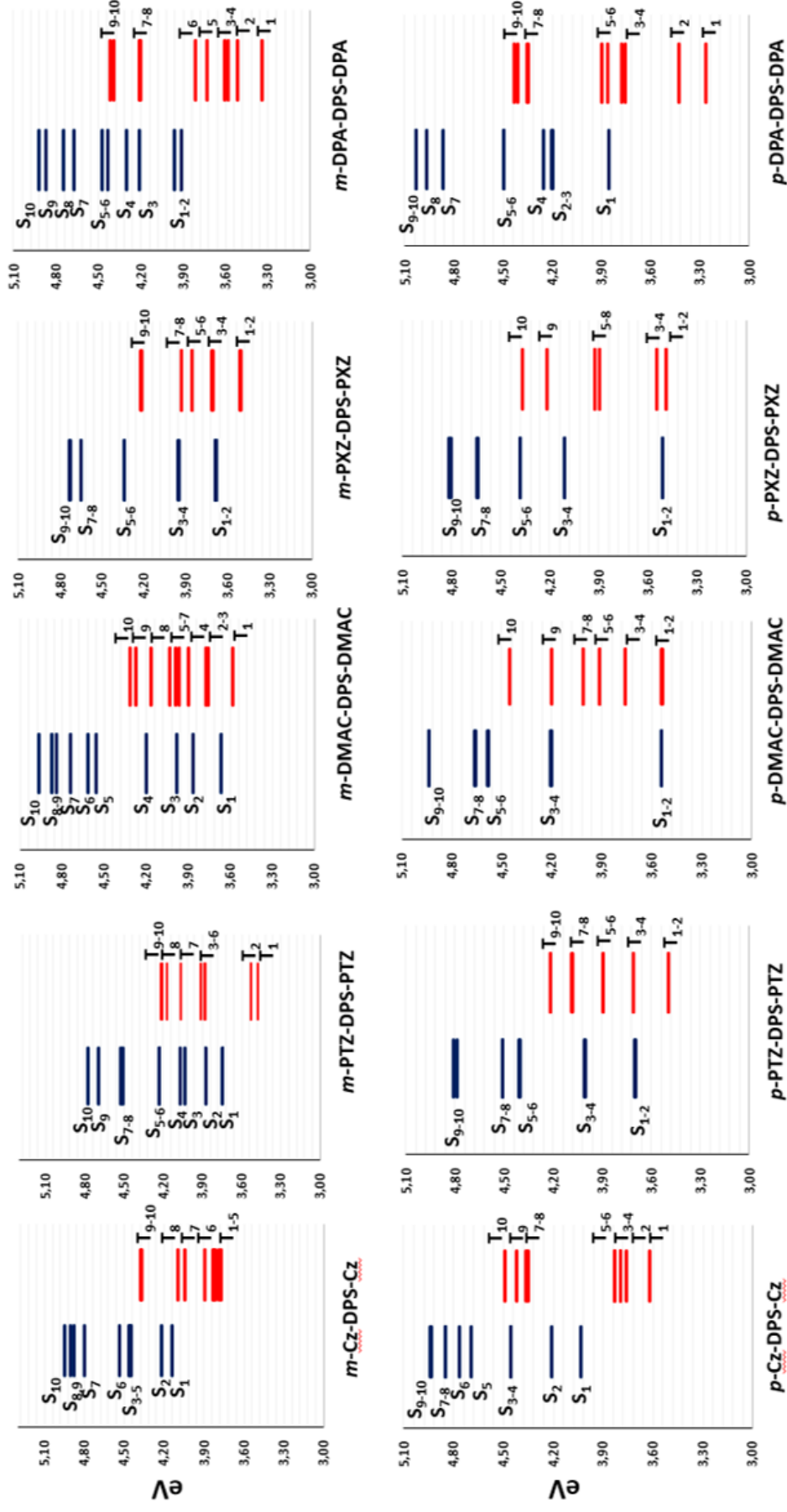


Figure 6.4. Energy levels of meta- (Group 1) and para-substituted (Group 2) TADF emitters computed at M062X/6-31+G(d,p) level of theory in toluene. Compounds: m-Cz-DPS-Cz [1], m-PTZ-DPS-PTZ [1], m-DMAC-DPS-DMAC [1], m-PXZ-DPS-PXZ [1], m-DPA-DPS-DPA [1], p-Cz-DPS-Cz [2], p-PTZ-DPS-PTZ [3], p-DMAC-DPS-DMAC [4], p-PXZ-DPS-PXZ [4], p-DPA-DPS-DPA [5].

As listed in Table 6.3, except for para-substituted Cz-DPS-Cz and DPA-DPS-DPA emitters, compounds usually exhibit negligible transition to S_1 level and strong transitions to higher singlet states. It is also shown that for meta-substituted Cz-DPS-Cz emitters, absorptions with relatively larger oscillator strengths are (>0.1) S4, S6, S8 and S9. On the other hand, its para-substituted analogue has $S_0 \rightarrow S_1$ transition with quite strong oscillator strength, $f=0.6433$. Similar to the Cz-DPS-Cz emitter, para-substituted DPA-DPS-DPA emitter exhibits strong $S_0 \rightarrow S_1$ transition ($f=0.9967$), while its meta- analogue has negligible transition to S_1 state, and quite strong transitions to higher singlet states. For meta- and para-substituted PTZ-DPS-PTZ, PXZ-DPS-PXZ and DMAC-DPS-DMAC emitters, strong excitations from S_0 to S_n states opens up alternative ISC channels for TADF emitters.

It is well-known that population of high energy excited states leads to more energy loss during the IC process to the S_1 level. Therefore, with the help of strong SOC values between high energy singlet and triplet states, instead of IC, emitters may experience ISC between S_n and neighboring triplet states, leading to decreased energy loss and hence, higher efficiency. Population of triplet states are affected by both the energy difference and the SOC between relevant singlet and triplet states.

Though strong SOC between high oscillator strength singlet states and T_1 or T_2 states is possible (such as in meta-Cz), a strong coupling between high-energy singlet levels and high-energy triplet levels can also be observed (such as in meta-PTZ). Moreover, we also observed that iso-energetic triplet states, such as, the ones observed in m/p-PXZ-DPS-PXZ, p-DMAC-DPS-DMAC and p-PTZ-DPS-PTZ compounds may exhibit SOC values in different strengths, which shows that these iso-energetic triplet levels are in different natures, $3^{CT}/3^{LE}$, and state mixing processes enhancing RISC is possible in these emitters.

Table 6.3. Oscillator strengths for singlet excitations of Group 1 and Group 2 emitters computed at M06-2X/6-31+G(d,p) level of theory.

	$S_0 \rightarrow S_1$	$S_0 \rightarrow S_2$	$S_0 \rightarrow S_3$	$S_0 \rightarrow S_4$	$S_0 \rightarrow S_5$	$S_0 \rightarrow S_6$	$S_0 \rightarrow S_7$	$S_0 \rightarrow S_8$	$S_0 \rightarrow S_9$	$S_0 \rightarrow S_{10}$
m-Cz-DPS-Cz	0.0185	0.0587	0.0191	0.1179	0.0371	0.3055	0.0052	0.3728	0.2308	0.0377
p-Cz-DPS-Cz	0.6433	0.2086	0.0743	0.0467	0.0025	0.0113	0.0318	0.0788	0.1359	0.3846
m-PTZ-DPS-PTZ	0.0006	0.0007	0.0002	0.0022	0.0025	0.0066	0.0526	0.0547	0.1105	0.1072
p-PTZ-DPS-PTZ	0.0007	0.0023	0.0002	0.0005	0.0248	0.038	0.0481	0.0555	0.0856	0.0993
m-DMAC-DPS-DMAC	0.0002	0.0154	0.0005	0.0124	0.0986	0.2999	0.0592	0.1863	0.4185	0.0124
p-DMAC-DPS-DMAC	0.0001	0.0003	0.0011	0.0014	0.1023	0.0484	0.3343	0.4996	0.0016	0.0101
m-PXZ-DPS-PXZ	0	0.0007	0.0061	0.0031	0.0748	0.0965	0.0048	0	0.1892	0.1712
p-PXZ-DPS-PXZ	0.0014	0.0008	0	0	0.1242	0.1707	0.0086	0.0028	0.13	0.1478
m-DPA-DPS-DPA	0.0052	0.0744	0.1228	0.5341	0.4195	0.2402	0.1032	0.0799	0.0343	0.0378
p-DPA-DPS-DPA	0.9967	0.1901	0.2356	0.0299	0.5097	0.0551	0.0391	0.0832	0.0261	0.0192

The role of state mixing in enhancing RISC has been explained in El Sayed rule. According to the El Sayed rule, the rate of intersystem crossing between the states of different electronic character is found to be much faster than that between two states of same electronic character [252]. Moreover, as first recognized by Monkman, when local excited states enter into the picture and mix with charge transfer triplets, they prevent the El Sayed constraint of S_1 and T_1 states which are mostly CT character in TADF molecules [253]. Therefore, the presence of states with different nature lying close in energy works as speeding up mechanism for RISC [254,255]. For instance, p-PXZ-DPS-PXZ emitter has iso-energetic T_1 and T_2 states which have 0.64 cm^{-1} and 1.61 cm^{-1} SOC values, respectively, and this difference in SOC values can be attributed to the different natures of T_1 and T_2 states (see Table 6.4).

Table 6.4. Natures of S_1 , T_1 - T_5 states of the emitters in Group 1 and Group 2 computed at M062X/6-31+G(d,p) level of theory in toluene.

Emitters	S_1	T_1	T_2	T_3	T_4	T_5
	(Φ_S)	(Φ_S)	(Φ_S)	(Φ_S)	(Φ_S)	(Φ_S)
m-Cz-DPS-Cz	CT	LE	LE	LE	LE	LE
	0.557	0.7721	0.8095	0.8065	0.9629	0.9618
p-Cz-DPS-Cz	CT-LE	CT-LE	CT-LE	LE	LE	LE
	0.7047	0.8405	0.8622	0.7503	0.7622	0.9676
m-PTZ-DPS- PTZ	CT-LE	CT-LE	LE	CT-LE	CT	LE
	0.4703	0.792	0.8164	0.5513	0.5599	0.703
p-PTZ-DPS- PTZ	CT	CT-LE	CT-LE	CT	CT	LE
	0.331	0.7845	0.7859	0.4534	0.4614	0.6823
m-DMAC-DPS-DMAC	CT	CT-LE	CT-LE	LE	LE	CT-LE
	0.3939	0.6062	0.5834	0.8424	0.7313	0.5798
p-DMAC-DPS-DMAC	CT	CT	CT	LE	LE	LE
	0.1642	0.1692	0.1677	0.88	0.8798	0.7097
m-PXZ-DPS-PXZ	CT	CT-LE	CT-LE	CT-LE	CT-LE	CT-LE
	0.4383	0.7597	0.7578	0.6758	0.6576	0.5843
p-PXZ-DPS-PXZ	CT	CT-LE	CT	CT-LE	CT-LE	LE
	0.2485	0.4301	0.3921	0.784	0.7951	0.7599
m-DPA-DPS-DPA	CT-LE	CT-LE	CT-LE	CT-LE	LE	LE
	0.7416	0.8193	0.7288	0.7987	0.8031	0.8448
p-DPA-DPS-DPA	CT-LE	CT-LE	CT-LE	LE	LE	LE
	0.7594	0.8375	0.8465	0.8208	0.8373	0.8241

As mentioned previously, multiple triplet states below the S_1 level creates multiple RISC possibilities. To analyze the probability of RISC from different triplet levels, SOC values between relevant states were calculated. SOC dependence of RISC has been reported in Fermi's Golden Rule approximation. According to the Fermi's Golden Rule approximation, the square of root mean square coupling element (RMSCE, V_{SOC}) is directly proportional to the RISC rate constant [256, 257]. Another parameter which plays an important role in kRISC is the Franck Condon weighted density of states (ρ_{FCWD}) which can be calculated in the framework of Marcus-Levich-Jortner theory [179]. Herein, since the calculation of ρ_{FCWD} is a high cost calculation for these wide molecule sets, we only calculated the $|V_{soc}|^2$ to foresee the RISC rates. The square of root mean square coupling element (RMSCE, V_{SOC}), has been calculated for all states (for transition between S_1 and T_1 states, $\left| \left\langle S_1 \left| \hat{H}_{soc} \right| T_1 \right\rangle \right|^2$ is divided into three to represent the average over the three triplet states for each possible value of the total angular momentum $J=-1,0,1$). These formula can be represented as:

$$k_{RISC} = \frac{2\pi}{\hbar} |V_{SOC}|^2 \times \rho_{FCWD}, \quad (6.2)$$

$$k_{RISC} = \frac{2\pi}{\hbar} |V_{SOC}|^2 \times \rho_{FCWD}. \quad (6.3)$$

It is obvious that transition from any triplet state below S_1 is possible with a strong SOC value. Importantly, it was observed that the energy gaps closest to the experimental value generally exhibit strongest $|V_{soc}|^2$, and generally, SOC values in para-substituted emitters are larger than the meta-substituted ones (except emitters Cz-DPS-Cz and PTZ-DPS-PTZ). These higher SOC values in para-substituted emitters can be attributed to the larger amount of state mixing in iso-energetic triplet levels below the S_1 state.

As represented in Table 6.5, among meta- and para-analogues, slight changes were observed in HOMO-LUMO energies and the energy difference between these two molecular orbitals (E_g). For compounds Cz-DPS-Cz, PTZ-DPS-PTZ and DMAC-DPS-DMAC, meta-substitution leads to larger HOMO energies, thus, stronger electron donating ability of Cz, PTZ and DMAC donor moieties. On the other hand, while the PXZ donor moiety represents almost equal HOMO energies in meta- and para-substituted emitters, their DPA analogues yield better donating ability with para-substitution.

Table 6.5. HOMO and LUMO energies, and energy gaps of Group 1 and Group 2 emitters computed at M062X/6-31+G(d,p) level of theory in toluene.

Emitters	HOMO	LUMO	LUMO - HOMO (Eg) (eV)	Experimental ΔE_{ST} (eV)	Theoretical ΔE_{ST} (eV)
m-Cz-DPS-Cz	-7.02	-1.25	5.77	0.44	0.36
p-Cz-DPS-Cz	-7.06	-1.24	5.82	0.25-0.31	0.27
m-PTZ-DPS- PTZ	-6.69	-1.3	5.39	0.01	0.04
p-PTZ-DPS- PTZ	-6.7	-1.33	5.37	0.4	0.21
m-DMAC-DPS-DMAC	-6.54	-1.21	5.33	0.05	0.09
p-DMAC-DPS-DMAC	-6.59	-1.27	5.32	0.09	0.01
m-PXZ-DPS-PXZ	-6.6	-1.3	5.3	0.06	0.03
p-PXZ-DPS-PXZ	-6.6	-1.36	5.24	0.08	0.02
m-DPA-DPS-DPA	-6.69	-0.88	5.81	-	0.33
p-DPA-DPS-DPA	-6.64	-0.85	5.79	0.54	0.42

This behavior of DPA-DPS-DPA emitter can be attributed to the highly sterically hindered and twisted structure in meta-compound, which results in disruption of conjugation within the molecule.

For the electron accepting ability, LUMO energies of meta- and para-substituted compounds were checked and it was observed that for PTZ-DPS-PTZ, DMAC-DPS-DMAC and PXZ-DPS-PXZ compounds, para-substitution leads to smaller LUMO energies and stronger electron withdrawing towards the acceptor moiety. Overall, the position of the donor moiety in these two molecule sets did not cause large differences in E_g values and these results are consistent with the similar ΔE_{ST} values of meta- and para- isomers (except Cz-DPS-Cz and PTZ-DPS-PTZ emitters).

To further compare the RISC behaviors of meta- and para-emitters, we theoretically calculated the energy gaps between singlet and triplet states. As reported in Table 6.5, experimental energy gaps were well reproduced and the largest absolute deviation was obtained as 0.29 eV for p-PTZ-DPS-PTZ emitter. Importantly, these energy gaps correspond to the gaps between S_1 and triplet state with largest RMSCE. In particular, proving the deterministic effect of SOC is consistent with our recent study published in 2022 [196].

To summarize our findings so far, changing the position of the donor moiety from para- to meta- results in an increase in the twisting angle between donor and acceptor moieties, which is beneficial for separation of frontier molecular orbitals. For the molecules in the first two groups, we have investigated the energy level alignments of excited states. Surprisingly, there are more than one triplet states below the S_1 level. Moreover, the presented results show that there are iso-energetic singlet and triplet states, which have the possibility to contribute to ISC and RISC processes.

It should also be noted that though the first ten excited states were calculated to observe the brightest states and the pathways for the possible ISC and internal conversions, the low lying states, especially for singlets, play the main role in RISC process. Further analyses

led us to conclude that the RISC process is mainly a SOC driven mechanism and it occurs between the states with strongest SOC values. Additionally, we also present our findings for the oscillator strength and its effect on IC/RISC pathways.

It should also be noted that Herzberg-Teller (HT) effect, which is a parameter that enhances the ISC/RISC processes and represents the dependence of oscillator strength on the internal coordinates is also an important factor in TADF efficiency [258]. Though we did not calculate the emission spectra in this study, it is known that small molecular deformations between S_1 and S_0 states may enhance the emission oscillator strengths, which is a phenomena named HT effect. Enhancement of the emission oscillator strength not only affects the transition intensity, but it also affects the competition between the fluorescence and ISC/RISC processes. Therefore, an important point to keep in mind is that the excited state characteristics obtained with the Franck Condon (FC) approach are not the only parameters that affect the TADF efficiency [44, 147, 259, 260]. In other words, photophysical properties of these kind of compounds are affected by both the FC and HT components.

6.4.2. Effects of Rigidity of The Acceptor Moiety on Photophysical Properties

According to molecular design strategies, rigid compounds are good candidates for spatially separated frontier molecular orbitals, which makes them CT based compounds due to their short π -conjugation length and high steric hindrance. Therefore, here we analyzed the behaviors of rigid TXO2, DBTO acceptor moieties and flexible DPS moiety to observe and compare the photophysical differences arising from the degree of rigidity.

As shown in Figure 6.5, TTR, DBTO and DPS acceptor moieties with different rigidities behave differently in photophysical properties. By virtue of the geometric analysis, we observed that these three acceptor moieties create perfectly orthogonal geometries with DMAC unit. On the other hand, their coupling with PXZ donor group leads to 10° shift from orthogonality. We further investigated their electron accepting abilities with the help of E_g values and observed that LUMO energies decrease in the order of TXO2-PXZ, p-PXZ-DPS-PXZ and DBTO-PXZ which indicates that DBTO is the strongest and TXO2 is the weakest

electron acceptor. On the other hand, ΔE_{ST} values of the six emitters under investigation are extremely small both experimentally and theoretically.

This indicates that any possible difference in RISC mechanisms of these compounds can arise from any other parameter, but not from the singlet-triplet energy gap. At this stage, since the natures of triplet states will be the determinative factor in RISC, the effects of these acceptor moieties on the natures of excited triplet states have been analyzed. The results obtained using metahybrid M062X functional are shown in Figure 6.5 and Table 6.6.

Table 6.6. Natures of S_1 , T_1 - T_5 states computed at M062X/6-31+G(d,p) level of theory in toluene (TXO2-PXZ, p-PXZ-DPS-PXZ, TXO2-DMAC, p-DMAC-DPS-DMAC, DBTO-DMAC) and in dichloromethane (DBTO-PXZ).

Emitters	S_1	T_1	T_2	T_3	T_4	T_5
	(Φ_S)	(Φ_S)	(Φ_S)	(Φ_S)	(Φ_S)	(Φ_S)
TXO2-PXZ	CT	LE	LE	CT	CT	LE
	0.2809	0.8393	0.8372	0.3879	0.3939	0.8082
p-PXZ-DPS-PXZ	CT	CT-LE	CT-LE	CT-LE	CT-LE	CT-LE
	0.2485	0.4301	0.3921	0.784	0.7951	0.7599
DBTO-PXZ	CT	CT	CT	CT-LE	CT-LE	LE
	0.1854	0.3842	0.4018	0.6394	0.6383	0.9497
TXO2-DMAC	CT	CT	CT	LE	LE	LE
	0.3465	0.3422	0.3206	0.8951	0.8951	0.7484
p-DMAC-DPS-DMAC	CT	CT	CT	LE	LE	LE
	0.1642	0.1692	0.1677	0.88	0.8798	0.7097
DBTO-DMAC	CT	CT	CT	LE	CT-LE	CT-LE
	0.1712	0.2102	0.2044	0.953	0.4715	0.4789

The S_1 state natures of all emitters were found to be in CT character with perfectly separated FMOs. Their T_1 and T_2 states are generally in CT character except TXO2-PXZ and para-PXZ. For T_2 , T_3 , T_4 and T_5 states, while para-PXZ emitter represents mixed character, DBTO-PXZ emitter represents an obvious increase in LE transitions. On the other hand, TXO2-PXZ does not represent any regular trend from T_2 to T_5 . $\Delta\Phi_S$ values in Figure 6.5 are in well agreement with the SOC values which represent an enhancement with the increase nature difference between singlet and triplet states.

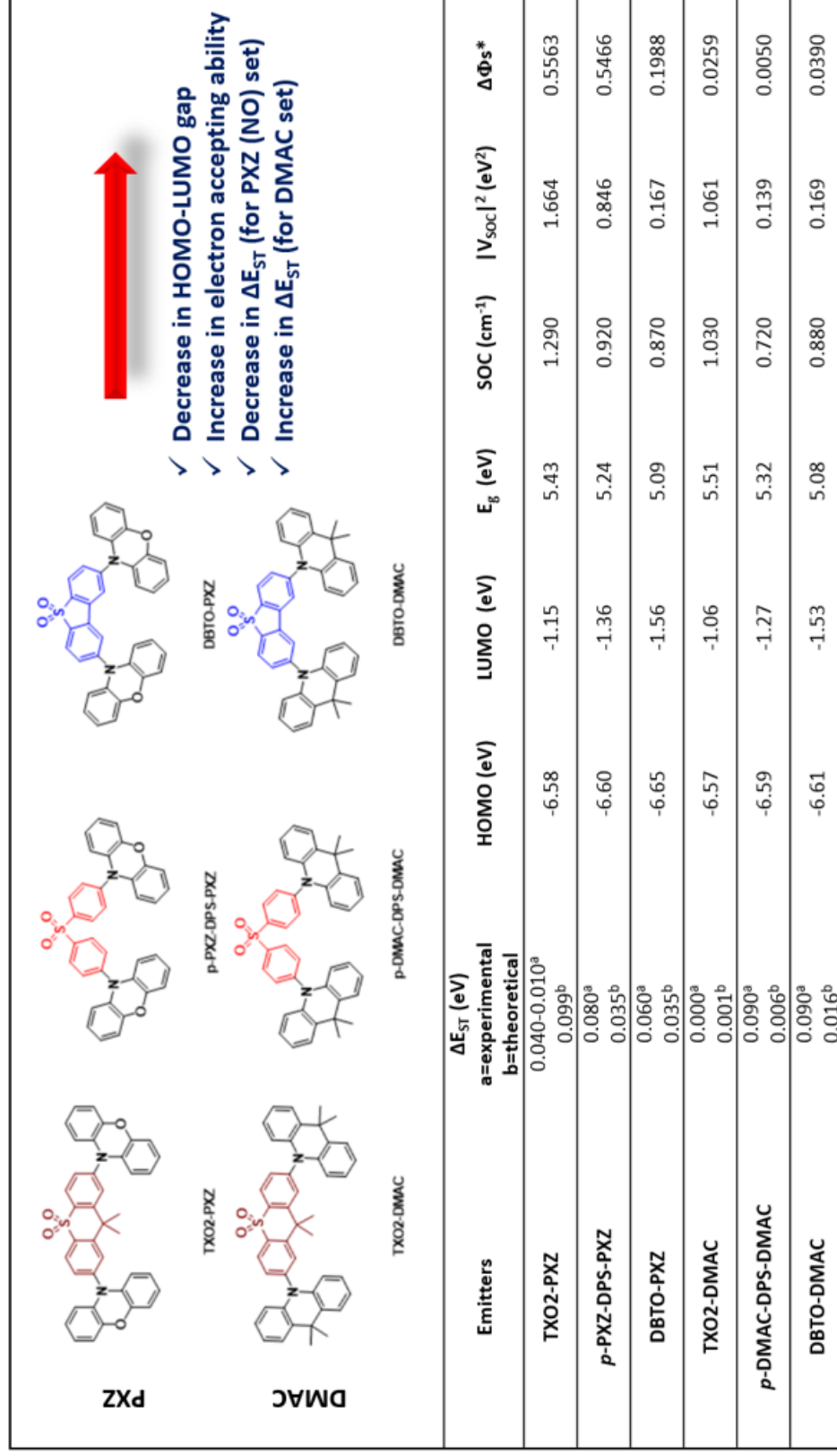


Figure 6.5. Comparison of different photophysical properties for different acceptor moieties computed at M062X/6-31+G(d,p) level of theory in toluene (TXO2-PXZ, *p*-PXZ-DPS-PXZ, TXO2-DMAC, *p*-DMAC-DPS-DMAC, DBTO-DMAC) and in dichloromethane (DBTO-PXZ).

Comparing with their phenoxazine analogues, we observed the better FMO separation of T_1 and T_2 states, which is reflected in Φ_S values, of DMAC containing emitters (see Table 6.6). Hence, the SOC from these low lying triplet states exhibit smaller values than their PXZ-analogues. Besides lower Φ_S indices of the first two triplet states, T_3 , T_4 and T_5 states show larger LE character, thus, larger SOC values. Considering all comparisons, we learned that the different acceptor moieties may yield various SOC values with higher triplet levels and there is no a regular trend between these acceptor groups.

Further analyses of excited state energies show that going from TXO2-PXZ to DBTO-PXZ, energies of the first singlet states decrease (see Figure 6.6), thus, compared to TXO2 acceptor moiety, DPS and DBTO yield bathochromically shifted absorption spectra. According to the our theoretical findings reported in Figure 6.6, energy comparisons are in well agreement with the experimental emission spectra of investigated compounds which emit in blue-green, blue and yellow for TXO2-PXZ [261], p-PXZ-DPS-PXZ [261] and DBTO-PXZ [262] compounds respectively. Moreover, we observed the similar decreasing energy trend for triplet states, and the energies of T_1 and T_2 states are iso-energetic in all emitters. This degeneracy of triplet states leads to state mixing between the states in different nature, thus, leading to larger SOC values and more efficient RISC processes.

To sum up, the nature of excited singlet states for TXO2, DPS and DBTO acceptor moieties are similar and surprisingly, Φ_S values of emitters with DPS (flexible) and DBTO (rigid) acceptor groups are found to be very close to each other (see Table 6.6). Additionally, LUMO energies of these emitters are also quite similar representing their similar electron accepting abilities, which is consistent with their similar absorption spectra. Moreover, energy level alignments of this molecule set was found to behave differently from the first two groups. In contrast to Groups 1 and 2, the molecule set under investigation have low lying iso-energetic singlet and triplet levels with similar nature of states.

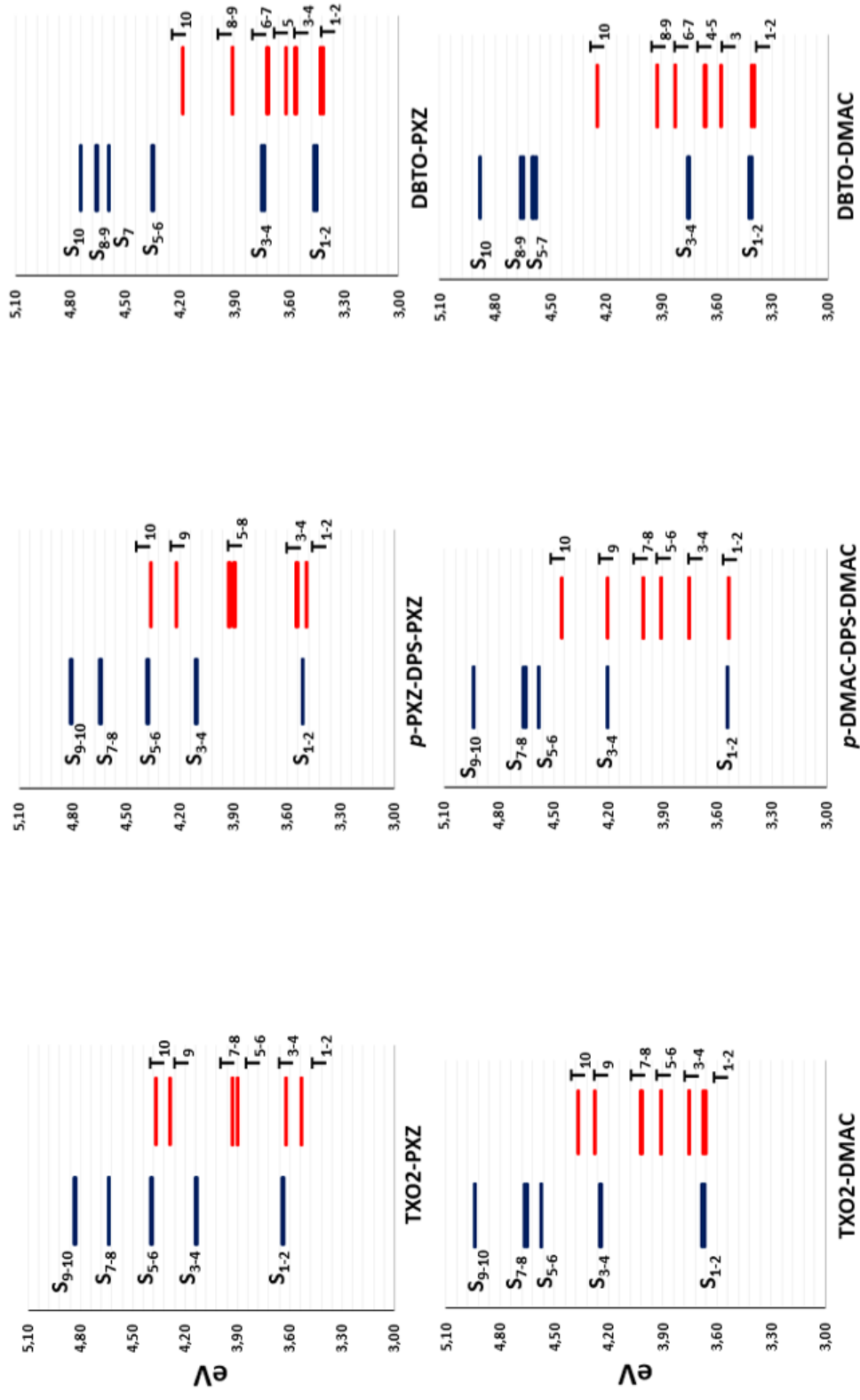


Figure 6.6. Energy levels of excited states for TTR, DPS and DBTO containing TADF emitters computed at M062X/6-31+G(d,p) level of theory in toluene (TXO2-PXZ, p-PXZ-DPS-PXZ, TXO2-DMAC, p-DMAC-DPS-DMAC) and in dichloromethane (DBTO-PXZ).

6.4.3. Effects of Phenyl Bridges on Photophysical Properties

Density functional theory calculations of Groups 3 and 4 were performed on ground state energy surfaces. As shown in Figure 6.7, Group 4 is the bridge-containing analogue of Group 3. Herein, we aimed to theoretically examine the effects of bridging the donor and acceptor moieties with a phenyl ring to observe the change in properties such as, geometric parameters, excited state energies, FMO separations, energy gaps between HOMO and LUMO orbitals and, energy gaps between the excited states involved in the RISC process.

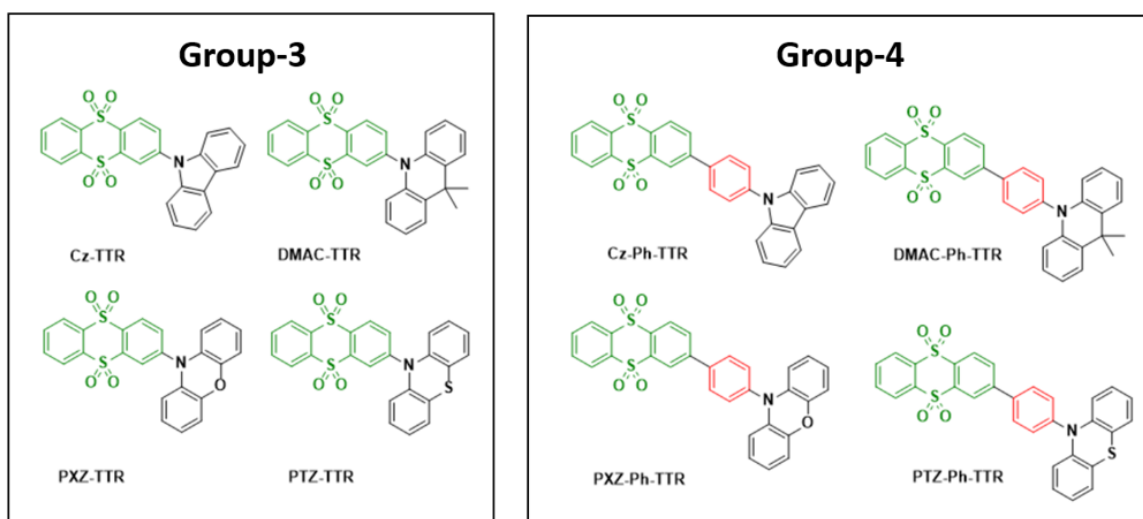


Figure 6.7. Bridged and non-bridged TADF emitters with TTR acceptor moiety. Compounds: Cz-TTR, DMAC-TTR, PXZ-TTR, PTZ-TTR, Cz-Ph-TTR, DMAC-Ph-TTR, PXZ-Ph-TTR and PTZ-Ph-TTR.

In the set of molecules under investigation, the TTR moiety with two sulfur atoms has been selected as the acceptor group and Cz, DMAC, PXZ and PTZ moieties with different steric hindrance and aromaticity have been selected as the donor moieties. As reported in Table 6.7 and Table 6.8, effect of inserting a phenyl bridge largely affected the torsion angles between acceptor groups and their adjacent moieties. As an expectation, the carbazole moiety in Cz-TTR and Cz-Ph-TTR exhibits 40° and 37° torsion angle, respectively; thus, inserting phenyl bridge in carbazole containing emitter do not cause large effect on torsion angle of Cz moiety.

Table 6.7. Torsion angles of Group 4 emitters computed at M06-2X/6-31+G(d,p) level of theory.

Compounds	$\theta(\text{D-A})_1 S_0/S_1/T_1$
Cz-TTR	49.02/65.43/45.36
DMAC-TTR	-9.57/-90.38/-5.43
PXZ-TTR	-83.98/-92.63/-102.05
PTZ-TTR	15.11/-90.76/5.53

Table 6.8. Torsion angles of Group 5 emitters computed at M06-2X/6-31+G(d,p) level of theory.

Compounds	$\theta(\text{D-A})_1 S_0/S_1/T_1$	$\theta(\text{D-A})_2 S_0/S_1/T_1$
Cz-Ph-TTR	37.70/13.59/-1.93	53.36/46.33/42.18
DMAC-Ph-TTR	-38.58/-10.41/-8.05	90.40/92.63/62.57
PXZ-Ph-TTR	-39.45/-10.79/-12.91	102.92/92.30/72.00
PTZ-Ph-TTR	36.08/20.08/2.63	17.34/-1.56/2.32

As reported in Table 6.9, both experimental and theoretical ΔE_{ST} values for the Cz-TTR emitter are smaller than their phenyl containing analogue (Cz-Ph-TTR), a situation which can be attributed to the larger electron-hole separation (see Phi-S indices in Table 6.10). On the other hand, DMAC and PTZ containing emitters were found to have two possible conformers, which are orthogonal and planar (see Figure 7). The relative energy differences between orthogonal and planar conformers of these emitters are very small, indicating the presence of iso-energetic low energy conformers in their D-A and D- π -A structures.

According to Table 6.9, effects of orthogonal geometries on singlet–triplet energy gap were well reproduced and their TADF activity due to the iso-energetic low energy conformers has been proved once again. Moreover, we also observed that the orthogonal geometries lead to a decrease in the LUMO and an increase in the HOMO energies, thus, they yield smaller E_g values.

Table 6.9. HOMO-LUMO energies, Eg and ΔE_{ST} values of Group 4 and 5 emitters computed at M062X/6-31+G(d,p) level of theory in toluene.

Emitters	HOMO	LUMO	LUMO - HOMO (Eg) (eV)	Experimental ΔE_{ST} Values (eV)	Theoretical ΔE_{ST}
					Values (eV)
Cz-TTR	-7.24	-1.81	5.43	0.10	0.55
Cz-Ph-TTR	-6.98	-1.82	5.16	0.30	0.15
DMAC-TTR (Planar)	-7.33	-1.50	5.83	0.45	0.33
DMAC-TTR (Orthogonal)	-6.90	-1.80	5.10	0.01	0.01
DMAC-Ph-TTR (Only orthogonal)	-6.51	-1.82	4.69	0.06	0
PXZ-TTR	-6.69	-1.84	4.85	-	0.37
PXZ-Ph-TTR	-6.50	-1.84	4.66	0.05	0.02
PTZ-TTR (Planar)	-7.41	-1.49	5.92	0.38	0.25
PTZ-TTR (Orthogonal)	-6.79	-1.83	4.96	0.1	0.01
PTZ-Ph-TTR (Planar)	-7.05	-1.66	5.39	0.57	0.2
PTZ-Ph-TTR (Orthogonal)	-6.62	-1.84	4.78	0.01	0.07

Table 6.10. Natures of S_1 , T_1 - T_5 states computed at M062X/6-31+G(d,p) level of theory in toluene (for Cz-Ph-TTR, DMAC-TTR, DMAC-Ph-TTR, PXZ-TTR, PXZ-Ph-TTR, PTZ-TTR, PTZ-Ph-TTR) and in ethy ethanoate (Cz-TTR).

Emitters	S_1	T_1	T_2	T_3	T_4	T_5
	(Φ_S)	(Φ_S)	(Φ_S)	(Φ_S)	(Φ_S)	(Φ_S)
Cz-TTR	CT-LE	LE	LE	LE	LE	LE
	0.5372	0.6815	0.9669	0.7556	0.6962	0.9489
Cz-Ph-TTR	CT-LE	LE	LE	LE	LE	LE
	0.7649	0.9017	0.7723	0.9601	0.9118	0.9495
DMAC-TTR (Planar)	CT-LE	LE	LE	LE	LE	LE
	0.715	0.7941	0.7471	0.9543	0.9551	0.9622
DMAC-TTR (Orthogonal)	CT	CT	CT	LE	LE	LE
	0.2008	0.2255	0.4256	0.8829	0.949	0.7289
DMAC-Ph-TTR (only Orthogonal)	CT	CT	LE	LE	LE	LE
	0.4644	0.4545	0.945	0.8793	0.7088	0.7127
PXZ-TTR	CT-LE	CT-LE	CT	LE	CT-LE	CT-LE
	0.5143	0.5045	0.4417	0.7709	0.5976	0.5589
PXZ-Ph-TTR	CT	CT-LE	LE	LE	LE	LE
	0.2247	0.521	0.7435	0.9473	0.8069	0.7076
PTZ-TTR (Planar)	LE	LE	LE	LE	LE	LE
	0.6951	0.8187	0.7689	0.9175	0.8723	0.963
PTZ-TTR (Orthogonal)	CT	CT	LE	CT-LE	LE	LE
	0.1588	0.1974	0.7363	0.5658	0.7236	0.945
PTZ-Ph-TTR (Planar)	CT-LE	LE	LE	LE	LE	LE
	0.6631	0.8496	0.8313	0.8525	0.904	0.8741
PTZ-Ph-TTR (Orthogonal)	CT	LE	CT-LE	LE	LE	LE
	0.3481	0.7746	0.4652	0.9449	0.6797	0.6983

Due to the smaller E_g values calculated for orthogonal geometries, their emission spectra were expected to be bathochromically shifted compared to their planar analogues, and although we did not calculate theoretical emission spectra, by way of comparing with experimental spectra reported in literature, we concluded that the calculated E_g values are consistent with the experimental data reported in literature [263]. To further study the effects of phenyl insertion and geometry changes on photophysical properties, we computed Phi-S indices at the M062X/6-31+G(d,p) level of theory in experimental solvents. As summarized in Table 6.10 and as represented in Figure 6.9, insertion of phenyl bridge may increase or decrease the electron and hole separation of triplet states differently.

Due to better separation in orthogonal geometries, going from planar to orthogonal conformers, a general decrease in Phi-S indices was observed. Since the S_1 states of orthogonal emitters were found to be in CT or mixed character, their SOC values with triplet states in strong LE character were observed to be the strongest couplings (see Figure 6.10).

We further compared the electron – hole overlaps of bridged and non-bridged emitters, and observed that for Cz, PXZ and PTZ containing emitters, significant differences arise from the presence of phenyl bridges. However, negative or positive effect of using phenyl bridge can vary in different emitters. For instance, while the insertion of a phenyl bridge to Cz-TTR and PTZ-TTR lead to increase in electron-hole overlap, separation increased in PXZ-Ph-TTR emitter.

The contribution of a phenyl bridge to excited state energies and energy gaps were also examined and the relative positions of the excited singlet and triplet states were reported in Figure 6.8. With the incorporation of the phenyl moiety, an increasing trend in S_1 energy levels was observed in all emitters, except for DMAC-Ph-TTR. This situation can be attributed to the larger decrease in the torsion angle of DMAC moiety in phenyl containing emitter compared to the other donor moieties which leads to larger increase in planarity and conjugation length, thus decrease in S_1 energy.

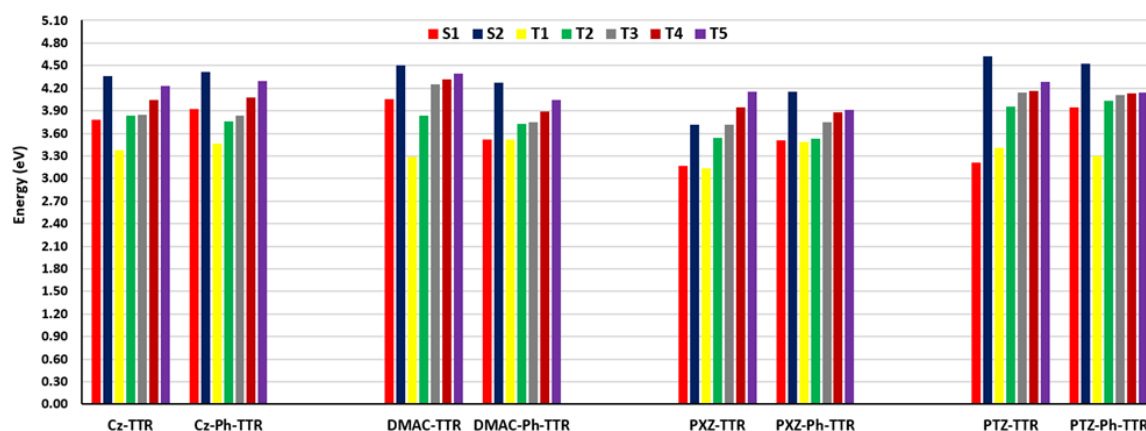


Figure 6.8. Energies of singlet and triplet excited states computed at M062X/6-31+G(d,p) level of theory in toluene (for Cz-Ph-TTR, DMAC-TTR, DMAC-Ph-TTR, PXZ-TTR, PXZ-Ph-TTR, PTZ-TTR, PTZ-Ph-TTR) and in ethyl ethanoate (Cz-TTR).

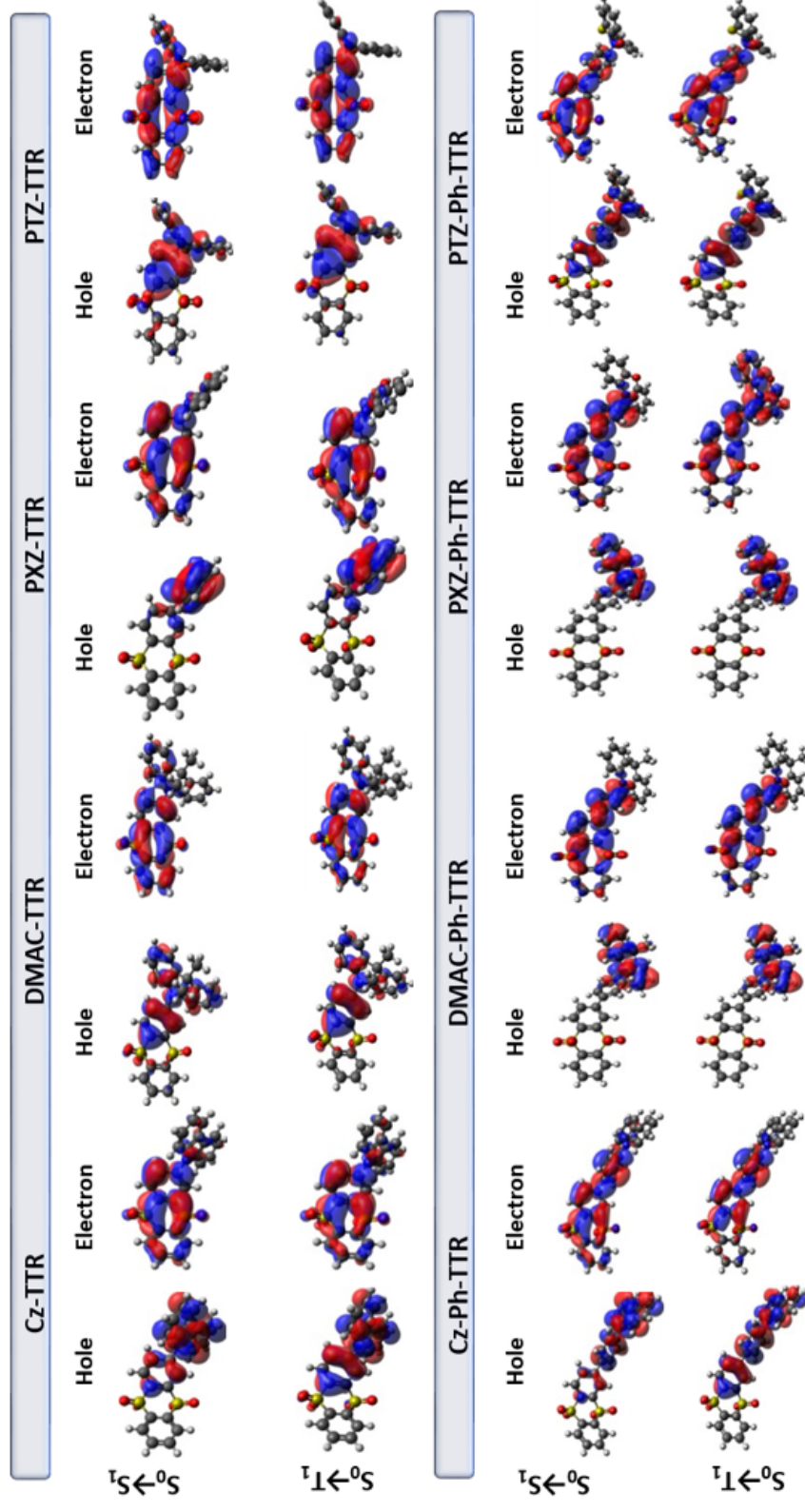


Figure 6.9. Frontier molecular orbital distributions of Group 4 and Group 5 emitters computed at M06-2X/6-31+G(d,p) level of theory in toluene (for Cz-Ph-TTR, DMAC-TTR, DMAC-Ph-TTR, PXZ-TTR, PXZ-Ph-TTR, PTZ-TTR, PTZ-Ph-TTR) and in ethyl ethanoate (Cz-TTR). Hole and electron orbitals correspond to the HOMO and LUMO orbitals respectively.

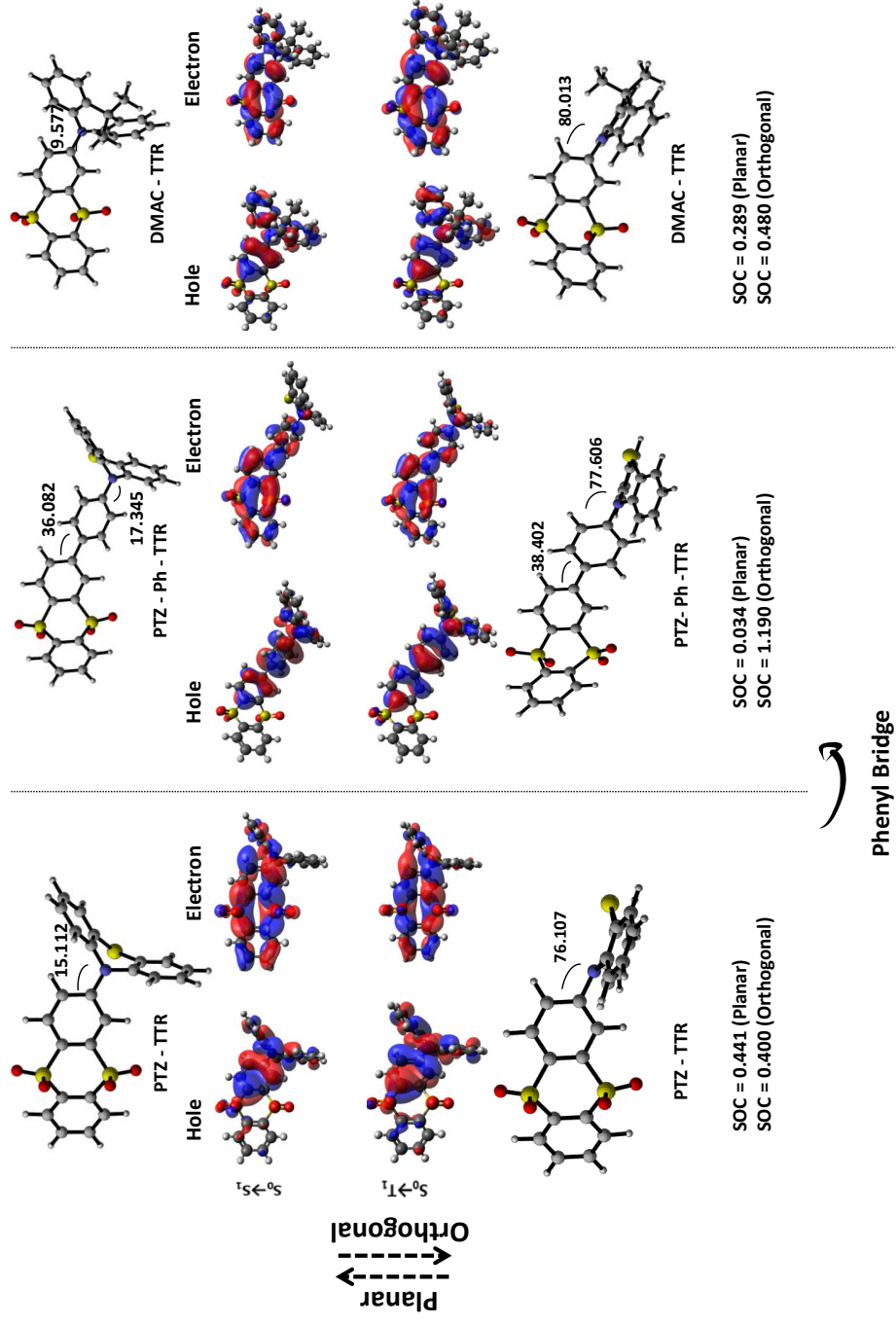


Figure 6.10. Optimized geometries and electron - hole orbitals of planar and orthogonal conformers of PTZ-TTR, PTZ-Ph-TTR and DMAC-TTR emitters computed at M06-2X/6-31+G(d,p) level of theory.

On the other hand, compared to the D-A emitters, T_1 energies of phenyl containing analogues were increased, except compound with the PTZ moiety. Despite the benefit of longer conjugation in bridge containing D- π -A emitters, increased electron-hole overlap generally led to an increase in the LE character of the T_1 state. Correspondingly, SOC values of phenyl containing emitters were increased, leading to larger RISC probabilities.

Summarizing, insertion of the π -bridge affected the behavior of emitters differently. While some materials exhibit larger ΔE_{ST} values with π -linkers, some of them represented smaller ΔE_{ST} values. On the other hand, HOMO-LUMO gaps of the emitters were found to be very close in emitters with or without π -bridges. Notably, DMAC-TTR and PTZ-TTR emitters were found to have iso-energetic low energy conformers with different photophysical properties. Our findings in ΔE_{ST} and nature of states analyses confirmed the TADF activity of orthogonal conformers. Lastly, in most of the emitters under investigation, phenyl unit containing TADF materials represented larger SOC values.

6.5. Conclusion

In summary, we present a comprehensive theoretical study on structural and photophysical properties of sulfone-based TADF emitters. Our investigations reveal that the molecule set under investigation presents various geometric behaviors, such as bearing bent conformations which prevent the formation of intermolecular excimers as well as having iso-energetic low energy conformers, which exhibit TADF or non-TADF activities. Notably, our analyses on the effects of meta- and para-conjugation showed that the regioisomers possess different photophysical properties. The first two molecule sets were shown to have multiple triplet levels below the S_1 state, which opens alternative ISC/RISC pathways. Moreover, we also presented the possibilities of IC, ISC and RISC processes between the high lying singlet and triplet levels. Additionally, we observed that the larger amount of state mixing in iso-energetic triplet levels below the S_1 state enhances the SOC values and RISC probabilities.

In the last part of our study, we discussed the effects of phenyl bridges on structures and photophysical properties. Our findings show that most of the phenyl bridge containing TADF emitters present larger SOC values. This work is intended to provide insight and pave

a way to design new TADF emitters. In light of our findings, it is possible to design new emitters with desired properties and give rise to the developments in TADF technology with new molecule designs.

7. INTERSYSTEM CROSSING IN A CARBAZOLE-BASED ROOM TEMPERATURE PHOSPHORESCENT LUMINOPHORE INVESTIGATED BY NONADIABATIC DYNAMICS

7.1. Overview

The use of phosphorescent luminophore is highly beneficial in diverse high-technological and biological applications. Yet, because of the formally forbidden character of intersystem crossing, the use of heavy metals or atoms is usually necessary to achieve high quantum yields. This choice imposes serious constraints in terms of high device cost and inherent toxicity. In this contribution we resort to density functional based surface hopping non-adiabatic dynamics of a potential organic luminophore intended for room-temperature applications. We confirm that intersystem crossing is operative in a ps time-scale without requiring the activation of large-scale movements, thus confirming the suitability of the El Sayed based strategy for the rational design of fully organic phosphorescent emitters.

7.2. Introduction

Organic luminescent materials have recently attracted considerable interest due to their suitability for applications in electroluminescence, organic lasers, and bioimaging [264–266]. Organic luminescence is produced by the radiative deactivation of sufficiently long-lived excited states. Luminescence can, in principle, be observed either from singlet or triplet states resulting in fluorescence or phosphorescence emission, respectively [267]. Fluorescence emission which following the well-known Kasha's rule occurs between the first singlet excited state and the ground state, does not involve any change in spin, and is thus fully allowed, resulting in relatively short lifetimes. Fluorescence is notably at the base of the functioning of organic light emitting devices (OLEDs). Despite some limitations, OLEDs offer several advantages such as flexible device structures, reduced power consumption, and high brightness [34]. However, OLEDs are also plagued by the insufficient device

efficiencies, partially due to the inherently short fluorescence lifetime, and the need of a high driving voltage, which severely limit their applications [196]. To overcome the efficiency problems plaguing OLEDs, a second generation of electro-luminescent materials based on phosphorescence, and collectively known as Phosphorescent organic light emitters (PhOLEDs) have been proposed.

Phosphorescence emission includes a forbidden transition between two states of different spin multiplicity, i.e. excited triplet and ground singlet states [268], thus significantly increasing the elision lifetime. Furthermore, in the case of electroluminescent materials, and because of spin statistics rules the applied electronic potential will generate 75% of the excitons in their triplet state [6]. Therefore, opening alternative emission channel through the engineering of room temperature phosphorescent materials has represented an important improvement in increasing the global device efficiency [269]. In addition, phosphorescence is usually red-shifted compared to fluorescence emission, thus allowing a deeper penetration of light in biological samples, which is a most beneficial effects for instance in the case of luminescent probes. Indeed, PhOLEDs, and more generally phosphorescent materials and compounds, have found widespread applications in electronics [20,21], optics [16,22] and biological sciences [23]. Yet, phosphorescence compounds due to the long-lived population of the triplet manifold, are more sensitive to the presence of molecular oxygen since they can sensitize the latter to its highly reactive singlet state. If the latter channel may be beneficial, for instance in photo dynamic therapy (PDT) applications, it may lead to luminescence quenching or material degradation [35]. Consequently, in some instances relevant phosphorescence is observed only under inert or cryogenic conditions, thus drastically limiting their use in portable devices or high technological applications. Therefore, the development of materials and luminophores showing efficient room-temperature phosphorescence (RTP) is highly sought [6].

RTP materials have attracted tremendous attention due to their applications in the field of intelligence security [27], optical detection [36], and biochemical imaging [37]. As a matter of fact, to be applicable RTP should require a relative fast ISC, to minimize the competition with other radiative and non-radiative channels, such as prompt fluorescence or internal

conversion (IC), conversely the depopulation of the triplet state manifold should be slow and life-times of more than 100 ms have, indeed, been reported [270]. The population of triplet states from singlet excited manifolds (Figure 7.2) is much slower than other fully allowed relaxations, and as such can be regarded as one of the key phenomena dictating the efficiency of phosphorescent luminophores. As stipulated by quantum mechanics laws, the selection rules formally forbidding ISC, may be relaxed under the effects of several favorable terms, such as a small energy gap between the involved singlet and triplet states, and a high spin orbit coupling (SOC) between the relevant states [271,272].

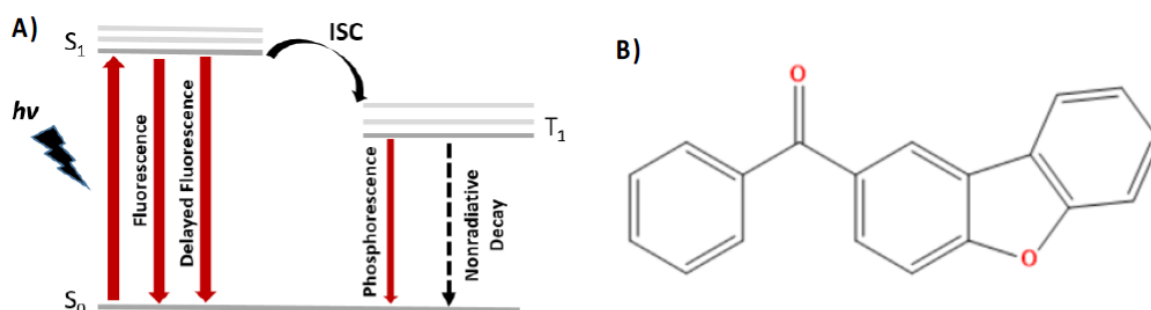


Figure 7.1. A) Schematic Jablonski diagram illustrating the relaxation processes operative in phosphorescent luminophores and B) the carbazole-based compound reported by Zhao et al. [6] and studied in the present contribution.

In a previous study devoted to Thermally Activated Delayed Fluorescent (TADF) materials, by investigating various molecular and electronic descriptors we observed that magnitude of SOC is, indeed, one of the most important parameters to control the efficiency of reverse intersystem crossing (RISC), and thus by extension ISC [244]. Indeed, as shown in the literature different strategies, and molecular engineering approaches, aimed at increasing SOC, also by favoring hydrogen bond and space restrictions are pursued to enhance phosphorence emission [273]. Usually, however, the most widespread strategy to increase SOC, and hence favor ISC or RISC, is the inclusion high atomic number atoms, to exploit the so-called heavy atom effect, since SOC is roughly proportional to the fourth power of nuclear charge [3,274]. In many instances this objective is achieved by the use of transition metal components, usually up to the second and third row of the d-elements. Indeed, while Ru complexes are known for ultrafast ISC, Ir-based compounds are among the most efficient

phosphorescent emitters, allowing not only a bright luminescence but also tuning the emission color. Conversely, metal complexed porphyrins are among the most common components for PDT applications, having, in some cases, already found clinical use. Yet, metal- or heavy-atom containing emitters also present significant drawbacks, in particular in terms of high cost and toxicity, low processability, low flexibility, and in some cases low stability [3, 34]. Furthermore, the rarity of heavy metals also poses significant burdens in terms of resources availability and sustainable development.

Therefore, the possible use of fully organic RTP compounds is regarded as highly suitable to overcome these drawbacks, yet strategies to maximize SOC and ISC rates should then be pursued. According to the well-known El Sayed rule, SOC will be maximum between singlet and triplet states having a different diabatic nature, since in this case the states can be coupled by the magnetic field operator. Thus, SOC and ISC will be maximized when involving transitions between a $^1(n, \pi^*)$ and a $^3(\pi, \pi^*)$ state. Consequently, the use of conjugated moieties involving the presence of carbonyl units is highly favorable, due to the presence of low-lying (n, π^*) states. Yet it has to be pointed out that the states in real molecular systems are rarely of a pure diabatic nature and instead a different degree of mixing between (n, π^*) and (π, π^*) character is observed, slightly complicating inferring general tendencies. In this instance, benzophenone is a paradigmatic organic moiety, which can reach a triplet conversion of up to 100% [13], also due to the extended three states quasi-degeneracy involving S_1 and two lowest triplet states T_1 and T_2 , as confirmed by a number of different experimental and computational studies involving non-adiabatic dynamics [275, 276]. The benzophenone facile ISC is also at the base of its inherent phototoxicity toward DNA [277].²⁹ Recently an extensive and systematic proposition of molecular rules for the enhancement of ISC in organic emitters has been proposed by Zhao et al [6]. based on the consideration of the El Sayed rule and the use of static density functional theory (DFT) calculations.

Among the different compounds, benzophenone and carbazole containing units have appeared as the most favorable candidates to enforce high SOC and ISC rates. As concerns carbazole, their rigid π -conjugated scaffold is also optimal to enforce aggregation and crystal formation. Indeed, the reduced vibrational disorder in the condensed phase may be beneficial

in slowing non-radiative decay pathways, hence favoring luminescence. Yet, in this case ISC should be achieved without the activation of large amplitude movements, which could be impeded in the solid state.

In this contribution we will resort to non-adiabatic dynamics in the surface hopping (SH) formalism to study ISC in the carbazole emitter presented in Figure 7.2, which despite lacking any heavy atoms is displaying optimal luminescence and a phosphorescence quantum yield of about 34% [6]. In particular, and going beyond the pure static picture, we will show that the favorable alignment of the involved states and their optimal symmetry, in terms of the El Sayed rule, translate into a ps-scale ISC rate, which, thus, should imply the facile population of the triplet manifold. Furthermore, our SH study will also confirm that ISC does not involve the activation of any large-scale movement, hence should remain operative also in condensed media, further pointing to the optimal characteristic of the chosen compound.

7.3. Computational Methodology

Prior to the propagation of the non-adiabatic dynamics, the carbazole luminophore's ground state (GS) has been optimized at DFT level using the Gaussian 16 software package [155]. The M06-2X [77] functional together with the 6-31+G(d,p) [278] basis set has been chosen to this aim. The choice of M06-2X functional is justified by its good performance in reproducing the geometries of aromatic compounds [156].

Integral equation formalism polarizable continuum model (IEF-PCM) is used in DFT calculations, to implicitly model the solvent environment [162]. Optimized structures were rendered with the CYLview software package.

Excited States have been calculated in the framework of Time Dependent-DFT (TDFT) approach, due to its optimal compromise between accuracy and computational cost. More specifically the Tamm Dancoff Approximation (TDA) has been consistently used for the excited states calculations of both singlet and triplet states. This choice is due to the fact that

the TDA provides a more balanced description of both triplet and singlet excited states, as compared to TD-DFT since it is free from triplet instability issues [164].

Furthermore, and in addition to the GS, also the geometries of the lowest singlet (S_1) and the three lowest triplet (T_1 , T_2 and T_3) states have been fully optimized. Additionally, and for benchmark purposes, the singlet and triplet excitation energies have been calculated from the GS, S_1 , T_1 , T_2 and T_3 equilibrium geometries using different functionals, namely, CAM-B3LYP [158], M06-2X, PBE0 [279], ω B97XD [208], and different basis sets of increasing size, 6-31G, 6-31G(d), 6-31G(d,p), 6-31+G(d), 6-31+G(d,p), 6-311++G(d,p).

The diabatic nature of the excited states have been evaluated using Natural Transition Orbitals (NTOs), which have been obtained post-processing Gaussian output with the Nancy-EX [168] code and visualized with the Avogadro [169] software package. To further characterized the nature of the excited states, the Φ_S index, defining the overlap between the attachment and the detachment density matrices, has been obtained.

SOC elements between S_1 and the lowest triplet states have been calculated, at the TDA level, by using the ORCA code [280] at the M06-2X/TZP [172] and CAM-B3LYP/TZP levels of theory and the TZP basis set.

To go beyond the simple static picture of ISC, we performed in vacuo SH dynamics using the SHARC code [281, 282] coupled with ORCA. Indeed, SHARC allows the use of a generalized coupling between the states, such as SOC, and hence may provide the time-scales of ISC. To simulate the effects of a wave-packet the SH dynamics has been averaged over 200 independent trajectories, whose initial conditions have been obtained sampling the Franck-Condon region through a Wigner distribution. The non-adiabatic dynamic trajectories have been propagated at TDA level, explicitly calculating the SOC element at each step, at CAM-B3LYP/6-31G level of theory, with a time-step of 0.5 fs for a total time of 2 ps (4000 steps). The common Persico correlation correction [276] was applied to avoid over-correlation as typical in SH formalism. Our model involved explicitly the first excited singlet state, and the lowest four triplet states. An initial total population of the S_1 state was considered, and

the time evolution of the states' population has been fitted with exponential models to obtain the corresponding kinetic model and the global time-scales.

7.4. Results and Discussion

Upon optimization the ground state geometry of the carbazole-based luminophore presents all the expected characteristics of these family of compounds. In particular, the rigid core and the extended π -conjugation enforce a globally planar structure, while a non-negligible torsion angle (30°) is observed between the carbonyl moiety and the phenyl ring to minimize the sterical hindrance with the carbazole, as it is the case for the parent benzophenone. The vertical excitation energies from the Franck-Condon region for the lowest-lying excited states, on either the singlet and triplet manifolds are reported in Table 7.1.

Table 7.1. Vertical excitation energies from the Franck-Condon geometry calculated at CAM-B3LYP/6-31G level of theory.

State	Excitation Energy (eV)	f (absorption)
S_1	3.98	0.0014
S_2	4.61	0.0303
S_3	4.87	0.1810
S_4	5.00	0.8612
T_1	3.37	-
T_2	3.56	-
T_3	3.84	-
T_4	3.88	-
T_5	4.07	-

The low energy portion of the absorption spectrum is dominated by two excitations, the lowest one being almost dark and the second one having a much higher oscillator strength. Yet, the S_1 state lies about 0.65 eV lower than the brighter S_2 states. Thus, even if the latter should be populated due to the higher oscillator strength it is reasonable to assume that an ultrafast, fs-based intersystem crossing, will drive an almost unitary population of the first excited state. Interestingly, 4 triplet states are found at lower energies than the S_1 state with

T_4 being quasi-degenerate with S_1 .

In Figure 2 we report the NTOs calculated for the most important states. The nature of S_1 is, thus, clearly identified as (n, π^*) , while the second excited singlet state has a (π, π^*) nature showing a partial charge-transfer character but being mainly localized on the carbazole unit. The same nature of the states is also found in the triplet manifold, with a pronounced (n, π^*) character for T_1 and a partially charge-transfer (π, π^*) nature for T_2 . Interestingly, the T_3 states, which will be relevant for the further discussion, can again be described as a (π, π^*) but is mainly localized on the phenyl ring.

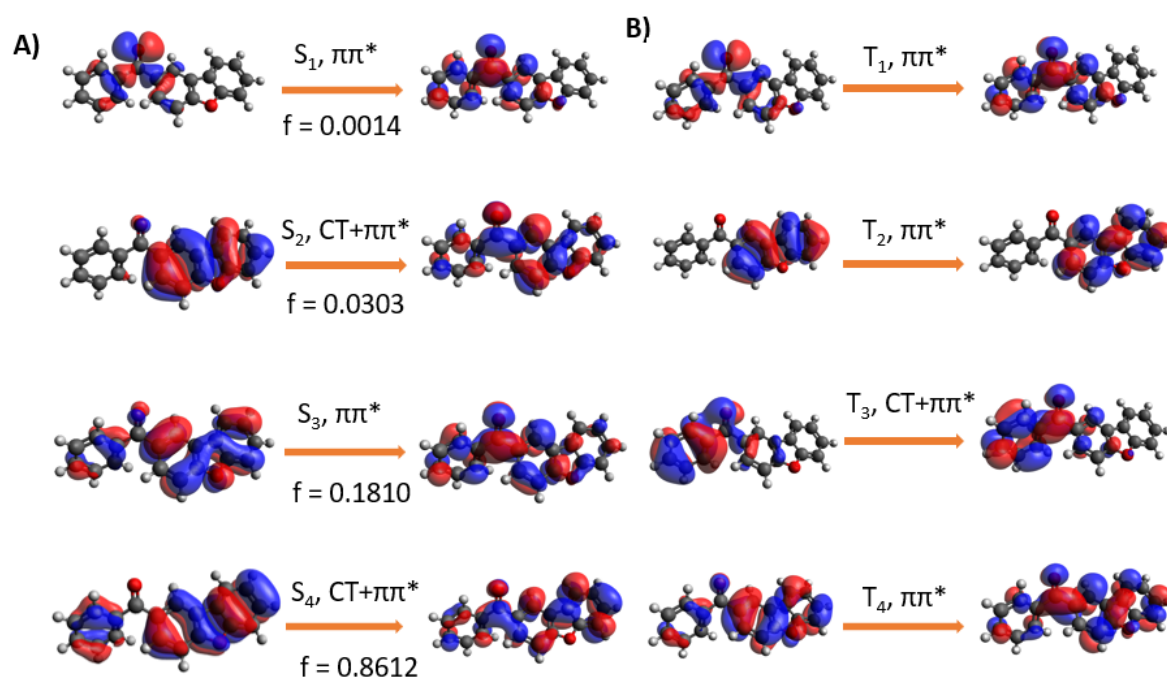


Figure 7.2. A) NTO study for S_n states computed at CAM-B3LYP/6-31G level of theory. B) NTO study for T_n states computed at CAM-B3LYP/6-31G level of theory.

The partial charge transfer character of the different states can also be appreciated by the values of the topological Φ_S index reported in Table 7.2.

Table 7.2. Topological Φ_S index of the S_1 , T_1 , T_2 , and T_3 states obtained from the S_0 equilibrium geometries with different functionals using the 6-31G basis set.

Functional	S_1	T_1	T_2	T_3
M062X	0.45	0.48	0.95	0.88
PBE0	0.47	0.61	0.92	0.76
ω B97XD	0.45	0.57	0.93	0.90
CAMB3LYP	0.45	0.65	0.91	0.89

The values of the SOC elements coupling the lowest triplet and singlet states are reported in Table 7.3, highlighting small but non negligible coupling of the S_1 states with the triplet manifold. The partial lifting of the El Sayed's rule is most probably due to the partially mixed nature of the states, to their partial charge-transfer character, and to the breaking of the σ/π symmetry due to the twisted carbonyl-phenyl arrangement. Yet, this situation appears as favorable to enforce efficient ISC.

Table 7.3. SOC elements between the different states calculated at CAM-B3LYP/6-31G level of theory and Franck-Condon geometry.

Excited States	SOC (cm^{-1})
S_1-T_1	7.43
S_1-T_2	8.48
S_1-T_3	17.23
S_1-T_4	7.00
S_2-T_1	2.13
S_2-T_2	0.27
S_2-T_3	0.92
S_2-T_4	0.17

Upon geometrical relaxation on the S_1 potential, as indicated on the Jablonski diagram reported in Figure 7.3, we may observe that the stabilization of S_1 closes the gap with T_2 and the two states are now separated by only 0.05 eV. This situation is again pointing toward a favorable, albeit non ultrafast ISC, involving those two states, also considering the non-negligible SOC between the two states.

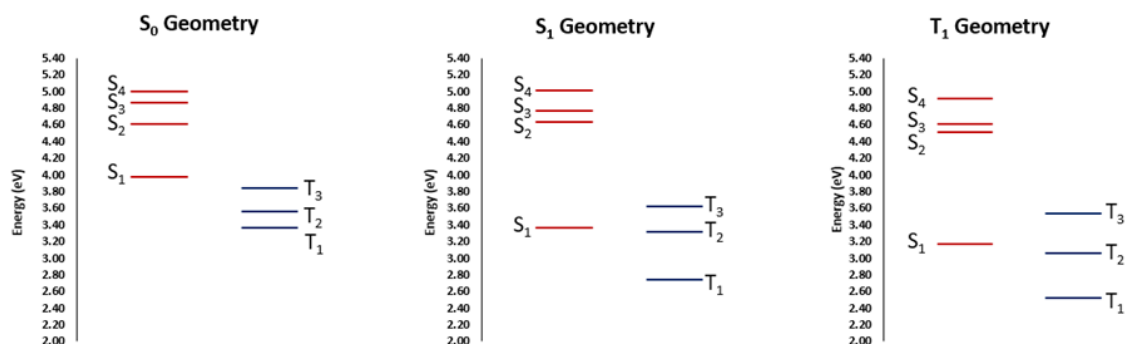


Figure 7.3. Jablonski diagrams at the most relevant equilibrium geometries obtained at CAM-B3LYP/6-31G level of theory.

As concerns the influence of the level of theory on the alignment of the states we report in Figure 7.4 the vertical excitation energies for the lowest singlet and triplet states computed using different exchange-correlation functionals and different basis set. It is evident that the choice of the basis set has a negligible effect on the quality of the excitation energies, thus justifying the following use of the smallest double-zeta basis for the non-adiabatic dynamics. A slightly more important influence of the functional can be appreciated. Yet, the effects are globally modest and the presence of partially charge-transfer excited states justifies the use of long-range corrected functionals for the following study.

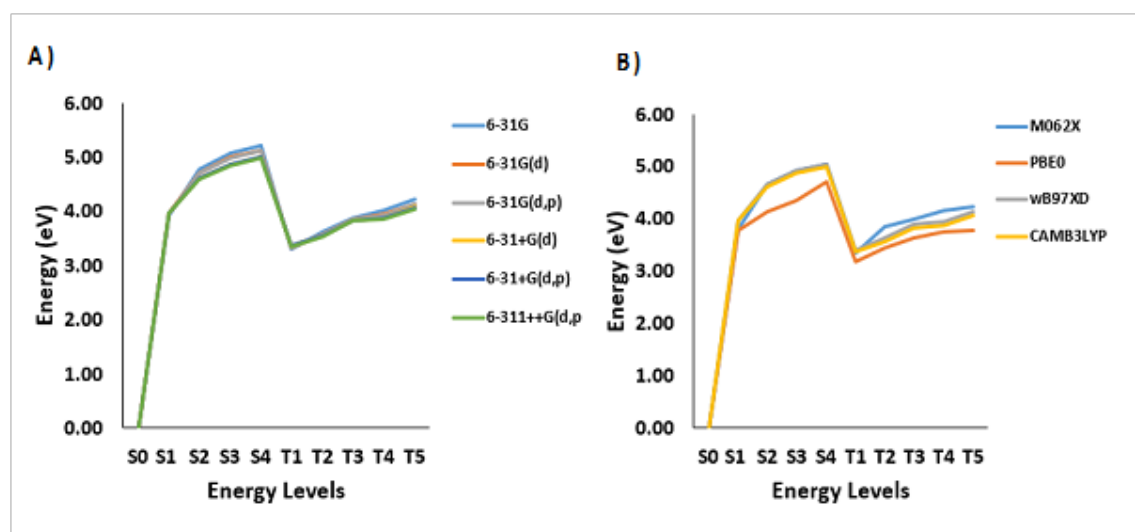


Figure 7.4. Vertical transitions energies calculated from the Franck-Condon geometry with different basis set (A) and exchange correlation functionals (B).

Finally, to assess the mechanisms and the time-scales of ISC we have performed SH dynamics over 200 independent trajectories. The results in terms of population of the different excited states are collected in Figure 7.5, together with the ensuing kinetic model inferred from the analysis of the hops between states of different multiplicity. Indeed, the population of the S_1 state decays slowly but steadily at the advantage of the triplet manifold, whose population increases. Interestingly, we may observe that after the raise in the population of T_2 , T_1 is also readily accessed and becomes the dominant triplet state after about 150 fs. At 2 ps we may observe a globally perfectly shared population between the singlet and the triplet manifold, with T_1 being now the largely dominant state. Yet, we may observe that the population of T_2 is persistent all along the SH dynamics being of about 10% at 2 ps. Furthermore, we may also observe the raising of the population of the T_3 state, which becomes non-negligible at around 500 fs and stays only slightly lower than the one of T_2 .

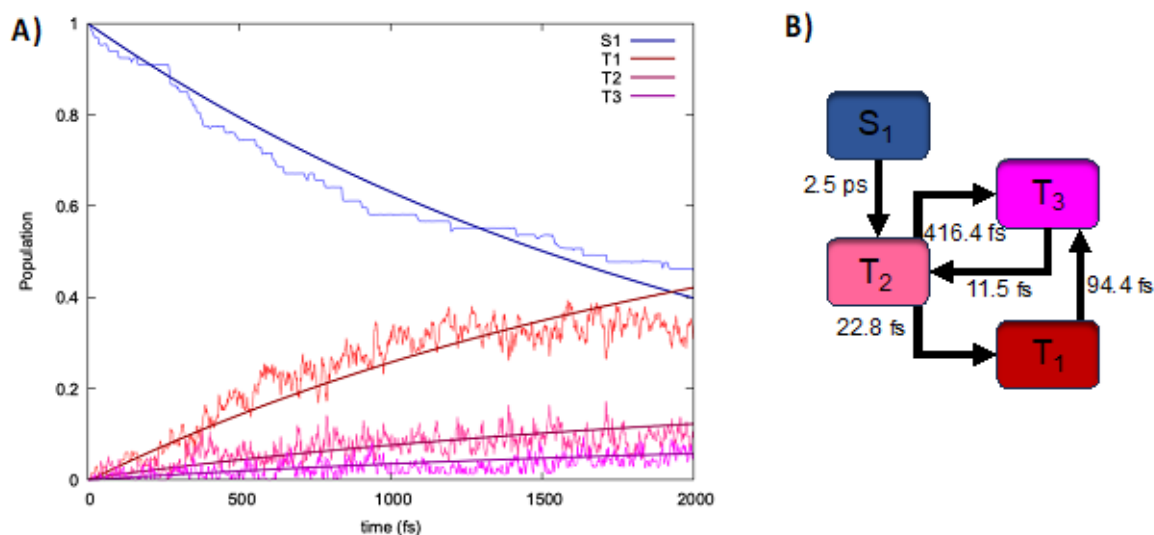


Figure 7.5. Time evolution of the population of the different states following the SH dynamics (A). Kinetic model used to fit the time evolution of the population; the obtained characteristic time constants are also reported. Note that the population obtained by applying the fitting is also indicated in panel A with darker color shades.

Globally, this behavior appears quite surprising since, from the simple analysis of the Jablonski diagram, one could have inferred a straightforward population drift going from S_1 to T_2 and then rapidly towards T_1 . Instead, and because of the quasi-degeneracy of the

triplet states, a more complicated mechanism takes place in the photophysics of the carbazole derivatives. Indeed, while the first process of the S_1 decay is ISC towards T_2 , which also represents the time limiting step with a time constant τ of about 2.5 ps, the population of this state open up a complex equilibrium involving T_1 and T_3 . If the IC towards the lowest triplet state is clearly the most favorable process having a time constant of only 23 fs, a population transfer towards T_3 is also active, albeit having a much slower, yet ultrafast characteristic time of about 400 fs. Interestingly, while T_3 readily relaxes back to T_2 (τ of 11 fs) a population drift from T_1 to T_3 is also possible and is relatively fast (τ of 94 fs).

Our SH dynamics have thus confirmed that ISC is operative in this carbazole systems, thus justifying its efficiency as a luminophore. The rate limiting step of the ISC, which amounts to 2.5 ps confirms that the process while possible is not ultrafast, probably due to the relatively modest values of the involved SOC. However, this process hides a complex equilibrium involving rather extended population transfers in the triplet manifold, which ultimately leads to the persistence of anon-negligible population of T_2 and T_3 up to the ps time-scale.

Furthermore, by analyzing the geometrical changes along the SH trajectories we may evidence that no large-scale movement is necessary to trigger ISC. Instead only the activation of small amplitude vibrational movements, mainly related to the carbonyl stretching are necessary. This aspect is mostly favorable for the possible triggering of aggregation induced phosphorescence, which is operative in the present carbazole-based luminophore.

7.5. Conclusion

In the present contribution we have studied by extensive TD-DFT modeling, complemented with non-adiabatic SH dynamics the behavior of a carbazole-based chromophore which is a most promising candidate for room temperature phosphorescence. In particular we have confirmed the interplay between (n, π^*) and (π, π^*) states in providing the most

favorable conditions for high SOC in full organic compounds, thus favoring the ensuing ISC. While we have confirmed that ISC takes place with a rate limiting step of about 2.5 ps, and involves the transition between S_1 and T_2 , we also identify the instauration of a complex equilibrium in the triplet manifold with multiple population transfers between the lowest lying triplet states. In turn this imply that the population of T_2 and T_3 is persisting all along the SH dynamics, thus exceeding the ps time-scale, and should be taken into account.

Furthermore, we have shown that ISC does not involve the activation of large amplitude degrees of freedom, and may remain possible also in condensed phase, opening up the possibility of aggregation induced phosphorescence behavior. Our results, show how SH dynamics may be used to unravel complex and subtle mechanisms which may be important in shaping the photophysical behavior of organic chromophores. They also point out the validity of the exploitation of the El Sayed rule, involving the coupling between states of different diabatic nature in providing efficient organic compounds featuring high ISC rates. In the following we preview to extend this study to the chromophore in condensed phase to take into account the effects of aggregation on its photophysical behavior.

8. GENERAL CONCLUSION

This dissertation presents the outcomes of molecular structure and computational methodology impacts on thermally activated delayed fluorescence and organic room temperature phosphorescence technology.

In the first part of the thesis, we explored the performance of different computational protocols on static photophysical analyses of a wide range of TADF emitters. The results obtained from static calculations of TADF molecules with various structural properties demonstrates that the M06-2X functional well reproduces the descriptors important for TADF mechanism, which are nature of states, spin orbit coupling, and singlet - triplet energy gap. On the other hand, the basis set analyses obtained from the each study showed that the increase in basis set does not cause any change in excited state properties. The most important finding obtained from the first study is the deterministic role of spin orbit coupling on TADF performance and its dominant effects compared to the other descriptors.

In the second study which is focused on the boron-based TADF emitters, the main target was observing the role of boron on photophysical properties. Benchmark analyses performed in this study reproduced the findings observed in the first article. Therefore, the same computational methodology has been used in the calculations of boron based TADF emitters. In this study, we observed that while the highly orthogonal structures affects singlet - triplet energy gap positively, it leads to extremely small oscillator strengths, which decreases emission probability, and small SOC values which decrease ISC/RISC probabilities. Geometry analyses in this study showed that while ground state and first excited singlet states represent highly similar geometries, an obvious geometry relaxation has been observed in first excited triplet state which leads to increase in LE character of triplet state, which in turn, causes greater amount of ISC/RISC processes. Another important finding of this study is that we observed that it is possible to increase the performance of carbazole donor moiety, which is known as a poor performing donor moiety due to its five membered central ring. The

strategy to increase the performance of carbazole moiety is locating it to the ortho position of acceptor unit and increase the steric hindrance, which is a situation enhancing the electron - hole separation, thus, decreasing the singlet - triplet energy gap. Moreover, π - π interactions were observed between the phenyl groups in close proximity, which reduces the free rotations and increases the PLQY.

The third study reported in this thesis targets the role of sulfone based emitters on TADF performance and static calculations obtained from a wide range of sulfone containing emitters with various structures, showed similar properties reported in the previous articles. However, differently from the first two article, we observed that the large amount spin mixing in low lying, iso-energetic triplet states may play a positive role in enhancing the degree of SOC, thus, RISC processes.

The last article reported in this thesis focuses on the dynamic processes of a model room temperature phosphorescent emitter. In this contribution, the ISC processes between first excited singlet and low lying triplet states were observed. The processes were found to be consistent with the spin orbit coupling values between the relevant states. Moreover, we observed that the kinetic model includes multiple states and all triplet states lying below and close to the first excited singlet contribute to the ISC/IC processes.

To summarize, at the beginning of this thesis project, our main purpose was investigating the structure - photophysical property relation of TADF emitters via computational methods. At the end of this thesis study, we are in a position to predict the photophysical properties such as SOC, oscillator strength, nature of states and ΔE_{ST} of TADF candidates before their device applications. Therefore, with the help of our findings on computational protocol and structure - descriptor relationship, we can design and suggest new TADF emitters for the experimental research groups. On the other hand, differently from the widely reported studies, the findings from surface hopping dynamic simulations show us that the ISC and IC processes can be in a complex equilibrium between the excited states. Thus, to predict the efficiency of emission as phosphorescence, surface hopping dynamic simulations performed with the SHARC software package are highly important. In light of all these findings, we highlight the importance

of understanding the photophysical properties via the computational methods because our findings and observations reported in this thesis will help the experimental research groups to save both time and cost for the synthesis and device applications of the emitters.

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APPENDIX A: ARTICLES

A.1. Computational Descriptor Analysis On Excited State Behaviours Of A Series Of TADF And Non-TADF Compounds



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Computational descriptor analysis on excited state behaviours of a series of TADF and non-TADF compounds†

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The thermally activated delayed fluorescence (TADF) behaviours of seventeen organic TADF emitters and two non-TADF chromophores bearing various donor and acceptor moieties were investigated, focusing on their torsion angles, singlet–triplet gap (ΔE_{ST}), spin orbit couplings (SOC) and topological Φ_s index. Electronic structure calculations were performed in the framework of the Tamm–Dancoff approximation (TDA) allowing the possible reverse intersystem crossing (RISC) pathways to be characterized. The electronic density reorganization of the excited states was checked also with respect to the different exchange–correlation functional and absorption spectra were obtained by considering vibrational and dynamical effects through Wigner sampling of the ground state equilibrium regions. Examining all the parameters obtained in our computational study, we rationalized the influence of electron-donating and electron-accepting groups and the effects of geometrical factors, especially torsion angles, on a wide class of diverse compounds ultimately providing an easy and computationally effective protocol to assess TADF efficiencies.

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Introduction

Since the original proposal of organic light-emitting diodes (OLEDs) by Tang and Van Slyke in 1987,¹ significant progresses have been achieved in their development and application in different technologies, including display apparatus. OLEDs represent an important innovation in lighting markets, providing improved image quality, high brightness, low fabrication costs, low power consumption and high durability.^{2,3} They operate based on the physical phenomenon known as electroluminescence (EL), i.e. the conversion of electrical energy into light.⁴ In OLEDs, EL is achieved by fluorescent materials, which undergo a two-step process, an initial absorption leading to the population of an electronically excited state and a subsequent radiative decay to the electronic ground state, which is known as prompt fluorescence.² However, despite possessing useful properties, several drawbacks still limit the development of OLEDs, notably related to technical issues, such as high-power consumption, insufficient device efficiency, and high driving voltage. Insufficient device efficiencies in

OLEDs have led to the use of high quantum yield phosphorescent materials utilizing alternative routes to achieve radiative decay. These are based on intersystem crossing (ISC) and hence the population of triplet states, leading to phosphorescence.⁵ The exploitation of both singlet and triplet excited states has led to an increase in internal quantum efficiencies (IQE) up to 100%. Although the use of phosphorescent materials significantly increased quantum efficiencies in OLEDs, the use of heavy metals, such as Ir or Pt, limited their application due to increased device costs, environmental pollution, and toxicity. Moreover, the lack of stability is an additional drawback of phosphorescent OLEDs (PhOLEDs). Indeed, chemical degradation leading to charge traps, non-radiative recombination sites, and luminance loss, are serious issues affecting PhOLEDs.⁵ In the quest to increase OLED efficiencies, thermally activated delayed fluorescence (TADF) materials have attracted great attention as they lead to the population of both singlet and triplet states without using any heavy metals (Fig. 1).^{6–12}

Soon after the first organic TADF emitter was reported in 2011, studies related to TADF based OLEDs gained momentum and nowadays, external quantum efficiencies (EQE) reaching up to 30% together with internal quantum efficiencies (IQE) of 100% have been reported.¹³ In addition to their applications in OLEDs, TADF materials also have applications in fluorescence lifetime imaging,¹⁴ and oxygen sensing.^{15–19}

TADF materials also possess the critical advantage of serving as host materials in emission layers,¹⁸ and enabling different

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† Electronic supplementary information (ESI) available: Optimized structures, Cartesian coordinates for optimized geometries, benchmark calculations charge distributions, spin orbit couplings, nature of states, absorption spectra, and energies of excited states. See DOI: <https://doi.org/10.1039/d2cp01323a>

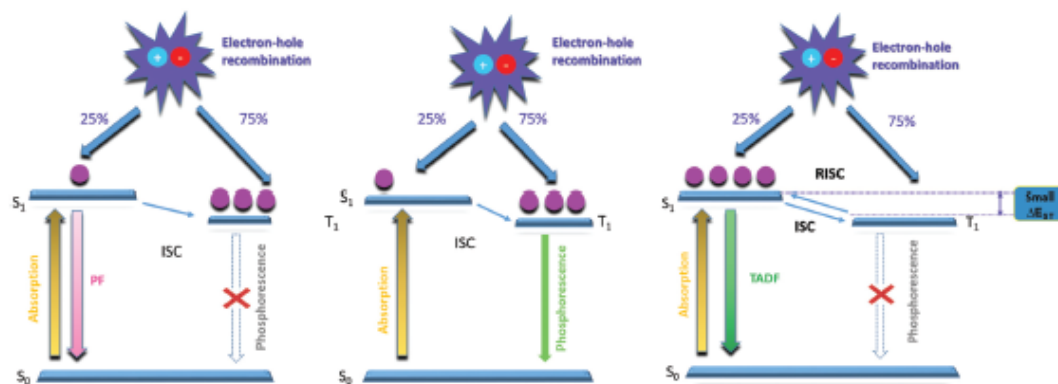


Fig. 1 Jablonski diagram for OLED, PHOLED and TADF materials, respectively.

color emission.^{19–34} Emission, which may span from blue to red, is mainly controlled by the degree of intramolecular charge transfer (ICT) of the involved excited states.^{31,32} Since ICT is one of the most important parameters in TADF activity, numerous design strategies were attempted to enhance this fundamental process. One strategy involves the use of donor–acceptor (D–A), D– π –A, D– π –A– π –D molecular frameworks, in which the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbital (LUMO) are localized on donor and acceptor units, respectively, hence leading to spatially separated frontier orbitals.³³ Various donor and acceptor groups were designed to enhance charge transfer in TADF luminophores. The most frequently used donor moieties are diphenylamine,^{2,14,35} carbazole,^{23,36–44} acridine,^{17,20,45} and phenoxazine derivatives,^{46–49} while the most common acceptor units include boron,^{50–58} sulfone,^{23,25,41} and benzophenone derivatives (Fig. 2).^{20,24,59,60} However, TADF systems are not limited to these building blocks, as other interesting frameworks were designed such as cyanobenzenes,⁵⁹ triazines,⁶¹ oxadiazoles,³¹ sulfones,⁶² and spiro derivatives.^{63,64}

From a photophysical point of view, TADF is based on the up conversion from the triplet (T_1) to the singlet (S_1) state, which is only possible if ΔE_{ST} is sufficiently small, *i.e.* less than 0.1 eV. This energetic alignment facilitates the reverse intersystem crossing process (RISC), which is also known as the up-intersystem crossing process (UISC).⁴⁶ Although TADF compounds with ΔE_{ST} values smaller than 0.1 eV show the best performances, some fluorophores with ΔE_{ST} values close to 0.5 eV exhibit TADF emission. However, though the TADF mechanism usually involves RISC between T_1 and S_1 states, an alternative possible pathway driven by higher excited triplet states is also observed. Indeed, in some circumstances more than one triplet state is present below the S_1 state, allowing reverse internal conversion (RIC) between T_1 and the upper lying triplet states. This is followed by a RISC between T_n , *i.e.* the triplet state closest to the first excited singlet state and S_1 .⁶⁶ Furthermore, rigid molecular architectures are usually preferred over flexible ones for high performance TADF devices, since they minimize non-radiative

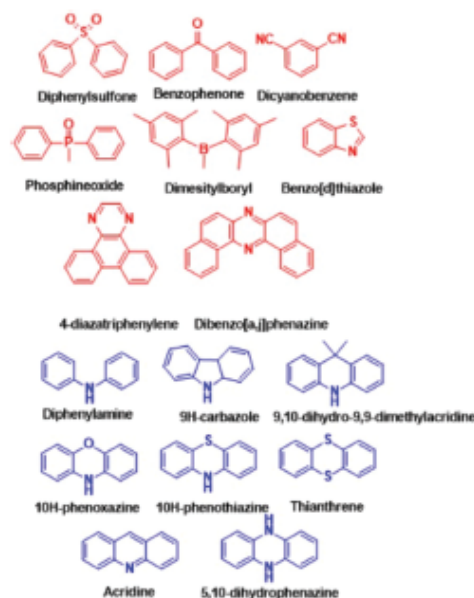


Fig. 2 Commonly used acceptor (red) and donor (blue) moieties in TADF molecules.⁷¹

decay due to vibrational and rotational motions.⁶⁷ In addition to a small ΔE_{ST} gap, the electronic coupling between charge transfer singlet (^1CT) and local triplet (^3LE) states strongly influences TADF efficiency.⁶⁸ Indeed, the magnitude of spin orbit coupling (SOC) is crucial to determine RISC efficiency and ultimately delayed fluorescence.⁶⁹

The rate of RISC (k_{RISC}) is usually expressed by combining Fermi's golden rule with Marcus' theory,⁷⁰ as:

$$k_{RISC} = \frac{2\pi}{\hbar} |H_{SD}|^2 (4\pi\lambda k_B T)^{-\frac{1}{2}} \exp\left(\frac{-E_A}{k_B T}\right) \quad (1)$$

$$E_A = \frac{(\Delta E_{ST} + \lambda)^2}{4\lambda} \quad (2)$$

The key parameters being the reorganization energy λ , the SOC expressed by H_{SO} , and E_A which is related to the ΔE_{ST} energy gap through eqn (2).

More topological descriptors of the electronic density reorganization such as the amount of CT (q^{CT}) and the effective CT distance (d^{CT}) for ground and excited states have also been used to computationally preview TADF performance.⁷² The CT character of T_1 states has also been analyzed through the excited state dipole moments.⁷³ Furthermore, environmental factors are also important in dictating the overall TADF efficiency, in particular the ISC rates, as shown by their sensitivity to solvent polarity.⁶⁵

In addition, as Yu-Zhong Xie and co-workers pointed out, minimum energy crossing points (MECP) between S_1 and T_1 states are crucial, since they represent funneling regions, allowing the non-adiabatic transition between different electronic states.⁷⁴

In our previous study, we investigated a series of benzophenone based TADF emitters and non-TADF chromophores by quantum chemical calculations. Our main goal in that contribution was to understand the photophysical properties of benzophenone emitters and their derivatives in terms of absorption spectra, charge separations in the excited states, ΔE_{ST} gaps and SOC magnitude.⁷⁵ Here, on the other hand, we plan to extend the objectives of the previous study investigating TADF emitters with various acceptor moieties and propose a new, more general, computational strategy applicable to a large variety of TADF emitters. For this purpose, we analyzed the relationship between molecular structures and photophysical properties of a wide range of emitters by means of *ab initio* calculations. To understand the correlation between the molecular structure and TADF properties, a comparative study is performed along molecules that possess TADF features and compounds known to be poor TADF emitters (henceforth, they will be referred to as non-TADF molecules). Indeed, a systematic study on the relationship between structural, electronic properties, and the TADF efficiency of different classes of compounds is somehow missing. We plan to bridge this gap by using molecular modelling and simulation to provide a unified description of the different parameters related to TADF performance.

For this purpose, ground state structural properties, such as the torsional angles, are explored and related to the optical properties and the singlet–triplet gap. Our analysis of different excited state descriptors, including singlet–triplet gap, SOC magnitude, and the amount of charge transfer provides a useful and computationally effective protocol to rationalize TADF efficiency.

Although the RISC probability decreases with the increase in ΔE_{ST} , H_{SO} which competes with ΔE_{ST} , albeit being usually overlooked, may play a significant role and hence, should be properly accounted for to sketch useful design rules for TADF compounds.

Computational methodology

Prior to the evaluation of all optical and photophysical properties, conformational analysis was performed using the Gaussian 16 software package⁷⁶ to characterize all possible conformers of the chosen TADF and non-TADF molecules. Density Functional Theory (DFT) calculations with the M06-2X^{77,78} meta-hybrid functional and the 6-31+G(d,p)⁷⁵ basis set have been carried out to optimize the ground state conformers and the corresponding S_1 and T_1 geometries. However, all conformers are expected to share the same TDA behavior since the latter is mainly dictated by the twisting angle between donor and acceptor moieties or between the donor and bridge moieties, which are highly conserved in the conformational space. While for ground state equilibrium geometries we have checked that no imaginary vibrational frequencies are present, this was not performed for S_1 and T_1 equilibrium geometries due to the lack of analytical Hessians. The choice of M06-2X functional is justified by its good performance in reproducing the geometries of aromatic compounds.⁷⁹ In our previous study, the excited state properties obtained by taking into account all the possible conformers of TADF molecules have been proven identical to the ones of the lowest energy conformer.⁷⁵ Thus, we continue our analysis considering the lowest energy conformers of each molecule only (see Tables S1–S5, ESI†). The energy and nature of excited states are assessed at the B3LYP⁸⁰/6-31+G(d,p), M06-2X/6-31+G(d,p), CAM-B3LYP⁸¹/6-31+G(d,p), and wB97XD⁸²/6-31+G(d,p) levels of theory, and 6-311++G(3df,3pd)⁸³ and 6-311++G(2d,2p)⁸⁴ basis sets were used, in all calculations, for sulfur and phosphorus atoms, respectively. A series of benchmark calculations with Becke's hybrid B3LYP functional and 6-31+G(d,p) and 6-311+G(d,p) basis sets are also performed. From this test, it is clearly observed that increasing the basis set does not induce any noticeable change in the calculated absorption spectra (see Tables S6 and S7, ESI†).

Integral equation formalism polarizable continuum model (IEF-PCM) is used in all calculations,⁸⁵ to implicitly model the solvent environment. Optimized geometries were rendered with the CYLview software package.⁸⁶

Tamm Dancoff Approximation (TDA) was employed for all the excited state calculations. This choice is due to the fact that the TDA method provides a more balanced description of both triplet and singlet excited states, and compared to Time-Dependent DFT (TD-DFT) is free from triplet instability issues.⁸⁷ All excited state calculations have been carried out with the Gaussian 16 software package. Absorption spectra were modeled as vertical transitions from the S_0 equilibrium geometry. Subsequently, to include dynamic and vibrational effects, 30 conformations, sampling the vicinity of the Frack-Condon region, were generated through a Wigner distribution⁸⁸ as implemented in the Newton-X⁸⁹ software package. Vertical transitions from each snapshot were convoluted using Gaussian functions of full-width at half length (FWHL) of 0.15 eV. Absorption spectra calculations *via* the Wigner distribution method have been performed with the B3LYP, PBE0, M062X, BLYP⁹⁰ and TPSSH⁹¹ functionals using the 6-31+G(d,p) basis set.

The nature of the excited states is evaluated using Natural Transition Orbitals (NTOs), obtained with the Nancy_EX code^{92,93} and visualized with the Avogadro⁹⁴ software package. In addition, Φ_s values, defining the overlap between the attachment and the detachment densities, were calculated. Spin-orbit couplings (SOC) between S_1 and T_1 states have been calculated at the TDA level by using the Amsterdam Density Functional (ADF) code^{95,96} at the B3LYP/DZP⁹⁷ and M06-2X/DZP levels of theory. DZP was used since Pople basis sets are not available in ADF.

Results and discussion

Herein, a series of different TADF emitters with various donor and acceptor groups were selected from the literature and were investigated by TDA-DFT methods (see Fig. 3). In an attempt to identify the presence of TADF characteristics in the selected emitters, several descriptors were assessed, such as the twisting angle between donor and acceptor units, ΔE_{ST} , NTO densities along with the charge transfer topology indices (Φ_s),⁹⁸ and SOC

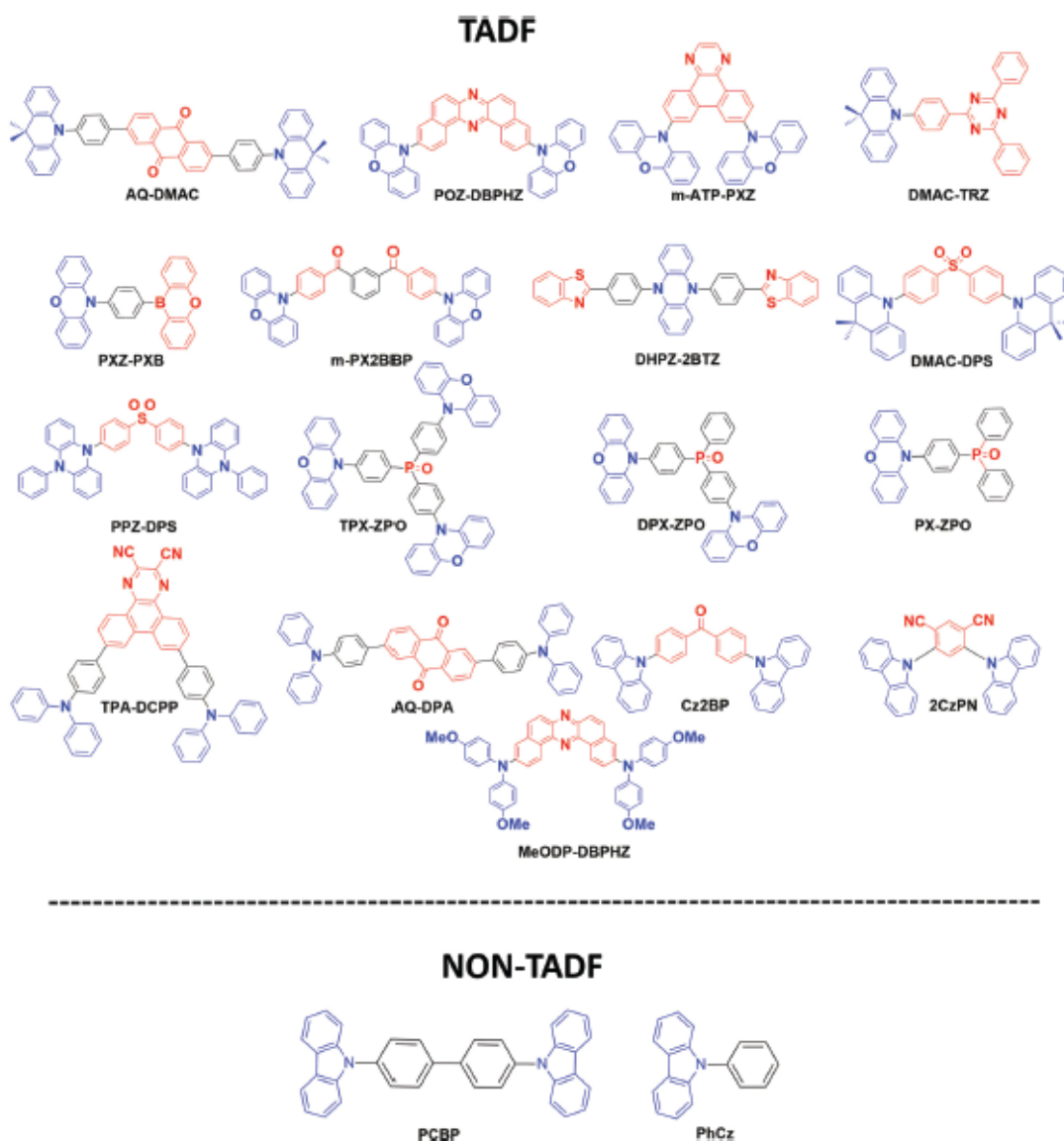


Fig. 3 TADF and non-TADF molecules investigated in this study. Blue: donor; red: acceptor; black: π -bridge.

values between the S_1 and T_n states involved in the RISC process.

We selected TADF compounds containing different acceptor groups, such as phosphine oxides, phenazines, anthraquinones, phenanthrenes, diphenylsulfones and benzophenones. Specifically, we consider the phosphine oxide (PX-ZPO, DPX-ZPO and TPX-ZPO⁹⁹), dibenzo[*a,f*] phenazine (MeODP-DBPHZ, POZ-DBPHZ),¹⁰⁰ anthraquinone-based compounds (AQ-DMAC, AQ-DPA),¹⁰¹ phenanthrene containing compounds (*m*-ATP-PXZ,¹⁰² TPA-DCPP¹⁰³) diphenylsulfone-based compounds (DMAC-DPS, PPZ-DPS)¹⁰⁴ and benzophenone containing compounds (*m*-PX2BBP and Cz2BP).¹⁰⁵ Additionally, we studied PXZ-PXB bearing a 10*H*-phenoxaboryl electron acceptor group,¹⁰⁶ DMAC-TRZ with a 2,4,6-triphenyl-1,3,5-triazine (TRZ) acceptor moiety,¹⁰⁷ and 2CzPN with a dicyanobenzene group.¹⁰⁸ Furthermore, and as a comparison, we also considered two non-TADF molecules namely, pCBP and PhCz.¹⁰⁹

Twist angle between donor (D), acceptor (A) and bridge (B) moieties

The torsion angle between donor/acceptor units and the bridge moieties is a straightforward descriptor allowing one to rationalize the TADF activity, and the calculated values are reported in Fig. 4. As a matter of fact, twisting angles of 90° will constitute the perfect arrangement to break conjugation, thus leading to small ΔE_{ST} values and, hence, enhance TADF. However, while minimizing ΔE_{ST} values, perfectly orthogonal geometries lead to an important disadvantage for luminescence,

since the oscillator strength, which is one of the key parameters for light emission, is then strongly reduced. Among seven different donor units we show that the best performing group is clearly DMAC with its ~90° twisting, while the PXZ moiety with ~80° twist angle is the second most efficient donor group.

As expected, the favorable value of the twist angle is reflected in PXZ-containing compounds which present small ΔE_{ST} values, as seen both experimentally and theoretically (Fig. S2, ESI†). PPZ and DHPZ display a twisting of ~100° between the adjacent neighboring groups. These structural features also correlate with ideal ΔE_{ST} values (<0.1 eV) and well separated frontier orbitals as can be seen from Fig. S3 (ESI†). On the contrary, TPA-DCPP, AQ-DPA and MeODP display relatively lower TADF activity due to their small twist angle, which is close to 30°. The small twisting can be attributed to the freely rotating phenyl rings, which cause a general planarization of the compounds. The last donor unit, Cz, induces a torsion angle of around 50–60°. The relatively low torsion angle of the carbazole moiety can be attributed to a smaller steric repulsion due to the five-membered ring in the donor group. In addition to the torsion angles between the donor and adjacent moieties, we also examined the twisting angles between acceptor units and their adjacent donor or bridge moieties (Fig. 4). While the triphenyl triazine acceptor induces a twisting angle of 90°, DBPHZ and *m*-ATP units reach approximately 80°.

On the other hand, the DPS moiety leads to an ideal 90° twisting with DMAC and 100° angle with the PPZ group. Instead, relatively low performance TADF emitters, such as Cz2BP and

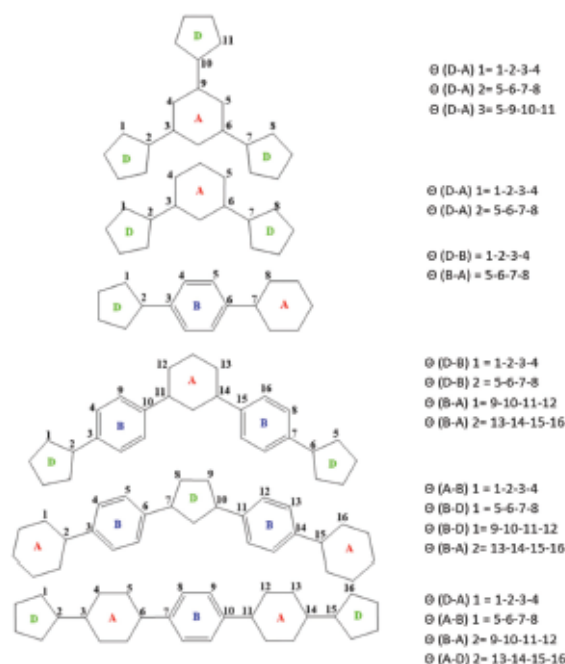
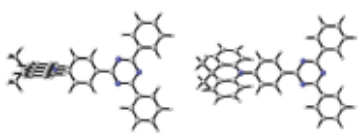
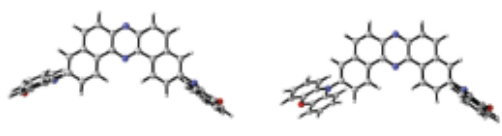
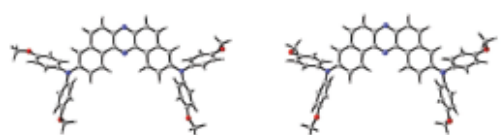
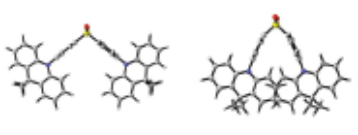
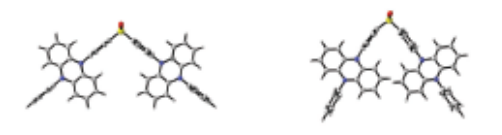
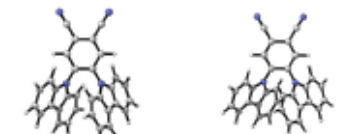
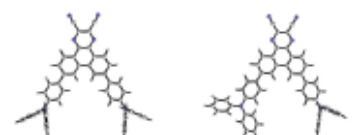
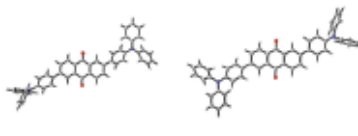


Fig. 4 Ground state twist angles of TADF and non-TADF molecules. D: donor unit, A: acceptor unit, B: bridge unit.

D-A	$\theta(\text{D-A})1$	$\theta(\text{D-A})2$	$\theta(\text{D-A})3$	
DMAC-TRZ	89.50	-	-	
TPX-ZPO	-103.6	9.85	-76.01	
DPX-ZPO	-103.62	-75.74	-	
PX-ZPO	76.76	-	-	
D-A-D	$\theta(\text{D-A})1$	$\theta(\text{D-A})2$		
POZ-DBPHZ	77.89	-104.66		
M-ATP-PXZ	77.44	77.39		
MeODP-DBPHZ	25.32	-27.27		
DMAC-DPS	-91.08	89.23		
PPZ-DPS	-103.56	102.96		
Cz2BP	51.43	51.43		
2CzPN	119.78	-59.80		
D-B-A	$\theta(\text{D-B})1$	$\theta(\text{B-A})2$		
PXZ-PXB	-78.74	53.94		
D-B-A-B-D	$\theta(\text{D-B})1$	$\theta(\text{A-B})1$	$\theta(\text{A-B})2$	$\theta(\text{D-B})2$
AQ-DMAC	89.39	-38.44	38.45	-89.26
TPA-DCPP	-34.98	-37.01	-36.93	-35.40
AQ-DPA	-35.84	-36.21	35.71	-36.20
A-B-D-B-A	$\theta(\text{A-B})1$	$\theta(\text{B-D})1$	$\theta(\text{B-D})2$	$\theta(\text{A-B})2$
DHPZ-2BTZ	0.00	102.18	102.18	0.00
D-A-B-A-D	$\theta(\text{D-A})1$	$\theta(\text{A-B})1$	$\theta(\text{A-B})2$	$\theta(\text{D-A})2$
m-PX2BBP	75.44	-30.90	-30.98	75.45
Non-TADF	$\theta(\text{D-B})1$	$\theta(\text{B1-B2})$	$\theta(\text{D-B})2$	
PCBP	-55.44	37.55	-55.45	
PhCz	-55.89			

Table 1 3D representations of S_0 and T_1 geometries of some compounds with different ground state and excited state geometries and changes in torsion angles (M06-2X/6-31+G(d,p) level of theory)

DMAC-TRZ (1)		POZ-DBPHZ (2)																																																																										
m-ATP-PXZ (3)		MeODP-DBPHZ (4)																																																																										
DMAC-DPS (5)		PPZ-DPS (6)																																																																										
2CzPN (7)		PXZ-PXB (8)																																																																										
TPA-DCPP (9)		<table><tr><th colspan="4">S_0/T_1 Geometries Torsion Angles</th></tr><tr><th></th><th>$\theta(D-A)1$</th><th>$\theta(D-A)2$</th><th></th></tr><tr><td>1</td><td>89.5/63.62</td><td></td><td></td></tr><tr><th></th><th>$\theta(D-A)1$</th><th>$\theta(D-A)2$</th><th></th></tr><tr><td>2</td><td>77.89/-69.93</td><td>-104.7/-103.4</td><td></td></tr><tr><td>3</td><td>77.44/75.74</td><td>77.39/66.03</td><td></td></tr><tr><td>4</td><td>25.32/29.27</td><td>-27.27/-30.34</td><td></td></tr><tr><td>5</td><td>-91.08/71.68</td><td>89.23/71.68</td><td></td></tr><tr><td>6</td><td>-103.56/-101.8</td><td>102.96/95.49</td><td></td></tr><tr><td>7</td><td>119.78/-56.63</td><td>-59.8/-56.63</td><td></td></tr><tr><th></th><th>$\theta(D-B)1$</th><th>$\theta(D-B)2$</th><th></th></tr><tr><td>8</td><td>-78.74/69.19</td><td>53.94/37.06</td><td></td></tr><tr><th></th><th>$\theta(D-B)1$</th><th>$\theta(A-B)1$</th><th>$\theta(A-B)2$</th><th>$\theta(D-B)2$</th></tr><tr><td>9</td><td>-34.98/-29.33</td><td>-37.01/-27.72</td><td>-36.93/-27.72</td><td>-35.4/-29.3</td></tr><tr><td>10</td><td>-35.84/-41.52</td><td>-36.21/35.79</td><td>35.71/-15.04</td><td>-36.2/-24.4</td></tr><tr><th></th><th>$\theta(A-B)1$</th><th>$\theta(B-D)1$</th><th>$\theta(B-D)2$</th><th>$\theta(A-B)2$</th></tr><tr><td>11</td><td>0/0</td><td>102.18/-90.34</td><td>102.18/90.24</td><td>0</td></tr></table>		S_0/T_1 Geometries Torsion Angles					$\theta(D-A)1$	$\theta(D-A)2$		1	89.5/63.62				$\theta(D-A)1$	$\theta(D-A)2$		2	77.89/-69.93	-104.7/-103.4		3	77.44/75.74	77.39/66.03		4	25.32/29.27	-27.27/-30.34		5	-91.08/71.68	89.23/71.68		6	-103.56/-101.8	102.96/95.49		7	119.78/-56.63	-59.8/-56.63			$\theta(D-B)1$	$\theta(D-B)2$		8	-78.74/69.19	53.94/37.06			$\theta(D-B)1$	$\theta(A-B)1$	$\theta(A-B)2$	$\theta(D-B)2$	9	-34.98/-29.33	-37.01/-27.72	-36.93/-27.72	-35.4/-29.3	10	-35.84/-41.52	-36.21/35.79	35.71/-15.04	-36.2/-24.4		$\theta(A-B)1$	$\theta(B-D)1$	$\theta(B-D)2$	$\theta(A-B)2$	11	0/0	102.18/-90.34	102.18/90.24	0
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2CzPN, assume a butterfly shape. Benzophenone-containing TADF emitters presenting a D-A-D scaffold, reach twist angles of $\sim 52^\circ$ and $\sim 120^\circ$ thus leading to a non-orthogonal geometry. Indeed, also due to its efficient ISC, benzophenone was previously explored as an OLED emitter.⁵⁹

In addition to the Franck-Condon region, the torsion angles at the equilibrium T_1 geometries were also examined, and, as reported in Table 1, only slight changes can be observed except for compound 7. Moreover, torsion angles at the S_1 equilibrium geometries were also obtained for AQ-DMAC, POZ-DBPHZ, DHPZ-2BTZ, PPZ-DPS, Cz2BP, TPA-DCPP, AQ-DPA and MeODP-DBPHZ. It has been observed that equilibrium geometries for the first excited singlet state are very close to those of the ground state. Therefore, to reduce computational costs, further analyses have been performed in the Franck-Condon region, only. Thus, geometry relaxation is important only for the T_1 state, leading to a decrease in orthogonality, and consequently to the increase of the HOMO-LUMO overlap and ΔE_{ST} . Indeed, excited state twisting is recognized as a key feature of TADF molecules.

To sum up, DMAC, PXZ and DHPZ units appear as the most appropriate donors to establish the desired orthogonality leading to twisting angles around 80° and 100° . On the other hand, DPA derivatives have smaller twisting angles ($\sim 40^\circ$), which lead to an increased HOMO-LUMO overlap and ΔE_{ST} . Moreover, when considering acceptor moieties, anthraquinone and diphenylsulfone groups provide almost ideal orthogonal arrangements. It should be pointed out, however, that the term ideal here refers to geometrical properties and twisting angle only and not to the device performance.

Electronic density reorganization and effect of the functional

The reorganization of the electronic density due to the excited state population has been analyzed by examining the behavior of the corresponding NTOs. Furthermore, we compare the natures of S_1 and T_1 states obtained using M06-2X, CAM-B3LYP and ω B97XD to assess the influence of the exchange-correlation functional in the topology of the electron density reorganization (Table S8, ESI†), and hence, in providing the correct diabatic description of the most relevant states.

In this respect, the B3LYP functional was excluded, since TADF compounds rely heavily on CT, exasperating the known deficiencies of hybrid functionals, especially for bridged compounds leading to spatially long-range CT states.¹¹⁰ Since the molecular set under investigation is composed of mostly donor- π -acceptor charge transfer molecules, we did a benchmark study with medium-range separated M06-2X and long range separated CAM-B3LYP and ω B97XD functionals. Though slightly unsatisfactory performances of CAM-B3LYP and ω B97XD have been reported for some donor-acceptor systems,¹¹¹ their behavior was not tested for the set of molecules under investigation, which are typical donor- π -acceptor systems.

Table 2 reports the Φ_S values of S_1 states computed with M06-2X, ω B97XD and CAM-B3LYP functionals, while the corresponding NTO densities are reported in Fig. S3 (ESI†). High Φ_S values indicate a large overlap between electron and hole densities, thus, LE character. On the other hand, small Φ_S

Table 2 Φ_S values of S_1 states computed at different levels of theory and the 6-31+G(d,p) basis set

Φ_S Values	M062X	ω B97XD	CAMB3LYP
AQ-DMAC	0.310	0.511	0.479
POZ-DBPHZ	0.094	0.841	0.099
M-ATP-PXZ	0.144	0.176	0.134
PXZ-PXB	0.064	0.487	0.511
DMAC-TRZ	0.213	0.503	0.519
m-PX2BBP	0.247	0.525	0.549
DHPZ-2BTZ	0.085	0.733	0.746
PPZ-DPS	0.160	0.612	0.591
DMAC-DPS	0.201	0.550	0.564
TPX-ZPO	0.252	0.601	0.254
DPX-ZPO	0.252	0.647	0.260
PX-ZPO	0.212	0.525	0.235
TPA-DCPP	0.728	0.588	0.612
AQ-DPA	0.610	0.517	0.642
Cz2BP	0.410	0.579	0.633
2CzPN	0.599	0.567	0.584
MeODP-DBPHZ	0.739	0.483	0.514
pCBP	0.782	0.497	0.587
PhCz	0.847	0.862	0.863

values indicate that the degree of overlap between electron and hole densities is small, and thus the presence of a CT excited state.

S_1 states computed with the M06-2X functional mostly present a noticeable CT character, which is known to favor TADF efficiency. Conversely, CAM-B3LYP and ω B97XD functionals preview a locally excited S_1 state for some TADF compounds. Also taking into account the orthogonal arrangement, which should indeed favor charge separation, it appears that the LE character should be regarded as an artifact as opposed to the more reliable M062X results (Table 3, see Tables S8 and S12 for the full list, ESI†). Hence, M062X will be consistently used hereafter.

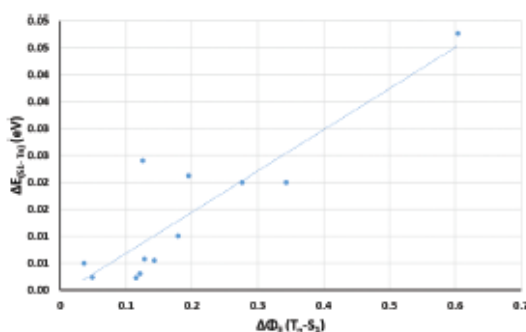
Fig. 5 reports the correlation between the change in the degree of overlap between S_1 and T_n states and $\Delta E_{S_1-T_n}$. We may observe that when the nature of S_1 and T_1 changes the energy gap increases. Though a linear relationship with $R^2 = 0.99$ could not be observed, a direct correlation with a positive slope has been observed. However, these should not be necessarily considered as a drawback to the RISC mechanism, since due to the El Sayed rule the SOC between states of different character should increase.

Correlation between $\Delta E_{S_1-T_1}$ and RISC efficiency

According to Kasha's Rule,⁷⁴ the population of high lying singlet states is followed by ultrafast internal conversion (IC) to S_1 , and eventually ISC leading to the population of the triplet manifold. IC is also active on the triplet manifold, hence leading to the T_1 population. Thus, RISC from T_1 to S_1 is not the only possible pathway, indeed reverse internal conversion (RIC) between T_1 and upper lying T_n states may be possible if the former are quasi-degenerate, which in turn will open a channel for RISC between excited T_n and S_1 states.^{66,112} Globally, however, RISC will be mainly determined by the energy order of singlet and triplet states, together with their efficient couplings. Bredas *et al.* have shown that the separation

Table 3 Torsion angles and natures of S_1 states with different functionals

Compounds	Torsion angle	M062X	CAM-B3LYP	wB97XD
		S_1	S_1	S_1
AQ-DMAC	89.39	CT	LE	CT + LE
PXZ-PXB	78.74	CT	LE	LE
DMAC-TRZ	89.50	CT	CT	CT
PPZ-DPS	103.56	CT	CT + LE	CT + LE
DMAC-DPS	91.08	CT	CT + LE	CT + LE
TPX-ZPO	103.60	CT	CT + LE	CT + LE
DPX-ZPO	103.62	CT	CT	CT + LE

Fig. 5 Correlation between ΔE_{ST} and the change in electronic density reorganization computed at the M062X/6-31+G(d,p) level of theory.

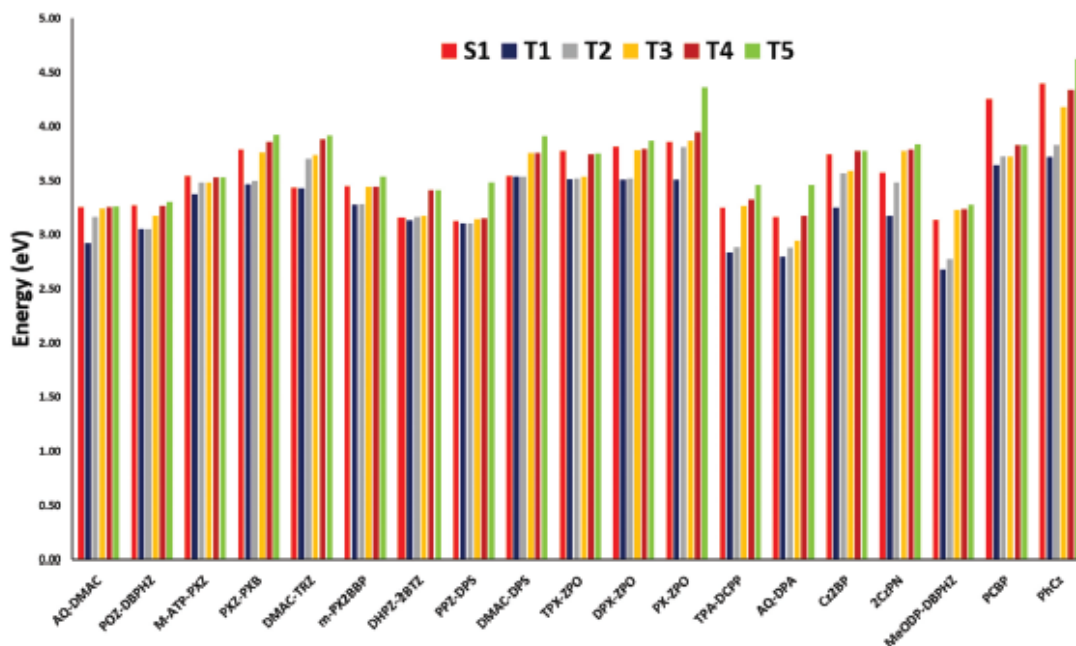
of frontier molecular orbitals alone is not sufficient to assure TADF efficiency and highlighted the fact that other factors, including the possibility of mixed CT T_1 states with a small ΔE_{ST} gap, are crucial.¹¹² The electron donating character of the donor moiety may also have a noticeable effect on ΔE_{ST} , with the increase of electron donation leading to its decrease. Additionally, using donor and acceptor moieties with appropriate ionization potentials and electron affinities is another key parameter in minimizing the ΔE_{ST} gap.⁷³

As shown in Fig. 6, the energy levels of singlet and triplet states indicate that for many compounds, more than one triplet state is lying below the S_1 level. Additionally, in some instances T_1 and T_2 states were found to be almost energetically degenerate. For some compounds, such as DHPZ-2BTZ and PPZ-DPS, a three-state degeneracy involving S_1 , T_1 and T_2 is observed. Globally, all these facts may point to the fact that higher triplet states may, indeed, contribute to the RISC process.

Therefore, to identify the states responsible for RISC, the specific value of SOC should be analysed together with the energetic gaps.

Correlation between SOC and RISC efficiency

Besides the ΔE_{ST} descriptor, we also determined the effects of structural modifications on the SOC between S_1 and T_1 states. Indeed, despite giving rise to low lying CT with negligible electron-hole overlap, orthogonal arrangement of donor and acceptor moieties may have a negative effect on SOC, hence influencing in a more subtle way the ultimate RISC rate.

Fig. 6 Energies of S_1 and T_1 - T_5 levels computed at the M062X/6-31+G(d,p) level of theory.

Although TADF compounds are generally known to have low SOC values, it is found that RISC occurs on a timescale shorter than 100 ns at 300 K.¹¹² Furthermore, LE triplet states may be involved in increasing the possibility of RISC due to the El Sayed's rule.^{113,114} In this context, Penfold and Monkman suggested a RISC mechanism which involves a three state degeneracy between S_{CT} , T_{CT} and T_{LE} .¹¹⁵

Herein, we computed the SOC between S_1 and the first five triplet states (see Fig. 8 and Table S11, ESI†). As represented in Fig. 7, striking differences in SOC between S_1 and different triplet states are observed. It should be pointed out that since the SOC value enters the Marcus's formula directly, couplings between the states involved in RISC are highly important. Detailed analysis of Fig. 7 shows that the energy gap between the singlet and triplet states with the largest SOC are very close to the experimental energy gaps. In other words, we observed that the experimental ΔE_{ST} values are very close to the calculated gaps between strongly-coupled singlet and triplet states.

For instance, for AQ-DMAC, *m*-ATP-PXZ, DHPZ-2BTZ, and AQ-DPA, the SOC between S_1 and T_3 are larger compared to all the other states, and the absolute deviations of the computed S_1 - T_3 energy gaps with the experimental values are smaller than 0.05 eV. For POZ-DBPHZ, PXZ-PXB and TPX-ZPO, S_1 and T_4 have the largest SOC and their gaps deviate by less than 0.1 eV compared to the experiment.

On the other hand, for DMAC-TRZ, DPX-ZPO, PX-ZPO and 2CzPN, the SOC between S_1 and T_1 states are the highest, moreover, their corresponding energy gaps deviate by approximately 0.1 eV from the experiment, suggesting a more classic scenario involving only the lowest triplet state. For the DMAC-TRZ emitter, it should be pointed out that the SOC between S_1 - T_2 states is larger than for S_1 - T_1 . However, while the T_2 state is higher, and hence shows a large energy gap, T_1 is almost degenerate with S_1 . Thus, when compared with the experiment, the gap between S_1 and T_1 states is approximately 0.006 eV.

As a matter of fact, SOC appears as a more promising, and crucial descriptor in determining the states involved in the RISC process. It should also be pointed out that various TADF groups are represented in our set, and in all the cases SOC was

able to reliably describe the experimental efficiency, even in the presence of wide and diverse donor and acceptor groups, and in general different functional moieties.

As a general rule, good TADF efficiency requires either moderate SOC and very small $\Delta E_{S_1-T_1}$ or moderate $\Delta E_{S_1-T_1}$ and very high SOC. Thus, almost perfectly orthogonal scaffolds including strong D and A moieties, which will result in very small $\Delta E_{S_1-T_1}$ and SOC values, will be less efficient than moderate strength D and A groups if they still present torsion angles leading to acceptable $\Delta E_{S_1-T_1}$ and strong SOC.

Another important role of SOC is its deterministic behaviour in competition between the direct transition from S_1 to S_1 and ISC/RISC. According to Hund's rule, the T_1 state is lower in energy than the S_1 state and though both ISC and RISC processes depend on the same SOC matrix element between S_1 and T_1 states, the ISC rate is always higher than RISC. Moreover, there is competition between fluorescence emissions and ISC; generally, fluorescence emissions are faster than the ISC, which is faster than the RISC process. However, in the case of TADF emitters, a small singlet-triplet energy gap with localized HOMO and LUMO orbitals leads to a small transition dipole for the $S_1 \rightarrow S_0$ transition, causing a slow radiative rate of fluorescence, hence, excited state dynamics favour the ISC to triplet states.¹¹⁶

For the molecule set under investigation, ΔE_{ST} and SOC descriptors support the preference of ISC over fluorescence emission. As reported in Fig. 7 and Table S11 (ESI†), TADF emitters under investigation exhibit strong SOC values, thus strong ISC to the triplet states. Moreover, Table S10 (ESI†) reports that these emitters exhibit CT character S_1 states, with localized HOMO and LUMO orbitals, thus, they are expected to have small transition dipole moments for the radiative decay between S_1 and S_0 states. Moreover, due to the very small energy gaps between the relevant states, the ΔE_{ST} descriptor also favors ISC over fluorescence emission.

Topological Φ_s index

The Φ_s index measures the degree of overlap between particle and hole densities, and the smaller its value the larger the

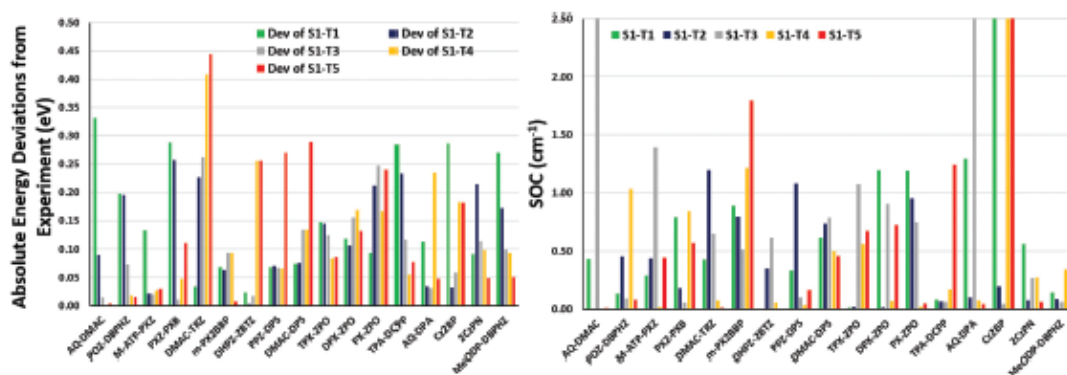


Fig. 7 Absolute deviations of S-T gaps from the experiment and the SOC values computed at the M062X/6-31+G(d,p) level of theory.

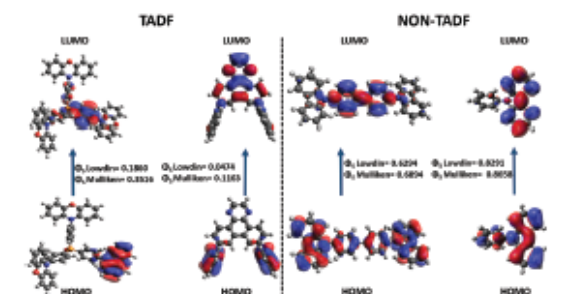


Fig. 8 Φ_s indices of S_1 states and frontier molecular orbital overlap differences of TADF TPX-ZPO, *m*-ATPPXZ and non-TADF pCBP, PhCz molecules, respectively.

charge separation in the excited states. Hence, the Φ_s index can be used as an indicator for TADF efficiencies. As represented in Fig. 8, going from TADF to non-TADF compounds, Φ_s indices definitely increase.

This situation is also coherent with the decrease of orthogonality and increase of ΔE_{ST} . The compounds with the smallest twisting angles between donor and acceptor units, such as Cz2BP, MeODP-DBPHZ, TPA-DCPP and AQ-DPA, or the non-TADF pCBP and PhCz present higher Φ_s indices, because of the highly delocalized π electrons, which result in hole and particle density overlap and increased LE character (Fig. S3, ESI†). On the other hand, compounds with higher twisting angles and lower ΔE_{ST} values exhibit lower Φ_s indices, which indicates an increased CT character.¹¹⁷

As shown in Fig. 8 and 9, while most of the TADF compounds have Φ_s values for S_1 smaller than 0.3, non-TADF compounds have Φ_s values close to unity. Namely this is the case for TADF active MeODP, Cz2BP, TPA-DCPP, AQ-DPA and non-TADF pCBP, PhCz. The latter also presents torsion angles

far from 90° and the hole and particle densities are delocalized over the conjugated bridges (Fig. S3, ESI†), thus justifying the high Φ_s values (see Table 2).

On the contrary, for compounds which have orthogonal D-A geometries, such as DMAC-TRZ, DMAC-DPS and AQ-DMAC, hole densities are distributed on the donor moieties while particle densities are almost perfectly localized on the acceptor groups.

In Fig. 9, Φ_s indices for S_1 , T_1 , T_2 , T_3 , T_4 and T_5 states have been reported. It is obvious that while S_1 generally has a CT character with small Φ_s indices, triplet states have larger Φ_s indices, thus indicating an increased LE character (see Table S12 for the full list of natures, ESI†). Since the change in the nature of the states is favorable to enhance SOC, this feature should be considered as beneficial for TADF efficiency. Moreover, when compared to Fig. 6, it has been observed that energetically degenerate states such as T_3 and T_4 in AQ-DMAC have remarkable differences in their Φ_s indices, which leads to differences in their SOC values with the S_1 state. This situation is a way of obtaining strong RISC between the singlet and isoenergetic, mixed triplet states.

In summary, five main descriptors: torsion angle, nature of states, ΔE_{ST} , Phi-S index and SOC, were investigated for a series of TADF emitters, including benchmark calculations via TDA approximation. Here are the main findings from the benchmark study:

✓ For the nature of states analyses, PBE0, B3LYP, M06-2X, CAM-B3LYP and ω B97XD functionals with the 6-31+G(d,p) basis set were used. In our calculations, we observed the deficiency of hybrid functionals for modelling CT emitters. On the other hand, CAM-B3LYP and ω B97XD were found to represent LE singlet states, which is not consistent with the structural properties of the TADF emitters. Our calculations on the nature of excited states indicate that the M06-2X is the only functional which well reproduces the nature of excited states for the TADF emitters under investigation.

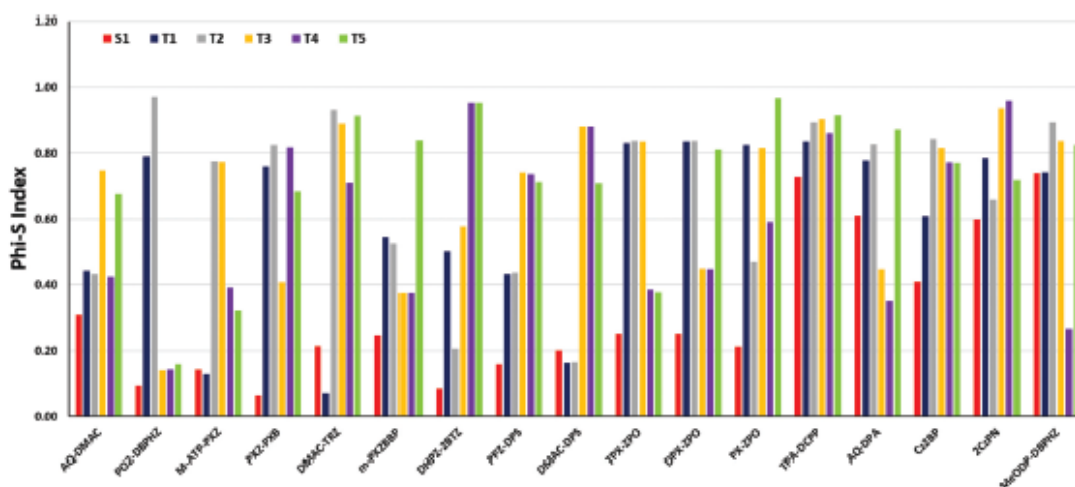


Fig. 9 Phi-S indices of S_1 , T_1 , T_2 , T_3 and T_4 states computed at the M062X/6-31+G(d,p) level of theory.

✓ To further check the degree of overlap between electron and hole orbitals, we reported Φ_s indices computed at the M06-2X/6-31+G(d,p), CAM-B3LYP/6-31+G(d,p) and ω B97XD/6-31+G(d,p) levels of theory. Our findings indicate that the M06-2X/6-31+G(d,p) level of theory provides the correct degree of separation between electron and hole orbitals.

✓ Based on the results from the nature of states analysis, we further modelled the ΔE_{ST} and SOC parameters with the M06-2X functional and observed that it nicely reproduces the experimental ΔE_{ST} data obtained from the literature and it represents reliable SOC values consistent with RISC processes.

Based on the findings from five descriptor analyses, we theoretically proposed a comprehensive methodological approach for TADF design strategies. Moreover, via considering the effects of five descriptors, we conclude that the SOC parameter has a determinative role in TADF efficiency. Thus, the primary target in designing and synthesizing new TADF emitters should be optimizing the SOC involved in the RISC process. Furthermore, we highlighted the role of intermediate triplet states on TADF performance, which should be taken into consideration when modelling the photophysical properties of TADF emitters.

Conclusion

Through a systematic study of a large panel of potential TADF chromophores we have elucidated the reasons behind the performance of the different descriptors, which may be used to forecast RISC probability. Singlet/triplet gap, ΔE_{ST} , is usually associated with twisting angles and the presence of strong electron donating and withdrawing groups. The results obtained with M06-2X are reliable and consistent with experimental data. Additionally, we also observed a significant deviation in the twisting angles of TADF molecules between ground and triplet excited state equilibrium geometries.

The identification of ΔE_{ST} values for the states presenting the larger SOC, allows us to identify RIC accessible channels and further supports the role of SOC as the most reliable descriptor of TADF performance. Indeed, for most of the studied cases, SOC is the determinant factor in determining the probability of RISC. Furthermore, as the electronic density reorganization seems fundamental to assure TADF, Φ_s indices have been explicitly considered. A good correlation has been observed with structural parameters, such as the twisting angles, or electronic properties, including ΔE_{ST} values, also coherently with previously reported trends.¹¹⁷

Oscillator strength may also be regarded as highly important, especially dictating luminescence efficiency and is strongly correlated with the geometric properties. Our results show that while designing new TADF emitters with favourable properties such as small ΔE_{ST} values and strong SOC, the geometrical features of the constituents should be carefully adjusted vanishing oscillator strengths. Therefore, instead of perfect orthogonal geometries, smaller torsions with moderate ΔE_{ST} values, strong SOC and strong oscillator strengths, will lead to more efficient TADF devices. To sum up, our calculations successfully explain the

TADF performance of a wide range of donor and acceptor groups and their characteristic structural behavior, also highlighting useful and computationally efficient indicators. We also further analyzed the possible RISC paths and showed that RIC involving the highest excited triplet states may play an important role in mediating RISC when leading to high SOC. Hence, ΔE_{ST} , oscillator strength, and SOC descriptors should be combined when performing computational screening and rational molecular design.

Conflicts of interest

There are no conflicts to declare.

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A.2. Photophysical Properties of Boron-Based Chromophores As Effective Moieties In TADF Devices: A Computational Study



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Photophysical Properties of Boron-Based Chromophores as Effective Moieties in TADF Devices: A Computational Study**

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Thermally activated delayed fluorescence (TADF) materials have shown great potential in the design of organic metal-free optoelectronic devices and materials and, therefore, are the subject of intense investigations. This contribution presents the effects of various parameters on the photophysical properties of a series of boron-based TADF emitters. These include torsion angle, the changes in the electronic density, energy gap between the first excited singlet (S_1) and the first excited triplet states (T_1), oscillator strength (f) and spin-orbit coupling (SOC). Through a comprehensive structural analysis, we first show the

most favorable conformation of the ground state of donor (D) and acceptor (A) moieties that are popular in TADF emitters. Further, the properties of the excited state manifolds are obtained with Tamm-Dancoff Approximation (TDA), thus rationalizing their optical and photophysical properties. Globally, our results settle the basis for the rationalization of the effects of different parameters on reverse intersystem crossing (RISC) probabilities, which is the rate-limiting step for TADF, thus favoring the rational design of novel highly efficient TADF materials with strong triplet exciton harvesting.

Introduction

Although organic light emitting diodes (OLEDs) are some of the most promising devices in displays and lighting technology, they still suffer from important drawbacks. Indeed, the overall device efficiency, which is fundamental in applications, is one of the weakest points of OLED technology. Due to the intrinsic limitations of spin-statistics, only 25% of the excitons produced by the applied electric potential are generated as singlets while the remaining 75% are in triplet states.^[1] However, while organic materials may usually be fluorescent their phosphorescence quantum yield is generally low, resulting in the loss of the majority of the excitons and in low electroluminescence.^[2] Furthermore, OLED efficiency is also limited by other non-radiative relaxation pathways of the singlet or triplet excitons.^[2]

To cope with such phenomena and hence with the challenges of electron-light conversion, other strategies, in addition to the optimization of fluorescence quantum yield,

have been proposed including triplet-triplet annihilation (TTA),^[4] singlet fission (SF),^[5] phosphorescence emission, and thermally activated delayed fluorescence (TADF) (see Figure 1).^[6] In TTA, one singlet excited state is originated from two low-lying triplet states leading to the increase of the external quantum efficiencies (EQE) compared to OLED materials.^[7] On the other hand, in SF, a molecule converts a singlet excited state into two triplet states, with spin densities localized on adjacent moieties, leading to a theoretical EQE of 200%, which can be highly attractive for solar cell applications.^[8] Phosphorescence emission is achieved with the second generation OLED devices, whose components include heavy metals, such as iridium and platinum, characterized by a high efficient triplet state radiative decay due to the increased spin-orbit coupling (SOC).^[9] Although, second generation emitters provide high efficiency devices, they also suffer from the need to include rare metals, which are plagued by undesirable environmental and economic shortcomings. Thus, the development of alternative approaches to harvest both singlet and triplet states is still highly attractive.

In this respect, TADF materials have been recently proposed since they are capable of exploiting triplet excited states. This is achieved via reverse intersystem crossing (RISC) in which low-lying triplets (T_1) are converted back to the singlet manifold (S_1). TADFs are highly promising emitters in display technology and thus, have become a hot research topic.^[9] They are also referred to as 'third generation' OLEDs and show important advantages such as high efficiency,^[10] low fabrication costs, and wide emission color range.^[11] Furthermore, it has been shown that TADF emitters may also be used as high-performance metal-free photosensitizers (PSs) with remarkable photosensitizing ability, including in the domain of photodynamic therapy. As an example, in 2019, mitochondria-targeting nanoparticles with TADF ability have been successfully used against cancer cells.^[12]

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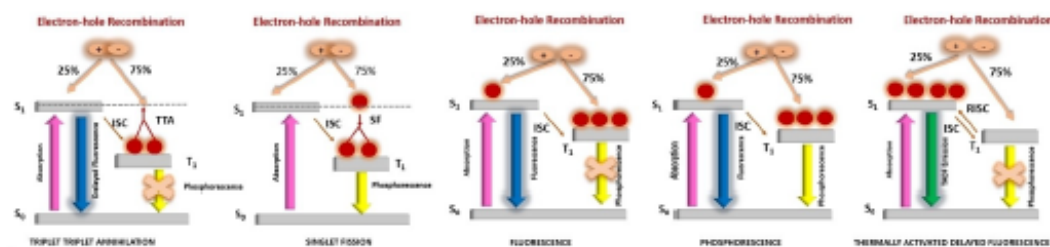


Figure 1. Photophysical processes observed in electronic excitations of optoelectronic materials.

From a photophysical point of view, in TADF materials, the population ratio between singlet and triplet states is largely controlled by the competition between RISC and phosphorescence.^[13] In particular, thermally activated RISC, which drives the population accumulation in the triplet states, should be maximized. Fortunately, tuning RISC efficiency should also lead to the concomitant minimization of competitive non-radiative decay. It is generally recognized that to attain an efficient RISC the energy gap between S_1 and T_1 states (ΔE_{ST}) should be sufficiently small to allow the population transfer between the two manifolds via thermal activation.^[14] However, the spin conversion between S_1 and T_1 is also influenced by the magnitude of the spin-orbit coupling (SOC), which should be high.

ΔE_{ST} in TADF materials can be minimized by adopting a donor (D) – acceptor (A) molecular design, where the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are spatially separated, thus reducing the exchange integral between S_1 and T_1 states and consequently closing the gap between the states.^[13,15]

On the other hand, as stated by El Sayed's rule, high SOC necessitates a large variation in the electronic density of the excited states, which can also be achieved by n -orbital participation.^[16] Several studies aiming at simulating the spin-forbidden non-radiative transition between S_1 and T_1 states have been reported. It is generally known that heavy metals such as Ir, Pt, and halogens have large SOC due to their relativistic effects, hence favoring (R)ISC. For pure organic molecules SOC are much smaller, however they can be increased when the triplet and singlet have a different electronic (diabatic) nature. Generally, large SOC are observed between a singlet state with $^1(n, \pi^*)$ or $^1(\pi, \pi^*)$ nature and a triplet state with $^3(\pi, \pi^*)$ or $^3(n, \pi^*)$ nature. On the contrary, transition from $^1(\pi, \pi^*)$ to $^3(\pi, \pi^*)$ and from $^1(n, \pi^*)$ to $^3(n, \pi^*)$ are unfavorable.^[17] Many molecular modeling studies have been devoted to the problem of ISC in organic materials. In 2012, Marian summarized the theoretical principles and calculation methods of SOC.^[18] In 2017, Bredas discussed how ΔE_{ST} and SOC influence the RISC rate constants.^[19] In 2016, Peng et al. defined a parameter, n -orbital composition, describing the effects of heteroatoms on SOC matrix elements and the states involved in ISC and RISC.^[17] It should also be noted that in RISC, in coherence with thermal activation, the rate constant depends also on the Boltzmann constant (k_B) and the temperature.

As reported in literature, D–A structures are not the only possible molecular arrangements for TADF materials, other designs, such as, D– π –A, D– π –A– π –D may be envisaged. In all these cases HOMOs and LUMOs are spatially separated leading to small ΔE_{ST} gaps, high SOC and blue color emission. The main aim of incorporating donor and acceptor groups is enhancing charge-transfer (CT) character leading to high efficiency emitters. The most commonly used donor moieties in TADF emitters are dimethylacridine (DMAC), phenoxazine (PXZ), carbazole (Cz), diphenylamine (DPA), spiroacridan, phenothiazine (PTZ) and dihydrophenazine. On the other hand, the most frequently used acceptor groups involve diphenyl sulfone (DPS), benzophenone (BP), boron derivatives, cyano-substituted aromatics, triazine and pyrimidine (see Figure 2).

In the various molecular modeling works published to date, TADF and RISC processes have been analyzed with the help of various parameters. The most frequently used descriptors are frontier molecular orbital (FMO) distributions, ΔE_{ST} , SOC, and reorganization energy, λ . Moreover, parameters related to the topological description of the changes in the electronic density in the excited states have also been proposed and their correlation with RISC has been reported.^[16] In addition to these electronic based descriptors, there have been studies focusing

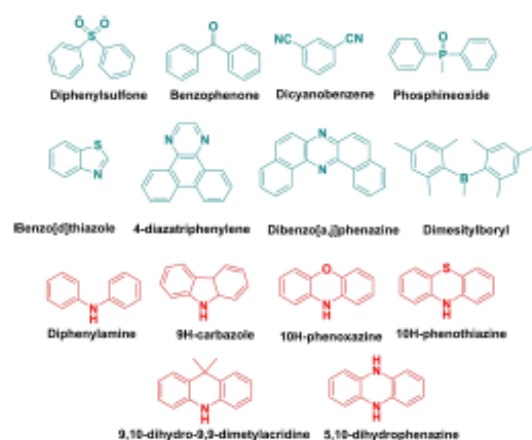


Figure 2. Widely used acceptor (blue) and donor (red) moieties in TADF literature.

on the correlation between geometric parameters and the evolution of the excited state.^[20] Furthermore, the probability of radiative decay from S_1 to S_0 has also been taken into account via the calculation of the corresponding oscillator strength, because a good OLED candidate should show good intrinsic luminescence via either prompt or delayed fluorescence.^[21]

In a previous contribution, we further investigated the effects of various descriptors to determine RISC efficiency and concluded that SOC plays an important role in shaping RISC pathways between triplet and singlet states.^[22] We have also investigated the behavior of different descriptors for benzophenone based TADF emitters and performed a functional benchmark study for the molecular set under investigation.^[23]

In the present contribution, we assess the relationship between molecular structure and photophysical properties for a range of boron-based TADF molecules (see Figure 3). Boron, participates in π -conjugation via its available p_z orbital, and thus enhances charge transport, and, therefore, represents an attractive choice for optoelectronic materials.^[24] In 2015, Adachi and coworkers reported the first boron-based TADF emitters consisting of 10H-phenoxaborin as acceptor and *N*-heterocyclic donor groups.^[25] In 2016, a new approach termed 'multi-resonance (MR) HOMO-LUMO separation' has been proposed by Hatakeyama and colleagues. MR is mainly observed in boron emitters in which the atom in *para* position with respect to Boron is substituted with nitrogen, thus enhancing the resonance effect and leading to remarkable HOMO and LUMO

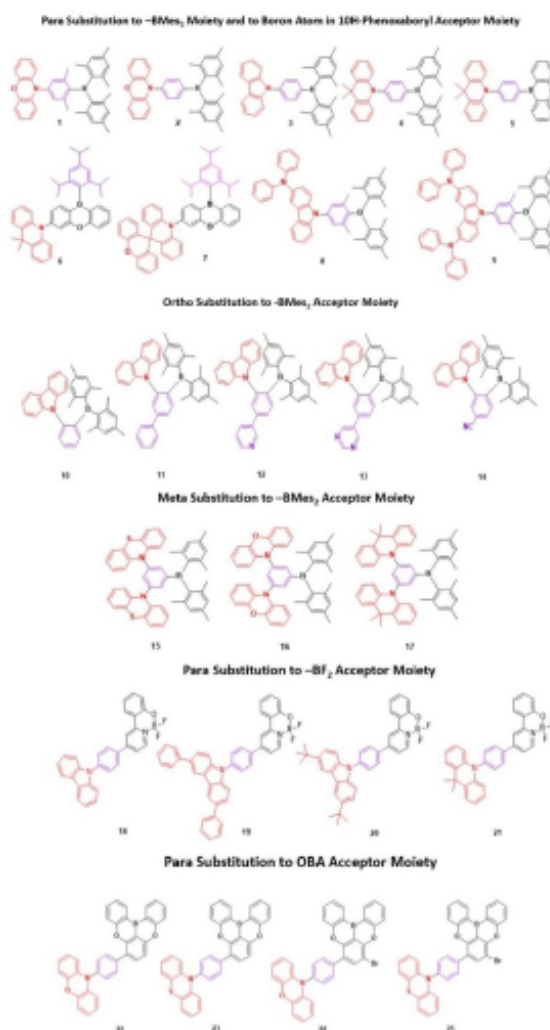


Figure 3. TADF emitters investigated in this study.

spatial separation.^[24,26,27] Furthermore, it has also been observed that MR-type blue TADF emitters have high device efficiencies, and narrow emission bands with high color purity.^[28] High color purity with very narrow emission bands is an important property of MR-TADFs, however, this feature is also accompanied by important drawbacks, such as, slower RISC rate compared to other TADF emitters.^[29] One of the main strategies which can be used to accelerate RISC rate is to provide a high density of close lying ³CT states, which can be achieved through peripheral substitution.^[30] Alternatively the inclusion of heavy main group atoms such as S or Se to the molecular skeleton can be considered.^[31] Finally, the inclusion of heavy metals is a suitable strategy to increase SOC values and improve RISC rates in MR-emitters, although this reduces the economic and ecological sustainability of the devices.^[32]

On the other hand, it has been reported that increasing the molecular rigidity and suppressing large excited state structural changes represents an efficient approach to achieve high color purity.^[33] Therefore, design strategies focused on rigidity of the scaffold have been implemented. As an alternative to fused π systems, ortho-substituted D–A structures that suppresses excited state structural changes can also be used to obtain devices with high color purity. Design strategies of boron based TADF emitters are not limited to these systems and other chromophores with various kinds of boron acceptors such as, dimesitylboryl (Mes₂B),^[33] 9,10-dihydro-9,10-diboraanthracene (DBA),^[34] phenoxaboronyl,^[35] B,N-doped analogues,^[36] have been proposed.

Herein, we mainly focused on the effects of various donors and boron-based acceptors on the character of the most relevant excited states. We also consider the relation between their donor acceptor strength and the emission colors as well as their influence in affecting RISC efficiencies. Moreover, we also analyze the possible electronic excitation pathways to understand the exact mechanism leading to the excited state relaxation while presenting a comprehensive comparison between the different emitting groups.

Computational Methodology

All the geometry optimizations were performed using Gaussian 16^[37] program package to model all the possible conformers of boron-based TADF emitters. Ground state geometries were optimized with Density Functional Theory (DFT) calculations; the corresponding S₀ and T₁ equilibrium geometries have been obtained at TDA level (see Tables S1–S37 for torsion angles and relative energies of different conformers). For geometry optimizations, a series of benchmark calculations with TPSSH^[38]/6-31+G(d,p), wB97XD^[39]/6-31+G(d,p) and M06-2X^[40]/6-31+G(d,p) levels of theory were used and meta-hybrid M06-2X functional was chosen (see Table S38). This choice is also justified since it is well known that this functional performs well in reproducing electronic energies, and equilibrium geometries of compounds bearing aromatic moieties.^[40] To increase the accuracy, 6-311++G(3df,3pd)^[41] basis set was used, in all calculations, for sulfur atom.

For selected model compounds, the energy order of the different conformers was checked using a series of single point calculations with B3LYP^[42] and TPSSH^[44] on top of M06-2X optimized geometries confirming that the lowest energy conformer does not depend on the choice of the functionals (see Table S39).

Following the assessment of the structural parameters, a comprehensive benchmark study on the excited state properties has been conducted using Tamm Dancoff Approximation (TDA) with LC- ω PBE,^[44] M06-2X, CAM-B3LYP^[45] and ω B97XD functionals (Figure S8). Excited state energies and oscillator strengths are the two main parameters used to judge the properties of the functionals; we observed that except for LC- ω PBE, the other three functionals behave similarly in both oscillator strength and excited state energies. In our previous study, which has been mainly focused on the effects of functionals on descriptor analyses, we investigated the performance of M06-2X, CAM-B3LYP and ω B97XD functionals in detail and we observed that the nature of excited state calculations with M06-2X and ω B97XD functionals yield more reliable results compared to the CAM-B3LYP functional.^[22] Figure S9 reports absolute deviations from experimental data and it is observed that except for some outliers such as; Spiroacridan-Phenoxaboronyl-TIPP, DACMES₂B, NOBF₂-Cz^[46] and NOBF₂-DPCz,^[46] calculations with M06-2X/6-31+G(d,p) gave deviations smaller than 0.05 eV. Moreover, absolute deviations from calculations with ω B97XD/6-31+G(d,p) also yielded small values, however, it has been observed that ω B97XD could not reproduce some of the most remarkable molecules such as PXZMES₂B, 10H-Phenoxaboronyl-Phenyl-DMAC, DACMES₂B, 2DACMES₂B, B-2PTZ and B-2DMAC. Overall, both M06-2X and ω B97XD are good performing functionals for energy gap calculations, however, compared to ω B97XD, calculations with M06-2X have smaller number of outliers. Furthermore, the effects of the basis were assessed taking into account 6-31G(d),^[47] 6-31G(d,p),^[48] 6-31+G(d),^[49] and 6-31+G(d,p)^[47] sets. It was clearly observed that increasing the basis set does not induce any significant change on the excited state energies and the corresponding oscillator strengths (see Figure S8). The choice of TDA over Time-Dependent DFT (TD-DFT) is due to its better performance in describing both singlet and triplet excited states, since it is not plagued with triplet instability issues.^[50] The effects of conformational variability on the excited state properties was also checked concluding that when the change in equilibrium geometries do not involve the angles close to the donor moieties, their effect on excited state energies is negligible (see Table S40). Moreover, it has also been observed that ground state conformational changes do not occur in the donor moieties (see Tables S1, S4, S7, S10, and S13), and instead involve the acceptor fragments.

All calculations were performed taking into account solvent effects, in accordance with experiments, by using the polarizable continuum model in the integral equation formalism (IEF-PCM).^[51]

The absorption spectra have been computed by generating 40 conformers through a Wigner distribution^[52] based on the calculation of the harmonic vibrational frequencies as implemented in the Newton-X^[53] software package. The final

spectrum is obtained by the convolution of all the vertical transitions and the corresponding oscillator strengths. Absorption spectra were modeled using B3LYP, BLYP,^[38] PBE0,^[34,35] M06-2X and ω B97XD functionals and 6-31+G(d,p) basis set. To reproduce the band shape the vertical transitions from each snapshot were convoluted using Gaussian functions of full-width at half-length (FWHM) of 0.15 eV.

The nature of excited states was assessed using Natural Transition Orbitals (NTOs) and Φ_s indices, defining the overlap between the attachment and the detachment densities that is, the electron density removed/rearranged during the excitation. NTOs and Φ_s were obtained with the Nancy_EX code^[36] and visualized with the Avogadro^[37] software package. Other parameters describing the degree of overlap between HOMO and LUMO orbitals, such as D-index, S-index and t-index were computed using the Multiwfn^[39] software package.

SOC elements between S_1 and T_n states involved in RISC mechanism were calculated with Amsterdam Density Functional Code (ADF),^[39] at the M06-2X/DZP^[40] level of theory. Since Pople basis sets are not available in ADF, the Slater type DZP was chosen.

Results and Discussion

We report the behavior of a series of D- π -A type TADF emitters bearing boron-containing acceptor moieties and different donor groups such as PXZ, PTZ, DMAC, Spiroacridan, Cz, Diphenylamino carbazole (DAC) and bis(diphenylamino) carbazole (2DAC) which are introduced to the *para*- (1–9, 18–25 in Figure 3) or *ortho*- (10–17 in Figure 3) position relative to the acceptor groups. Four important and widely used acceptors, namely Dimesitylboryl (Mes_2B), 10H-Phenoxaboron, Difluoroboron ($-\text{BF}_2$), and 5,9-dioxo-13b-boranaphtho[3,2,1-de]anthracene (OBA) are selected to understand their effects on the electronic properties. Indeed, Mes_2B unit has strong electron accepting ability coupled with p - π^* conjugation and is one of the most popular acceptor groups in TADF literature.^[41] 10H-Phenoxaboron is important due to its rigid structure, which is highly efficient in assuring orthogonal arrangements, hence favoring small singlet-triplet gaps.^[42] On the other hand, the $-\text{BF}_2$ unit, thanks to its strong electron withdrawing capability provides low

LUMO levels leading to an increase in intramolecular charge-transfer (ICT) character.^[43] The last acceptor unit OBA is usually described as providing large torsion angle making it an efficient acceptor group in blue emitting TADF materials.^[44]

Torsion angle analyses

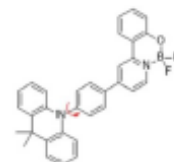
A comprehensive conformational analysis was firstly performed to investigate the geometrical features of TADF molecules. As reported in literature, orthogonality, which results in decreased Electron-Hole overlap and small ΔE_{ST} values is one of the key features for TADF performance.^[45] Table 1 reports the torsion angles between donor groups and phenyl linkers in the boron-based TADF emitters (see also the schematic representation in Table 1).

As shown in Table 1, dimethylacridine and spiroacridan stand out with their perfectly orthogonal geometry (compounds 4–7), followed by phenoxazine and phenothiazine with torsion angle close to 80°. On the other hand, carbazole, which is known for its poor TADF activity has a torsion angle of ~50° (*para* position) most probably since its five-membered central ring has smaller steric hindrance compared to the other donors presenting six-membered rings. This fact is also partially justified by the observation that replacing the substituent to the *ortho* position increases orthogonality and leads to an acceptable torsion of about 75° as shown for Cz-o-B (10),^[46] Cz-Ph-o-B (11),^[46] Cz-Pyridine-o-B (12),^[46] Cz-Pyrimidine-o-B (13) and Cz-CN-o-B (14).^[46] In light of these results, it can be stressed that changing the location of carbazole from *para* to *ortho* position appears as an effective strategy to increase steric hindrance and induce orthogonality, thus, decreasing ΔE_{ST} . In other carbazole containing donor moieties, namely DAC and 2DAC, it was observed that the addition of phenyl rings on carbazole does not change steric hindrance, keeping the torsion angles close to 50°. Thus, while DMAC, PXZ, Spiroacridan, and PTZ donors have favorable orthogonal geometrical arrangements, carbazole geometry may be tuned by changing its regioisomery and increasing its steric hindrance.

The torsion angles of the acceptor moieties were also studied to infer the degree of separation between π -linkers and acceptor moieties, and hence the possible disruption of

Table 1. Optimized torsion angles of the donor units modeled in this study and the representation of torsion angle in model NOBF_2 -DMAC^[46] emitter.

Donor Moiety	Torsion Angle (D – π linker)
Phenoxazine (PXZ)	~80
Carbazole (Cz) – in <i>para</i> position	~50
Carbazole (Cz) – in <i>ortho</i> position	~75
Dimethylacridine (DMAC)	~90
Spiroacridan	~90
Diphenylamino carbazole (DAC)	~50
Bis(Diphenylamino carbazole) (2DAC)	~50
Phenothiazine (PTZ)	~80



conjugation leads to the separation of electron and hole orbitals.

As reported in Tables S1, S4, S7, S10 and S13, the acceptor groups discussed in this study have a torsion angle of $\sim 50^\circ$ and thus their effect on TADF efficiency seems more limited. This structural feature further suggests that the modifications in donor moiety should lead to a greater change in ICT. This assumption will be examined in more detail in the following sections.

To assess the excited state properties of the emitters we also optimized S_1 and T_1 geometries and in particular we evidenced the appearance of 'Excited State Twisting' as pictorially represented in Figure 4 (See also Table S2, S3, S5, S6, S8, S9, S11, S12, S14, S15). Indeed, the orthogonality between donor and acceptor moieties decreases in the case of the lowest triplet states. The twisted geometry partially reinstates conjugation and will favor more local excited states.

Moreover, the optimized structures reported in Figure 5 show that the ortho substituted TADF emitters exhibit intramolecular π - π interactions between the carbazole unit and the mesityl group of acceptor moiety, the two interacting unit being at about 3.43–3.55 Å distance. Within the whole set, intramolecular π - π interactions were observed only in emitters where D/A groups are in close proximity and showing face-to-face arrangement.

Similarly, this kind of intramolecular interaction is expected to induce an increased rigidity via the suppression of rotation

around C–C bond between the central phenyl group and donor moiety or the mesityl group of the acceptor. This feature is expected to affect not only the TADF descriptors reported in our study such as Electron/Hole separation and ΔE_{ST} , but also the photoluminescence quantum yield (PLQY) of these kinds of emitters, reducing occurrence of competitive non-radiative decays.^[67] Thus, *ortho*-substitution can lead to favorable device properties, such as, high PLQY and faster RISC which can be observed via the smaller Electron/Hole overlap and ΔE_{ST} values. Moreover, SOC for these kind of emitters are larger than for the *para*-substituted ones, such as Cz-Ph-Mes₂B. The larger SOC values of *ortho*-substituted emitters can be attributed to the hybridization of charge transfer and local excitation states, which is a behavior observed in molecules exhibiting intramolecular π - π interactions between cofacially packed donor and acceptor moieties.^[68]

Energy splitting between S_1 and T_n states (ΔE_{ST})

Although, usually TADF compounds should have ΔE_{ST} values smaller than 0.1 eV, some TADF emitters with singlet-triplet energy splitting larger than this threshold have been reported.^[69] For the set of molecules under investigation, the energy gaps between S_1 and the first five triplet states have been computed at M06-2X/6-31+G(d,p) and ω B97XD/6-31+G(d,p) levels of theory (see Table 2 and Table S42). The calculated energy gaps were compared with experimental data and, as reported in Table 2, we found that the experimental energy gaps involved in RISC are, globally, well reproduced when considering the gaps between S_1 and the closest triplet states. It should also be underlined that some energy gaps represented in Table 2 have negative signs, which indicate that the relevant triplet state is higher than the S_1 state. This includes different kind of compounds such as PXZMES₂B, 10H-Phenoxaboryl-Phenyl-DMAC 2DACMES₂B, Cz-Pyridine-*o*-B, Cz-Pyrimidine-*o*-B, Cz-CN-*o*-B, B-2PXZ, B-2DMAC, NOBF2-DTCz,^[40] NOBF2-DMAC, OBA-*o*, OBA-*s*, OBA-Br-*o*, OBA-Br-*s*. Thus, possible reverse internal conversion R(IC) pathways between T_1 and T_n levels^[70] cannot be excluded for these compounds.

In addition to ISC/RISC analyses based on ΔE_{ST} values, we also examined the relation between torsion angles and the ΔE_{ST} values. As we discussed previously, the analyses of torsion

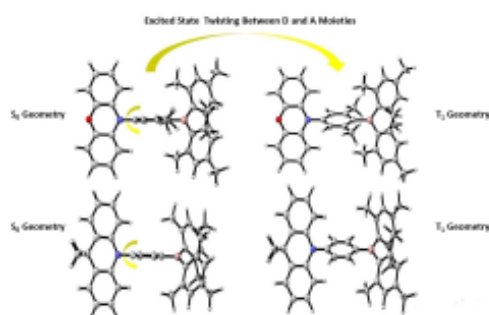


Figure 4. Excited state twisting observed in T_1 geometries.

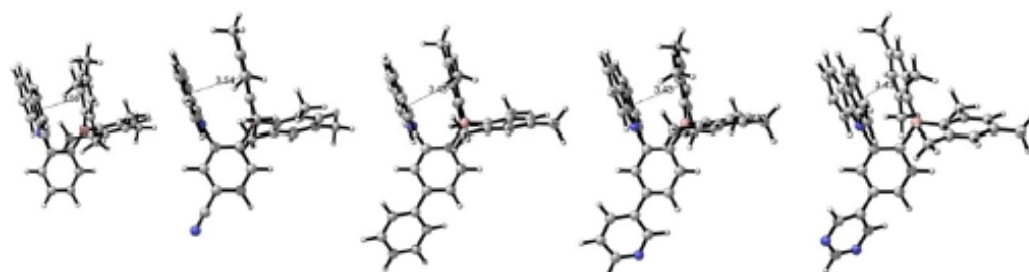


Figure 5. Distances (Angstrom) between the centroids of aromatic rings computed at M06-2X/6-31+G(d,p) level of theory.

Table 2. Energy splitting (in eV) between S_1 and first five triplet levels computed at M06-2X/6-31 + G(d,p) level of theory.

Compounds	$\Delta E(S_1-T_1)$	$\Delta E(S_1-T_2)$	$\Delta E(S_1-T_3)$	$\Delta E(S_1-T_4)$	$\Delta E(S_1-T_5)$	Experiment	Ref.
PXZMES ₂ B (1)	0.231	0.185	0.156	0.008	−0.063	0.008	[33]
PXZ-Ph-Mes ₂ B (2)	0.030	−0.006	−0.059	−0.116	−0.351	0.033	[71]
Cz-Ph-Mes ₂ B (3)	0.463	0.319	0.248	0.177	0.085	0.460	[71]
DMAC-Ph-Mes ₂ B (4)	0.010	−0.047	−0.103	−0.198	−0.342	0.041	[71]
10H-Phenoxaboryl-Phenyl-DMAC (5)	0.341	0.085	0.005	−0.062	−0.223	0.013	[72]
DMAC-Phenoxaboryl-TIPP (6)	0.014	−0.022	−0.220	−0.358	−0.573	0.060	[25]
Spiroacridan-Phenoxaboryl-TIPP (7)	0.933	0.476	−0.065	−0.222	−0.390	0.010	[25]
DACMES ₂ B (8)	0.413	0.348	−0.212	−0.456	−0.543	0.019	[33]
2DACMES ₂ B (9)	0.476	0.304	0.173	0.144	0.058	0.021	[33]
Cz-o-B (10)	0.240	0.127	0.056	−0.106	−0.133	0.150	[66]
Cz-Ph-o-B (11)	0.234	0.056	0.027	−0.055	−0.141	0.180	[66]
Cz-Pyridine-o-B (12)	0.215	0.053	0.007	−0.085	−0.165	0.130	[66]
Cz-Pyrimidine-o-B (13)	0.192	0.036	−0.020	−0.146	−0.209	0.080	[66]
Cz-CN-o-B (14)	0.156	−0.005	−0.087	−0.311	−0.342	0.050	[66]
B-2PTZ (15)	0.180	0.166	0.059	−0.021	−0.049	0.030	[73]
B-2PXZ (16)	0.083	0.021	−0.109	−0.139	−0.161	0.039	[73]
B-2DMAC (17)	0.367	0.066	−0.101	−0.124	−0.188	0.030	[73]
NOBF ₂ -Cz (18)	0.571	0.433	0.044	−0.006	−0.051	0.200	[46]
NOBF ₂ -DPCz (19)	0.361	0.163	−0.331	−0.368	−0.429	0.080	[46]
NOBF ₂ -DTCz (20)	0.664	0.416	0.335	0.276	0.167	0.220	[46]
NOBF ₂ -DMAC (21)	0.583	0.392	0.329	0.200	0.087	0.200	[46]
OBA-O (22)	0.606	0.386	0.075	0.024	−0.011	0.090	[64]
OBA-S (23)	0.606	0.418	0.078	0.024	−0.061	0.090	[64]
OBA-Br-O (24)	0.608	0.327	0.052	−0.034	−0.059	0.040	[64]
OBA-Br-S (25)	0.608	0.357	0.054	−0.036	−0.101	0.070	[64]

*Energy differences represented as bold have the smallest absolute deviations from experiment.

angles show that PXZ, DMAC, Spiroacridan and PTZ moieties lead to orthogonal structures. On the other hand, Cz based emitters have ~50° torsion angles which are far from orthogonality. In light of this structural analysis, ΔE_{ST} values of PXZ, DMAC, Spiroacridan and PTZ containing emitters are expected to be smaller than the Cz containing emitters.

As shown in Table 2, the calculated ΔE_{ST} values sufficiently reproduces the expected correlation. For instance, while PXZ-Ph-Mes₂B, DMAC-Ph-Mes₂B and Spiroacridan-Phenoxaboryl-TIPP have ΔE_{ST} smaller than 0.1 eV; Cz-Ph-Mes₂B, Cz-o-B and NOBF₂-Cz emitters have ΔE_{ST} larger than 0.1 eV.

Singlet triplet alignment

As represented in Figure 6, the Jablonski diagrams obtained at GS, S_1 and T_1 equilibrium geometries show different trends in both the energy and the nature of the involved states. In particular, large differences in the state alignment depending on the equilibrium geometry are present. This in turn limits considerably the possibility to rationalize TADF from considerations drawn at Franck-Condon, without considering the excited state relaxation. Indeed, for the compounds represented

in Figure 6, at Franck-Condon geometry, S_1 is in close proximity to a manifold of triplet states, which could possibly lead to thermally activated ISC towards different states. However, this quasi-degeneracy in the triplet manifold is lifted at both S_1 and T_1 equilibrium geometry, where only the lowest triplet state remains accessible. Furthermore, we also observed that the natures of S_1 and T_1 states depends on the geometry.

Indeed, at the S_1 equilibrium geometry both states have CT character, which in turn should lead to small SOC and low ISC probability. Conversely, at T_1 equilibrium geometries the two states are respectively local and charge-transfer, hence the SOC increases, favoring RISC, despite the slight increase of the energy gap.

Nature of states

In our previous studies, we have stressed the importance of Natural Transition Orbitals (NTOs) in analyzing the changes of the electronic density in the S_1 and T_1 states.^[22] Herein, we characterize such changes with different parameters such as: the density based descriptor D-index, which is the distance between electron and hole centroids, the S_{H} index, defining the

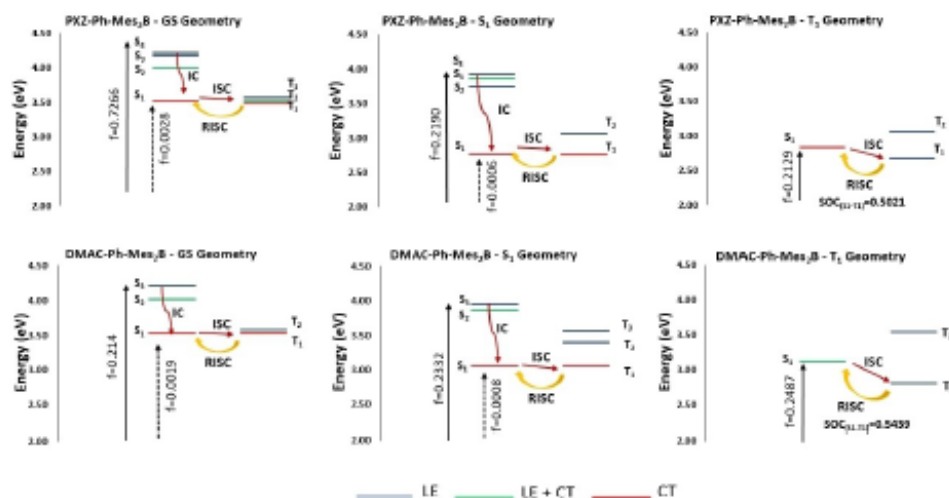


Figure 6. Jablonski diagrams for GS (S_0), S_1 and T_1 geometries of PXZ-Ph-Mes₂B and DMAC-Ph-Mes₂B computed at M06-2X/6-31 + G(d,p) level of theory. Blue, green and red lines correspond to LE, LE + CT mixed and CT states respectively.

overlap between electrons and holes, the t -index, which measures the degree of separation between frontier molecular orbitals, and finally, the Φ_s index which can be defined as the overlap between attachment (electron) and detachment (hole) densities.^[26]

The most important structural reorganizations are observed for the T_1 states and our calculations predict that the corresponding planarization is enhancing the LE nature of the state. This effect can also be witnessed by the change in the topological descriptors computed at T_1 or Franck-Condon geometries, suggesting a different diabatic nature for this state. As shown in Table 3, the nature of S_1 and T_1 states are different at S_0 and T_1 equilibrium geometries. The reason behind this behavior may be traced to the large structural reorganization, which is observed upon excitation. As we stated previously, the decrease in orthogonality, which is observed in T_1 state geometries, leads to higher LE character. Due to the time-scales of TADF-involved processes, the systems have enough time to equilibrate along the T_1 potential energy surface. Thus, since we are mostly interested in RISC starting from T_1 state, we mainly focused on the descriptors obtained from the optimized T_1 geometries. As can be seen from Table 4, the D indices of the T_1 states are systematically smaller than the corresponding indices for the S_1 states, again pointing to a larger LE character of the former. Moreover, we observe that the D indices of S_1 are generally larger than 3 Å clearly identifying these states as charge-transfer. However, D indices of the S_1 states for the OBA-S₁ and OBA-Br-S₁ are found to be smaller than 1 Å, which can indicate that LE character is here dominant. The same behavior is also confirmed by the other complementary descriptors including Φ_s . However, a sharp separation between LE (close to 1.0) and CT (close to 0.0) value is observed for this descriptor while smoother transitions were observed for the D index. Thus,

Φ_s index appears, at least to this respect, as a more reliable indicator for precisely assigning the natures of these states.

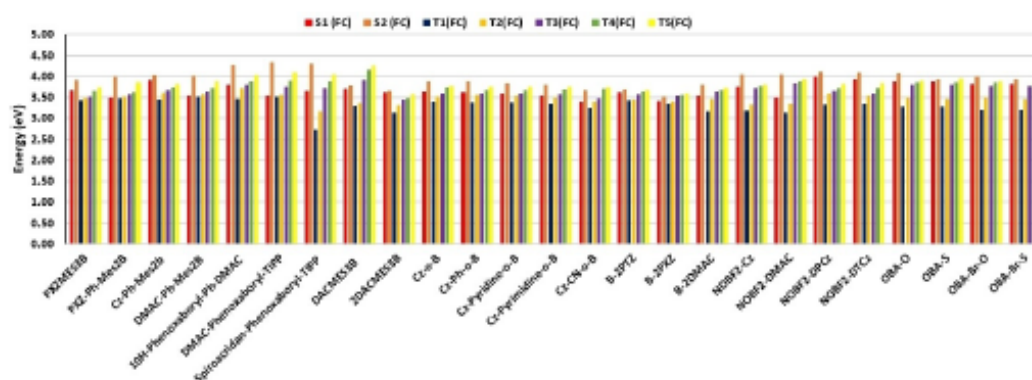
Indeed, as shown in Table 4, for the S_1 state Φ_s , especially for PXZ and DMAC containing molecules, is mostly around 0.5 indicating mixed CT-LE character, while Cz-containing molecules exhibit dominant LE character with high Φ_s values around 0.7. On the other hand, Φ_s for the T_1 state are generally found to lie close to 0.8, indicating dominant LE natures. To have a deeper understanding of the interplay between structural effects and changes in the electronic density, Φ_s has also been computed at the ground state geometries and as reported in Table S47, these values are found to be smaller than those at the T_1 geometries, which is again coherent with the observed excited state twisting.

Table 5 summarizes the main geometry changes observed in the excited states of DMAC-Ph-Mes₂B, Cz-o-B, NOBF₂-DMAC and OBA-S together with the HOMO and LUMO orbitals computed at S_0 and T_1 geometries. The main geometrical changes involve the degree of orthogonality, or in some compounds such as OBA-S, the planarization of donor moieties. It is clear that the decreased orthogonality in T_1 states leads to an increased LE character in FMO. Besides this, FMO analysis of OBA-S compound shows that the donor groups, which are folded in the ground state, can stay planar in the excited state.

As reported in Table S49 and Table S50, unlike previous groups with CT/ S_1 and LE/ T_1 states, OBA- and NOBF₂- groups exhibit LE character in both singlet and triplet states. However, these compounds may still be characterized by small singlet triplet energy gap and large SOC, thus leading to efficient RISC. Moreover, as reported in Figure 7 and Table S60, our calculations show that in addition to T_1 other higher triplet states, whose population could be thermally allowed, lay below S_1 . Hence, a competition between RISC-assisted TADF (involving

Table 3. Natures of S_1 and T_1 states computed from S_0 and T_1 geometries at M062X/6-31 + G(d,p) level of theory.

Compounds	S_0 Geometry		T_1 Geometry		Torsion Angle Between D and A Groups or D and π Bridges	
	S_1	T_1	S_1	T_1	S_0 Geometry	T_1 Geometry
PXZMES ₂ B (1)	CT	LE	LE + CT	LE + CT	−101.01	−64.63
PXZ-Ph-Mes ₂ B (2)	CT	LE + CT	LE + CT	LE + CT	−101.76	68.34
Cz-Ph-Mes ₂ B (3)	CT + LE	LE	LE + CT	LE + CT	−52.44	42.46
DMAC-Ph-Mes ₂ B (4)	CT	CT	LE + CT	LE + CT	−90.41	−63.60
10H-Phenoxaboryl-Phenyl-DMAC (5)	CT	LE	CT	LE + CT	90.64	64.85
DMAC-Phenoxaboryl-TIPP (6)	CT	CT	CT	CT	88.39	69.92
Spiroacridan-Phenoxaboryl-TIPP (7)	CT	LE	CT	CT	−82.55	−66.18
DACMES ₂ B (8)	LE + CT	LE + CT	LE + CT	LE + CT	−53.76	49.88
2DACMES ₂ B (9)	CT	LE + CT	LE + CT	LE + CT	−52.43	48.90
Cz-o-B (10)	LE + CT	LE	LE + CT	LE + CT	75.25	49.10
Cz-Ph-o-B (11)	CT	LE	LE + CT	LE + CT	75.71	−47.58
Cz-Pyridine-o-B (12)	CT	LE	LE + CT	LE + CT	−77.91	−47.94
Cz-Pyrimidine-o-B (13)	CT	LE	LE + CT	LE + CT	75.75	−77.96
Cz-CN-o-B (14)	CT	LE + CT	LE + CT	LE + CT	78.30	50.82
B-2PTZ (15)	CT	LE	CT	LE + CT	−102.26	81.05
B-2PXZ (16)	CT	LE + CT	CT	CT	101.69	82.38
B-2DMAC (17)	CT	LE	CT	LE + CT	11.88	−80.48
NOBF2-Cz (18)	LE + CT	LE + CT	LE + CT	LE + CT	−52.30	−50.48
NOBF2-DPCz (19)	LE + CT	LE + CT	CT	LE + CT	51.78	43.08
NOBF2-DTCz (20)	LE + CT	LE	LE + CT	LE + CT	50.07	42.49
NOBF2-DMAC (21)	LE + CT	LE	LE + CT	LE + CT	−89.52	68.96
OBA-O (22)	LE	LE	LE + CT	LE	78.40	112.63
OBA-S (23)	LE	LE	LE	LE	101.13	91.69
OBA-Br-O (24)	LE	LE	CT	LE	−77.72	73.94
OBA-Br-S (25)	LE	LE	LE	LE	−101.79	−91.56

**Figure 7.** Energies of S_1 , S_2 and first five triplet states computed at M062X/6-31 + G(d,p) level of theory. FC refers to the Franck Condon, i.e. the ground state equilibrium geometry.

higher lying triplet states) and direct RISC from T_1 to S_1 can be expected. To check, more generally the involvement of higher triplet states in our set, the energy differences between T_1 and

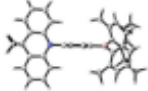
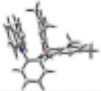
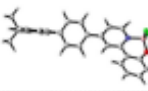
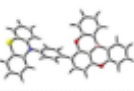
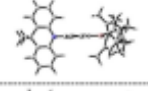
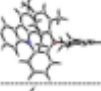
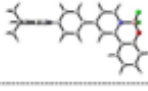
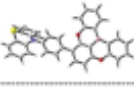
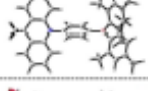
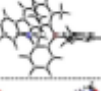
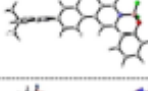
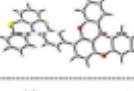
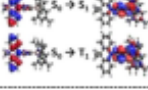
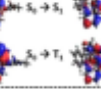
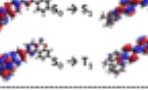
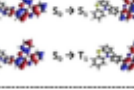
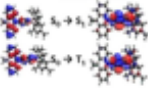
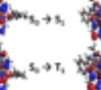
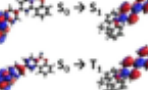
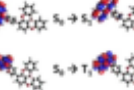
T_2 states has been considered and close triplet states were analyzed.

In Figure 7 we report the energy of the first two singlet and five triplet states, and we observe that generally, compounds

Table 4. D, Sm, t indices and Φ_S values for S_1 and T_1 states computed at M06-2X/6-31 + G(d,p) level of theory at T_1 geometry.

Compounds	S_1 State				T_1 State			
	D (Angstrom)	S_m (a.u.)	t (angstrom)	Φ_S	D (angstrom)	S_m (a.u.)	t (angstrom)	Φ_S
PXZMES ₂ B (1)	5.790	0.089	3.774	0.535	3.887	0.237	1.344	0.649
PXZ-Ph-Mes ₂ B (2)	5.167	0.072	3.281	0.563	4.723	0.136	2.579	0.557
Cz-Ph-Mes ₂ B (3)	3.137	0.278	0.151	0.721	1.938	0.380	−0.667	0.846
DMAC-Ph-Mes ₂ B (4)	4.684	0.112	2.636	0.508	3.602	0.244	1.171	0.779
10H-Phenoxaboryl-Phenyl-DMAC (5)	5.183	0.104	2.992	0.478	3.551	0.267	0.703	0.652
DMAC-Phenoxaboryl-TIPP (6)	4.834	0.083	2.972	0.419	4.366	0.132	2.232	0.623
Spiroacridan-Phenoxaboryl-TIPP (7)	4.758	0.105	2.744	0.500	3.921	0.208	1.542	0.697
DACMES ₂ B (8)	6.128	0.129	3.435	0.561	4.576	0.223	1.669	0.729
2DACMES ₂ B (9)	5.611	0.168	2.762	0.565	4.191	0.247	1.155	0.735
Cz-o-B (10)	2.477	0.217	0.629	0.608	1.668	0.286	−0.089	0.716
Cz-Ph-o-B (11)	2.546	0.229	0.640	0.619	1.528	0.316	−0.404	0.779
Cz-Pyridine-o-B (12)	2.770	0.212	0.879	0.629	1.641	0.314	−0.280	0.763
Cz-Pyrimidine-o-B (13)	3.559	0.100	1.858	0.489	2.429	0.215	0.665	0.484
Cz-CN-o-B (14)	3.104	0.169	1.211	0.555	2.330	0.272	0.407	0.688
B-2PTZ (15)	5.229	0.035	3.582	0.336	3.794	0.201	1.965	0.557
B-2PXZ (16)	3.584	0.048	2.000	0.242	3.230	0.081	1.619	0.372
B-2DMAC (17)	4.907	0.041	3.328	0.308	2.709	0.309	0.795	0.752
NOBF ₂ -Cz (18)	4.803	0.214	1.819	0.717	2.560	0.387	−0.538	0.838
NOBF ₂ -DPCz (19)	4.856	0.235	1.702	0.697	2.897	0.369	−0.323	0.832
NOBF ₂ -DTCz (20)	5.414	0.179	2.487	0.715	3.058	0.353	−0.068	0.835
NOBF ₂ -DMAC (21)	5.972	0.076	3.743	0.450	5.156	0.173	2.442	0.690
OBA-O (22)	5.458	0.204	1.989	0.738	5.458	0.204	1.989	0.814
OBA-S (23)	0.525	0.414	−1.007	0.716	0.525	0.414	−1.007	0.801
OBA-Br-O (24)	7.151	0.091	4.367	0.638	0.099	0.441	−1.606	0.823
OBA-Br-S (25)	0.584	0.412	−1.056	0.713	0.519	0.401	−1.087	0.795

Table 5. Geometric relaxations in excited states and NTO distributions computed at M062X/6-31 + G(d,p) level of theory.

	DMAC-Ph-Mes ₂ B	Cz-o-B	NOBF ₂ -DMAC	OBA-S
S_0 Geometry				
S_1 Geometry				
T_1 Geometry				
FMO S_0 Geometry				
FMO T_1 Geometry				

with dimethylboryl acceptor moiety and PXZ, DMAC donor groups, (PXZMES₂B,^[22] PXZ-Ph-Mes₂B,^[71] DMAC-Ph-Mes₂B,^[71] DACMES₂B,^[22] B-2PXZ and B-2DMAC^[72]), have closer T₁ and T₂. Since T₂ levels are very close to S₁ and T₁, a possible RISC from T₂ to S₁ can be envisaged. To analyze the effects of these close lying T₂ states, their nature has been determined (see Table S49) and SOC between T₂ and S₁ states have been obtained (see Table S51). As shown in Table S49–S50, T₂ presents an increased LE character compared to T₁, which further supports the contribution of mixed triplet states to RISC. Furthermore, in all the cases reported in Figure 7 the low energy triplet states are found below S₁. Therefore, RISC from multiple triplet states may represent a possible deactivation pathway affecting the excited state dynamics and life-times.

Spin-orbit coupling (SOC)

SOC which arises from the one-electron Dirac equation is responsible for mixing orbital and spin degrees of freedom, and thus allows the coupling of electronic states of different multiplicities.^[73] As reported in literature,^[74–76] reducing ΔE_{ST} should be accompanied by the optimization of SOC, which in organic TADF molecules is challenging.

As reported in Table S51, for compounds 1, 2, 3, 4, 6 and 7, the SOC values between S₁–T₂ are larger than the ones between S₁–T₁. Moreover, SOC from upper triplet states are generally lower than the SOC's between S₁–T₂, which suggests that the upper triplet states may undergo internal conversion to T₂ and T₁ followed by RISC through T₁→S₁ and T₂→S₁ channels.

The role of higher triplet states, in providing a potential pathway for RISC, has been extensively discussed in the previous studies. As reported in the literature, this has been

observed in anthracene derivatives, organic dyes, and excited state intramolecular proton transfer (ESIPT) materials.^[77] For anthracene, as reported by Kobayashi et al., RISC from T₂ to S₁ state can be observed when the T₁ states further excited to higher triplet states.^[77] On the other hand, the origin of RISC from upper triplet states can also be attributed to the large T₂–T₁ energy gap or the presence of heavy atom substitutions. It has been observed that the RISC from high-lying triplet exciton (hot exciton process) is an effective way of increasing device efficiencies and is mainly controlled by the energy level alignment of the excited states.^[78,79]

Figure 8 represents the Jablonski diagrams of compounds Cz-Ph-Mes₂B and Cz-o-B computed at M06-2X/6-31+G(d,p) level of theory. Due to the lack of orthogonality between the donor and π -bridge, Cz-Ph-Mes₂B was found to have large overlap in electron and hole orbitals which lead to high ΔE_{ST} value (ΔE_{ST} =0.463 eV). In the case of *ortho*-substituted Cz-o-B emitter with the same donor and acceptor moieties but different isomerism, a larger separation between S₁ and T₂ states, and larger SOC (0.3008 cm⁻¹) between S₁ and T₁ states are observed. This result is attributed to the change in the nature of S₁ states in more sterically hindered *ortho* Cz-o-B. Indeed, this regioisomery causes a mixed CT+LE character with the increase in torsion angle with π bridge (~75°), which leads to an increase in SOC value with both T₁ and T₂ states. Overall, though larger SOC values are obtained between states of different character, these values are still very small, which is a known consequence of charge transfer contribution in TADF emitters.^[80]

Mainly, based on the magnitude of SOC, we tried to compare our theoretical data to experimental external quantum efficiencies (see Table S61). Yet, this underlies that the computed SOC's are sufficient to fully reproduce the experimental

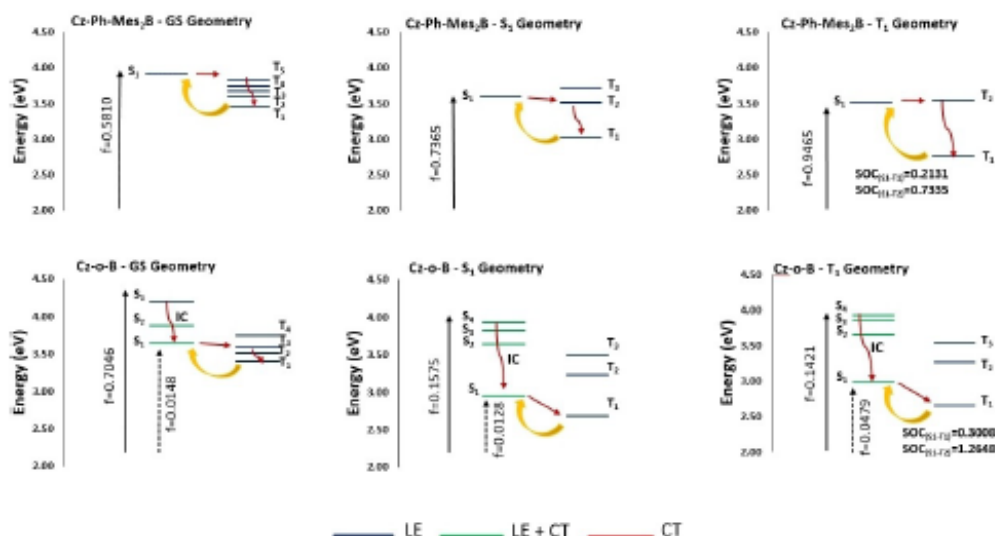


Figure 8. Energy level diagrams for GS, S₁ and T₁ geometries of Cz-Ph-Mes₂B and Cz-o-B emitters computed at M06-2X/6-31+G(d,p) level of theory.

results. Yet, care should be taken when analyzing the experimental efficiencies, since the conditions of the preparation of the device may be important in dictating the overall performance. Yet, even if the selected molecules have been studied under different conditions some valuable tendencies can be extracted. Indeed, compounds with SOC above 0.4 cm^{-1} usually exhibit efficiencies between 14.0% and 23.0%. Conversely, SOC below the 0.4 cm^{-1} threshold correlates with efficiency lower than 14.0%, with two exceptions which are DACMes₂B, 2DACMes₂B and PXZ-Mes₂B, whose efficiency is high despite the small SOC. However, the high efficiencies of these emitters can be attributed to their extremely small ΔE_{ST} less 0.04 eV, which can thus favor RISC from an energetical point of view.

Donor-acceptor strengths

Herein, we focused our attention on two important points, the desired geometries of selected donor and acceptor moieties, and the relative strengths of these units. As reported in literature, one of the crucial strategies in designing high efficiency TADF molecules is achieving a structure with spatially separated HOMO and LUMO orbitals and using strong donor and acceptor moieties is a way of having localized and separated frontier molecular orbitals. The spatial separation between HOMO and LUMO orbitals decreases the energy gap between S_1 and T_1 states, which leads to enhanced RISC processes.^[2] This implies that as the strength of donating and accepting moieties increases, leading to more effective π electron transfer in conjugated systems, the HOMO–LUMO gaps

(E_g) decreases.^[80–82] Thus, reducing ΔE_{ST} is achieved by using strong donor and acceptor units.^[83,84] Furthermore, the electron donating and accepting ability of D and A groups do not only affect ΔE_{ST} , but they also have an important role in tuning the emission color of TADF emitters.^[85] The experimental emission wavelengths are reported in SI showing that the molecules covers efficiently the blue and green portion of the electromagnetic spectrum.

In our molecular set, we benefited from the electron accepting ability of the boron atom and we have analyzed its effect on LUMO orbitals. In general, acceptor moieties affect LUMO orbitals by reducing their energies and for boron-based emitters this behavior is globally reproduced. However, we observed that for NOBF₂-based compounds, the boron atoms do not contribute to the LUMO orbitals, differently from other molecules (Tables S52–S57). Indeed, while for NOBF₂-Cz, NOBF₂-DTCz, NOBF₂-DPCz and NOBF₂-DMAC boron has 1.061%, 1.279%, 1.274% and 1.184% contribution to the LUMO, respectively, in Cz-Ph-Mes₂B and DMAC-Ph-Mes₂B boron achieves 25.431% and 26.150% contributions. This behavior indicates that the electron accepting ability of NOBF₂- moiety is mainly controlled by the nitrogen atom in NOBF₂- unit and the carbon atom in pyridine ring. On the other hand, in Cz-Ph-Mes₂B and DMAC-Ph-Mes₂B emitters with dimethylboron acceptor moiety, boron has a more pronounced effect on the LUMO.

It is known that as HOMO energy increases, electron donating ability increases, and as LUMO energy decreases, electron accepting ability increases, hence tuning the HOMO–LUMO gap. In Figure 9, HOMO–LUMO energies and ΔE_{ST} values computed at M06-2X/6-31+G(d,p) level of theory were re-

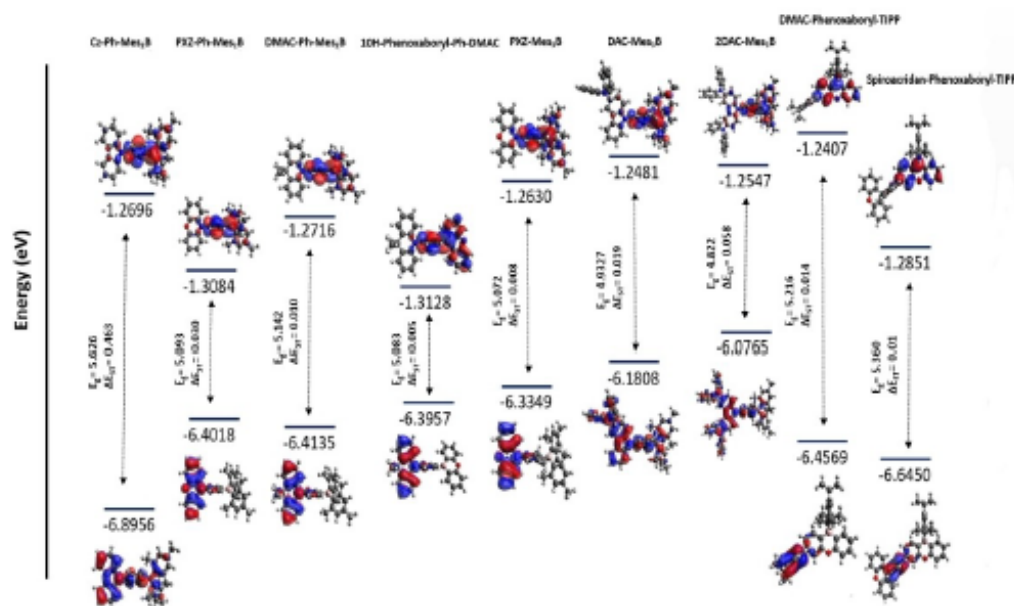


Figure 9. HOMO and LUMO energies of first nine compounds and frontier molecular orbital distributions computed at M06-2X/6-31+G(d,p) level of theory.

ported. We may observe that the donor strength order is as: 2DAC > DAC > PXZ > DMAC > Spiroacridan > Cz (HOMO energies of related compounds are: -6.0765 eV, -6.1808 eV, -6.3349 eV, -6.4135 eV, -6.6450 eV, -6.8956 eV for compounds 2DAC-Mes₂B, DAC-Mes₂B, PXZ-Ph-Mes₂B, DMAC-Ph-Mes₂B, Spiroacridan-Phenoxaboryl-TIPP and Cz-Ph-Mes₂B respectively).

On the other hand, with the help of LUMO energies, the acceptor strength order may be sketched as: 10H-Phenoxaboryl > Mes₂B. Moreover, as reported in Figure 9 the relation between ΔE_{ST} and E_g values is consistent with the expected behavior correlating the decrease of E_g with ΔE_{ST} . This observation once again proves that the strong electron accepting and donating abilities of donor and acceptor moieties are highly beneficial for achieving small singlet-triplet energy gaps.

The electron accepting and donating strength can also be considered via the simulated absorption spectra (see Figure S10). Although, the presence of multiple absorption bands, arising from different $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, leads to a rather complicated absorption spectrum, a trend of the absorption wavelength can be easily observed, especially for the brighter $\pi \rightarrow \pi^*$ band. As shown in Figure S10, the lowest energy absorption band of 2DAC-Mes₂B (9) takes place at longer wavelength than DAC-Mes₂B (8), which is followed by PXZ-Ph-Mes₂B (2), DMAC-Ph-Mes₂B (5), Cz-Ph-Mes₂B (3) and 10H-Phenoxaboryl-Ph-DMAC (5) respectively. On the other hand, no significant change in the absorption spectra between 6 and 7 is observed.

Conclusions

Herein, a series of tri-coordinated and tetra-coordinated boron-based TADF emitters, which are widely used in display technology have been systematically investigated to understand their RISC pathways and efficiencies. Indeed, due to their contribution to π -conjugation through the empty p_z orbital, coordinated boron-based emitters show high photoluminescence quantum yield. Moreover, due to their low electron withdrawing ability, they usually exhibit blue emission, it is possible, however, by various design strategies, to obtain different color emissions.

Globally, our systematic investigation has shown several important aspects: 1) creating highly orthogonal structures with sterically hindered donor moieties helps to reduce singlet-triplet energy gaps, however, this strategy leads to a decrease of oscillator strength, inherent emission probability, and SOC; 2) boron-based acceptor moieties used in this study usually induce a $\sim 50^\circ$ torsion angle, 3) the ground state geometries are very similar to S_1 equilibrium geometries, however, more pronounced geometry changes are observed at T_1 equilibrium geometries, 4) the geometry changes in T_1 lead to a corresponding change in the nature of the excited states, thus increasing RISC efficiency; 5) while S_1 states generally have CT character, T_1 can be characterized as LE or mixed CT-LE; 6) unlike other TADF emitters, NOBF₂- and OBA- based compounds have LE- S_1 states and LE- T_1 states, 7) the efficiency

of the carbazole moiety can be increased by forcing appropriate geometrical arrangements, for instance via *ortho*- or *para*-regioisomery 8) the presence of quasi-degenerate T_1 and T_2 states opens alternative efficient channels for RISC, 9) up-conversion from higher triplet states to S_1 has been identified as a possible pathway for RISC 10) unexpectedly, NOBF₂- and OBA- based emitters, despite the same nature of S_1 and T_1 states, have high SOC.

In light of all these findings, we highlight the importance of selecting the correct connectivity between donor and acceptor moieties. Our results and observations reported in this manuscript strongly suggest that possible alternative pathways may be operative for RISC. In turn, this would require a careful selection of donor and acceptor moieties to achieve the desired electron exchange energy, HOMO-LUMO gap, strong oscillator strength and high SOC. Finally, we observed that boron emitters can be used in different architectures either as tri-coordinated or tetra-coordinated; boron atom may or may not contribute to LUMOs and they can achieve small ΔE_{ST} and strong enough SOC to allow efficient RISC.

Supplementary Material

Supplementary data file consists of 3D representations of the geometries, their torsion angles and conformer energies. Benchmark calculation results and oscillator strengths together with other data from excited state calculations such as nature of states, absorption spectra, spin-orbit coupling and Cartesian coordinates are also included in the SI file.

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Conflict of Interests

There are no conflicts of interest to declare.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: boron • donor-acceptor systems • intersystem crossing • organic light-emitting diodes • reverse intersystem crossing • thermally activated delayed fluorescence

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A.3. The Photophysical Properties of Sulfone-Based TADF Emitters In Relation to Their Structural Properties

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The photophysical properties of sulfone-based TADF emitters in relation to their structural properties†

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In this work, thermally activated delayed fluorescence (TADF) of a series of emitters with sulfone-based acceptor moieties was studied by density functional theory (DFT) methods. Sulfone derivatives were shown to be high performing TADF emitters over recent years. When discussing the TADF efficiency, various properties, such as the singlet–triplet energy gap (ΔE_{ST}), spin–orbit coupling (SOC) and the nature of states, stand out due to their roles in reverse intersystem crossing (RISC). Here, we mainly focused on three important structural parameters that affect the intersystem crossing (ISC) and RISC pathways and their efficiencies. These three parameters are: (1) the effect of *meta*- and *para*-conjugation, (2) the effect of rigid acceptor moieties and (3) the effect of the phenyl bridge on photophysical properties.

Introduction

In recent years, thermally activated delayed fluorescence (TADF) materials have attracted considerable attention due to their 100% exciton harvesting abilities and high device efficiencies.¹ For traditional fluorescent materials, known as organic light emitting diodes (OLEDs), only 25% of excitons lead to luminescence, and the remaining 75% are triplets that are deactivated by nonradiative transitions.^{2–4} To overcome low device efficiencies of fluorescent emitters, phosphorescent materials (PhOLEDs) containing heavy metals were developed and due to their emission from the triplet state to the ground state, the loss of triplet excitons was prevented.^{5,6} Although the loss of excitons was prevented, the heavy metals in their structure led to undesirable consequences, such as high cost and environmental pollution.⁷ In 2012, Adachi and co-workers developed TADF materials as a promising technology, which provides high efficiency, cost saving and environmentally friendly applications (Fig. 1).^{2,8–10} Due to the efficient harvesting of triplet excitons, TADF materials offer advanced applications in electroluminescence,¹¹ sensors,¹² bioimaging,^{10,12} and organic lasers.¹³ Metal free TADF emitters can achieve 100% internal quantum efficiencies by harvesting triplet excitons *via* the RISC process from the first excited triplet state (T_1) to the first excited singlet state (S_1) under thermal activation.^{14–17}

Many TADF materials usually adopt a twisted donor (D)–acceptor (A) geometry to minimize the overlap between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO), which lead to small S_1 – T_1 energy gaps (ΔE_{ST}).¹⁸

$$\Delta E_{ST} = 2 \iint \Phi_L(1)\Phi_H(2) \frac{e^2}{r_{12}} \Phi_L(2)\Phi_H(1) d\tau_1 d\tau_2 \quad (1)$$

As represented in eqn (1), decreasing the exchange interaction integral of the HOMO and the LUMO wavefunctions is an efficient way to minimize the ΔE_{ST} . Recent studies reported that in a cofacial configuration of D and A moieties, emitters have the possibility to exhibit through-space charge-transfer (TSCT) which leads to separation between the HOMO and LUMO, thus leading to small ΔE_{ST} values. However, compared to through-bond charge-transfer (TBCT) systems, TSCT systems have relatively lower electronic interactions between D and A moieties, which lead to increased rotations between D and A groups and strong non-radiative decays.¹⁹ To sum up, there are two possible ways of separating frontier molecular orbitals, which is rationally designing TBCT and TSCT systems.

Furthermore, the TADF efficiency is not only dependent on ΔE_{ST} , but also highly related to the spin–orbit coupling (SOC), that is, effective RISC relies on both small ΔE_{ST} and large SOC.^{11,12,16,20,21} For many TADF emitters, due to their purely organic structures, SOC were found to be intrinsically weak, which makes it difficult to obtain efficient RISC in TADF and ISC in phosphorescence. To enhance SOC values in TADF emitters, the heavy-atom effect was used; since SOC is proportional to the fourth power of the nuclear charge, the most

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‡ These authors contributed equally to this study.

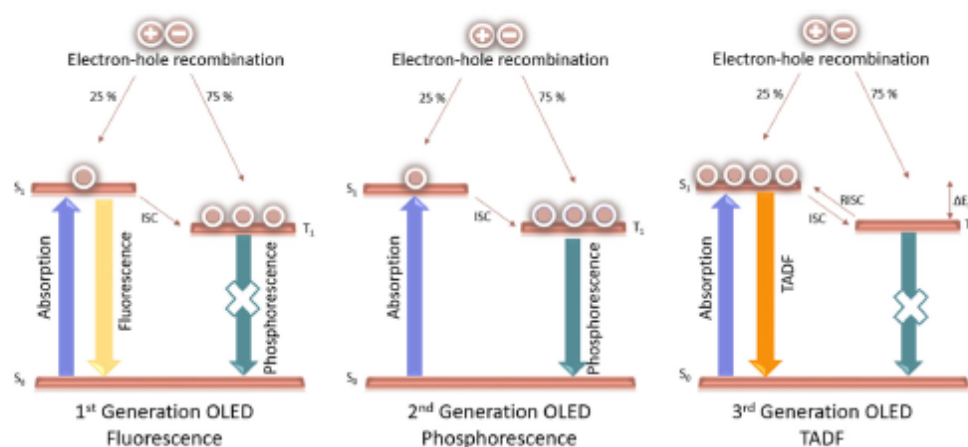


Fig. 1 OLED, PhOLED and TADF mechanism.

common strategy for improving SOC is introducing non-metal atoms into the molecular structure, such as halogens.^{18,22}

In this work, we demonstrate the photophysical properties and structural behaviors of a series of sulfone-based TADF emitters using computational methods. As listed in Fig. 2, the set of molecules under investigation has various sulfone-based acceptor moieties such as diphenylsulfone (DPS), dibenzo-thiophene-*S,S*-dioxide (DBTO2), 9,9-dimethyl-9H-thioxanthene-10,10-dioxide (TXO2), and thianthrene 5,5,10,10-tetraoxide (TTR).

The acceptor moieties depicted in this molecule set (Fig. 2) were reported in our previous studies as well as in recent TADF literature.^{7,23} In our previous reports, we theoretically investigated the characteristics of dimethylacridine (DMAC), carbazole (Cz), phenoxazine (PXZ), phenothiazine (PTZ) and diphenylamine (DPA) as donor moieties.^{7,24} By simulating a wide molecule set with different donor and acceptor moieties, we study the effects and significance of the sulfur atom in various structures. As reported in the literature, DPS is a multi-talented acceptor moiety, with a strong electron withdrawing

ability due to the highly electronegative oxygen atoms, and provides excellent TADF activity due to its central twist.^{25,26} Moreover, since it has tetrahedral geometry, it is known to restrict the π -conjugation of the emitters leading to CT compounds. While the DBTO2 and TXO2 acceptor moieties were used to understand the influence of acceptor rigidity on descriptors, the TTR group was selected to predict the effects of two iso-energetic low energy conformers and phenyl bridges on TADF descriptors.

Computational methodology

To better understand the structural and photophysical properties of the emitters discussed in this study, a computational analysis was conducted using the Gaussian16²⁷ and Amsterdam density functional (ADF)²⁸ software packages. Geometries in the ground and excited S_1 and T_1 states were optimized at the M062X²⁹/6-31+G(d,p)³⁰ level of theory. Tamn Dancoff Approximation (TDA)³¹ calculations for the $S_0 \rightarrow S_n$ and $S_0 \rightarrow T_n$

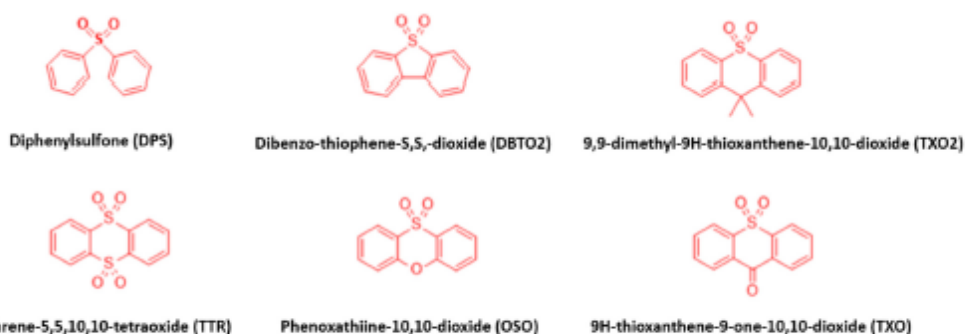


Fig. 2 Sulfone based acceptor moieties investigated in this study.

transitions using the M062X/6-31+G(d,p) and ω B97XD³²/6-31+G(d,p) levels were performed with respect to the optimized S_0 state geometries.

In our previous contribution, we modeled the excited state behaviors of a series of TADF emitters with various functionals such as M062X, ω B97XD and CAMB3LYP and the results obtained with M062X were found to be reliable and consistent with experimental data.²³ The reliability of data obtained with the M062X functional was tested with the nature of state and ΔE_{ST} analyses. In light of our previous findings from a methodological study, we chose to model sulfone based emitters with the M062X functional and, ω B97XD was used only for benchmark purposes. TDA choice is due to the fact that the TDA method provides a more balanced description of both triplet and singlet excited states, and compared to time-dependent DFT (TD-DFT), it is free from triplet instability issues.³³ The 6-311++G(3df,3pd)³⁴ extra basis set was used for the sulfur atom in all calculations. From the theoretical calculations, it can be observed that different acceptor and donor moieties exhibit characteristic torsions (see Tables S2–S6, ESI†). Moreover, some compounds exhibit two different iso-energetic low energy conformers presenting TADF as well as non-TADF activities. While near orthogonal geometries resulted in very small ΔE_{ST} values making the RISC process viable, planar conformers were shown to yield larger ΔE_{ST} values representing non-TADF behavior.

In order to better analyze electron processes at excited states, including internal conversion (IC), ISC and RISC processes, we report the lowest 5 states for singlet and triplet excitations. Surprisingly, energy differences between excited states show the possibility of high-energy hot exciton pathways in ISC processes. Moreover, the nature of the excited singlet and triplet states is evaluated using natural transition orbitals (NTOs), obtained with the Nancy_EX code³⁵ and visualized with the Avogadro³⁶ software package. Additionally, Φ_s values, defining the overlap between the attachment and the detachment densities were calculated. In other words, it measures the degree of overlap between particle and hole densities and while the smaller its value the larger the charge transfer character, the larger its value the larger the local excitation character. Data obtained from calculations at the ω B97XD/6-31+G(d,p) level of theory were reported in Tables S7–S20 (ESI†). In consideration of the first-order perturbation theory, SOC values between excited singlet and triplet geometries were computed at S_1 and T_1 geometries using the ADF software package at the M062X/DZP³⁷ level of theory. The choice of M062X functional for SOC calculations is based on the analyses of the nature of states that we performed in our previous contribution.²³ In our previous contribution, we modeled a TADF active molecule set consisting various structures and aimed to investigate the best functional which well reproduces the nature of excited states. In light of our data, we observed and reported that the S_1 states that we modeled via the M062X functional mostly present a noticeable CT character, which is known to favor TADF efficiency. On the other hand, ω B97XD presents locally excited S_1 states for most of the TADF emitters. Moreover, due to the

structural properties of TADF emitters, they should favor a CT character, therefore, LE states observed by the ω B97XD functional should be regarded as an artifact compared to the reliable performance of M062X. According to the El Sayed rule, the nature of excited states plays an important role on SOC, therefore, the functional which best reproduces the nature of states will be the most appropriate functional for the SOC calculations. The excited state energies, oscillator strengths and, Φ -S indices, obtained from excited state calculations were calculated using two different functionals, ω B97XD and M062X. Herein, M062X was chosen for further SOC analyses, which is highly important for (R)ISC processes and controlled by the nature of states. ω B97XD has been used only for benchmark purposes.

The ultraviolet-visible (UV-Vis) absorption spectra of the investigated emitters were modeled by generating 30 conformers through a Wigner distribution as implemented in the Newton-X software package.³⁸ Vertical transitions from each snapshot were convoluted using Gaussian functions of a full-width at half length (FWHM) of 0.15 eV (see Fig. S7, ESI†). An integral equation formalism polarizable continuum model (IEF-PCM) was used in all calculations, to implicitly model the solvent environment.^{39–41} Toluene is used for all emitters except DBTO-PXZ and Cz-TTR, which have been modelled in dichloromethane and ethyl ethanoate, respectively. Optimized geometries were rendered with the CYLview software package.⁴²

Results and discussion

Effects of *meta*- and *para*-conjugation on photophysical properties

Although sulfone-based TADF emitters have been reported by several research groups, the majority of these studies focus on *para*-substituted materials. Comparatively, we theoretically investigated both *meta*- and *para*-substituted sulfone-based emitters to clarify the effects of different positions of the donor moieties on photophysical properties. As depicted in Fig. 3, we modeled five *meta*- and five *para*-substituted molecules with the DPS donor moiety and various donor groups, such as, Cz, PTZ, PXZ, DMAC and DPA.

It is well-known that the photophysical properties of organic compounds are highly affected by geometric parameters. The majority of the studies in the literature focus exclusively on symmetric emitters with D–A–D skeletons.⁴³ However, a few studies have been reported to clarify the effects of asymmetric emitters in TADF efficiencies.⁴³ Optimized geometries of *meta*- and *para*-substituted TADF emitters show that for S_0 state structures, the tetrahedral geometry of the DPS moiety do not change, however, significant changes were observed in the bending of donor moieties. As reported in Tables S2 and S3 (ESI†), while *para*-substituted DPS containing TADF emitters yield highly symmetrical structures, their *meta*-substituted analogues have asymmetric geometries. Herein, a comprehensive analysis on the effects of symmetric and asymmetric geometries as well as the bends in donor groups was

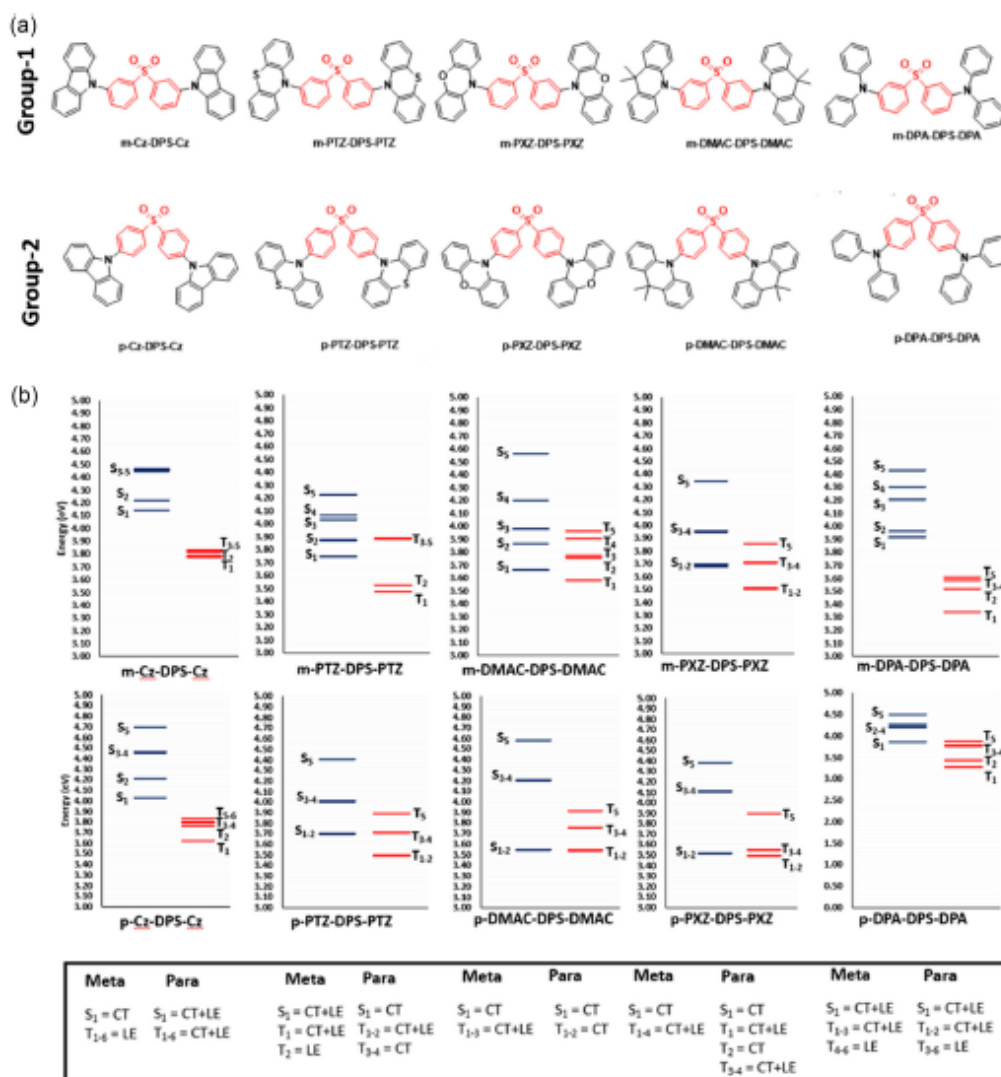


Fig. 3 (A) *meta*- (group 1) and *para*-substituted (group 2) TADF emitters with DPS acceptor moieties. (B) Energy levels and nature of excited states for *meta*- (group 1) and *para*-substituted (group 2) TADF emitters computed at the M062X/6-31+G(d,p) level of theory in toluene. Compounds: *m*-Cz-DPS-Cz,⁴⁵ *m*-PTZ-DPS-PTZ,⁴⁵ *m*-DMAC-DPS-DMAC,⁴⁵ *m*-PXZ-DPS-PXZ,⁴⁵ *m*-DPA-DPS-DPA,⁴⁵ *p*-Cz-DPS-Cz,⁴⁵ *p*-PTZ-DPS-PTZ,⁴⁷ *p*-DMAC-DPS-DMAC,⁴⁸ *p*-PXZ-DPS-PXZ,⁴⁸ and *p*-DPA-DPS-DPA.⁴⁹

performed. Bent conformations in the ground state are known to avoid molecular aggregation and the formation of intermolecular excimers.⁴⁴

Therefore, emitters with bent donor moieties are expected to be favorable in preventing molecular aggregation, which leads to non-emissive decays.⁴⁴ Following the geometry analyses, we further modeled the energy alignments of singlet and triplet states and aimed to investigate the differences between *meta*- and *para*-substituted emitters.

Fig. 3B demonstrates that except for the DPA-derivative, *para*-substituted emitters yield lower energy triplet levels compared to their *meta*-counterparts; and low-lying singlet state energies decreased in *para*-substituted emitters. Moreover, we also observed that many compounds in the first two groups exhibit iso-energetic S_1 and S_2 states, which may cause multiple emission bands with identical or different natures. On the other hand, lower energy triplet states in *para*-emitters create a greater number of possible pathways for the RISC process,

which also leads to a greater amount of exciton harvesting from iso-energetic triplet states below the S_1 level.

As shown in Fig. S7 (ESI†), the absorption spectra of *para*-substituted emitters yield lower energy bands compared to the *meta*-substituted compounds. This behavior of *para*-substitution suggests that geometries with smaller distortion cause stronger electron conjugation in the excited state. It should also be noted that the theoretical absorption spectra of both *meta*- and *para*-emitters exhibit dominant high intensity bands in higher energies, indicating that while $S_0 \rightarrow S_1$ absorptions are almost negligible, strong excitations to upper singlet states are highly dominant in both group 1 and 2 (Table S21, ESI†). Comparisons between *meta*- and *para*-substituted emitters showed that *para*-substituted compounds have larger oscillator strengths, which is an important parameter in understanding excited state transitions. As listed in Table S21 (ESI†), except for *para*-substituted **Cz-DPS-Cz** and **DPA-DPS-DPA** emitters, compounds usually exhibit negligible transition to the S_1 level and strong transitions to higher singlet states. It is also shown that for *meta*-substituted **Cz-DPS-Cz** emitters, absorptions with relatively larger oscillator strengths are (>0.1) $S_0 \rightarrow S_4$, $S_0 \rightarrow S_6$, $S_0 \rightarrow S_8$ and $S_0 \rightarrow S_{10}$. On the other hand, its *para*-substituted analogue has $S_0 \rightarrow S_1$ transition with quite strong oscillator strength, $f = 0.6433$. Similar to the **Cz-DPS-Cz** emitter, the *para*-substituted **DPA-DPS-DPA** emitter exhibits strong $S_0 \rightarrow S_1$ transition ($f = 0.9967$), while its *meta*-analogue has negligible transition to the S_1 state, and quite strong transitions to higher singlet states. For *meta*- and *para*-substituted **PTZ-DPS-PTZ**, **PXZ-DPS-PXZ** and **DMAC-DPS-DMAC** emitters, strong excitations from S_0 to S_n states open up alternative ISC channels for TADF emitters.

It is well-known that the population of high energy excited states leads to more energy loss during the IC process to the S_1 level. Therefore, with the help of strong SOC values between high energy singlet and triplet states, instead of IC, emitters may experience ISC between S_n and neighboring triplet states, leading to decreased energy loss and hence, higher efficiency.⁵⁰ The population of triplet states is affected by both the energy difference and the SOC between relevant singlet and triplet states. As reported in Table S22 (ESI†), though strong SOC between high oscillator strength singlet states and T_1 or T_2 states is possible (such as in *meta*-Cz), a strong coupling between high-energy singlet levels and high-energy triplet levels can also be observed (such as in *meta*-PTZ). Moreover, we also observed that iso-energetic triplet states, such as, the ones observed in *m/p*-**PXZ-DPS-PXZ**, *p*-**DMAC-DPS-DMAC** and *p*-**PTZ-DPS-PTZ** compounds may exhibit SOC values in different strengths, which shows that these iso-energetic triplet levels are in different natures, $^3CT/LE$, and state mixing processes enhancing RISC is possible in these emitters. The role of state mixing in enhancing RISC has been explained using the El Sayed rule. According to the El Sayed rule, the rate of inter-system crossing between the states of different electronic character is found to be much faster than that between two states of the same electronic character.⁵¹ Moreover, as first recognized by Monkman, when local excited states enter into

the picture and mix with charge transfer triplets, they prevent the El Sayed constraint of S_1 and T_1 states which are mostly CT character in TADF molecules.⁵² Therefore, the presence of states with a different nature lying close in energy works as a speeding up mechanism for RISC.^{53,54} For instance, the *p*-**PXZ-DPS-PXZ** emitter has iso-energetic T_1 and T_2 states which have 0.64 cm^{-1} and 1.61 cm^{-1} SOC values, respectively, and this difference in SOC values can be attributed to the different natures of T_1 and T_2 states (Table S23, ESI†).

As mentioned previously, multiple triplet states below the S_1 level creates multiple RISC possibilities. To analyze the probability of RISC from different triplet levels, the SOC values between relevant states were calculated. The SOC dependence of RISC has been reported in Fermi's Golden Rule approximation represented in eqn (2). According to the Fermi's Golden Rule approximation, the square of root mean square coupling element (RMSCE, V_{SOC}) is directly proportional to the RISC rate constant.^{55,56} Another parameter which plays an important role in k_{RISC} is the Franck-Condon-weighted density of states (pFCWD) which can be calculated in the framework of Marcus-Levich-Jortner theory.⁵⁷ Herein, since the calculation of pFCWD is a high cost calculation for these wide molecule sets, we only calculated the $|V_{SOC}|^2$ to foresee the RISC rates. As reported in Table S22 (ESI†), the square of root mean square coupling element (RMSCE, V_{SOC}) has been calculated for all states (for transition between S_1 and T_1 states, $|\langle S_1 | \hat{H}_{SOC} | T_1 \rangle|$ is divided into three to represent the average over the three triplet states for each possible value of the total angular momentum $J = -1, 0, 1$, see eqn (3)).

$$k_{RISC} = \frac{2\pi}{\hbar} |V_{SOC}|^2 \times \rho_{FCWD} \quad (2)$$

$$V_{SOC} = \frac{1}{3} |\langle S_1 | \hat{H}_{SOC} | T_1 \rangle| \quad (3)$$

It is obvious that transition from any triplet state below S_1 is possible with a strong SOC value. Importantly, it was observed that the energy gaps closest to the experimental value generally exhibit the strongest $|V_{SOC}|^2$, and generally, SOC values in *para*-substituted emitters are larger than the *meta*-substituted ones (except emitters **Cz-DPS-Cz** and **PTZ-DPS-PTZ**). These higher SOC values in *para*-substituted emitters can be attributed to the larger amount of state mixing in iso-energetic triplet levels below the S_1 state.

As represented in Table 1, among *meta*- and *para*-analogues, slight changes were observed in HOMO-LUMO energies and the energy difference between these two molecular orbitals (E_g). For compounds **Cz-DPS-Cz**, **PTZ-DPS-PTZ** and **DMAC-DPS-DMAC**, *meta*-substitution leads to larger HOMO energies, thus, the stronger electron donating ability of Cz, PTZ and DMAC donor moieties. On the other hand, while the PXZ donor moiety represents almost equal HOMO energies in *meta*- and *para*-substituted emitters, their DPA analogues yield a better donating ability with *para*-substitution. This behavior of the **DPA-DPS-DPA** emitter can be attributed to the highly sterically hindered and twisted structure in *meta*-compound, which

Table 1 HOMO and LUMO energies, and energy gaps of group 1 and group 2 emitters computed at the M062X/6-31+G(d,p) level of theory in toluene

Emitters	HOMO	LUMO	LUMO-HOMO (E_g) (eV)	Experimental ΔE_{ST} values ^a (eV)	Theoretical ΔE_{ST} values (eV)
<i>m</i> -Cz-DPS-Cz	-7.02	-1.25	5.77	0.44	0.36
<i>p</i> -Cz-DPS-Cz	-7.06	-1.24	5.82	0.25-0.31	0.27
<i>m</i> -PTZ-DPS-PTZ	-6.69	-1.30	5.39	0.01	0.04
<i>p</i> -PTZ-DPS-PTZ	-6.70	-1.33	5.37	0.40	0.21
<i>m</i> -DMAC-DPS-DMAC	-6.54	-1.21	5.33	0.05	0.09
<i>p</i> -DMAC-DPS-DMAC	-6.59	-1.27	5.32	0.09	0.01
<i>m</i> -PXZ-DPS-PXZ	-6.60	-1.30	5.30	0.06	0.03
<i>p</i> -PXZ-DPS-PXZ	-6.60	-1.36	5.24	0.08	0.02
<i>m</i> -DPA-DPS-DPA	-6.69	-0.88	5.81	—	0.33
<i>p</i> -DPA-DPS-DPA	-6.64	-0.85	5.79	0.54	0.42

^a Experimental ΔE_{ST} values obtained from the references: *m*-Cz-DPS-Cz,⁴⁵ *m*-PTZ-DPS-PTZ,⁴⁵ *m*-DMAC-DPS-DMAC,⁴⁵ *m*-PXZ-DPS-PXZ,⁴⁵ *m*-DPA-DPS-DPA,⁴⁵ *p*-Cz-DPS-Cz,⁴⁶ *p*-PTZ-DPS-PTZ,⁴⁷ *p*-DMAC-DPS-DMAC,⁴⁸ *p*-PXZ-DPS-PXZ,⁴⁸ and *p*-DPA-DPS-DPA.⁴⁹

results in disruption of conjugation within the molecule. For the electron accepting ability, the LUMO energies of *meta*- and *para*-substituted compounds were checked and it was observed that for PTZ-DPS-PTZ, DMAC-DPS-DMAC and PXZ-DPS-PXZ compounds, *para*-substitution leads to smaller LUMO energies and stronger electron withdrawing towards the acceptor moiety. Overall, the position of the donor moiety in these two molecule sets did not cause large differences in E_g values and these results are consistent with the similar ΔE_{ST} values of *meta*- and *para*-isomers (except Cz-DPS-Cz and PTZ-DPS-PTZ emitters).

To further compare the RISC behaviors of *meta*- and *para*-emitters, we theoretically calculated the energy gaps between singlet and triplet states. As reported in Table 1, experimental energy gaps were well reproduced and the largest absolute deviation was obtained as 0.29 eV for the *p*-PTZ-DPS-PTZ emitter. Importantly, these energy gaps correspond to the gaps between S_1 and triplet states with the largest RMSCE. In particular, proving the deterministic effect of SOC is consistent with our recent study published in 2022.²³

To summarize our findings so far, changing the position of the donor moiety from *para*- to *meta*- results in an increase in the twisting angle between donor and acceptor moieties, which is beneficial for separation of Frontier molecular orbitals. For the molecules in the first two groups, we have investigated the energy level alignments of excited states. Surprisingly, there are more than one triplet states below the S_1 level. Moreover, the presented results show that there are iso-energetic singlet and triplet states, which have the possibility to contribute to ISC and RISC processes. It should also be noted that though the first ten excited states were calculated to observe the brightest states and the pathways for the possible ISC and internal conversions, the low-lying states, especially for singlets, play the main role in the RISC process. Further analyses led us to conclude that the RISC process is mainly a SOC driven mechanism and it occurs between the states with the strongest SOC values. Additionally, we also present our findings for the oscillator strength and its effect on IC/RISC pathways.

It should also be noted that the Herzberg-Teller (HT) effect, which is a parameter that enhances the ISC/RISC processes and represents the dependence of oscillator strength on the internal

coordinates is also an important factor in TADF efficiency.⁵⁰ Though we did not calculate the emission spectra in this study, it is known that small molecular deformations between S_1 and S_0 states may enhance the emission oscillator strengths, which is a phenomena named the HT effect. Enhancement of the emission oscillator strength not only affects the transition intensity, but also affects the competition between the fluorescence and ISC/RISC processes. Therefore, an important point to keep in mind is that the excited state characteristics obtained with the Franck Condon (FC) approach are not the only parameters that affect the TADF efficiency.⁵⁹⁻⁶² In other words, the photophysical properties of these kinds of compounds are affected by both the FC and HT components.

Effect of rigidity of the acceptor moiety on photophysical properties

According to molecular design strategies, rigid compounds are good candidates for spatially separated Frontier molecular orbitals, which makes them CT based compounds due to their short π -conjugation length and high steric hindrance. Therefore, here we analyzed the behaviors of rigid TXO2 and DBTO acceptor moieties and a flexible DPS moiety to observe and compare the photophysical differences arising from the degree of rigidity. As shown in Fig. 4, TTR, DBTO and DPS acceptor moieties with different rigidities behave differently in terms of photophysical properties. By virtue of the geometric analysis, we observed that these three acceptor moieties create perfectly orthogonal geometries with a DMAC unit. On the other hand, their coupling with the PXZ donor group leads to $\sim 10^\circ$ shift from orthogonality (Table S4, ESI†). We further investigated their electron accepting abilities with the help of E_g values and observed that LUMO energies decrease in the order of TXO2-PXZ, *p*-PXZ-DPS-PXZ and DBTO-PXZ which indicates that DBTO is the strongest and TXO2 is the weakest electron acceptor. On the other hand, the ΔE_{ST} values of the six emitters under investigation are extremely small both experimentally and theoretically. This indicates that any possible difference in RISC mechanisms of these compounds can arise from any other parameter, but not from the singlet-triplet energy gap. At this stage, since the nature of triplet states will be the determinative factor in RISC, the effects of these acceptor

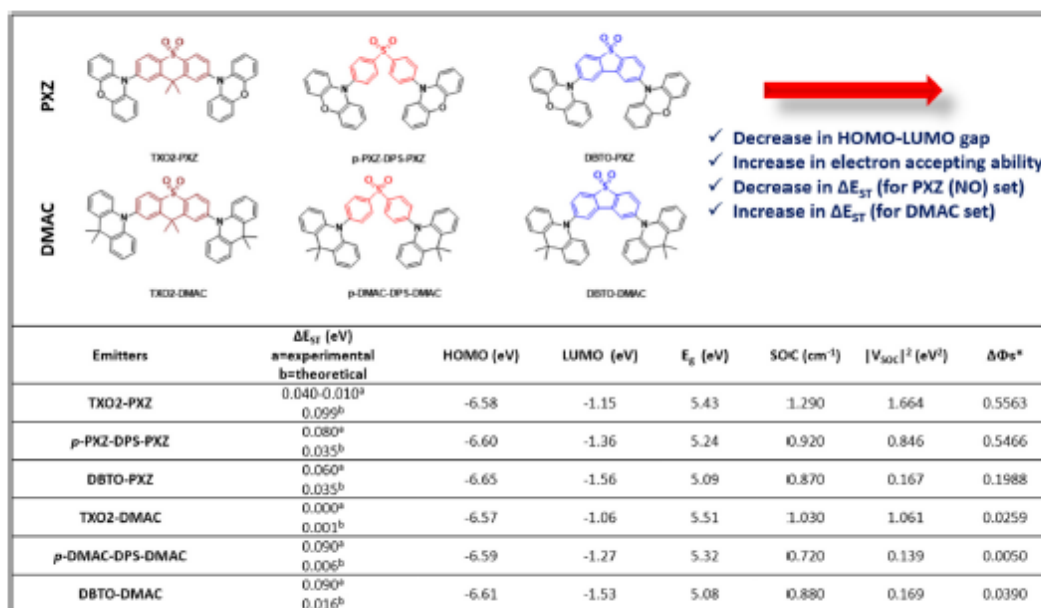


Fig. 4 Comparison of different photophysical properties for different acceptor moieties computed at the M062X/6-31+G(d,p) level of theory in toluene (TXO2-PXZ, *p*-PXZ-DPS-PXZ, TXO2-DMAC, *p*-DMAC-DPS-DMAC, and DBTO-DMAC) and in dichloromethane (DBTO-PXZ). * $\Delta\Phi_s$ is the difference between Φ_s values of singlet and triplet states with the strongest SOC values. ^aExperimental ΔE_{ST} values are obtained from the references; TXO2-PXZ,⁶³ *p*-PXZ-DPS-PXZ,⁶⁴ DBTO-PXZ,⁶⁵ TXO2-DMAC,²⁵ *p*-DMAC-DPS-DMAC and DBTO-DMAC.²⁵

moieties on the nature of excited triplet states have been analyzed. The results obtained using the meta-hybrid M062X functional are shown in Fig. 4 and Table S24 (ESI†). The S_1 state natures of all emitters were found to be in CT character with perfectly separated FMOs. Their T_1 and T_2 states are generally in CT character except TXO2-PXZ and *para*-PXZ. For T_2 , T_3 , T_4 and T_5 states, while the *para*-PXZ emitter represents a mixed character, the DBTO-PXZ emitter represents an obvious increase in LE transitions. On the other hand, TXO2-PXZ does not represent any regular trend from T_2 to T_5 . $\Delta\Phi_s$ values in Fig. 4 are in good agreement with the SOC values which represent an enhancement with the increase in nature difference between singlet and triplet states. Comparing with their phenoxazine analogues, we observed better FMO separation of T_1 and T_2 states, which is reflected in the Φ_s values of DMAC containing emitters (see Table S24, ESI†). Hence, the SOC from these low lying triplet states exhibit smaller values than their PXZ-analogues. Besides the lower Φ_s indices of the first two triplet states, T_3 , T_4 and T_5 states show a larger LE character, thus, larger SOC values. Considering all comparisons, we learned that the different acceptor moieties may yield various SOC values with higher triplet levels and there is not a regular trend between these acceptor groups.

Further analyses of excited state energies show that going from TXO2-PXZ to DBTO-PXZ, energies of the first singlet states decrease (see Fig. 5), thus, compared to the TXO2 acceptor moiety, DPS and DBTO yield bathochromically shifted absorption spectra (see Fig. S7 ESI†). According to our theoretical

findings reported in Fig. 5, the energy comparisons are in good agreement with the experimental emission spectra of investigated compounds which emit in blue-green, blue and yellow for TXO2-PXZ,⁶³ *p*-PXZ-DPS-PXZ⁶³ and DBTO-PXZ⁶⁵ compounds respectively. Moreover, we observed a similar decreasing energy trend for triplet states, and the energies of T_1 and T_2 states are iso-energetic in all emitters. This degeneracy of triplet states leads to state mixing between the states in different nature, thus, leading to larger SOC values and more efficient RISC processes.

To sum up, the nature of excited singlet states for TXO2, DPS and DBTO acceptor moieties are similar and surprisingly, the Φ_s values of emitters with DPS (flexible) and DBTO (rigid) acceptor groups are found to be very close to each other (see Table S24, ESI†). Additionally, the LUMO energies of these emitters are also quite similar representing their similar electron accepting abilities, which is consistent with their similar absorption spectra (see Fig. S7, ESI†). Moreover, the energy level alignments of this molecule set were found to behave differently from the first two groups (Fig. 3). In contrast to groups 1 and 2, the molecule set under investigation has low lying iso-energetic singlet and triplet levels with a similar nature of states.

Effects of phenyl bridges on photophysical properties

Density functional theory calculations of groups 3 and 4 were performed on ground state energy surfaces. As shown in Fig. 6, group 4 is the bridge-containing analogue of group 3. Herein,

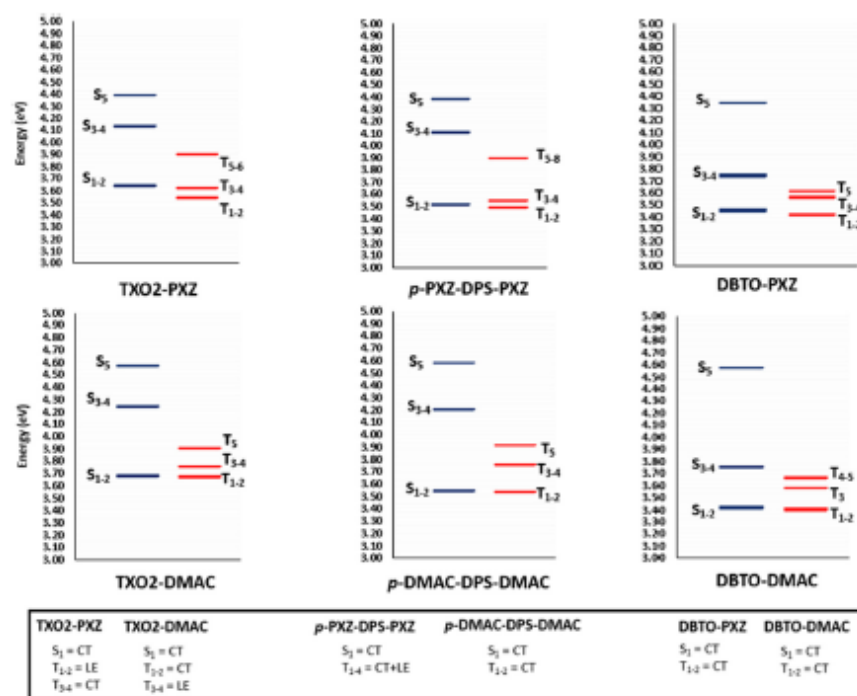


Fig. 5 Energy levels and natures of excited states for TTR, DPS and DBTO containing TADF emitters computed at the M062X/6-31+G(d,p) level of theory in toluene (TXO2-PXZ, p-PXZ-DPS-PXZ, TXO2-DMAC, p-DMAC-DPS-DMAC, DBTO-DMAC) and in dichloromethane (DBTO-PXZ).

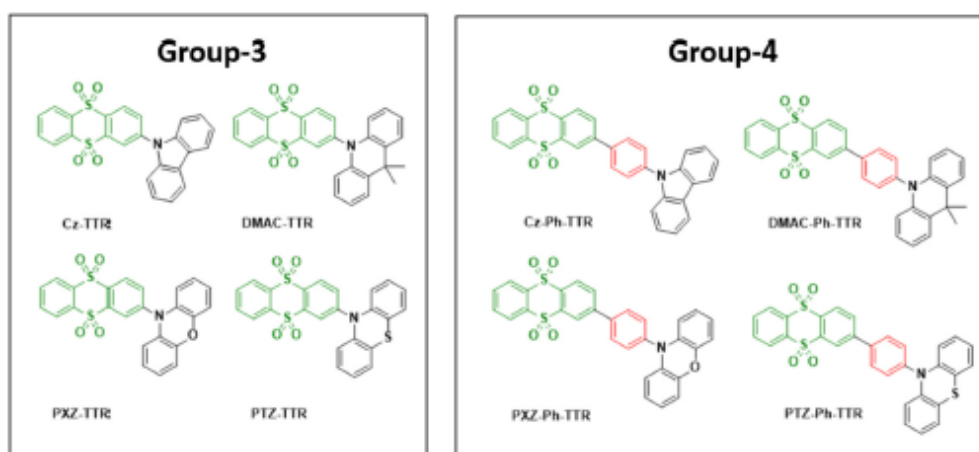


Fig. 6 Bridged and non-bridged TADF emitters with the TTR acceptor moiety. Compounds: Cz-TTR,⁶⁶ DMAC-TTR,⁶⁷ PXZ-TTR,⁶⁸ PTZ-TTR,⁶⁷ Cz-Ph-TTR,⁶⁹ DMAC-Ph-TTR,⁶⁷ PXZ-Ph-TTR⁷⁰ and PTZ-Ph-TTR.⁶⁷

we aimed to theoretically examine the effects of bridging the donor and acceptor moieties with a phenyl ring to observe the change in properties such as, geometric parameters, excited state energies, FMO separations (energy gaps between HOMO

and LUMO orbitals) and energy gaps between the excited states involved in the RISC process. In the set of molecules under investigation, the TTR moiety with two sulfur atoms has been selected as the acceptor group and Cz, DMAC, PXZ and PTZ

Table 2 HOMO–LUMO energies, E_g and ΔE_{ST} values of group 4 and 5 emitters computed at the M062X/6-31+G(d,p) level of theory in toluene (for Cz-TTR, Ph-TTR, DMAC-TTR, DMAC-Ph-TTR, PXZ-TTR, PXZ-Ph-TTR, PTZ-TTR, PTZ-Ph-TTR) and in ethy ethanoate (Cz-TTR)

Emitters	HOMO	LUMO	LUMO–HOMO (E_g) (eV)	Experimental ΔE_{ST} values ^a (eV)	Theoretical ΔE_{ST} values (eV)
Cz-TTR	−7.24	−1.81	5.43	0.10	0.55
Cz-Ph-TTR	−6.98	−1.82	5.16	0.30	0.15
DMAC-TTR (planar)	−7.33	−1.50	5.83	0.45	0.33
DMAC-TTR (orthogonal)	−6.90	−1.80	5.10	0.01	0.01
DMAC-Ph-TTR (only orthogonal)	−6.51	−1.82	4.69	0.06	0.00
PXZ-TTR	−6.69	−1.84	4.85	—	0.37
PXZ-Ph-TTR	−6.50	−1.84	4.66	0.05	0.02
PTZ-TTR (planar)	−7.41	−1.49	5.92	0.38	0.25
PTZ-TTR (orthogonal)	−6.79	−1.83	4.96	0.10	0.01
PTZ-Ph-TTR (planar)	−7.05	−1.66	5.39	0.57	0.20
PTZ-Ph-TTR (orthogonal)	−6.62	−1.84	4.78	0.01	0.07

^a Experimental ΔE_{ST} values are obtained from the references; Cz-TTR,⁶⁶ DMAC-TTR,⁶⁷ PXZ-TTR,⁶⁸ PTZ-TTR,⁶⁷ Cz-Ph-TTR,⁶⁸ DMAC-Ph-TTR,⁶⁷ PXZ-Ph-TTR⁷⁰ and PTZ-Ph-TTR.⁶⁷

moieties with different steric hindrance and aromaticity have been selected as the donor moieties. As reported in Tables S5 and S6 (ESI[†]), the effect of inserting a phenyl bridge largely affected the torsion angles between acceptor groups and their adjacent moieties. As an exception, the carbazole moiety in Cz-TTR and Cz-Ph-TTR exhibits ~ 40 and ~ 37 torsion angle, respectively; thus, inserting a phenyl bridge in the carbazole

containing emitter does not have a large effect on the torsion angle of the Cz moiety. As reported in Table 2, both experimental and theoretical ΔE_{ST} values for the Cz-TTR emitter are smaller than their phenyl containing analogue (Cz-Ph-TTR), a situation which can be attributed to the larger electron–hole separation (see the Φ -S indices in Table S25, ESI[†]). On the other hand, DMAC and PTZ containing emitters were found to

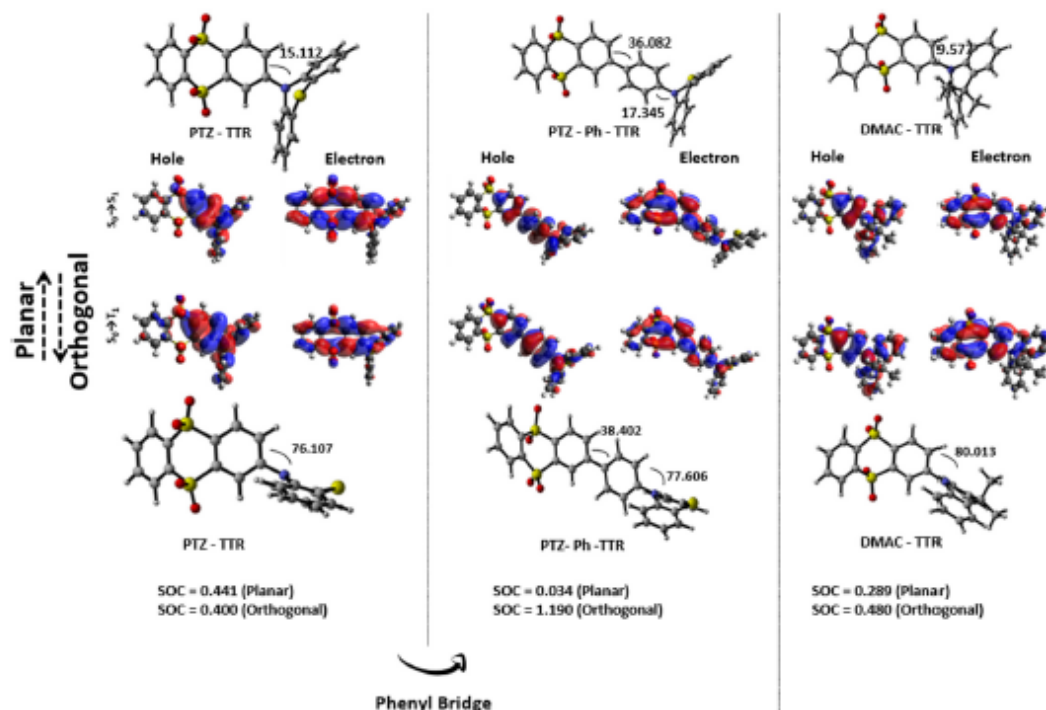


Fig. 7 Optimized geometries and electron–hole orbitals of planar and orthogonal conformers of PTZ-TTR, PTZ-Ph-TTR and DMAC-TTR emitters computed at the M06-2X/6-31+G(d,p) level of theory. Hole and electron orbitals correspond to the HOMO and LUMO orbitals, respectively.

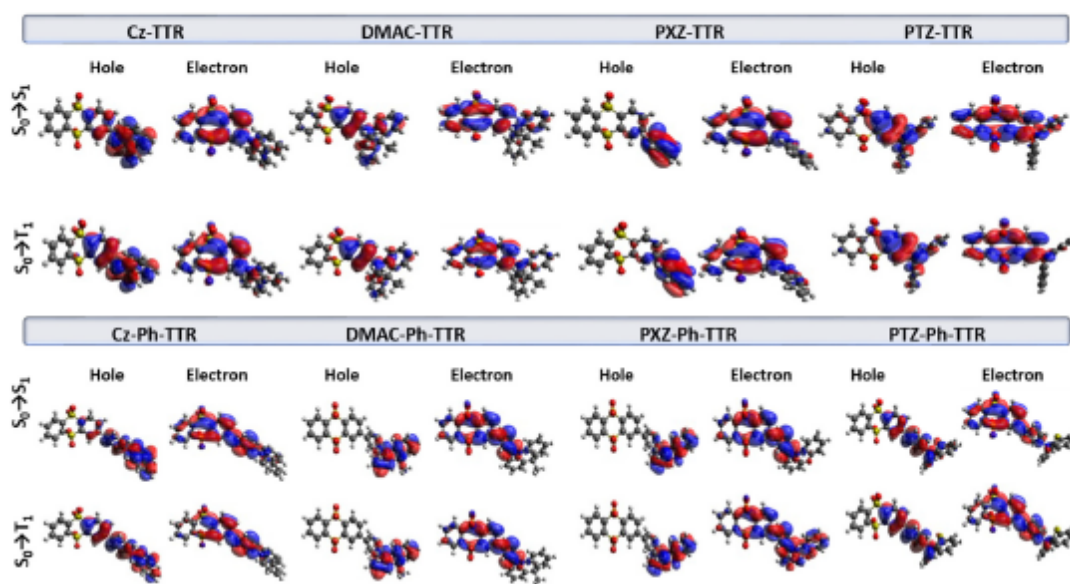


Fig. 8 Frontier molecular orbital distributions of group 4 and group 5 emitters computed at the M06-ZX/6-31+G(d,p) level of theory in toluene (for Cz-Ph-TTR, DMAC-TTR, DMAC-Ph-TTR, PXZ-TTR, PXZ-Ph-TTR, PTZ-TTR, PTZ-Ph-TTR) and in ethyl ethanoate (Cz-TTR). Hole and electron orbitals correspond to the HOMO and LUMO orbitals respectively.

have two possible conformers, which are orthogonal and planar (see Fig. 7). The relative energy differences between orthogonal and planar conformers of these emitters are very small, indicating the presence of iso-energetic low energy conformers in their D-A and D- π -A structures.

According to Table 2, the effects of orthogonal geometries on the singlet-triplet energy gap were well reproduced and their TADF activity due to the iso-energetic low energy conformers has been proved once again. Moreover, we also observed that the orthogonal geometries lead to a decrease in the LUMO and an increase in the HOMO energies, thus, they yield smaller E_g

values. Due to the smaller E_g values calculated for orthogonal geometries, their emission spectra were expected to be bathochromically shifted compared to their planar analogues, and although we did not calculate theoretical emission spectra, by way of comparing with experimental spectra reported in the literature, we concluded that the calculated E_g values are consistent with the experimental data reported in the literature.⁶⁷ To further study the effects of phenyl insertion and geometry changes on photophysical properties, we computed Phi-S indices at the M062X/6-31+G(d,p) level of theory in experimental solvents.

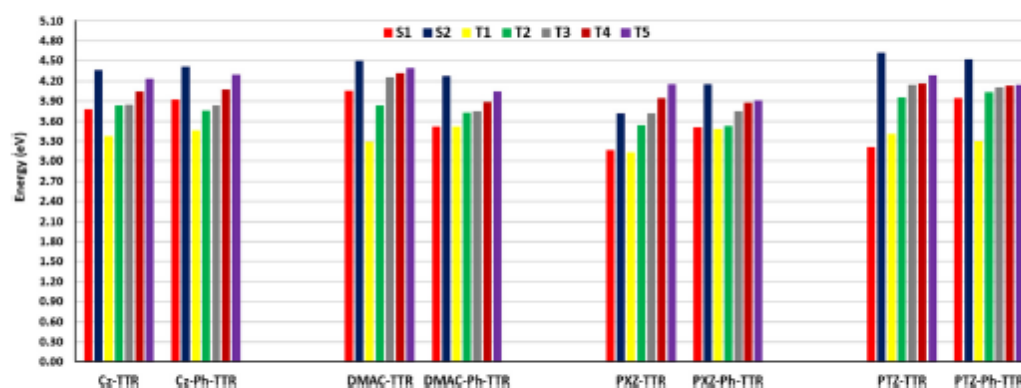


Fig. 9 Energies of singlet and triplet excited states computed at the M062X/6-31+G(d,p) level of theory in toluene (for Cz-Ph-TTR, DMAC-TTR, DMAC-Ph-TTR, PXZ-TTR, PXZ-Ph-TTR, PTZ-TTR, PTZ-Ph-TTR) and in ethyl ethanoate (Cz-TTR).

As summarized in Table S25 (ESI†) and as represented in Fig. 8, insertion of a phenyl bridge may increase or decrease the electron and hole separation of triplet states differently. Due to better separation in orthogonal geometries, going from planar to orthogonal conformers, a general decrease in Φ_{IS} indices was observed. Since the S_1 states of orthogonal emitters were found to be in CT or mixed character, their SOC values with triplet states in strong LE character were observed to be the strongest couplings (see Fig. 7). We further compared the electron-hole overlaps of bridged and non-bridged emitters, and observed that for Cz, PXZ and PTZ containing emitters, significant differences arise from the presence of phenyl bridges. However, negative or positive effects of using a phenyl bridge can vary in different emitters. For instance, while the insertion of a phenyl bridge to Cz-TTR and PTZ-TTR lead to an increase in electron-hole overlap, separation increased in the PXZ-Ph-TTR emitter.

The contribution of a phenyl bridge to excited state energies and energy gaps was also examined and the relative positions of the excited singlet and triplet states are reported in Fig. 9. With the incorporation of the phenyl moiety, an increasing trend in S_1 energy levels was observed in all emitters, except for DMAC-Ph-TTR. This situation can be attributed to the larger decrease in the torsion angle of the DMAC moiety in phenyl containing emitter compared to the other donor moieties which leads to a larger increase in planarity and conjugation length, thus a decrease in S_1 energy (see Tables S5 and S6, ESI†).

On the other hand, compared to the D-A emitters, the T_1 energies of phenyl containing analogues were increased, except for the compound with the PTZ moiety. Despite the benefit of longer conjugation in bridge containing D- π -A emitters, increased electron-hole overlap generally led to an increase in the LE character of the T_1 state. Correspondingly, the SOC values of phenyl containing emitters were increased, leading to larger RISC probabilities.

In summary, the insertion of the π -bridge affected the behavior of emitters differently. While some materials exhibit larger ΔE_{ST} values with π -linkers, some of them represented smaller ΔE_{ST} values. On the other hand, the HOMO-LUMO gaps of the emitters were found to be very close in emitters with or without π -bridges. Notably, DMAC-TTR and PTZ-TTR emitters were found to have iso-energetic low energy conformers with different photophysical properties. Our findings in ΔE_{ST} and nature of states analyses confirmed the TADF activity of orthogonal conformers. Lastly, in most of the emitters under investigation, the phenyl unit containing TADF materials represented larger SOC values.

Conclusions

In summary, we present a comprehensive theoretical study on the structural and photophysical properties of sulfone-based TADF emitters. Our investigations reveal that the molecule set under investigation presents various geometric behaviors, such as bearing bent conformations which prevent the formation of

intermolecular excimers as well as having iso-energetic low energy conformers, which exhibit TADF or non-TADF activities. Notably, our analyses of the effects of *meta*- and *para*-conjugation showed that the regioisomers possess different photophysical properties. The first two molecule sets were shown to have multiple triplet levels below the S_1 state, which opens alternative ISC/RISC pathways. Moreover, we also presented the possibilities of IC, ISC and RISC processes between the high lying singlet and triplet levels. Additionally, we observed that the larger amount of state mixing in iso-energetic triplet levels below the S_1 state enhances the SOC values and RISC probabilities.

In the last part of our study, we discussed the effects of phenyl bridges on structures and photophysical properties. Our findings show that most of the phenyl bridge containing TADF emitters present larger SOC values. This work is intended to provide insight and pave a way to design new TADF emitters. In light of our findings, it is possible to design new emitters with the desired properties and give rise to developments in TADF technology with new molecule designs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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A.4. Intersystem Crossing in a Carbazole-Based Room Temperature Phosphorescent Luminophore Investigated by Non-Adiabatic Dynamics

Intersystem Crossing in a Carbazole-Based Room Temperature Phosphorescent Luminophore Investigated by Non-Adiabatic Dynamics.

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KEYWORDS. Room Temperature Phosphorescence; Intersystem Crossing; Phosphorescent Emitters, Benzophenone-based luminophores Surface Hopping Dynamics; Intersystem Crossing.

ABSTRACT. The use of phosphorescent luminophore is highly beneficial in diverse high-technological and biological applications. Yet, because of the formally forbidden character of intersystem crossing, the use of heavy metals or atoms is usually necessary to achieve high quantum yields. This choice imposes serious constraints in terms of high device cost and inherent toxicity. In this contribution we resort to density functional based surface hopping non-adiabatic dynamics of a potential organic luminophore intended for room-temperature applications. We confirm that intersystem crossing is operative in a ps time-scale without requiring the activation of large-scale movements, thus confirming the suitability of the El Sayed based strategy for the rational design of fully organic phosphorescent emitters.

INTRODUCTION.

Organic luminescent materials have recently attracted considerable interest due to their suitability for applications in electroluminescence, organic lasers, and bioimaging ¹⁻³. Organic luminescence is produced by the radiative deactivation of sufficiently long-lived excited states. Luminescence can, in principle, be observed either from singlet or triplet states resulting in fluorescence or phosphorescence emission, respectively ⁴. Fluorescence emission which following the well-known Kasha's rule occurs between the first singlet excited state and the ground state, does not involve any change in spin, and is thus fully allowed, resulting in relatively short lifetimes. Fluorescence is notably at the base of the functioning of organic light emitting devices (OLEDs). Despite some limitations, OLEDs offer several advantages such as flexible device structures, reduced power consumption, and high brightness ⁵. However, OLEDs are also plagued by the insufficient device efficiencies, partially due to the inherently short fluorescence lifetime, and the need of a high driving voltage, which severely limit their applications ⁶. To overcome the efficiency problems plaguing OLEDs, a second generation of electro-luminescent materials based on phosphorescence, and collectively known as Phosphorescent organic light emitters (PhOLEDs)

have been proposed. Phosphorescence emission includes a forbidden transition between two states of different spin multiplicity, i.e. excited triplet and ground singlet states,⁷ thus significantly increasing the elision lifetime. Furthermore, in the case of electroluminescent materials, and because of spin statistics rules the applied electronic potential will generate 75% of the excitons in their triplet state ⁸. Therefore, opening alternative emission channel through the engineering of room temperature phosphorescent materials has represented an important improvement in increasing the global device efficiency ⁹. In addition, phosphorescence is usually red-shifted compared to fluorescence emission, thus allowing a deeper penetration of light in biological samples, which is a most beneficial effects for instance in the case of luminescent probes. Indeed, PhOLEDs, and more generally phosphorescent materials and compounds, have found widespread applications in electronics,^{10,11} optics,^{12,13} and biological sciences.¹⁴ Yet, phosphorescence compounds due to the long-lived population of the triplet manifold, are more sensitive to the presence of molecular oxygen since they can sensitize the latter to its highly reactive singlet state. If the latter channel may be beneficial, for instance in photo dynamic therapy (PDT) applications, it may lead to luminescence quenching or material

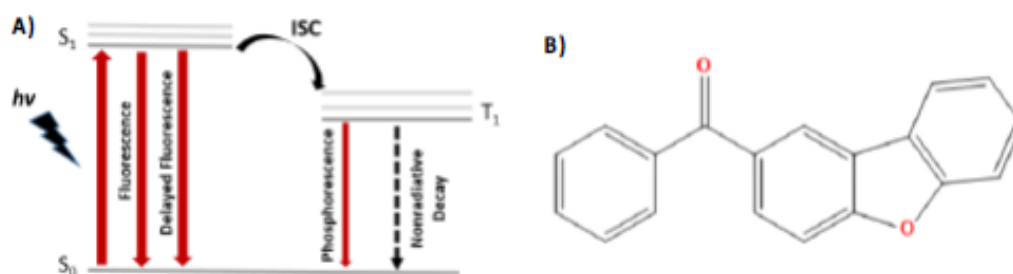


Figure 1) Schematic Jablonski diagram illustrating the relaxation processes operative in phosphorescent luminophores and B) the carbazole-based compound reported by Zhao et al.⁸ and studied in the present contribution

degradation.¹⁵ Consequently, in some instances relevant phosphorescence is observed only under inert or cryogenic conditions, thus drastically limiting their use in portable devices or high technological applications. Therefore, the development of materials and luminophores showing efficient room-temperature phosphorescence (RTP) is highly sought.⁸ RTP materials have attracted tremendous attention due to their applications in the field of intelligence security,¹⁶ optical detection,¹⁷ and biochemical imaging.¹⁸

As a matter of fact, to be applicable RTP should require a relative fast ISC, to minimize the competition with other radiative and non-radiative channels, such as prompt fluorescence or internal conversion (IC), conversely the depopulation of the triplet state manifold should be slow and life-times of more than 100 ms have, indeed, been reported.¹⁹

The population of triplet states from singlet excited manifolds (Figure 1) is much slower than other fully allowed relaxations, and as such can be regarded as one of the key phenomena dictating the efficiency of phosphorescent luminophores. As stipulated by quantum mechanics laws, the selection rules formally forbidding ISC, may be relaxed under the effects of several favorable terms, such as a small energy gap between the involved singlet and triplet states, and a high spin orbit coupling (SOC) between the relevant states.^{20,21}

In a previous study devoted to Thermally Activated Delayed Fluorescent (TADF) materials,

by investigating various molecular and electronic descriptors we observed that magnitude of SOC is, indeed, one of the most important parameters to control the efficiency of reverse intersystem crossing (RISC), and thus by extension ISC.⁶ Indeed, as shown in the literature different strategies, and molecular engineering approaches, aimed at increasing SOC, also by favoring hydrogen bond and space restrictions are pursued to enhance phosphorescence emission.²² Usually, however, the most widespread strategy to increase SOC, and hence favor ISC or RISC, is the inclusion high atomic number atoms, to exploit the so-called heavy atom effect, since SOC is roughly proportional to the fourth power of nuclear charge.²³ In many instances this objective is achieved by the use of transition metal components, usually up to the second and third row of the d-elements. Indeed, while Ru complexes are known for ultrafast ISC, Ir-based compounds are among the most efficient phosphorescent emitters, allowing not only a bright luminescence but also tuning the emission color. Conversely, metal complexed porphyrins are among the most common components for PDT applications, having, in some cases, already found clinical use. Yet, metal- or heavy-atom containing emitters also present significant drawbacks, in particular in terms of high cost and toxicity, low processability, low flexibility, and in some cases low stability.^{24,25} Furthermore, the rarity of heavy metals also poses significant burdens in terms of resources availability and sustainable development.

Therefore, the possible use of fully organic RTP compounds is regarded as highly suitable to overcome these drawbacks, yet strategies to maximize SOC and ISC rates should then be pursued. According to the well-known El Sayed rule, SOC will be maximum between singlet and triplet states having a different diabatic nature, since in this case the states can be coupled by the magnetic field operator. Thus, SOC and ISC will be maximized when involving transitions between a $^1(n\pi^*)$ and a $^3(\pi\pi^*)$ state. Consequently, the use of conjugated moieties involving the presence of carbonyl units is highly favorable, due to the presence of low-lying $n\pi^*$ states. Yet it has to be pointed out that the states in real molecular systems are rarely of a pure diabatic nature and instead a different degree of mixing between $n\pi^*$ and $\pi\pi^*$ character is observed, slightly complicating inferring general tendencies. In this instance, benzophenone is a paradigmatic organic moiety, which can reach a triplet conversion of up to 100%²⁶, also due to the extended three states quasi-degeneracy involving S_1 and two lowest triplet states T_1 and T_2 , as confirmed by a number of different experimental and computational studies involving non-adiabatic dynamics.^{27,28} The benzophenone facile ISC is also at the base of its inherent phototoxicity toward DNA.²⁹ Recently an extensive and systematic proposition of molecular rules for the enhancement of ISC in organic emitters has been proposed by Zhao et al.⁸ based on the consideration of the El Sayed rule and the use of static density functional theory (DFT) calculations. Among the different compounds, benzophenone and carbazole containing units have appeared as the most favorable candidates to enforce high SOC and ISC rates. As concerns carbazole, their rigid π conjugated scaffold is also optimal to enforce aggregation and crystal formation. Indeed, the reduced vibrational disorder in the condensed phase may be beneficial in slowing non-radiative decay pathways, hence favoring luminescence. Yet, in this case ISC should be achieved without the activation of large amplitude movements, which could be impeded in the solid state.

In this contribution we will resort to non-adiabatic dynamics in the surface hopping (SH)

formalism to study ISC in the carbazole emitter presented in Figure 1b, which despite lacking any heavy atoms is displaying optimal luminescence and a phosphorescence quantum yield of about 34%.⁸ In particular, and going beyond the pure static picture, we will show that the favorable alignment of the involved states and their optimal symmetry, in terms of the El Sayed rule, translate into a ps-scale ISC rate, which, thus, should imply the facile population of the triplet manifold. Furthermore, our SH study will also confirm that ISC does not involve the activation of any large-scale movement, hence should remain operative also in condensed media, further pointing to the optimal characteristic of the chosen compound.

COMPUTATIONAL METHODOLOGY.

Prior to the propagation of the non-adiabatic dynamics, the carbazole luminophore's ground state (GS) has been optimized at DFT level using the Gaussian 16 software package³⁰. The M06-2X³¹ functional together with the 6-31+G(d,p)³² basis set has been chosen to this aim. The choice of M06-2X functional is justified by its good performance in reproducing the geometries of aromatic compounds³³. Integral equation formalism polarizable continuum model (IEF-PCM) is used in DFT calculations, to implicitly model the solvent environment³⁴. Optimized structures were rendered with the CYLview software package³⁵.

Excited States have been calculated in the framework of Time Dependent-DFT (TDFT) approach, due to its optimal compromise between accuracy and computational cost. More specifically the Tamm-Dancoff Approximation (TDA) has been consistently used for the excited states calculations of both singlet and triplet states. This choice is due to the fact that the TDA provides a more balanced description of both triplet and singlet excited states, as compared to TD-DFT since it is free from triplet instability issues³⁶. Furthermore, and in addition to the GS, also the geometries of the lowest singlet (S_1) and the three lowest triplet (T_1 , T_2 and T_3) states have been fully optimized. Additionally, and for benchmark purposes, the singlet and triplet excitation energies have been calculated from the GS, S_1 , T_1 ,

T₂ and T₃ equilibrium geometries using different functionals, namely, CAM-B3LYP³⁷, M06-2X, PBE0³⁸, ω B97XD³⁹, and different basis sets of increasing size, 6-31G, 6-31G(d), 6-31G(d,p), 6-31+G(d), 6-31+G(d,p), 6-311++G(d,p).

Table 1) Vertical excitation energies from the Franck-Condon geometry calculated at CAM-B3LYP/6-31G level of theory.

State	Excitation Energy (eV)	f ^(a)
S ₁	3.98	0.0014
S ₂	4.61	0.0303
S ₃	4.87	0.1810
S ₄	5.00	0.8612
T ₁	3.37	-
T ₂	3.56	-
T ₃	3.84	-
T ₄	3.88	-
T ₅	4.07	-

The diabatic nature of the excited states have been evaluated using Natural Transition Orbitals (NTOs), which have been obtained post-processing Gaussian output with the Nancy_EX⁴⁰ code and visualized with the Avogadro⁴¹ software package. To further characterized the nature of the excited states, the Φ_s index, defining the overlap between the attachment and the detachment density matrices, has been obtained calculated,^{40,42} as shown in SI. SOC elements between S₁ and the lowest triplet states have been calculated, at the TDA level, by using the Amsterdam Density Functional (ADF) code^{40,42} at the M06-2X/TZP⁴³ and CAM-B3LYP/TZP levels of theory and the TZP basis set.

To go beyond the simple static picture of IS, we performed *in vacuo* SH dynamics using the SHARC code^{44,45} coupled with ORCA⁴⁶. Indeed, SHARC allows the use of a generalized coupling between the states, such as SOC, and hence may provide the time-scales of ISC. To simulate the effects of a wave-packet the SH dynamics has been averaged over 200 independent trajectories, whose initial

conditions have been obtained sampling the Franck-Condon region through a Wigner distribution. The non-adiabatic dynamic trajectories have been propagated at TDA level, explicitly calculating the SOC element at each step, at CAM-B3LYP/6-31G level of theory, with a time-step of 0.5 fs for a total time of 2 ps (4000 steps). The common Persico correlation correction⁴⁷ was applied to avoid over-correlation as typical in SH formalism. Our model involved explicitly the first excited singlet state, and the lowest four triplet states. An initial total population of the S₁ state was considered, and the time evolution of the states' population has been fitted with exponential models to obtain the corresponding kinetic model and the global time-scales.

RESULTS AND DISCUSSION

Upon optimization the ground state geometry of the carbazole-based luminophore presents all the expected characteristics of these family of compounds. In particular, the rigid core and the extended π -conjugation enforce a globally planar structure, while a non-negligible torsion angle ($\sim 30^\circ$) is observed between the carbonyl moiety and the phenyl ring to minimize the steric hindrance with the carbazole, as it is the case for the parent benzophenone. All the optimized geometries for the different states are explicitly provided in SI. The vertical excitation energies from the Franck-Condon region for the lowest-lying excited states, on either the singlet and triplet manifolds are reported in Table 1.

The low energy portion of the absorption spectrum is dominated by two excitations, the lowest one being almost dark and the second one having a much higher oscillator strength. Yet, the S₁ state lies about 0.65 eV lower than the brighter S₂ states. Thus, even if the latter should be populated due to the higher oscillator strength it is reasonable to assume that an ultrafast, fs-based intersystem crossing, will drive an .

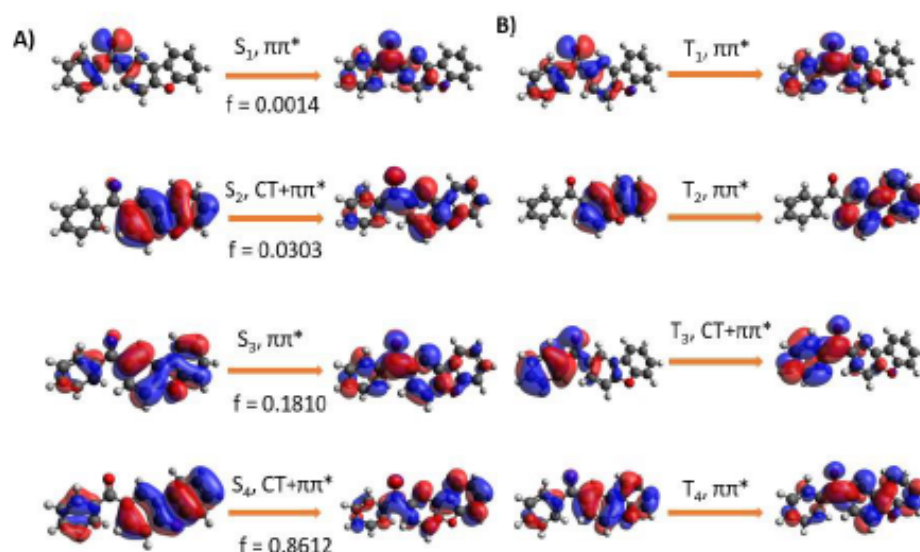


Figure 2) A) NTO study for S_n states computed at CAM-B3LYP/6-31G level of theory. B) NTO study for T_n states computed at CAM-B3LYP/6-31G level of theory.

almost unitary population of the first excited state. Interestingly, 4 triplet states are found at lower energies than the S_1 state with T_4 being quasi-degenerate with S_1 . In Figure 2 we report the NTOs calculated for the most important states. The nature of S_1 is, thus, clearly identified as $\pi\pi^*$, while the second excited singlet state has a $\pi\pi^*$ nature showing a partial charge-transfer character but being mainly localized on the carbazole unit. The same nature of the states is also found in the triplet manifold, with a pronounced $\pi\pi^*$ character for T_1 and a partially charge-transfer $\pi\pi^*$ nature for T_2 . Interestingly, the T_3 states, which will be relevant for the further discussion, can again be described as a $\pi\pi^*$ but is mainly localized on the phenyl ring. The partial charge transfer character of the different states can also be appreciated by the values of the topological Φ_s index reported in Table S3. The values of the SOC elements coupling the lowest triplet and singlet states are reported in Table 2, highlighting small but non negligible coupling of the S_1 states with the triplet manifold. The partial lifting of the El Sayed's rule is most probably due to the partially mixed nature of the states, to their partial charge-transfer character, and to the breaking of the $\pi\pi$ symmetry due to the

twisted carbonyl-phenyl arrangement. Yet, this situation appears as favorable to enforce efficient ISC.

Table 2) SOC elements between the different states calculated at CAM-B3LYP/6-31G level of theory and Franck-Condon geometry.

	SOC (cm^{-1})
S_1-T_1	7.43
S_1-T_2	8.48
S_1-T_3	17.23
S_1-T_4	7.00
S_2-T_1	2.13
S_2-T_2	0.27
S_2-T_3	0.92
S_2-T_4	0.17

Upon geometrical relaxation on the S_1 potential, as indicated on the Jablonski diagram reported in Figure 3, we may observe that the stabilization of S_1 closes the gap with T_2 and the two states are now separated by only 0.05 eV. This situation is again pointing toward a favorable, albeit non ultrafast ISC, involving those two states, also considering the non-negligible SOC between the two states.

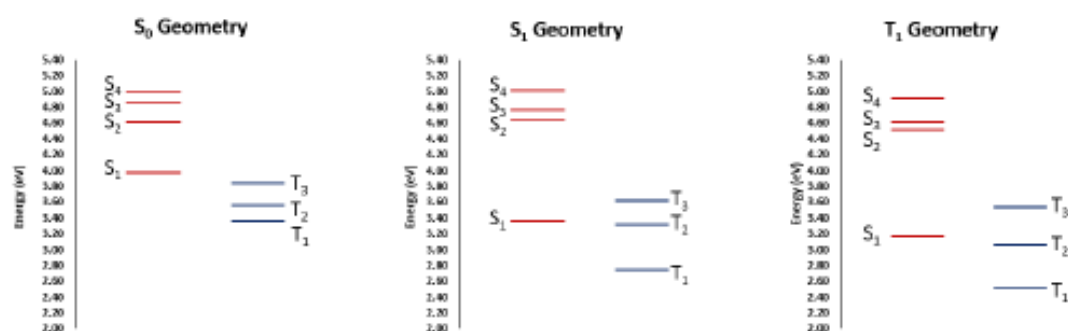


Figure 3) Jablonski diagrams at the most relevant equilibrium geometries obtained at CAM-B3LYP/6-31G level of theory.

As concerns the influence of the level of theory on the alignment of the states we report in Figure 4 the vertical excitation energies for the lowest singlet and triplet states computed using different exchange-correlation functionals and different basis set. It is evident that the choice of the basis set has a negligible effect on the quality of the excitation energies, thus justifying the following use of the smallest double-zeta basis for the non-adiabatic dynamics. A slightly more important influence of the functional can be appreciated. Yet, the effects are globally modest and the presence of partially charge-transfer excited states justifies the use of long-range corrected functionals for the following study. Finally, to assess the mechanisms and the time-scales of ISC

we have performed SH dynamics over 200 independent trajectories. The results in terms of population of the different excited states are collected in Figure 5, together with the ensuing kinetic model inferred from the analysis of the hops between states of different multiplicity. Indeed, the population of the S_1 state decays slowly but steadily at the advantage of the triplet manifold, whose population increases. Interestingly, we may observe that after the raise in the population of T_2 , T_1 is also readily accessed and becomes the dominant triplet state after about 150 fs. At 2 ps we may observe a globally perfectly shared population between the singlet and the triplet manifold, with T_1 being now the largely dominant state.

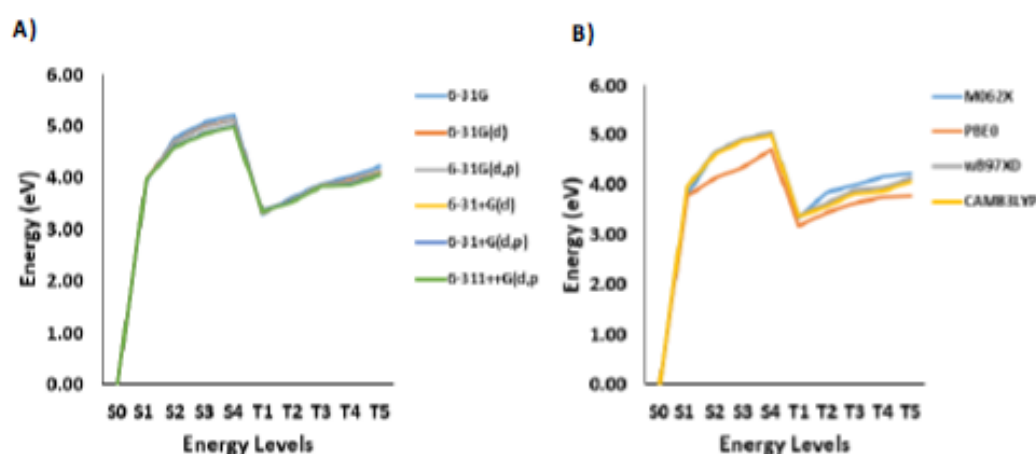


Figure 4) Vertical transitions energies calculated from the Franck-Condon geometry with different basis set (A) and exchange correlation functionals (B).

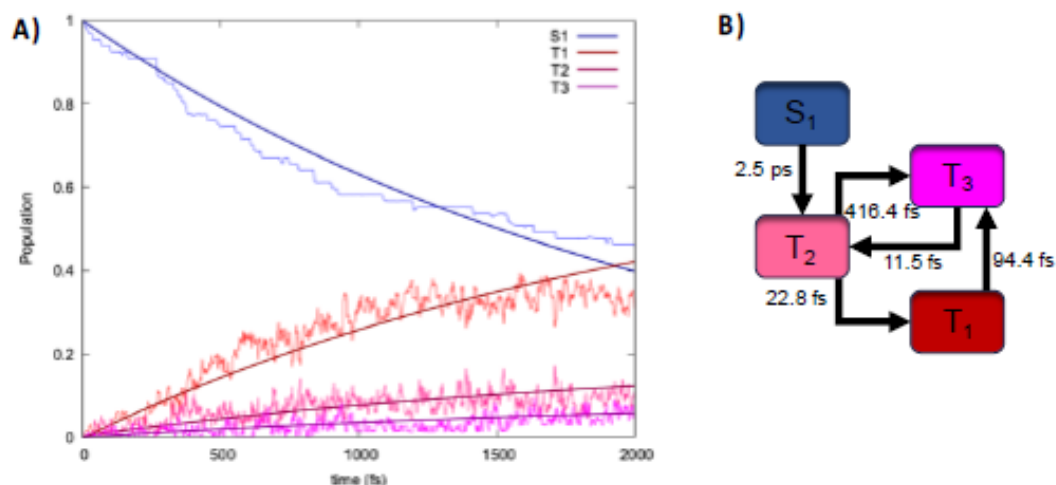


Figure 5) Time evolution of the population of the different states following the SH dynamics (A). Kinetic model used to fit the time evolution of the population; the obtained characteristic time constants are also reported. Note that the population obtained by applying the fitting is also indicated in panel A with darker color shades.

. Yet, we may observe that the population of T_2 is persistent all along the SH dynamics being of about 10% at 2 ps. Furthermore, we may also observe the raising of the population of the T_3 state, which becomes non-negligible at around 500 fs and stays only slightly lower than the one of T_2 . Globally, this behavior appears quite surprising since, from the simple analysis of the Jablonski diagram, one could have inferred a straightforward population drift going from S_1 to T_2 and then rapidly towards T_1 . Instead, and because of the quasi-degeneracy of the triplet states, a more complicated mechanism takes place in the photophysics of the carbazole derivatives. Indeed, while the first process of the S_1 decay is ISC towards T_2 , which also represents the time limiting step with a time constant τ of about 2.5 ps, the population of this state open up a complex equilibrium involving T_1 and T_3 . If the IC towards the lowest triplet state is clearly the most favorable process having a time constant of only 23 fs, a population transfer towards T_3 is also active, albeit having a much slower, yet ultrafast characteristic time of about 400 fs. Interestingly, while T_3 readily relaxes back to T_2 (τ of 11 fs) a

population drift from T_1 to T_3 is also possible and is relatively fast (τ of 94 fs).

Our SH dynamics have thus confirmed that ISC is operative in this carbazole systems, thus justifying its efficiency as a luminophore. The rate limiting step of the ISC, which amounts to 2.5 ps confirms that the process while possible is not ultrafast, probably due to the relatively modest values of the involved SOC. However, this process hides a complex equilibrium involving rather extended population transfers in the triplet manifold, which ultimately leads to the persistence of a non-negligible population of T_2 and T_3 up to the ps time-scale.

Furthermore, by analyzing the geometrical changes along the SH trajectories we may evidence that no large-scale movement is necessary to trigger ISC. Instead only the activation of small amplitude vibrational movements, mainly related to the carbonyl stretching are necessary. This aspect is mostly favorable for the possible triggering of aggregation induced phosphorescence, which is operative in the present carbazole-based luminophore.

CONCLUSION

In the present contribution we have studied by extensive TD-DFT modeling, complemented with non-adiabatic SH dynamics the behavior of a carbazole-based chromophore which is a most promising candidate for room temperature phosphorescence. In particular we have confirmed the interplay between $n\pi^*$ and $\pi\pi^*$ states in providing the most favorable conditions for high SOC in full organic compounds, thus favoring the ensuing ISC. While we have confirmed that ISC takes place with a rate limiting step of about 2.5 ps, and involves the transition between S_1 and T_2 , we also identify the instauration of a complex equilibrium in the triplet manifold with multiple population transfers between the lowest lying triplet states. In turn this imply that the population of T_2 and T_3 is persisting all along the SH dynamics, thus exceeding the ps time-scale, and should be taken into account. Furthermore, we have shown that ISC does not involve the activation of large amplitude degrees of freedom, and may remain possible also in condensed phase, opening up the possibility of aggregation induced phosphorescence behavior. Our results, show how SH dynamics may be used to unravel complex and subtle mechanisms which may be important in shaping the photophysical behavior of organic chromophores. They also point out the validity of the exploitation of the El Sayed rule, involving the coupling between states of different diabatic nature in providing efficient organic compounds featuring high ISC rates. In the following we preview to extend this study to the chromophore in condensed phase to take into account the effects of aggregation on its photophysical behavior.

ASSOCIATED CONTENT

Supporting Information. A listing of the contents of each file supplied as Supporting Information should be included. For instructions on what should be included in the Supporting Information as well as how to prepare this material for publications, refer to the journal's Instructions for Authors.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript

DEDICATION

This work is dedicated to the celebration of Roland Lindh's scientific achievements. His work has pioneered the correct description of complex excited states in complex environments and has, thus, made possible to study in silico photophysics and photochemistry with an unprecedented degree of precision.

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Publication Title	Physical chemistry chemical physics: PCCP	Rightsholder	Royal Society of Chemistry
Article Title	A Computational Descriptor Analysis on Excited State Behaviours of a Series of TADF and Non-TADF Compounds	Publication Type	Journal
Author/Editor	Royal Society of Chemistry (Great Britain), Deutsche Bunsen-Gesellschaft für Physikalische Chemie., Koninklijke Nederlandse Chemische Vereniging., Società chimica Italiana.	Start Page	16167
Date	01/01/1999	End Page	16182
Language	English	Issue	26
Country	United Kingdom of Great Britain and Northern Ireland	Volume	24

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NEW WORK DETAILS

Title	Static and Dynamic Simulations of Photoprocesses in Organic Phosphorescent and Thermally Activated Delayed Fluorescent Materials	Institution Name	Bogazici University
Instructor Name	Pelin Ulukan	Expected Presentation Date	2023-11-28

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Title, Description or Numeric Reference of the Portion(s)	A Computational Descriptor Analysis on Excited State Behaviours of a Series of TADF and Non-TADF Compounds	Title of the Article / Chapter the Portion Is From	A Computational Descriptor Analysis on Excited State Behaviours of a Series of TADF and Non-TADF Compounds
Editor of Portion(s)	Ulukan, Pelin; Baş, Ekin Esme; Özek, Rengin Busra; Dal Kaynak, Cansu; Monari, Antonio; Avlyente, Viktorya; Catak, Saran	Author of Portion(s)	Ulukan, Pelin; Baş, Ekin Esme; Özek, Rengin Busra; Dal Kaynak, Cansu; Monari, Antonio; Avlyente, Viktorya; Catak, Saran
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e) The License described in the Order Confirmation shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such license shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.

Last updated October 2022

B.2. The License for Article 2 in Chapter 5

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v1.10 Last updated September 2015

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B.3. The License for Article 3 in Chapter 6



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LICENSED CONTENT

Publication Title	Physical chemistry chemical physics : PCCP	Rightsholder	Royal Society of Chemistry
Article Title	Photophysical Properties of Sulfone-Based TADF Emitters in Relation To Their Structural Properties	Publication Type	Journal
Author/Editor	Royal Society of Chemistry (Great Britain), Deutsche Bunsen-Gesellschaft für Physikalische Chemie., Koninklijke Nederlandse Chemische Vereniging., Società chimica italiana.	Start Page	31457
Date	01/01/1999	End Page	31470
Language	English	Issue	45
Country	United Kingdom of Great Britain and Northern Ireland	Volume	25

REQUEST DETAILS

Portion Type	Chapter/article	Rights Requested	Main product
Page Range(s)	31457-31470	Distribution	Worldwide
Total Number of Pages	14	Translation	Original language of publication
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NEW WORK DETAILS

Title	Static and Dynamic Simulations of Photoprocesses in Organic Phosphorescent and Thermally Activated Delayed Fluorescent Materials	Institution Name	Bogazici University
Instructor Name	Pelin Ulukan	Expected Presentation Date	2023-12-08

ADDITIONAL DETAILS

Order Reference Number	N/A	The Requesting Person / Organization to Appear on the License	PELİN ULUKAN
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REQUESTED CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	The photophysical properties of sulfone-based TADF emitters in relation to their structural properties	Title of the Article / Chapter the Portion Is From	Photophysical Properties of Sulfone-Based TADF Emitters in Relation To Their Structural Properties
Editor of Portion(s)	Hepguler, Aslihan; Ulukan, Pelin; Catak, Saron	Author of Portion(s)	Hepguler, Aslihan; Ulukan, Pelin; Catak, Saron
Volume / Edition	25	Issue, if Republishing an Article From a Serial	45
Page or Page Range of Portion	31457-31470	Publication Date of Portion	2023-11-22

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iii) Subject to any Publisher Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the academic pay-per-use service is limited as follows:

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D) no User may sell or distribute any particular anthology, whether photocopied or electronic, at more than one institution of learning;

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B) Posting e-reserves, course management systems, e-coursepacks for material consisting of photographs or other still images not embedded in text, which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorization: to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above, including any necessary resizing, reformatting or modification of the resolution of such requested material (provided that such modification does not alter the underlying editorial content or meaning of the requested material, and provided that the resulting modified content is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms), but not including any other form of manipulation, alteration or editing of the requested material;

C) Posting e-reserves, course management systems, e-coursepacks or other academic distribution for audiovisual content, which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorizations: (i) to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above; (ii) to display and perform the requested material to such members of such class in the physical classroom or remotely by means of streaming media or other video formats; and (iii) to "dip" or reformat the requested material for purposes of time or content management or ease of delivery, provided that such "dipping" or reformatting does not alter the underlying editorial content or meaning of the requested material and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms. Unless expressly set forth in the relevant Order Confirmation, the License does not authorize any other form of manipulation, alteration or editing of the requested material.

ii) Unless expressly set forth in the relevant Order Confirmation, no License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied or, in the case of Works subject to Sections 14(b)(i)(B) or (C) above, as described in such Sections) (ii) permit "publishing ventures" where any particular course materials would be systematically marketed at multiple institutions.

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