

INVESTIGATING THE PHOTOPHYSICAL PROPERTIES OF BENZOPHENONE
BASED TADF EMITTERS: A COMPUTATIONAL APPROACH

by

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ABSTRACT

INVESTIGATING THE PHOTOPHYSICAL PROPERTIES OF BENZOPHENONE BASED TADF EMITTERS: A COMPUTATIONAL APPROACH

In this study, several TADF and non-TADF emitters containing benzophenone or its derivatives as the electron acceptor units have been investigated by implementing computational methods. M06-2X/6-31+G(d,p) method has been used to optimize ground state (S_0) and first triplet excited state (T_1) geometries, and solvent effects have been taken into account implicitly. Furthermore, a wide range of TADF descriptors have been determined and investigated. Torsion angles between the donor and acceptor units have been measured to gain insight into the spatial separation of the frontier orbitals. Absorption spectra have been generated by implementing Wigner distribution to include dynamic effects. Singlet-triplet energy gaps (ΔE_{ST}) have been calculated by employing Tamm-Dancoff Approximation (TDA). Natural transition orbitals (NTO) and ϕ_S indices have been computed to examine the amount of overlap between the frontier orbitals. Lastly, spin-orbit coupling (SOC) constants have been calculated to assess the RISC possibilities. In addition to the descriptor analysis, benchmark calculations have been performed to determine the most suitable functionals with respect to experimental data. With this purpose, excited state calculations have been carried out with B3LYP, PBE0, BLYP and M06-2X functionals together with 6-31+G(d,p) basis set. The results clearly indicate that rigidity of the molecular structure and spatial separation of the frontier orbitals are the most important factors that influence the efficiencies of the photophysical processes which cause TADF emission. The computational methods and photophysical descriptors employed in this study may contribute to the design of novel TADF materials as they reproduce well the experimental findings.

ÖZET

BENZOFENON TABANLI TADF YAYICILARIN FOTOFİZİKSEL ÖZELLİKLERİNİN İNCELENMESİ: HESAPSAL BİR YAKLAŞIM

Bu çalışmada, elektron alıcı birim olarak benzofenon veya türevlerini içeren bir dizi TADF ve TADF olmayan yayıcı hesapsal yöntemler uygulanarak araştırılmıştır. Temel hal (S_0) ve ilk triplet uyarılmış hal (T_1) geometrilerini optimize etmek için M06-2X/6-31+G(d,p) yöntemi kullanılmış ve çözücü etkileri kapalı çözümlü olarak dikkate alınmıştır. Ayrıca, çeşitli TADF tanımlayıcıları belirlenmiş ve araştırılmıştır. Sınır orbitallerin uzaysal ayrımı hakkında fikir edinmek için verici ve alıcı birimler arasındaki bükülme açıları ölçülmüştür. Absorpsiyon spektrumları, dinamik efektleri içerecek şekilde Wigner dağılımı uygulanarak oluşturulmuştur. Singlet-triplet enerji aralıkları (ΔE_{ST}), Tamm-Dancoff Yaklaşımı (TDA) kullanılarak hesaplanmıştır. Sınır orbitaller arasındaki örtüşme miktarını inceleyebilmek için, doğal geçiş orbitalleri (NTO'lar) ve ϕ_S indeksleri raporlanmıştır. Son olarak, RISC olasılıklarını değerlendirebilmek için spin-yörünge etkileşimi (SOC) sabitleri hesaplanmıştır. Tanımlayıcı analizine ek olarak, deneysel verilere göre en uygun fonksiyonelleri belirleyebilmek adına kıyaslama hesaplamaları yapılmıştır. Bu amaçla, B3LYP, PBE0, BLYP ve M06-2X fonksiyonelleri ve 6-31+G(d,p) baz seti ile uyarılmış hal hesaplamaları yapılmıştır. Sonuçlar açıkça göstermektedir ki, moleküler yapının bükülmezliği ve sınır orbitallerin uzaysal olarak ayrışması, TADF emisyonuna neden olan fotofiziksel süreçlerin verimliliğini etkileyen en önemli faktörlerdir. Bu çalışmada kullanılan hesapsal yöntemler ve fotofiziksel tanımlayıcılar, deneysel bulguları iyi bir şekilde yeniden ürettikleri için yeni TADF materyallerinin tasarımına katkıda bulunabilir.

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LIST OF SYMBOLS

$E_c[\rho]$	Correlation Energy
$E_x[\rho]$	Exchange Energy
$E_{XC}[\rho(r)]$	Exchange-Correlation Energy Functional
f	Oscillator Strength
G_{gs}^{HF}	Ground State Energy
$\hat{H}$	Hamiltonian Operator
h_{KS}	Kohn-Sham Hamiltonian Operator
$J[\rho(r)]$	Coulomb Energy
k_B	Boltzmann's Constant
k_r	Radiative Decay Rate
k_{RISC}	Reverse Intersystem Crossing Rate
R_v	Position of the Nucleus
S_n	Singlet Excited States
T_n	Triplet Excited States
$T_{ni}[\rho(r)]$	Kinetic Energy of Non-Interacting Electrons
$T[\rho(r)]$	Kinetic Energy of Interacting Electrons
$V_{XC}[\rho(r)]$	Exchange-Correlation Potential
Z	Atomic Number
ΔE_{ST}	Singlet-Triplet Energy Gap
Φ_{PL}	Photoluminescence Quantum Yield
η_{ext}	External Quantum Efficiency
η_{int}	Internal Quantum Efficiency
τ	Delayed fluorescence lifetime
$\rho(r)$	Electron Density
φ_j	Number of Atomic Orbitals
θ	Torsion Angle
ω_p	TDA Excitation Energy

X_p	Amplitude Vector
ϕ_S	Quantitative Topological Descriptor
Γ	Detachment Density Matrix
λ	Attachment Density Matrix
Ψ	Wavefunction

LIST OF ACRONYMS/ABBREVIATIONS

3D	Three Dimensional
A	Acceptor
ACG	Aggregation Caused Quenching
ADF	Amsterdam Density Functional
AIE	Aggregation Induced Emission
B3LYP	Becke-3-parameter Lee-Yang-Parr Functional
BLYP	Becke-Lee-Yang-Parr Functional
BS	Bethe-Salpeter
C1	Compound 1
C2	Compound 2
CT	Charge Transfer
CTR	Cathode Ray Tube
Cz	Carbazole
D	Donor
DF	Delayed Fluorescence
DMAC	Dimethylacridine
DPA	Diphenylamine
EL	Electroluminescent
GGA	Generalized Gradient Approximation
GTO	Gaussian Type Orbital
HF	Hartree-Fock
HOMO	Highest Occupied Molecular Orbital
ICT	Intramolecular Charge Transfer
IEF-PCM	Integral Equation Formalism Polarizable Continuum Model
ISC	Intersystem Crossing
KS-DFT	Kohn-Sham Density Functional Theory
L	Lowdin Charge Distribution
LCAO	Linear Combination of Atomic orbitals

LCD	Liquid Crystal Display
LDA	Local Density Approximation
LE	Local Excited
LED	Light Emitting Diode
LUMO	Lowest Unoccupied Molecular Orbital
M	Mulliken Charge Distribution
M06-2X	Hybrid Meta Exchange-Correlation Functional
MC2	Model Compound 2
NTO	Natural Transition Orbital
OLED	Organic Light Emitting Diode
PBE0	Perdew–Burke–Ernzerhof Hybrid Functional
PCM	Polarizable Continuum Model
PL	Photoluminescence
PLQY	Photoluminescence Quantum Yield
PTZ	Phenothiazine
PXZ	Phenoxazine
RG	Runge-Gross
RISC	Reverse Intersystem Crossing
SOC	Spin-Orbit Coupling
STO	Slater Type Orbital
TADF	Thermally Activated Delayed Fluorescence
TDA	Tamm-Dancoff Approximation
TD-DFT	Time Dependent Density Functional Theory

1. INTRODUCTION

Display systems are essential elements of lighting industry as they have a wide range of applications in daily life, including smart phones, tablets, desktop monitors and televisions. Flat-panel light-emitting diode (LED) and liquid crystal display (LCD) systems were invented in the late 1960s and gained widespread attention as they were lighter and thinner than the conventional cathode ray tube (CTR) television sets [1]. However, LED and LCD panels require a backlight unit, which leads to high power consumption and increased panel thickness [2]. As an alternative to conventional LED and LCD, Organic Light-Emitting Diode (OLED) displays have aroused widespread interest since the first practical organic electroluminescent (EL) device constructed by Tang and Van Slyke in 1987 [3]. OLEDs are self-illuminating and do not require a backlight unit, which makes them less power consuming and more sustainable. Sustainability of OLEDs makes them promising examples of organic electronics for future demands regarding ecological concerns [4]. Other beneficial features of OLEDs include wide viewing angles, reduced panel thickness, increased flexibility and higher response time [2, 5].

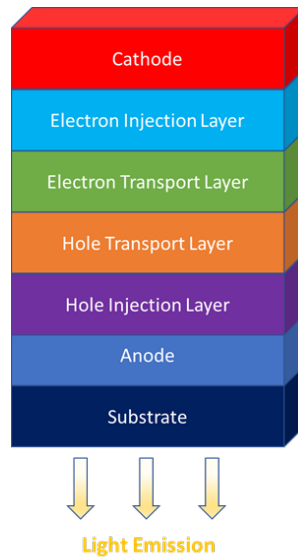


Figure 1.1. Multi-layer structural diagram of an OLED.

As depicted in Figure 1.1, OLEDs are mainly composed of cathode, electron transport layer, organic emissive layer, hole injection layer and anode, which are deposited on a substrate. Organic layers of OLEDs are conductive due to the delocalized π molecular orbitals introduced by conjugation [6]. When the voltage is applied, holes which are injected from the anode migrate through the panel and eventually recombine with the electrons injected from the cathode. This recombination causes energy release in the form of light from the emissive layer. This process is called electroluminescence [7, 8].

The recombined electron-hole pairs are called excitons. Spin statistics indicate that only the 25% of the excitons can be generated in the singlet state and the remaining excitons will be in the triplet state [9]. Radiative decay of the singlet excitons to the ground state is called fluorescence and it is generally very rapid. On the other hand, direct decay of the triplet excitons to the ground state, which is called phosphorescence, is generally slow and occurs only at lower temperatures, hence it is considered a forbidden process [8, 10, 11]. This means that the internal quantum efficiency (IQE) of the conventional fluorescent OLEDs is limited to 25% [5, 12].

Several attempts have been made to increase the internal efficiencies of the conventional OLEDs. One of them was the development of a new generation of OLEDs called phosphorescent organic-light emitting diodes (PhOLEDs) which contain transition metals. In PhOLEDs, triplet excitons can also be harvested along with the singlet ones with the help of the increased spin-orbit coupling (SOC) [5, 13, 14]. However, rarity of the heavy metals renders them expensive and restricts the commercial use of PhOLEDs. Besides rarity and high cost, toxicity of the heavy metal wastes raises environmental concerns [13].

Due to the drawbacks of the organometallic PhOLEDs, the third generation of pure organic OLEDs which utilize the thermally activated delayed fluorescence (TADF) principles were introduced by Adachi *et al.* in 2011 [15]. TADF process can occur if the energy gap between the first singlet excited state (S_1) and the first triplet excited state (T_1) is sufficiently low. The reduced singlet-triplet energy gap (ΔE_{ST}) facilitates

reverse intersystem crossing (RISC) where triplet excitons can be up-converted into singlet excitons and radiate back to the ground state via delayed fluorescence. By TADF, an internal quantum of efficiency of 100% can be achieved since harvesting of both singlet and triplet excitons becomes feasible [8, 16]. The three general emission mechanisms utilized in the three generations of OLEDs are depicted in Figure 1.2.

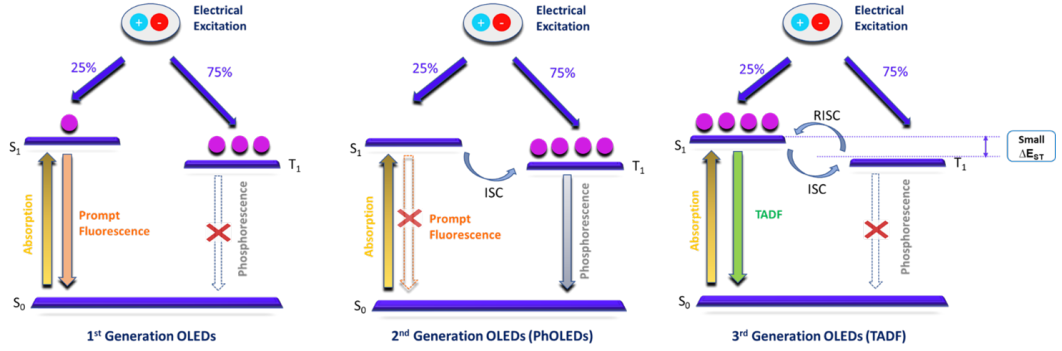


Figure 1.2. Schematic representations of the three generations of OLED emission mechanisms.

As mentioned above, ΔE_{ST} is a significant TADF descriptor due to its direct influence on the RISC process. The equation for the singlet-triplet energy gap is as follows:

$$\Delta E_{ST} = 2J_{LU} \quad (1.1)$$

where J_{LU} is the exchange integral between the spatial wavefunctions of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) [15].

As Equation 1.1 states, there is a direct correlation between the degree of HOMO-LUMO overlap and ΔE_{ST} . Therefore, if the overlap between HOMO and LUMO is negligible, ΔE_{ST} is expected to be small as well. The reduced ΔE_{ST} can be realized by intramolecular charge transfer (ICT). ICT requires spatially separated electron donating and accepting units, and this can be achieved by steric hindrance. This physical separation disrupts π -conjugation and leads to well localized HOMO and LUMO levels on the donor and acceptor units, respectively [8, 15]. While the donor (D) and accep-

tor (A) units can be arranged in D-A, D-A-D, A-D-A forms, phenyl links (π -bridges) can also be introduced between the donor and acceptor moieties to ensure a better separation [17].

Another important factor for an efficient TADF emission is the radiative decay rate (k_r). In contrast to the $n-\pi^*$ transitions which exhibit small k_r , $\pi-\pi^*$ transitions generally yield higher k_r . However, $\pi-\pi^*$ transitions usually generate larger ΔE_{ST} due to the large overlap between the π orbitals. Hence, balancing a small ΔE_{ST} and a moderate k_r is of great importance [15].

To sum up, an effective molecular design is essential in TADF process. Remarkable progress has been made since the first examples of TADF emitters introduced in the early 2010s. There are various donor and acceptor combinations that have been proven to exhibit TADF properties. Some of the commonly used electron acceptors comprise dicyanobenzene [8, 18, 19], benzonitrile [20, 21], triazine [22–27], sulfone [28–32], boron [33, 34], pyrazine [35, 36], pyridine [37–39], benzophenone [32, 40–48], anthraquinone [49, 50] and xanthone [41, 51–53]. These acceptors were combined with a wide range of donors, such as phenoxazine, phenazine, phenothiazine, carbazole, benzofurocarbazole, benzothienocarbazole, 3,3-bicarbazole, indolocarbazole, diphenylamine, diphenylaminocarbazole, dimethylacridine, and indenoacridine.

Benzophenone is a frequently used electron acceptor among the TADF based compounds. There are many other acceptors that can be classified as a benzophenone derivative due to the structural similarities, such as anthraquinone, xanthone, dibenzothiophene-benzoyl [54, 55] and phenylcarbazole-benzoyl [56]. Some of the electron donating and accepting compounds commonly used in the design of benzophenone based TADF emitters are given in Figure 1.3.

The first attempt to investigate the TADF efficiencies of benzophenone based compounds was made by Adachi *et al.* in 2014 [42]. They concluded that donor-acceptor-donor (D-A-D) type compounds employing benzophenones as acceptor units may give rise to efficient blue to orange-red TADF emission. Besides D-A-D, there are

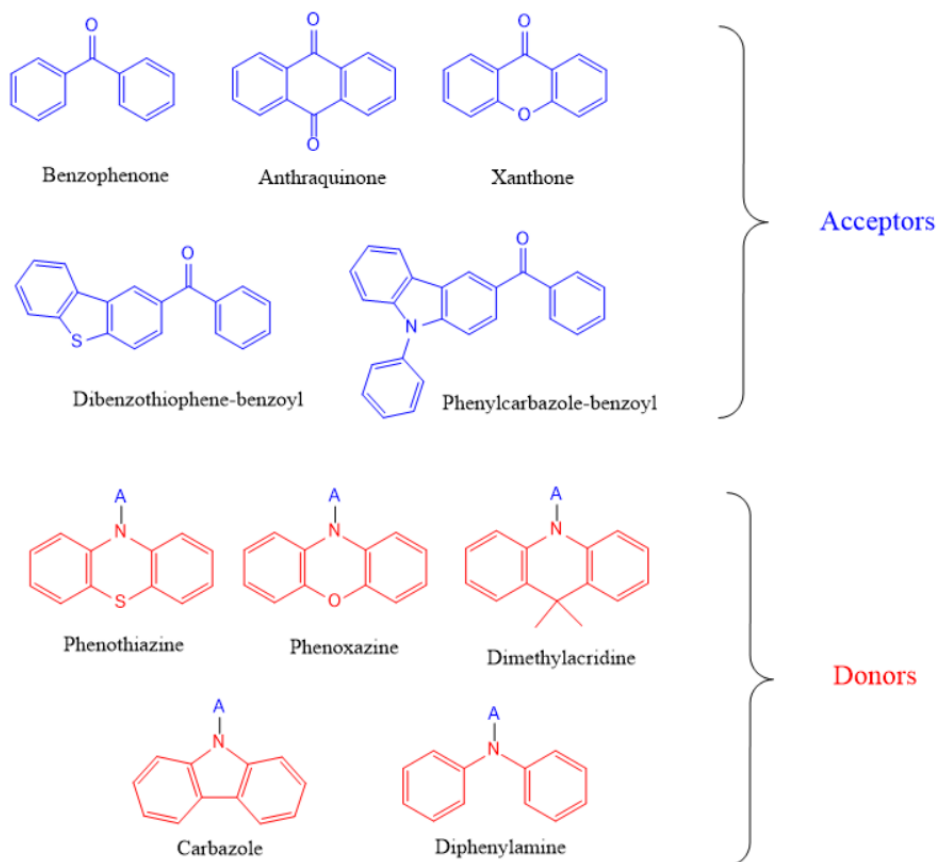


Figure 1.3. Some of the electron donating and accepting compounds commonly used in the benzophenone based TADF emitters. (A: Acceptor).

also efficient D-A type benzophenone based TADF compounds [43, 48, 52].

Other than OLED devices, benzophenones are also widely used in triplet sensitizers and photoinitiators due to their relatively high spin-orbit couplings and T_1 energy levels which enhance the intersystem crossing rate [57]. Benzophenone units can also be used in polymers and soaps as UV-blockers to prevent photodegradation in polymers, since they strongly absorb UV light [58]. These photophysical properties and good electron accepting abilities of benzophenone units widen their applicabilities as building blocks in various fields of chemistry [59].

In this study, compounds employing benzophenone and its derivatives as electron accepting units were analysed in terms of their TADF efficiencies. Investigating TADF

compounds with a certain acceptor also provides an insight into the influence of the different donor groups and donor-acceptor attachments on the TADF efficiencies. Also, efficiencies of benzophenone-like acceptor groups can be compared in this way.

There is a broad experimental literature on TADF emitters. There are certain experimental descriptors utilized to indicate the presence of TADF in a molecule, such as UV-Vis absorption and photoluminescence (PL) spectra, singlet-triplet energy gap (ΔE_{ST}), photoluminescence quantum yield (Φ_{PL}), internal quantum efficiency (η_{int}), external quantum efficiency (η_{ext}), delayed fluorescence lifetime (τ) and radiative decay rate (k_r) [15, 60]. UV-Vis absorption and PL spectra are necessary to determine the type, color and intensity of the electronic transitions. Moreover, ΔE_{ST} can be calculated from the onsets of the fluorescence and phosphorescence spectra. Φ_{PL} , η_{int} , and η_{ext} are useful to determine the efficiency of the emitter [61]. Delayed fluorescence lifetime (τ) and radiative decay rate (k_r) may provide insight into the rate of the emission from the S_1 state to the ground state. The photophysical properties can be given in solution and/or solid matrix. However, better TADF characteristics can be obtained from the solid state of an emitter as free rotations that can cause non-radiative transitions are restricted in this state [62].

A theoretical approach is essential to evaluate the validity of the experimental findings. Furthermore, computational simulations shed light on the charge transfer (CT) or local excitation (LE) character of the transitions, providing insight into the electronic and geometric properties. So far, the frequently used computational TADF descriptors are the torsion angle between donor and acceptor (θ), ΔE_{ST} , natural transition orbitals (NTO), ϕ_S index, spin-orbit coupling (SOC) and oscillator strength (f) [49, 63–69]. Fluorescence or TADF/RISC rates and lifetimes can also be computed [17, 65–69]. The photophysical properties have been mostly calculated from the ground state geometries, although there are examples where computations from the T_1 and S_1 geometries were also conducted [17, 49, 66, 68, 70–72].

ΔE_{ST} can be calculated by a time-dependent density functional theory (TD-DFT) calculation. In addition to TD-DFT, Tamm-Dancoff approximation (TDA) can

also be used [73]. TDA formalism generally reduces the deviations due to the triplet instability problem and yields results closer to experiment. Hence, TDA is superior to TD-DFT in terms of accuracy [65, 74, 75].

NTO analysis and ϕ_S index are useful to detect and visualize the degree of overlap between the frontier orbitals. NTO analysis is a commonly used method to identify the LE/CT character of an excited state [76]. ϕ_S index is defined as the spatial overlap between the attachment and detachment matrices and it gives an insight into the charge-separation nature of a potential emitter [77].

Spin-Orbit coupling (SOC) is a significant descriptor to attain an efficient RISC process. In the context of the semiempirical Marcus theory formalism, the rate of RISC (k_{RISC}) can be formulated as follows:

$$k_{RISC} = \frac{4\pi^2}{\hbar} \frac{\left| S_1 \langle \hat{H}_{SO} \rangle T_1 \right|^2}{\sqrt{4\pi k_B T \lambda}} \exp \left(-\frac{(\Delta E_{ST} + \lambda)^2}{4k_B T \lambda} \right) \quad (1.2)$$

where $\hbar$ is the Reduced Planck's constant, k_B is the Boltzmann constant, T is the temperature, λ is the reorganization energy between the S_1 and T_1 states and $\left| S_1 \langle \hat{H}_{SO} \rangle T_1 \right|^2$ denotes the SOC matrix element between the S_1 and T_1 states [64, 66, 78].

As Equation 1.2 states, there is a direct correlation between SOC and k_{RISC} . Nonetheless, SOC for direct transitions between CT states is considered to be negligible according to the El-Sayed's rules [65]. Thus, compounds possessing low ΔE_{ST} values usually have low SOC values as well.

Oscillator strength (f) gives information about the possibility of an electronic transition. In other words, oscillator strength of a transition from the S_1 to the S_0 energy level directly governs the radiative decay rate (k_r). The mathematical expression for k_r is given in Equation 1.3:

$$k_r = \frac{2\pi e^2 n^3 f \omega^2}{\varepsilon_0 m_e c} \quad (1.3)$$

where f is the oscillator strength of the radiative decay from the S_1 to the ground state, n is the refractive index of the medium, ε_0 is the electric constant, ω is the excitation energy, c is the speed of light, m_e is the electron mass and e is the charge [65]. The Jablonski diagram given in Figure 1.4 depicts the processes of k_r and k_{RISC} .

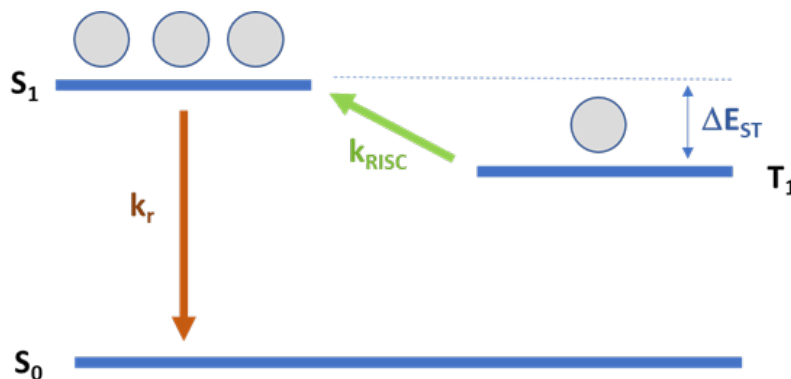


Figure 1.4. Jablonski diagram depicting the processes of radiative decay rate (k_r) and reverse intersystem crossing rate (k_{RISC}).

Similar to SOC, it is well known that the oscillator strength is closer to zero for the orthogonal donor-acceptor type charge transfer emitters [65]. This renders the design of efficient TADF emitters challenging since it is of great importance to maintain a balance between a small ΔE_{ST} and a reasonable k_r .

1.1. Aim of the Study

Herein, a series of benzophenone based TADF active and non-active compounds have been selected from the literature and investigated by computational methods. Benzophenone and its derivatives have been assessed as potential electron acceptors from a theoretical point of view. The influence of the donor groups and the donor-acceptor linkage positions on TADF efficiencies have been also investigated under the guidance of the calculated photophysical and optical properties. For the excited state calculations, TDA-DFT method has been used to reach higher accuracy. As a novel approach, excited state behaviors have been examined at both the S_0 and T_1 optimized geometries since the RISC process involves the up-conversion of the triplet excitons.

Photophysical properties obtained from the S_0 and T_1 geometries have been compared with the experimental data.

Additionally, absorption spectra of the selected compounds have been modeled within the framework of the Wigner distribution approach and compared with the experimental spectra. This method, along with the calculated ΔE_{ST} values, has been utilized to determine the best performing DFT functional for the excited state calculations. NTOs, ϕ_S indices and SOC values have been calculated with the purpose of having a better vision on the charge-transfer characteristics and radiative decay rates. Correlations have been made between the molecular structures and computed photophysical descriptors, since TADF process is highly dependent on the structural modifications.

To sum up, the relationship between the structure and TADF efficiency has been investigated based on the chromophores employing benzophenone and its derivatives, while determining the most suitable DFT functional with respect to experimental data. This study may eventually be useful for new experimental/computational studies concerning OLEDs and may inspire the design of novel efficient TADF materials.

2. METHODOLOGY

2.1. Density Functional Theory

Density Functional Theory (DFT) is a widely used quantum chemical method and its primary aim of use is to examine the properties and electronic structures of many-body systems by offering a solution to the complex Schrödinger equation [79]. DFT was first developed by Kohn and Hohenberg in 1964 [80], and it was based on the assumption that total electron density can be used to determine the properties of many-electron systems [81]. According to DFT, electron density ($\rho(r)$) can be represented as the spatial coordinates (x,y,z) since it depends solely on these variables. Electron density can be defined as follows:

$$\rho(r) = N \int \dots \int |\Psi(r_1, r_2, \dots, r_n)|^2 dr_1 dr_2 \dots dr_n \quad (2.1)$$

where r_i represents spin and spatial coordinates of electrons. Variational principle can be introduced to obtain ground state energies, as demonstrated by Equation 2.2:

$$E[\rho(r)] = \int V(r)\rho(r)dr + T[\rho(r)] + V_{ee}[\rho(r)] \quad (2.2)$$

where $V(r)\rho(r)dr$ stands for the interaction between electrons and external potential, $T[\rho(r)]$ represents the kinetic energy introduced by interacting electrons, and $V_{ee}[\rho(r)]$ corresponds to the interelectronic interaction energy. After Kohn and Sham developed the concept of non-interacting electrons within the framework of Kohn-Sham DFT (KS-DFT) in 1965 [82], the equation has become:

$$E[\rho(r)] = \int V(r)\rho(r)dr + T_{ni}[\rho(r)] + J[\rho(r)] + E_{XC}[\rho(r)] \quad (2.3)$$

where $T_{ni}[\rho(r)]$ represents the kinetic energy of non-interacting electrons, $J[\rho(r)]$ stands for the coulomb energy and $E_{XC}[\rho(r)]$ denotes the exchange-correlation en-

ergy functional [83]. In order to include the correlation for the motion of electrons, Coulomb energy term can be rewritten as follows,

$$J[\rho(r)] = - \sum_{A=1}^M \int \frac{Z_A}{|r - R_A|} \rho(r) dr + \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 \quad (2.4)$$

where M denotes the total number of nuclei and Z_A is the nuclear charge. The exchange-correlation energy functional $E_{XC}[\rho(r)]$ in Equation 2.3 can be expressed as the sum of exchange and correlation terms as demonstrated in Equation 2.5:

$$E_{XC}[\rho(r)] = \int \rho(r) \epsilon_{XC}(\rho(r)) dr \quad (2.5)$$

Regarding electron density, Equation 2.5 can be rewritten as:

$$V_{XC}[\rho(r)] = \rho(r) \frac{d\epsilon_{XC}(\rho(r))}{d\rho(r)} + \epsilon_{XC}(\rho(r)) \quad (2.6)$$

Solving Kohn-Sham equations with Kohn-Sham Hamiltonian operator (h_{KS}) leads to the estimation of Kohn-Sham orbitals (ψ_i):

$$h_{KS}\psi_i = \varepsilon_i\psi_i \quad (2.7)$$

The equation for Kohn-Sham Hamiltonian operator is given in Equation 2.8:

$$h_{KS} = -\frac{\nabla^2}{2} - \sum_{A=1}^N \int \frac{Z_A}{|r - R_A|} + \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 + V_{XC}[\rho(r)] \quad (2.8)$$

in which $V_{XC}[\rho(r)]$ represents the exchange-correlation potential.

Exact density can be obtained through Kohn-Sham orbitals, if the exact form of the exchange correlation functional is given, as stated by Equation 2.9:

$$\rho(r) = \sum_{i=1}^N |\psi_i|^2 \quad (2.9)$$

However, functionals are required to represent different approximations since it is not possible to know the exact form of exchange-correlation functional.

2.2. Functionals

Several approximations have been developed to bring a solution to the issue of exchange-correlation functionals. Local Density Approximation (LDA) is one of the most prominent approximations to establish the base of the exchange-correlation functionals [84]. LDA is based on the assumption that the electron density of a system is homogeneous, and the electrostatic energy of positivity (E_b) is employed to make the system neutral. The energy can be expressed as follows:

$$E[\rho] = T_{ni} + \int \rho(r) v(r) dr + J[\rho] + E_{XC}[\rho] + E_b \quad (2.10)$$

Electron density and positive charge density are assumed to be equal, thus Equation 2.10 can be reformulated as given in Equation 2.11 where the exchange and correlation functionals are provided in separate terms:

$$E[\rho] = T_{ni}[\rho] + E_x[\rho] + E_c[\rho] \quad (2.11)$$

The kinetic energy term $T_{ni}[\rho]$ can be written as:

$$T_{ni}[\rho] = C_F \int \rho(r)^{5/3} dr \quad (2.12)$$

Since C_F is a known constant which is equal to 2.8712, it becomes possible to estimate the exchange functional by Equation 2.13:

$$E_x[\rho] = -C_x \int \rho(r)^{4/3} dr \quad (2.13)$$

in which C_x is a constant and is equal to 0.7386. Since distribution of electron density in a system is not homogeneous in real life, LDA is not sufficient to determine the exact

form of exchange-correlation functional.

Generalized Gradient Approximation (GGA) method provides a more realistic approach, where the electron density of a system is not considered uniform, and the exchange and correlation functionals are associated with density gradient [85]. Therefore, the energy can be expressed as follows:

$$E_{XC}^{GGA}[n] = \int n(r) \epsilon_{XC}(n(r), |\nabla n(r)|) dr \quad (2.14)$$

Hybrid density functionals were developed with the aim of combining GGA with a degree of Hartree-Fock (HF) exchange. There are various hybrid functionals which utilize different approximations. B3LYP is a commonly used hybrid functional [86], in which LDA and GGA functionals are used together:

$$E_{XC}^{B3LYP} = (1 - a) E_X^{LSDA} + a E_X^{HF} + b \Delta E_X^B + (1 - c) E_C^{LSDA} + c E_C^{LYP} \quad (2.15)$$

where X refers to the percentage of HF exchange. Minnesota functionals, including the well known M06-2X functional [87], are based on the meta-GGA approximation and they contain terms related with kinetic energy density. Equation 2.16 represents the hybrid-exchange correlation for M06-2X:

$$E_{XC}^{hyb} = \frac{X}{100} E_X^{HF} + \left(1 - \frac{X}{100}\right) E_X^{DFT} + E_C^{DFT} \quad (2.16)$$

in which X is taken as 54 [87].

2.3. Basis Sets

In DFT or Hartree-Fock method, electronic wave functions, which are the approximate solutions to the Schrödinger equation, can be represented by basis sets [88]. Molecular orbitals can be generated through the linear combination of basis sets and they are used to construct wave functions for electronic states. The mathematical

expression for the linear combination of atomic orbitals (LCAO) is as follows,

$$\psi_i = \sum_j c_{ij} \varphi_j \quad (2.17)$$

where i is the number of molecular orbitals, φ_j is the number of atomic orbitals, and c_{ij} represents the coefficients. Constant coefficients in the linear combination can be obtained via implementing variational method.

Slater Type Orbitals (STOs) and Gaussian Type Orbitals (GTOs) are the major classes of basis sets. STOs provide more accurate solutions to Schrödinger equations of hydrogen-like atoms and they can describe the electron density around the nucleus. However, electron-state correlations are not accurately described by STOs since many-electron interactions are absent in hydrogen-like atoms.

Because of the computational difficulty of integral calculation with STOs, GTOs were later developed by S. Francis Boys, in which STOs are approximated as linear combinations of GTOs [89]. Various GTO basis sets are available, however basis sets with more accurate solutions increase computational cost.

John Pople introduced the concept of split valence basis sets with the aim of reducing the computational cost [90]. In this method, one basis function is used for core electrons, since they are less influenced by the environment as compared to valence electrons. In valence electrons, larger basis is used to obtain higher accuracy. For instance, in the case of widely used 6-31+G**, the first number 6 indicates the primitive Gaussians for core atomic orbitals. The presence of two numbers after the hyphen means that the basis set is a split-valence double-zeta basis set and two basis functions are used for valence orbitals. There are also available triple-zeta and quadrupole-zeta basis sets. Additionally, polarization and diffuse functions can be used for a better approximation [90]. Polarization functions provide higher angular momentum on heavy atoms and they can be represented as * or (d), and polarization function for hydrogen can be included by a second asteriks ** or (d,p). Also, diffuse functions which enable

the orbitals larger spaces, can be used. Adding a plus sign "+" includes the diffuse functions for heavy atoms, while addition of two plus signs "(++)" implies that diffuse functions are used for hydrogen.

2.4. Polarizable Continuum Model

Solvation models are necessary to include in quantum chemical calculations to obtain more accurate results. Solvation models can be added to the system either implicitly or explicitly. Explicit solvation models require high computational cost, since each solvent molecule is treated separately. Considering the solvent environment as a polarizable continuum instead of individual molecules is useful to increase the computational efficiency [91]. Several physical effects can be included in implicit solvation model. The total solvation free energy is given in Equation 2.18:

$$\Delta G_{solvation} = \Delta G_{cavity} + \Delta G_{dispersion} + \Delta G_{electrostatic} + \Delta G_{repulsion} \quad (2.18)$$

in which ΔG_{cavity} can be expressed as the solute addition to the system, $\Delta G_{dispersion}$ represents the interaction energy between solvent and solute, the electrostatic interaction energy between solvent and solute is taken into account in the term $\Delta G_{electrostatic}$, and $\Delta G_{repulsion}$ corresponds to the exchange solute-solvent interactions.

The concept of Polarizable Continuum Model (PCM) was first introduced by Tomasi *et al* [92]. In PCM, a cavity is defined by Van der Waals spheres around the atoms, then the solute is placed in the defined cavity. The point charges on the cavity surface are used to represent the reaction field. In PCM, it is assumed that a single dielectric constant is present and a polarization is induced through the charge distribution around the solute. There are various PCM methods, including Dielectric PCM (D-PCM), Conductor-like PCM (C-PCM), and Integral Equation Formalism PCM (IEF-PCM). C-PCM was developed from the preliminary D-PCM and it treats the medium as a conductor rather than a dielectric [93]. In IEF-PCM, which has been used in this thesis, an integral equation formalism is introduced [94].

2.5. Time Dependent Density Functional Theory (TD-DFT)

Time Dependent Density Functional Theory (TD-DFT) is a widely used method to compute the electronic and dynamic excited state properties of many-body systems. Its foundation is the Runge-Gross (RG) theorem which was introduced in 1984 [95]. According to the RG theorem, time-dependent external potential and time-dependent density are associated for a given wavefunction. It is a more accurate approximation as compared with DFT, since there is no general minimization principle in the base of it. The main concept of TD-DFT includes the representation of the systems by the many-body Schrödinger equation:

$$i\frac{\partial}{\partial t}\psi(\{r\},t) = \hat{H}(\{r\},t)\Psi(\{r\},t) \quad (2.19)$$

in which $\hat{H}$ denotes the Hamiltonian operator and r refers to the coordinates of N number of electrons. If the state of the system at an initial time t_0 is known, at a given time the wave function can be estimated.

Within the framework of TD-DFT, the Hamiltonian operator can be represented as follows:

$$\hat{H}(\{r\},t) = \hat{T}(\{r\},t) + \hat{W}(\{r\},t) + \hat{V}_{ext}(\{r\},t) \quad (2.20)$$

where the kinetic energy function $\hat{T}(\{r\},t)$ can be expressed as:

$$\hat{T}(\{r\}) = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 \quad (2.21)$$

And the electron-electron repulsion term $\hat{W}(\{r\},t)$ can be written as follows:

$$\hat{W}(\{r\},t) = -\frac{1}{2} \sum_{i,j=1}^N \sum_{i \neq j} \frac{1}{|r_i - r_j|} \quad (2.22)$$

Lastly, the external potential term can be expressed as:

$$\hat{V}_{ext}(\{r\}, t) = \sum_{i=1}^N v_{ext}(r_i, t) \quad (2.23)$$

The term associated with the Coulomb interaction of electrons, which is v_{ext} , can be formulated as:

$$v_{ext}(r, t) = - \sum_{v=1}^{N_n} \frac{Z_v}{|r - R_v(t)|} \quad (2.24)$$

where v and N_n represent the total number of nuclei in the system, Z_v is the charge of the nucleus, and R_v refers to the position of the nucleus.

The probability of locating an electron at a given time can be obtained by taking the square of the wave function as demonstrated in Equation 2.25:

$$\rho(r, t) = N \int d^3r_2 \dots d^3r_N |\Psi(r, r_2 \dots r_N, t)|^2 \quad (2.25)$$

where $\rho(r, t)$ becomes the basis variable which is normalized to the total number of electrons in the system.

2.6. Tamm-Dancoff Approximation (TDA)

Time Dependent Density Functional Theory (TD-DFT) is a feasible and convenient method to reproduce excited state energies and geometries of many-body systems. Still, because of the approximate nature of the exchange and correlation functionals, performance of TD-DFT may not be sufficient in some situations, especially considering its description of Rydberg states. Also it is remarkable to state that TD-DFT is not suitable to handle the triplet instability problem [96].

Applying Tamm-Dancoff Approximation (TDA) to the formalism of TD-DFT significantly improves the accuracy by solving the triplet instability problem in an

efficient way [97]. In TDA formalism, only the positive energy electron-hole pairs are taken into account and the negative energies are not considered. Also, it is assumed that only one electron-hole pair propagates in a given time interval, and this approximation neglects the interplay between electrons and holes at opposite charged energies.

Without the use of external parameters, polarization functions can be computed accurately via the ab-initio Bethe-Salpeter (BS) equation. However, the large amount of the electron-hole pairs in a given system renders the solution of BS equation extremely difficult [98]. By employing TDA, non-Hermitian Bethe-Salpeter (BS) problem can be solved by reducing it to solvable Hermitian problem with the help of the stable iterative methods [99]. The reduced Hermitian equation employed in TDA can be expressed as follows:

$$\widetilde{M}X_p = \omega_p X_p \quad (2.26)$$

where the X_p can be described as the amplitude vector. The excitation energy term ω_p can be written as follows:

$$\omega_p = \sum_{ai} (\epsilon_a - \epsilon_i) X_{ai}^2 + \sum_{abij} [\langle ib || aj \rangle + B_{ai,bj}] X_{ai} X_{bj} \quad (2.27)$$

When the solvent effects are taken into account, the total TDA energy for the excited state of p becomes:

$$G_p^{TDA} = G_{gs}^{HF} + \omega_p \quad (2.28)$$

where G_{gs}^{HF} denotes the ground state energy and ω_p term represents the TDA excitation energy.

2.7. Wigner Distribution Function

Wigner Distribution Function, also known as the Wigner quasi-probability distribution or Wigner-Ville distribution, is a quantum mechanical method used to relate wave function with the probability distribution in phase space. It was first proposed by Eugene Wigner in 1932 [100], and it has a wide range of applications, including amplitude and phase retrieval, signal processing, optical systems and devices, and calculation of coupling coefficients in phase space [101]. Coordinate-space or momentum-space wave functions can be utilized to generate the Wigner distribution. By using the coordinate-space function, Wigner transform for one dimensional system can be expressed as:

$$W(x, p) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \psi^* \left(x + \frac{s}{2} \right) \psi \left(x - \frac{s}{2} \right) e^{ips} ds \quad (2.29)$$

in which ψ represents the wave function, p is the momentum, and x is the position. The term $\psi^* \left(x + \frac{s}{2} \right)$ can be rewritten as follows:

$$\psi^* \left(x + \frac{s}{2} \right) = \left\langle \psi \mid x + \frac{s}{2} \right\rangle \quad (2.30)$$

And the term $\psi \left(x - \frac{s}{2} \right)$ in Equation 2.29 can be expressed as:

$$\psi \left(x - \frac{s}{2} \right) = \left\langle x - \frac{s}{2} \mid \psi \right\rangle \quad (2.31)$$

The following equation includes the multiplication of the third term e^{ips} in Equation 2.29 by $1/2\pi$, and the third term becomes:

$$\frac{1}{2\pi} e^{ips} = \frac{1}{\sqrt{2\pi}} e^{ip \left(x + \frac{s}{2} \right)} \frac{1}{\sqrt{2\pi}} e^{-ip \left(x - \frac{s}{2} \right)} \quad (2.32)$$

Equation 2.32 can be rewritten as:

$$\frac{1}{\sqrt{2\pi}} e^{ip \left(x + \frac{s}{2} \right)} \frac{1}{\sqrt{2\pi}} e^{-ip \left(x - \frac{s}{2} \right)} = \left\langle x + \frac{s}{2} \mid p \right\rangle \left\langle x - \frac{s}{2} \mid \psi \right\rangle ds \quad (2.33)$$

Expansion of Equation 2.29 with the expressions of Equations 2.30, 2.31 and 2.32 results in the following equation:

$$W(x, p) = \int_{-\infty}^{\infty} \left\langle \psi \mid x + \frac{s}{2} \right\rangle \left\langle x + \frac{s}{2} \mid p \right\rangle \left\langle p \mid x - \frac{s}{2} \right\rangle \left\langle x - \frac{s}{2} \mid \psi \right\rangle ds \quad (2.34)$$

where the first term represents the amplitude of a particle in the state ψ with the position of $(x - \frac{s}{2})$, the second term is the amplitude of a particle with the position of $(x - \frac{s}{2})$ and momentum p , the third term is the amplitude of a particle with the position of $(x + \frac{s}{2})$ and momentum p , and the last term is the amplitude of a particle in the state ψ with the position of $(x + \frac{s}{2})$. The superposition of the possible trajectories can be generated with integration over s , which eventually leads to a quasi-probability distribution in phase space [102].

2.8. ϕ_S Index

ϕ_S index can be defined as the spatial overlap between the attachment and detachment density matrices [77]. It can be used to elucidate the charge transfer nature of compounds upon absorption of light quantitatively [103]. The theorem behind ϕ_S index proposes that for a given system with N -electrons and K -sized basis set the difference between the density matrices of the ground state (P_0) and an excited state (P_X) can be estimated with the help of the basis set overlap matrix (S) [77], as illustrated in Equation 2.35:

$$\Delta = P_X - P_0 \Rightarrow \sum_{k=1}^K (\Delta S)_{kk} = 0 \quad (2.35)$$

where the trace of ΔS should be equal to 0 since there is no electron transfer occurring in the system. The eigenvalues of Δ in the diagonal matrix δ can be found by conducting an unitary similarity transformation:

$$\exists U \mid \delta = U^\dagger \Delta U; (\delta)_{ij} = 0 \quad \forall i \neq j \quad (2.36)$$

Diagonalization of the Δ provides the so-called detachment and attachment orbitals. Hence, two new diagonal matrices with opposite charges, Γ and Λ , are defined and expressed in the space of K atomic orbitals. Then the equation becomes:

$$\sum_{\mu=1}^K (\Gamma S)_{\mu\mu} = \sum_{\mu=1}^K (\Lambda S)_{\mu\mu} \quad (2.37)$$

Since there is no electron loss during the excitation process, the detachment and attachment densities can be defined in the 3D space:

$$\varrho_{\tau(\xi_1, \xi_2, \xi_3)} = \sum_{\mu=1}^K \sum_{\nu=1}^K (\tau)_{\mu\nu} \varphi_{\mu}(\xi_1, \xi_2, \xi_3) \varphi_{\nu}^*(\xi_1, \xi_2, \xi_3) \quad (2.38)$$

$$\tau \equiv \Gamma, \Lambda \quad (2.39)$$

These two functions represent the spatial distribution of the removed and reorganized electron densities during the excitation process. The detached and attached charges can be defined as follows:

$$\vartheta = \int_R d\xi_1 \int_R d\xi_2 \int_R d\xi_3 \varrho_{\tau}(\xi_1, \xi_2, \xi_3) \equiv \int_{R^3} d^3\xi \varrho_{\tau}(\xi) \quad (2.40)$$

Thus, ϕ_S index can be defined as the overlap between the attachment and detachment matrices:

$$\phi_S = \vartheta^{-1} \int_{R^3} d^3\xi \sqrt{\varrho_{\Gamma}(\xi) \varrho_{\Lambda}(\xi)} \quad (2.41)$$

where the term ϑ can be expressed as:

$$\vartheta \equiv \frac{1}{2} \left[\int_{R^3} d^3\xi \sum_{\tau=\Gamma, \Lambda} \varrho_{\tau}(\xi) \right] \quad \phi_S \in [0; 1] \quad (2.42)$$

ϕ_S index can be given in Mulliken and Lowdin charge densities, and a value closer to 0 in the range from 0 to 1 indicates the presence of charge transfer in a chromophore. On the contrary, a value closer to 1 implies that there is a large amount of overlap between the attachment and detachment densities and therefore the local excitation character of the electronic transition is more pronounced. In Figure 2.1, the ϕ_S index is illustrated as the overlap between the attachment and detachment densities.

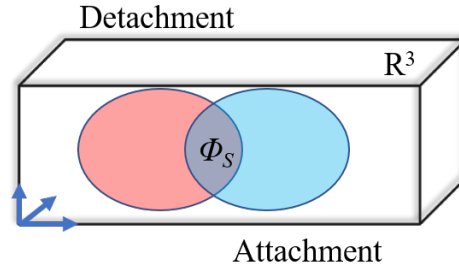


Figure 2.1. Description of the ϕ_S index as the overlap between the attachment and detachment densities.

2.9. Spin-Orbit Coupling

Spin-orbit coupling (SOC), also called spin-orbit interaction, is described as the interaction of the magnetic moment of an electron with the effective magnetic field, and it was first proposed by Thomas within a classical relativistic approach [104]. Later, the concept of spin-orbit coupling was further elucidated by the relativistic quantum electron theory introduced by Dirac [105]. Spin-orbit coupling causes shifts in the atomic energy levels of an electron because of the electromagnetic interaction between the magnetic dipole of the electron, electron's orbital motion and the electrostatic field induced by the nucleus [106]. The interaction of the magnetic moments of the nucleus and electron can be described as spin-orbit coupling.

The total angular momentum ($\vec{j}$) of an electron can be estimated by the summation of its orbital angular momentum and spin angular momentum, as given by the

following equation:

$$\vec{j} = \vec{l} + \vec{s} \quad (2.43)$$

The total momentum ($\vec{j}$) cannot be a negative value, it can be either a whole number or a half one. Therefore, the total momentum can be expressed by the following equations:

$$j_{max} = l + s = l + \frac{1}{2} \quad (2.44)$$

$$j_{min} = l - s = l - \frac{1}{2} \quad (2.45)$$

The magnetic moment of an electron is represented as follows:

$$\mu = -\frac{e}{2M}L \quad (2.46)$$

where M is the electron's mass and L is the electron's angular momentum.

In the quantum case, Equation 2.46 becomes:

$$\hat{\mu}_z = -\frac{1}{2M}\hat{L}_z \quad (2.47)$$

where $\hat{\mu}_z$ can be rewritten as:

$$\hat{\mu}_z = -\frac{e\hbar}{2M}m_l \equiv -\mu_B m_l \quad (2.48)$$

where μ_B denotes Bohn magneton. Thus, the Hamiltonian with respect to the interaction between the magnetic moments can be expressed as:

$$\hat{H}_{SO} = f(r)\hat{L}\hat{S} \quad (2.49)$$

in which $f(r)$ can be written as:

$$f(r) = \frac{1}{2M^2c^2r} \frac{dV(r)}{dr} \quad (2.50)$$

Taking the square of the total momentum ($\hat{J}^2 = \hat{L}^2 - \hat{S}^2$), Equation 2.49 can be rewritten as:

$$H_{S-O} = \frac{1}{2}f(r)\hat{J}^2 - \hat{L}^2 - \hat{S}^2 \quad (2.51)$$

where the term $f(r)$ can be expressed as:

$$\langle f(r) \rangle = \frac{Z^3}{8\pi\epsilon_0 M^2 C^2} \int_0^\infty \frac{1}{r^3} |R_{nl}(r)|^2 r^2 dr \quad (2.52)$$

in which Z is the atomic number. Increased amount of SOC effectively enhances the rate of the process of intersystem crossing. Since SOC is directly related with the atomic number as demonstrated in Equation 2.52, heavy atoms possess higher SOC. Thus, phosphorescence based materials usually contain heavy metals.

3. RESULTS

3.1. Background

Conventional OLEDs consisting of pure organic compounds have commercial limitations since singlet excitons and weakly emissive triplet excitons are generated in the 1:3 ratio due to spin statistics [107]. Use of thermally activated delayed fluorescence (TADF) materials in the emissive layer of OLEDs enables the up-conversion of triplet excitons into singlet ones with the help of the reduced singlet-triplet energy gap. As a consequence, an internal quantum efficiency of 100% can be achieved in OLED devices utilizing the principles of TADF. Molecular design strategies are important for an effective TADF emission since intramolecular charge transfer (ICT) is required for a small singlet-triplet gap. Therefore, the relationship between molecular structure and photophysical properties must be well understood [108].

TADF characteristics of chromophores can be investigated by means of computational approaches. In this study, D-A and D-A-D type TADF emitters employing benzophenone derivatives have been investigated since benzophenone is a frequently used electron accepting unit in the design of TADF emitters thanks to its desirable high-lying triplet energy levels, good electron accepting properties, strong SOC values and efficient absorptivity of UV light [58,59]. Based on this criterion, 21 emitters, given in Figures 3.1-3.4, have been selected from the literature. Also, 7 non-TADF benzophenone emitters, which are displayed in Figure 3.5, have been investigated, since their comparison with the TADF emitters is crucial to comprehend the structural conditions which lead to an effective TADF emission.

The studied TADF compounds have been divided into subgroups based on their structural similarities. Group 1 (Figure 3.1) contains D-A-D type para-substituted benzophenone emitters with different electron donating groups. The donor groups are the same in some of the compounds, such as Px2BP [42] with phenoxazine donors, DMAC-BP [32] with dimethylacridine donors, Cz2BP [42] with carbazole donors and

CC2BP [42] with bicarbazole donors, making them their molecular structures symmetrical. The other two emitters, A-BP-TA [109] and OPDPO [40], have different donor groups, thus they are referred as asymmetric D-A-D type emitters. A-BP-TA contains dimethylacridine and thianthrene donors, while OPDPO has diphenylphosphineoxide and phenothiazine donor groups.

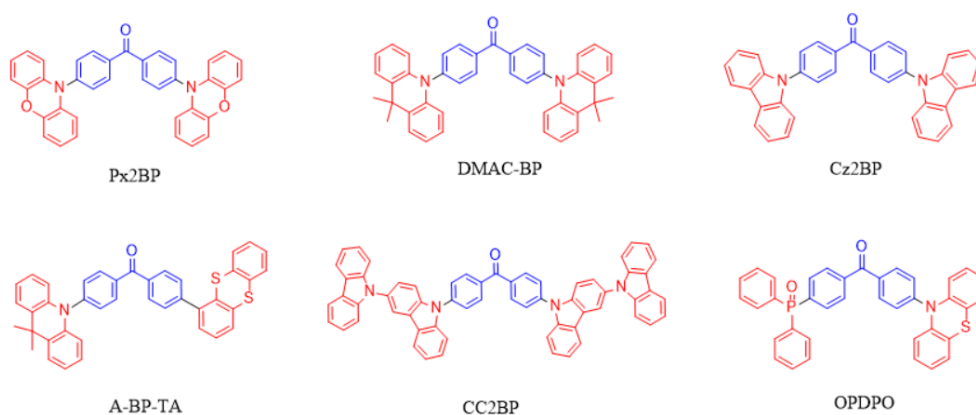


Figure 3.1. TADF emitters which have been included in Group 1.

Group 2 (Figure 3.2) includes asymmetric D-A type emitters with different donor groups. The acceptor unit of DBT-BZ-PXZ [55], DBT-BZ-PTZ [55] and DBT-BZ-DMAC [54] is dibenzothiophene-benzoyl, while the acceptor unit employed in CP-BP-PXZ [54] and CP-BP-DMAC [54] is phenylcarbazole-benzoyl. DBT-BZ-PXZ and CP-BZ-PXZ employ phenoxazine donors whereas DBT-BZ-DMAC and CB-BP-DMAC contain the dimethylacridine donor group. In DBT-BZ-PTZ, phenothiazine has been employed as the donor group.

Group 3 (Figure 3.3) includes six symmetric TADF emitters with anthraquinone acceptors. The compounds a1, a2, a3 and a4 are D-A-D type of emitters whereas the compounds b1 and b4 contain phenyl bridges between the donor acceptor units, making them D- π -A- π -D type emitters. The compounds a1 and b1 contain diphenylamine donor groups while dimethylacridine donor groups are employed in a4 and b4. The compounds a2 and a3 include bis(4-biphenyl)amine and 3,6-di-tert-butylcarbazole donors, respectively. All of the Group 3 emitters have been selected from the experi-

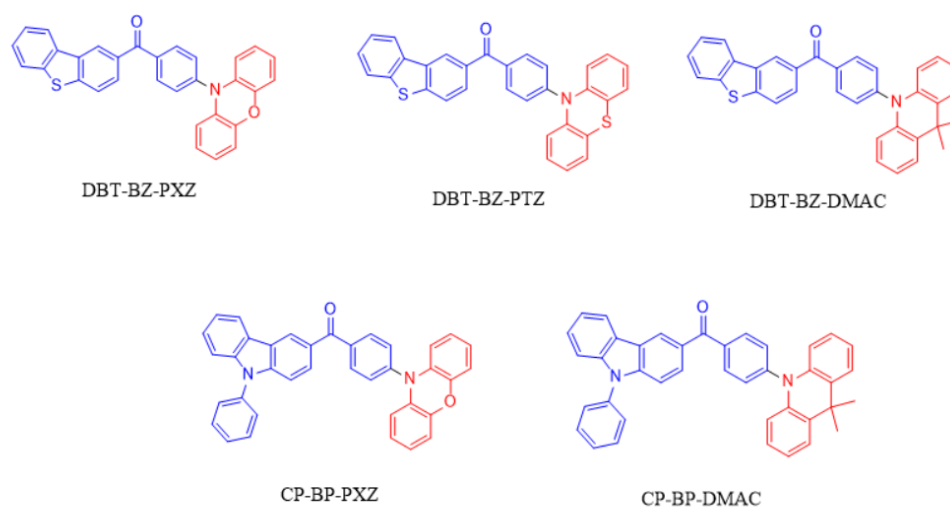


Figure 3.2. TADF emitters which have been included in Group 2.

mental and computational study of Zhang *et al.* [49].

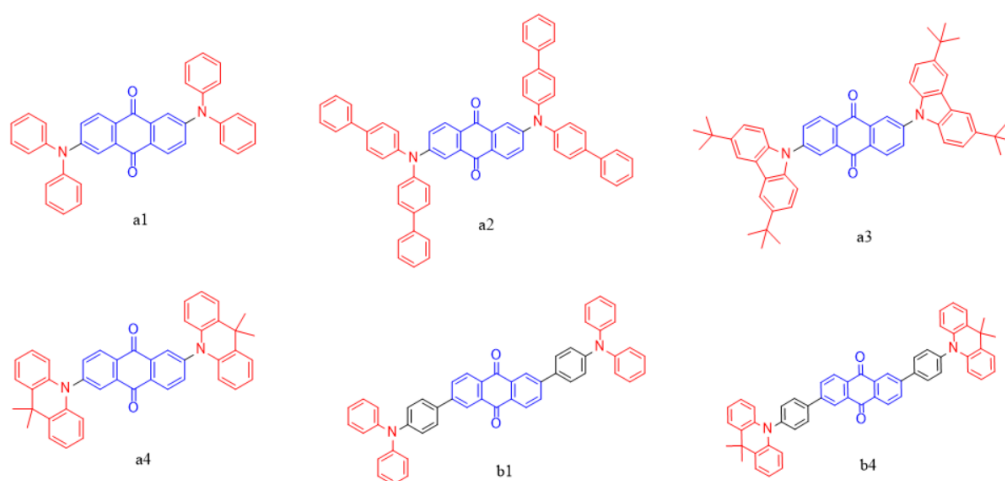


Figure 3.3. TADF emitters which have been included in Group 3.

Group 4 (Figure 3.4) contains D-A type TADF emitters where the acceptor unit is xanthone. While ACRXTN [53] and MCz-XT [51] have the donor groups of dimethylacridine and 1,3,6,8-tetramethylcarbazole, 3-PXZ-XO [41] and PTZ-XT [28] employ phenoxazine and phenothiazine donor groups, respectively.

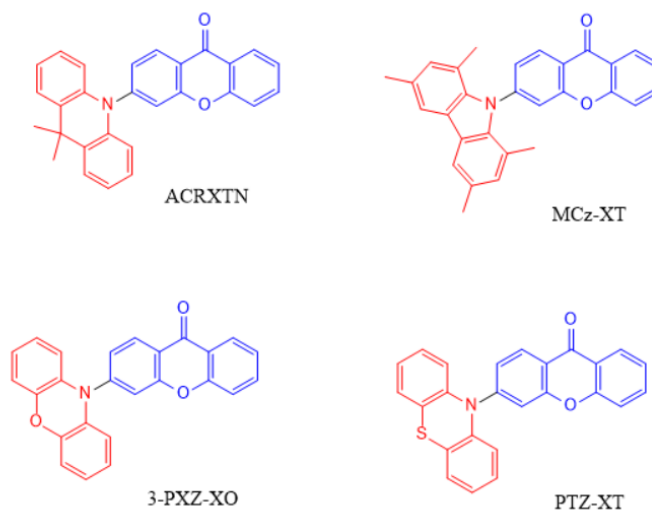


Figure 3.4. TADF emitters which have been included in Group 4.

Finally, a series of benzophenone based non-TADF compounds (Figure 3.5) have been modeled in order to compare their structural and photophysical properties with the TADF active ones. The non-TADF compounds include D-A type emitters such as Model Compound 2 [110], OPM [111] and p-Cz [112]; asymmetric para-substituted D-A-D type emitters including ODFRCZ [113] and ODBTCZ [114]; and symmetric meta-substituted D-A-D type emitters named as Compound 1 [115] and Compound 2 [115]. The structural and photophysical factors causing poor TADF activities in these compounds have been analyzed in detail in further discussions.

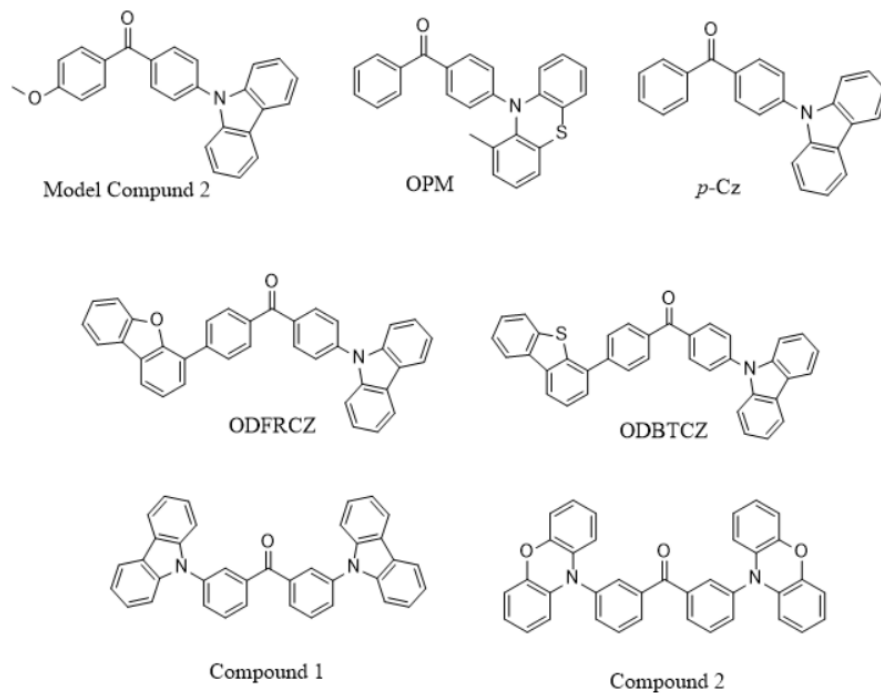


Figure 3.5. Non-TADF emitters employing benzophenone acceptor cores.

3.2. Computational Procedure

Density Functional Theory (DFT) calculations have been performed using Gaussian 16 program package [116]. Ground state and excited state optimizations were carried out with meta-hybrid M06-2X functional and 6-31+G(d,p) basis set for all of the molecules. M06-2X functional is known to reproduce well the geometries, π - π interactions and electronic energies of a wide range of compounds containing aromatic rings [117]. For the compounds containing sulfur and phosphorus elements, 6-311++G(3df,3pd) [118] and 6-311++G(2d,2p) [119] extra basis sets were applied, respectively. Inclusion of extra basis sets for the ground state optimizations and excited state calculations of the compounds containing third row elements is useful to increase accuracy. Conformational search has been applied to all compounds in an attempt to find the most stable ground state geometry. The further excited state calculations have been carried out using the most stable conformations. Integral equation formalism polarizable continuum model (IEF-PCM) has been implemented implicitly to take

into account solvent effects, and experimental solvent has been used for each emitter; toluene for Px2BP, Cz2BP, CC2BP, a1, a2, a3, a4, b1, b4, MCz-XT, 3-PXZ-XO, Model Compound 2 and OPM; THF for DBT-BZ-PXZ, DBT-BZ-PTZ, DBT-BZ-DMAC, CP-BP-PXZ, CP-BP-DMAC, PTZ-XT, *p*-Cz, Compound 1 and Compound 2; DCM for DMAC-BP, ACRXTN, ODFRCZ and ODBTCZ.

Tamm-Dancoff Approximation (TDA) has been employed for the excited state calculations. Benchmark calculations have been carried out to a set of emitters to determine the most promising functionals for the TDA-DFT computations. For this purpose, some of the widely used DFT functionals, including BLYP, B3LYP, M06-2X and PBE0, have been tested. The accuracy of the functionals has been determined with respect to their coherency with experimental data. Pople’s basis set 6-31+G(d,p) has been used for the TDA calculations. Energies of the first singlet and triplet excited states have been determined through these computations.

Absorption spectra for each compound have been generated as vertical electronic transitions from S_0 to S_1 energy level. Wigner distribution has been applied using Newton-X software package [120] and 40 conformations have been generated to simulate the absorption spectra. The obtained absorption spectra for each emitter have been compared with the experimental UV-Vis absorption spectra in order to evaluate the performances of the DFT functionals which have been used.

Spin-orbit coupling (SOC) values for the intersystem crossing transitions from T_1 to S_1 energy states have been calculated at the TDA-DFT level using the Amsterdam Density Functional (ADF) program [121] to investigate the plausibility of the process of reverse intersystem crossing. The calculations have been carried out by using the geometries optimized at T_1 energy level.

In order to investigate the distribution of the frontier orbitals, Natural Transition Orbitals for the vertical transitions from S_0 to S_1 energy states have been obtained with the Nancy_EX code [103] and visualized by Avogadro program package [122]. ϕ_S index, quantifying the spatial overlap between the attachment and detachment

densities, have been computed via Nancy_EX software package [77] and reported in Lowdin and Mulliken charge densities.

TDA-DFT and NTO calculations have also been performed with the geometries obtained from the first excited triplet state (T_1) optimizations and the calculated photophysical properties have been compared with the experimental results. The differences between the photophysical properties computed at the S_0 and T_1 levels have also been discussed.

3.3. Benchmark Calculations

Benchmark calculations have been carried out with the aim of determining the most appropriate DFT functional for the TDA-DFT computations of the benzophenone based TADF emitters. Comparison of the calculated ΔE_{ST} values with the experimental ones is one way to evaluate the performances of the functionals. In addition to this, experimental UV-Vis absorption spectrum and computed absorption spectra with different functionals have been compared for each compound. The evaluated functionals include some of the commonly used DFT functionals in TD-DFT calculations of TADF compounds, such as BLYP, B3LYP, PBE0 and M06-2X. The benchmark calculations have been applied to Group 1 and three molecules from Group 2, and the geometries optimized at S_0 energy level have been used. At the end of the calculations, the most promising functionals for the TDA-DFT computations have been determined with respect to experimental data. In all of the TDA calculations, 6-31+G(d,p) basis set has been used in conjunction with different DFT functionals.

3.3.1. Comparison of the Experimental and Calculated ΔE_{ST} Values

ΔE_{ST} values for the most energetically stable conformations have been calculated with BLYP, B3LYP, PBE0 and M06-2X functionals to determine the most promising functionals. For each emitter, the experimental solvent has been used for the calculations. The energy differences between the S_1 and T_1 states (ΔE_{S1-T1}) and S_1 and T_2 states (ΔE_{S1-T2}) for the Group 1 emitters are given in Table 3.1.

The missing $\Delta E_{S_1-T_2}$ values in Table 3.1 indicate that the T_2 energies are higher than the S_1 energies for the corresponding compounds. In general, BLYP, B3LYP and PBE0 yielded similar results which are expectedly low and in line with experimental ones. On the other hand, the energy gap between the first singlet and triplet excited states is relatively large in M06-2X calculations, which results in relatively high $\Delta E_{S_1-T_1}$ values.

Histograms have been generated in order to visualize the TDA-DFT results obtained from different functionals. For simplicity, only the $\Delta E_{S_1-T_1}$ values have been shown in the histograms. Histogram chart for Group 1 molecules is depicted in Figure 3.6 and it clearly demonstrates that unlike BLYP, B3LYP and PBE0, M06-2X produces relatively high ΔE_{ST} values which are not consistent with the experimental ones.

Table 3.1. Benchmark calculations for Group 1 emitters with different functionals together with the experimental values ($\Delta E_{S_1-T_1}$, $\Delta E_{S_1-T_2}$ and experimental values are given in eV, the basis set is 6-31+G(d,p)).

Compound	Nature	BLYP	B3LYP	PBE0	M06-2X	Exp.
Px2BP	$\Delta E_{S_1-T_1}$	0.004	0.007	0.010	0.162	0.03
	$\Delta E_{S_1-T_2}$	0.002	0.005	0.007	0.008	
DMAC-BP	$\Delta E_{S_1-T_1}$	0.004	0.006	0.009	0.178	0.07
	$\Delta E_{S_1-T_2}$	0.001	0.003	0.006	0.001	
Cz2BP	$\Delta E_{S_1-T_1}$	0.099	0.232	0.321	0.496	0.21
	$\Delta E_{S_1-T_2}$	0.090	0.165	0.216	0.179	
CC2BP	$\Delta E_{S_1-T_1}$	0.017	0.085	0.165	0.484	0.14
	$\Delta E_{S_1-T_2}$	0.013	0.069	0.114	0.169	
A-BP-TA	$\Delta E_{S_1-T_1}$	0.004	0.006	0.008	0.215	0.06
	$\Delta E_{S_1-T_2}$	-	-	-	0.003	
OPDPO	$\Delta E_{S_1-T_1}$	0.003	0.006	0.010	0.361	0.02
	$\Delta E_{S_1-T_2}$	-	-	-	0.155	

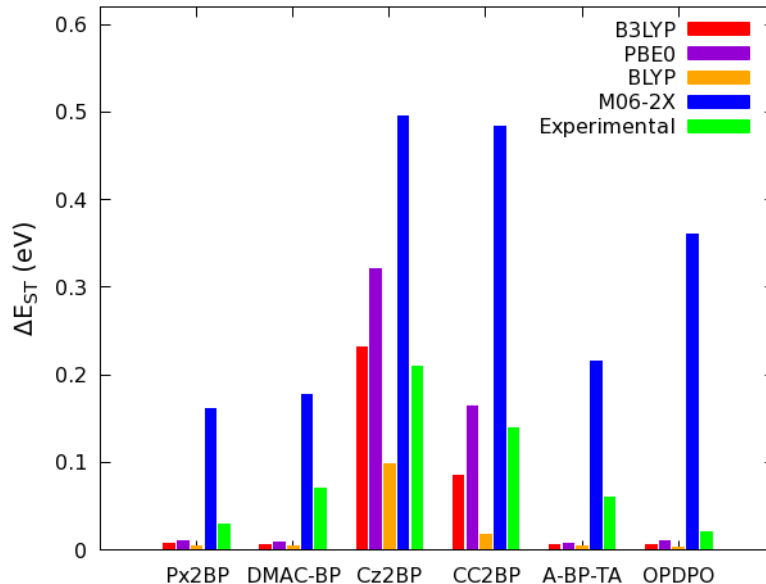


Figure 3.6. Histogram chart including ΔE_{S1-T1} values calculated with different functionals for Group 1 emitters together with the experimental values (The basis set is 6-31+G(d,p)).

Similarly, ΔE_{S1-T1} and ΔE_{S1-T2} values for three molecules from Group 2, which have been calculated with different functionals, are displayed in Table 3.2. The histogram chart for the results summarized in Table 3.2 is depicted in Figure 3.7.

The histogram chart given in Figure 3.7 and the ΔE_{ST} values in Table 3.2 display similar results where M06-2X produces the largest singlet-triplet energy gaps. The results for the Group 2 emitters are in line with those for the Group 1 emitters. Therefore, in terms of ΔE_{ST} , the performance of M06-2X as a potential TDA-DFT functional is poor based on the TDA calculations conducted for Group 1 and Group 2 emitters.

Table 3.2. Benchmark calculations for three molecules from Group 2 emitters with different functionals together with the experimental values (ΔE_{S1-T1} , ΔE_{S1-T2} and experimental values are given in eV, the basis set is 6-31+G(d,p)).

Compound	Nature	BLYP	B3LYP	PBE0	M06-2X	Exp.
DBT-BZ-PXZ	ΔE_{S1-T1}	0.004	0.008	0.011	0.241	0.09
	ΔE_{S1-T2}	-	-	-	0.047	
DBT-BZ-PTZ	ΔE_{S1-T1}	0.004	0.009	0.015	0.402	0.05
	ΔE_{S1-T2}	-	-	-	0.256	
DBT-BZ-DMAC	ΔE_{S1-T1}	0.004	0.006	0.009	0.235	0.08
	ΔE_{S1-T2}	-	-	-	0.002	

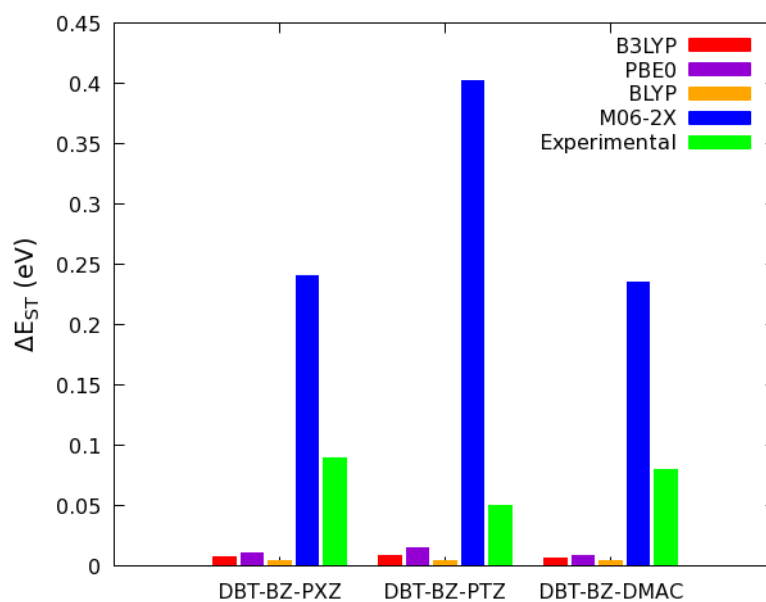


Figure 3.7. Histogram chart including ΔE_{S1-T1} values calculated with different functionals for three molecules from Group 2 emitters together with the experimental values (The basis set is 6-31+G(d,p)).

3.3.2. Comparison of the Experimental and Calculated UV-Vis Absorption Spectra

Absorption spectra of the selected compounds have been calculated with the functionals BLYP, B3LYP, PBE0 and M06-2X by using Wigner distribution in order to include dynamic effects. The excitation nature of S_0 to S_1 has been investigated in each compound and 40 conformations have been generated through Wigner distribution. Besides the functionals, influence of conformations have also been analyzed for the molecules Px2BP, Cz2BP, DBT-BZ-PXZ and DBT-BZ-DMAC by including all possible conformations of these emitters, and the generated spectra have been compared with the spectra calculated from the most stable conformation. Mirror images of the conformations are not included since they produce nearly the same Gibbs Free energies and photophysical properties. All of the computed absorption spectra have been compared with the experimentally available UV-Vis absorption spectra. In all of the calculations, 6-31+G(d,p) basis set and experimental solvents have been used. In order to gain a clear vision, the oscillator strengths corresponding to the $\lambda_{\max}$ values have been normalized to a value of 1.

First of all, the effects of conformations on the absorption spectra have been investigated. Figure 3.8 displays the influence of including all conformations on the calculated absorption spectra. Three functionals have been chosen to investigate the conformational effects, which are B3LYP, PBE0 and M06-2X. It has been clearly observed that all possible conformations have similar photophysical properties as they reproduce close $\lambda_{\max}$ values and spectral shapes in general. Therefore, further Wigner distribution calculations generating absorption spectra have been based on the geometries of only the most stable conformations.

After the analysis of the conformational effects, the performances of BLYP, B3LYP, PBE0 and M06-2X have been tested in terms of the absorption spectra of Px2BP, DMAC-BP, Cz2BP, CC2BP, A-BP-TA, OPDPO, DBT-BZ-PXZ, DBT-BZ-PTZ and DBT-BZ-DMAC. The computed spectra are displayed in Figures 3.9-3.11 together with the experimental $\lambda_{\max}$ values.

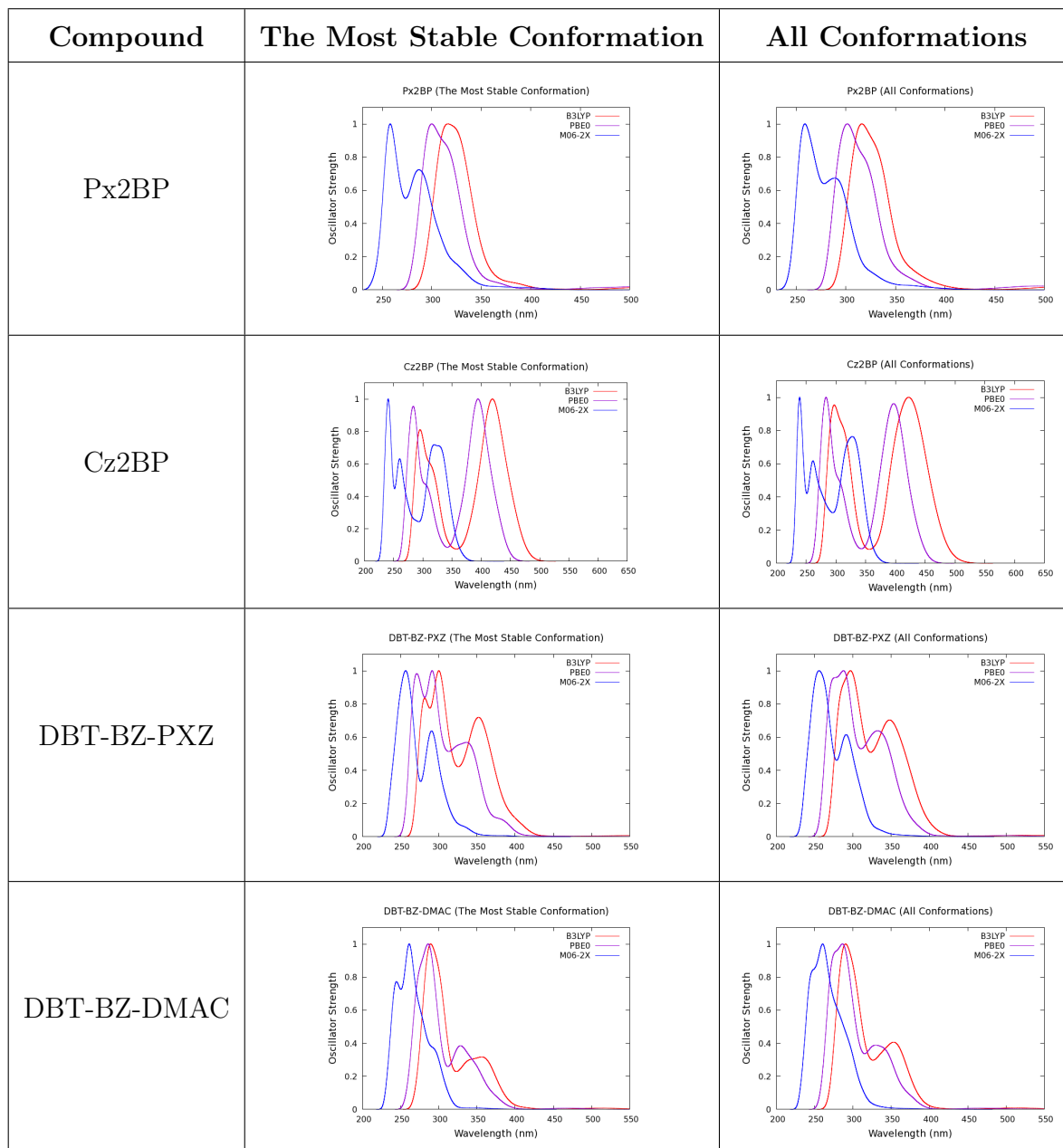


Figure 3.8. Absorption spectra calculated from the most stable conformation and all conformations at different levels of theory.

In general, hypsochromic shift has been observed in the spectral band for the calculations with M06-2X, whereas bathochromic shift is present in the spectra calculated with BLYP. The other two functionals, B3LYP and PBE0, yielded approximate $\lambda_{\max}$ values and spectral shapes. With respect to the experimental $\lambda_{\max}$ values, M06-2X produced low $\lambda_{\max}$ values which are usually below 300 nm. On the other hand,

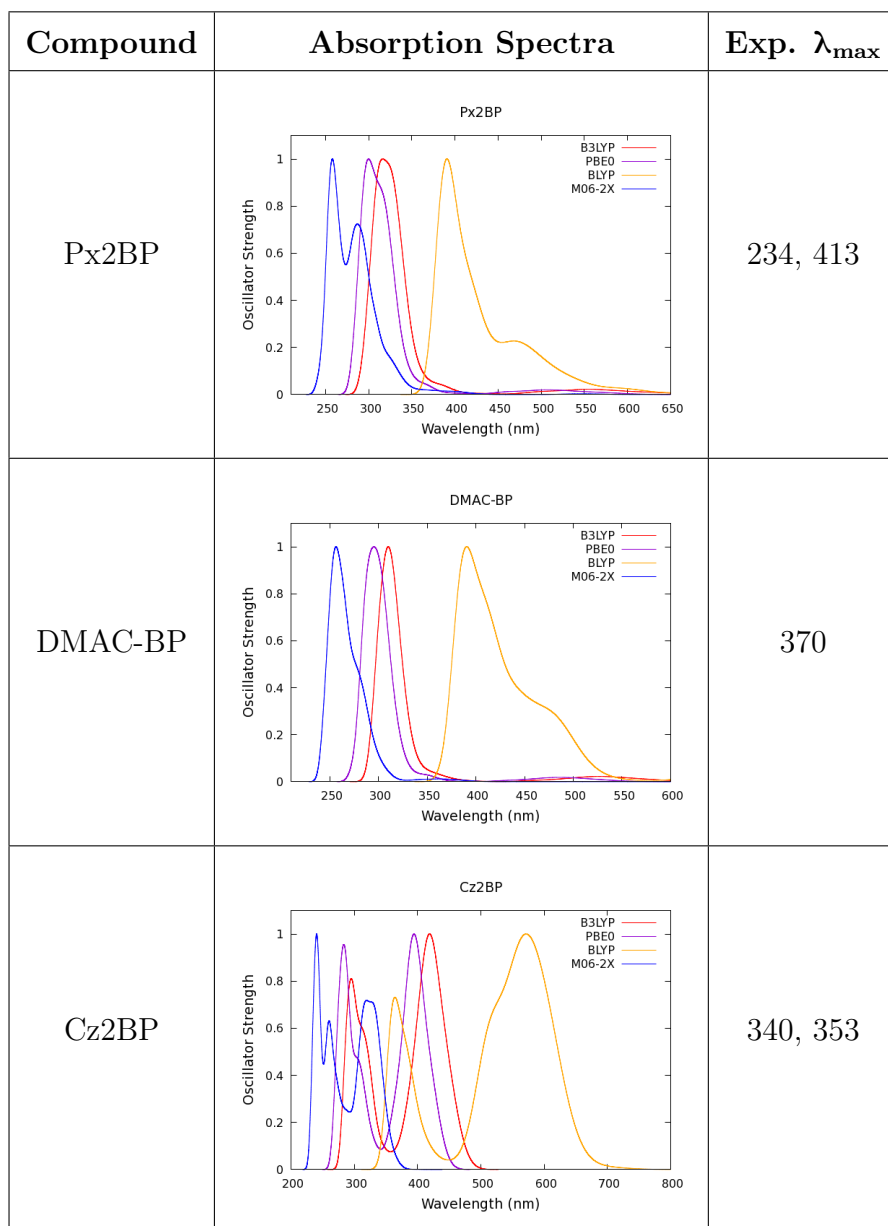


Figure 3.9. Absorption spectra for Px2BP, DMAC-BP and Cz2BP calculated at different levels of theory and experimental $\lambda_{\max}$ values in nm.

BLYP produced higher $\lambda_{\max}$ values when compared to the experimental results, except the emitters Px2BP and DMAC-BP. These results are in line with the results obtained from the ΔE_{ST} calculations, since bathochromic shift is observed when the charge transfer (CT) states are involved [123]. BLYP produced lower ΔE_{ST} values in general, together with the observed red-shift in the spectra generated with BLYP,

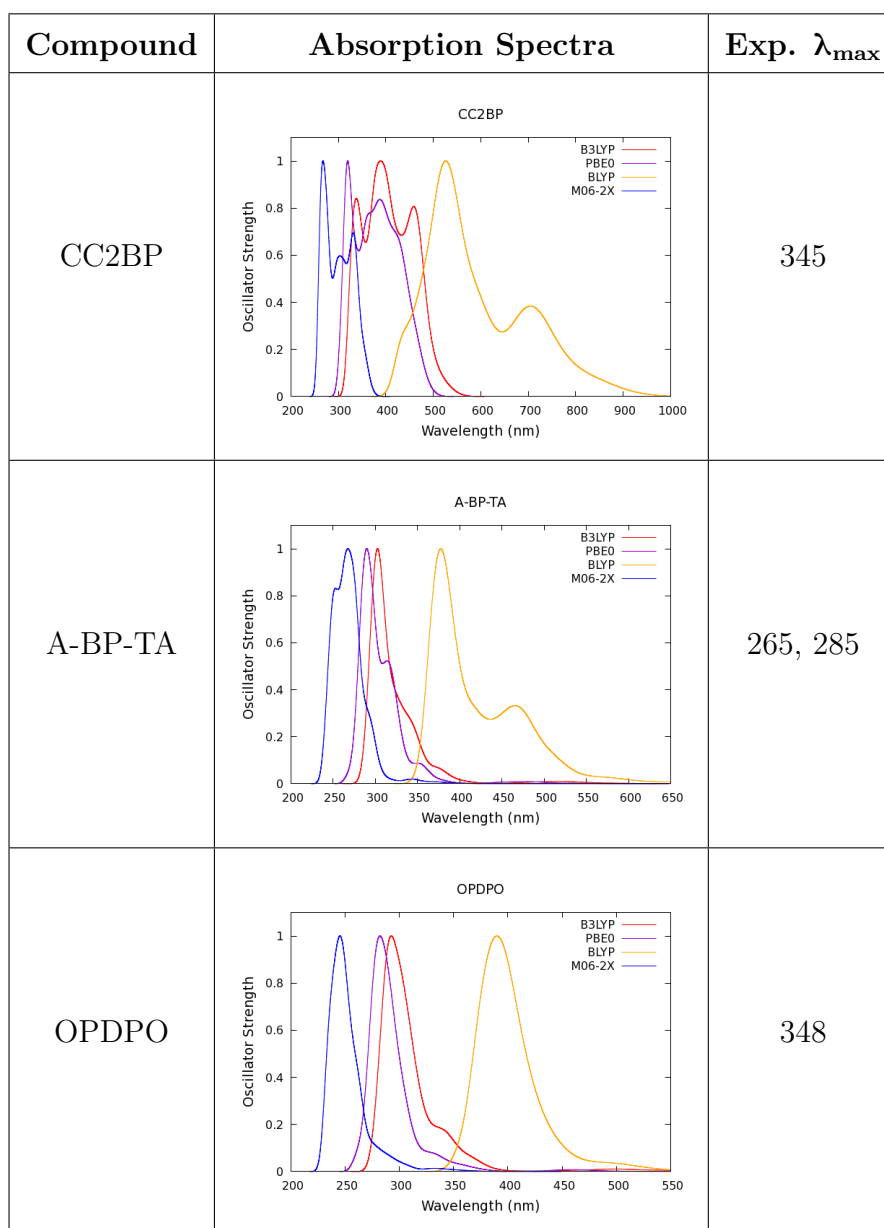


Figure 3.10. Absorption spectra for CC2BP, A-BP-TA and OPDPO calculated at different levels of theory and experimental $\lambda_{\max}$ values in nm.

it can be concluded that CT characters of the compounds are more pronounced in the calculations with BLYP. On the contrary, the increased ΔE_{ST} values and the observed hypsochromic shift indicates that local excitation (LE) character becomes more prominent in the calculations with M06-2X.

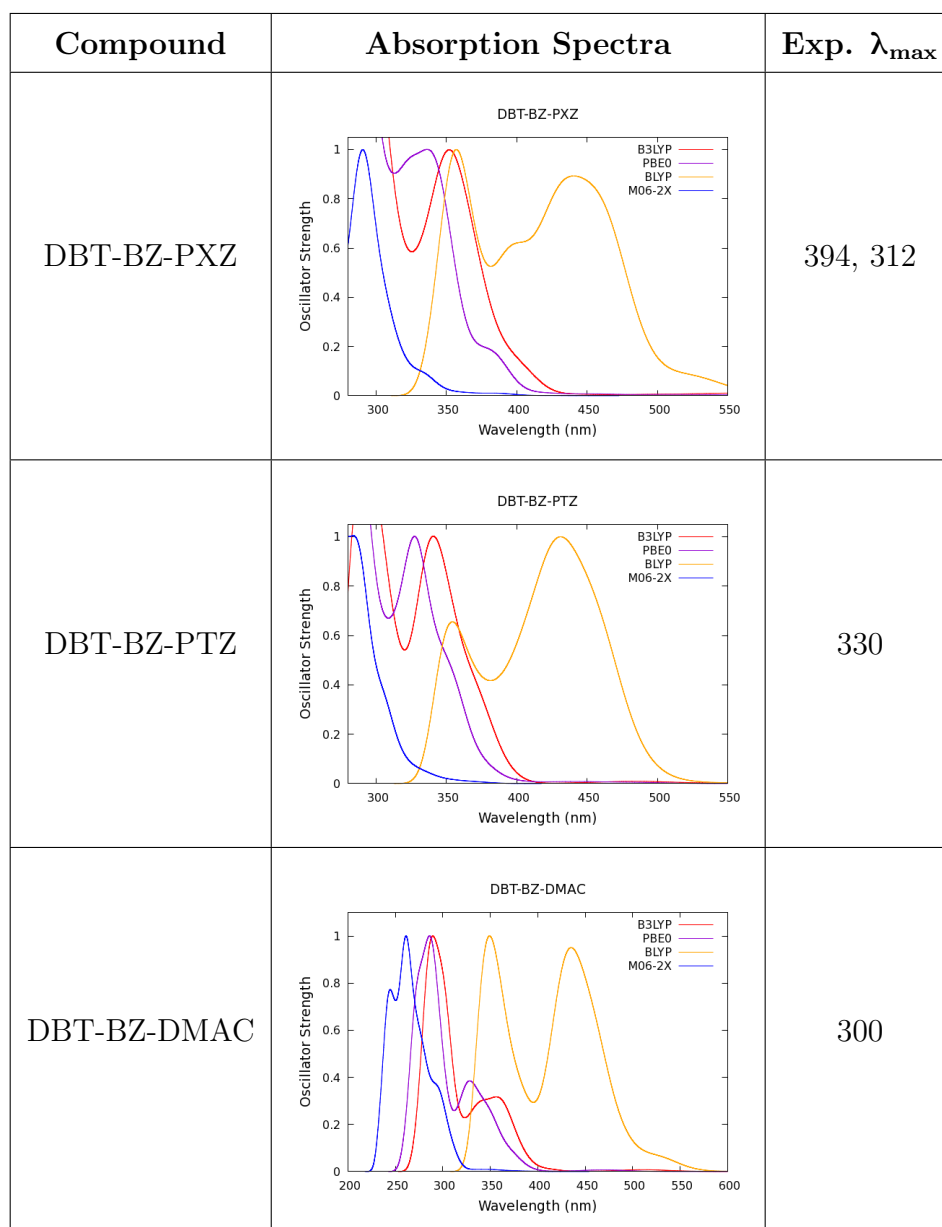


Figure 3.11. Absorption spectra for DBT-BZ-PXZ, DBT-BZ-PTZ and DBT-BZ-DMAC calculated at different levels of theory and experimental $\lambda_{\max}$ values in nm.

The spectra obtained from B3LYP and PBE0 are in reasonably well agreement with the experimental results, in contrast to the higher λ_{max} values generated with BLYP and lower λ_{max} values generated with M06-2X. However, given the satisfactory performance of BLYP in estimating the ΔE_{ST} values, further TDA calculations have been performed with BLYP as well, along with B3LYP and PBE0. Discussions featuring the relationship between spectral properties and molecular structures are made in the following sections.

3.4. Optimized Geometries at S_0 and T_1 Levels

As previously mentioned in the “Computational Procedure” chapter, all of the geometry optimizations have been carried out at M06-2X/6-31+G(d,p) level. After a careful conformational search, the most stable ground state conformations have been used for the optimizations at the T_1 level. The optimized geometries at the S_0 and T_1 levels have been used to conduct excited state calculations in order to investigate the photophysical properties at these energy states. Changes in the optimized molecular structure have been observed between the two energy states. For each emitter, the optimized geometries at S_0 and T_1 levels are shown in Figures 3.12-3.17.

According to the molecular structures of the TADF and non-TADF emitters given in Figures 3.12-3.17, some molecules have similar S_0 and T_1 geometries, including the ones with the diphenylamine (DPA), carbazole (Cz), bis(4-biphenyl)amine, 3,6-di-tert-butylcarbazole and dimethylacridine (DMAC) donor groups, such as DMAC-BP, Cz2BP, CC2BP, DBT-BZ-DMAC, CP-BP-DMAC, a1, a2, a3, a4, b4, ACRXTN, MC2, OPM, p-Cz, ODFRCZ, ODBTCZ and Compound 1. However, there are exceptions like b1 and MCz-XT, where the difference between the S_0 and T_1 geometries is remarkable. Despite the presence of the DPA donors, the structure of the π -bridge containing b1 emitter has changed significantly at the T_1 level due to the extended conjugation at this level induced by the rotated phenyl bridge. Also, C-N bond bending has been observed in the optimized geometry of MCz-XT at the S_0 level. A similar C-N bond bending is also present in the non-TADF compound OPM which might be linked to the methyl group on the thianthrene donor.

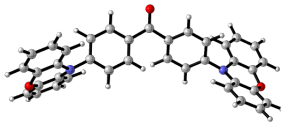
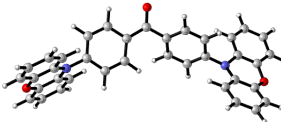
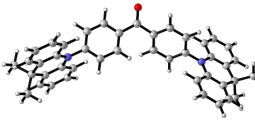
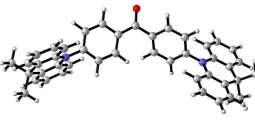
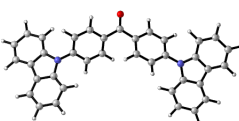
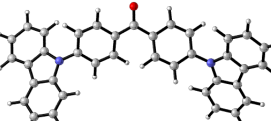
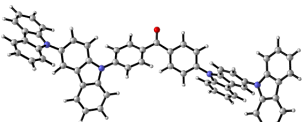
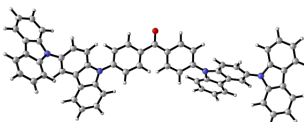
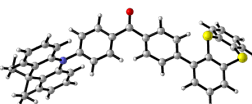
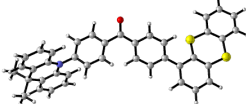
Compound	S_0 Level	T_1 Level
Px2BP		
DMAC-BP		
Cz2BP		
CC2BP		
A-BP-TA		

Figure 3.12. Optimized geometries of Px2BP, DMAC-BP, Cz2BP, CC2BP and A-BP-TA at S_0 and T_1 energy levels.

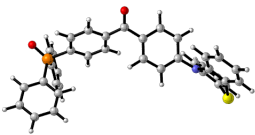
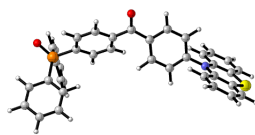
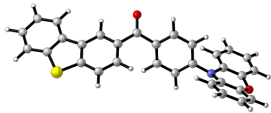
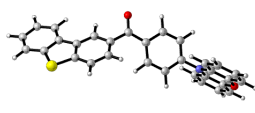
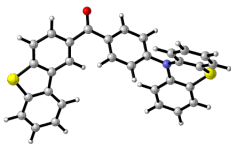
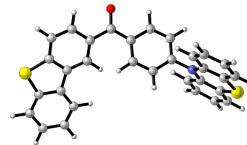
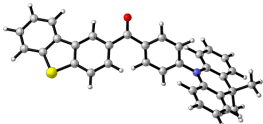
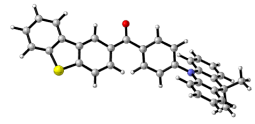
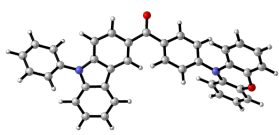
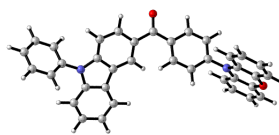
Compound	S_0 Level	T_1 Level
OPDPO		
DBT-BZ-PXZ		
DBT-BZ-PTZ		
DBT-BZ-DMAC		
CP-BP-PXZ		

Figure 3.13. Optimized geometries of OPDPO, DBT-BZ-PXZ, DBT-BZ-PTZ, DBT-BZ-DMAC and CP-BP-PXZ at S_0 and T_1 energy levels.

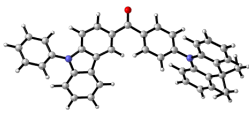
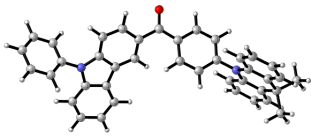
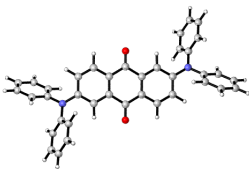
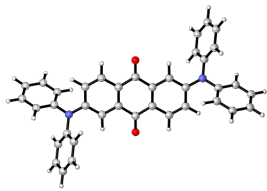
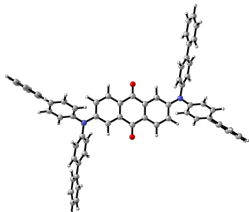
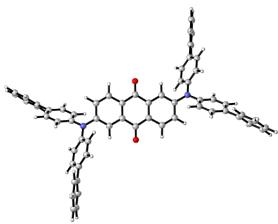
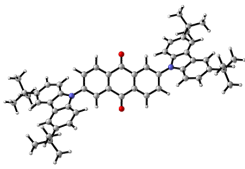
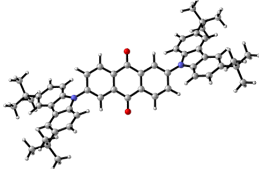
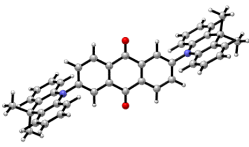
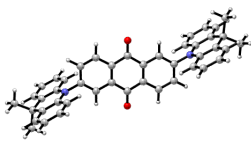
Compound	S_0 Level	T_1 Level
CP-BP-DMAC		
a1		
a2		
a3		
a4		

Figure 3.14. Optimized geometries of CP-BP-DMAC, a1, a2, a3 and a4 at S_0 and T_1 energy levels.

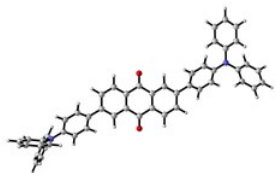
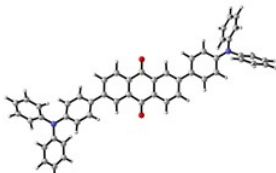
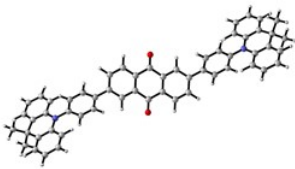
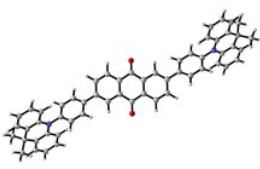
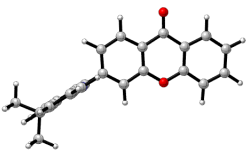
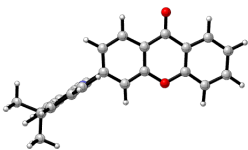
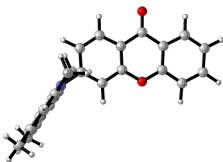
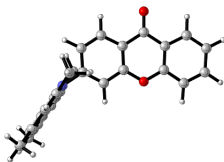
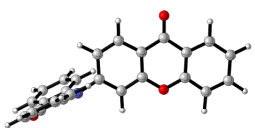
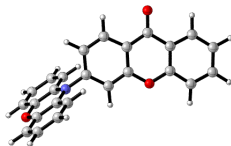
Compound	S_0 Level	T_1 Level
b1		
b4		
ACRXTN		
MCz-XT		
3-PXZ-XO		

Figure 3.15. Optimized geometries of b1, b4, ACRXTN, MCz-XT and 3-PXZ-XO at S_0 and T_1 energy levels.

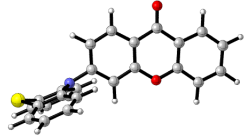
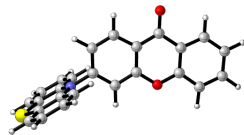
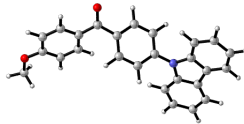
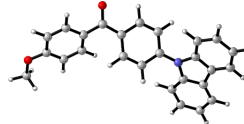
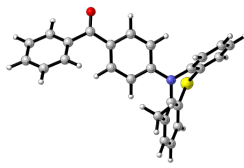
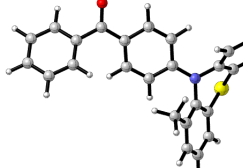
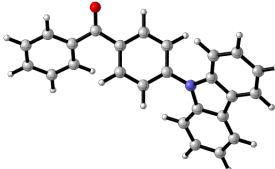
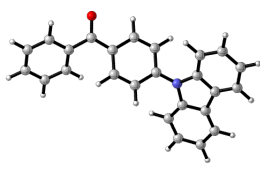
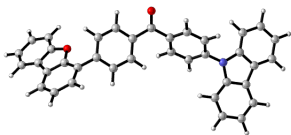
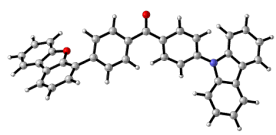
Compound	S_0 Level	T_1 Level
PTZ-Xt		
MC2		
OPM		
<i>p</i> -Cz		
ODFRCZ		

Figure 3.16. Optimized geometries of PTZ-Xt, Model Compound 2 (MC2), OPM, *p*-Cz and ODFRCZ at S_0 and T_1 energy levels.

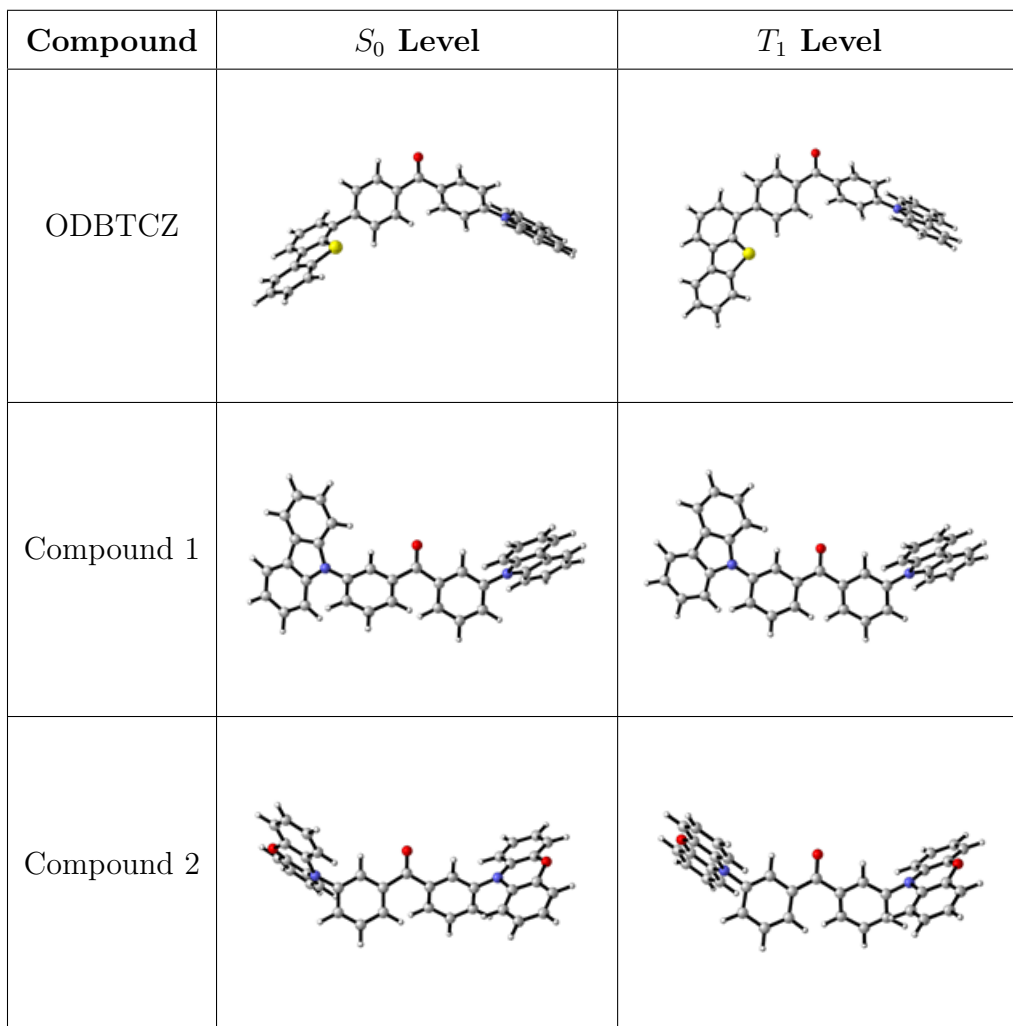


Figure 3.17. Optimized geometries of ODBTCZ, Compound 1 (C1) and Compound 2 (C2) at S_0 and T_1 energy levels.

The butterfly shaped donating groups, such as phenoxazine (PXZ), phenothiazine (PTZ) and thianthrene, became planar in the T_1 state, as it can be observed in the cases of A-BP-TA, OPDPO, DBT-BZ-PXZ, DBT-BZ-PTZ, CP-BZ-PXZ, 3-PXZ-XO and PTZ-XT. However, if there are two butterfly shaped donating groups in a molecule, only one of them is planar in the T_1 geometry, as in para-substituted Px2BP and its meta-substitute analogue Compound 2.

The structural changes between the optimized geometries at different energy levels substantially influence the photophysical properties of the emitters, such as ΔE_{ST} , HOMO-LUMO distributions and ϕ_S indices, since these descriptors are closely associated with torsion angles. Hence, comprehension of the structural attributes is essential.

3.5. Spectral Features

After a careful evaluation of the benchmark results, the rest of the excited state calculations have been performed with BLYP, B3LYP and PBE0 functionals. With these functionals, absorption spectrum of each emitter has been generated through a Wigner distribution calculation. The most stable conformation of each emitter has been used for the calculations since the conformations exhibit similar spectral properties.

The computed absorption spectra are given in Figures 3.18-3.23 for each group. Usually, bathochromic shift is attributed to the formation of the charge transfer (CT) states upon excitation [124]. What is more, CT bands are generally structureless and broad [123]. The compounds bearing PXZ, PTZ and DMAC electron donating groups which are more rigid and stronger, usually exhibit a broadened CT band following the high intensity local excited (LE) band. While this situation is observed in most of the TADF emitters, in non-TADF compounds more peaks have been observed instead of a featureless spectrum. Remarkably, Cz2BP, CC2BP, a1, a2, a3 and b1, which contain the freely rotating Cz and DPA donors, also exhibit excessive peaks. This can be ascribed to the less pronounced CT character in these compounds, which also gives rise to higher ΔE_{ST} values and ϕ_S indices which will be discussed in the following sections.

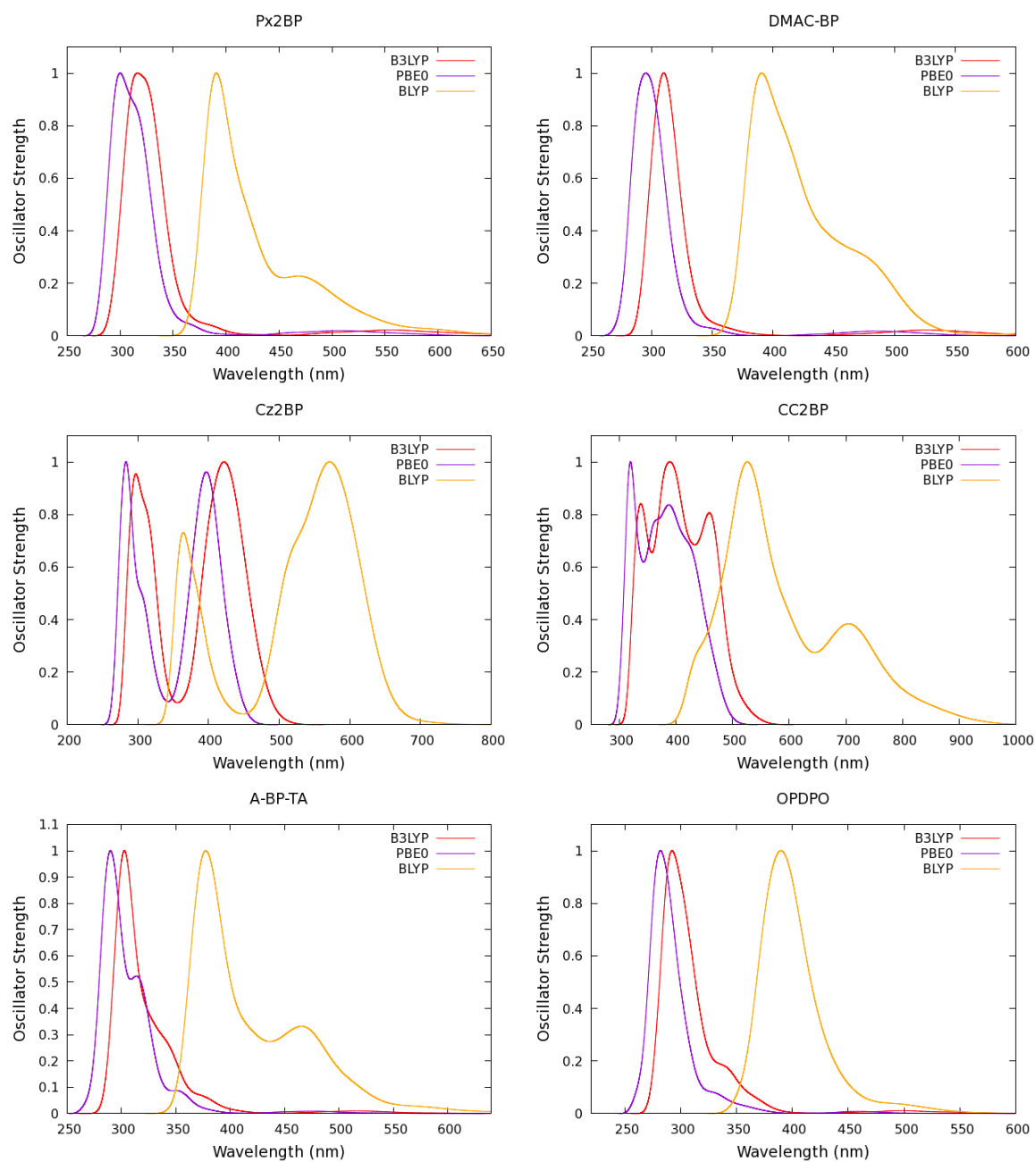


Figure 3.18. Absorption spectra of Group 1 emitters calculated with different functionals.

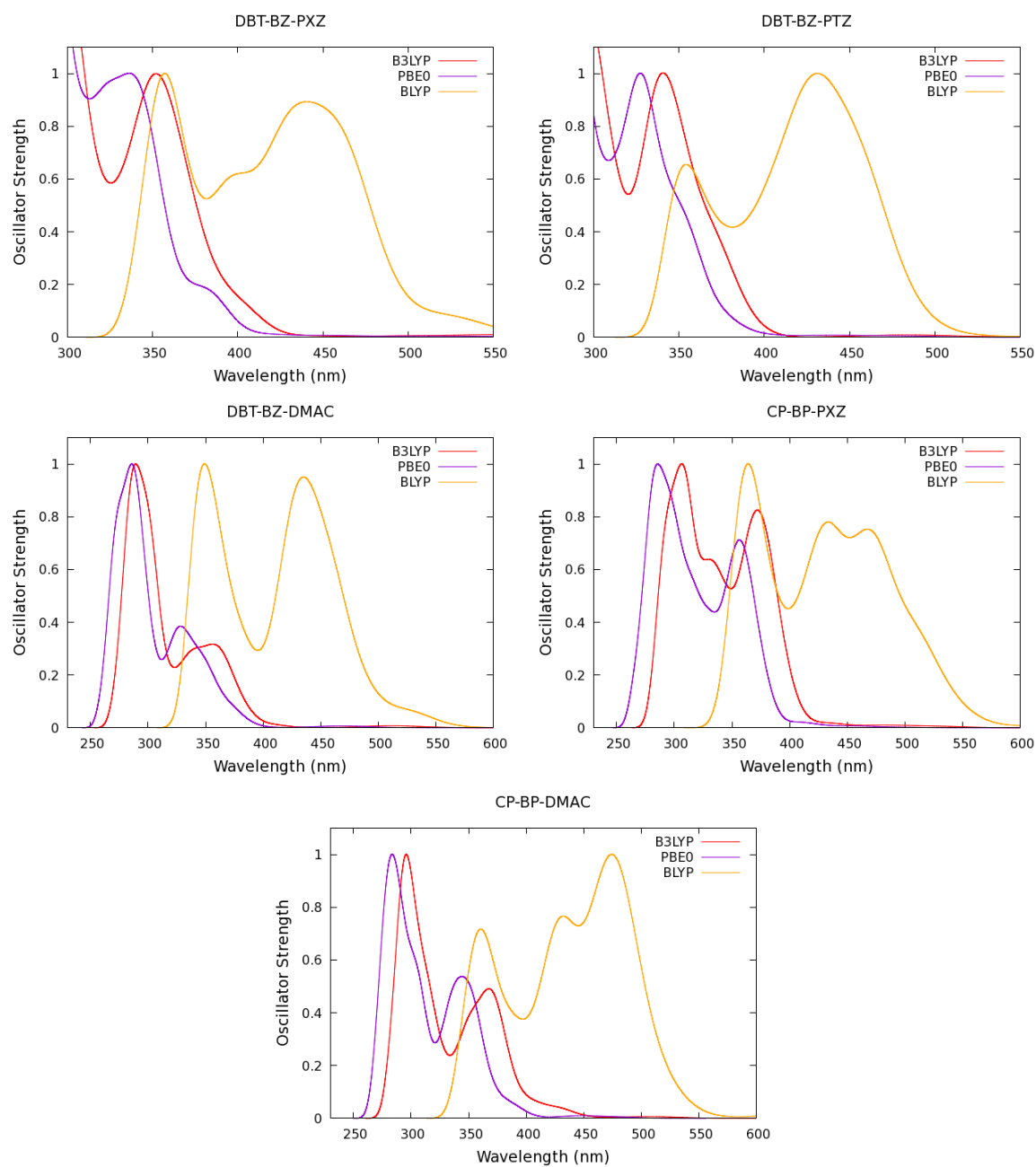


Figure 3.19. Absorption spectra of Group 2 emitters calculated with different functionals.

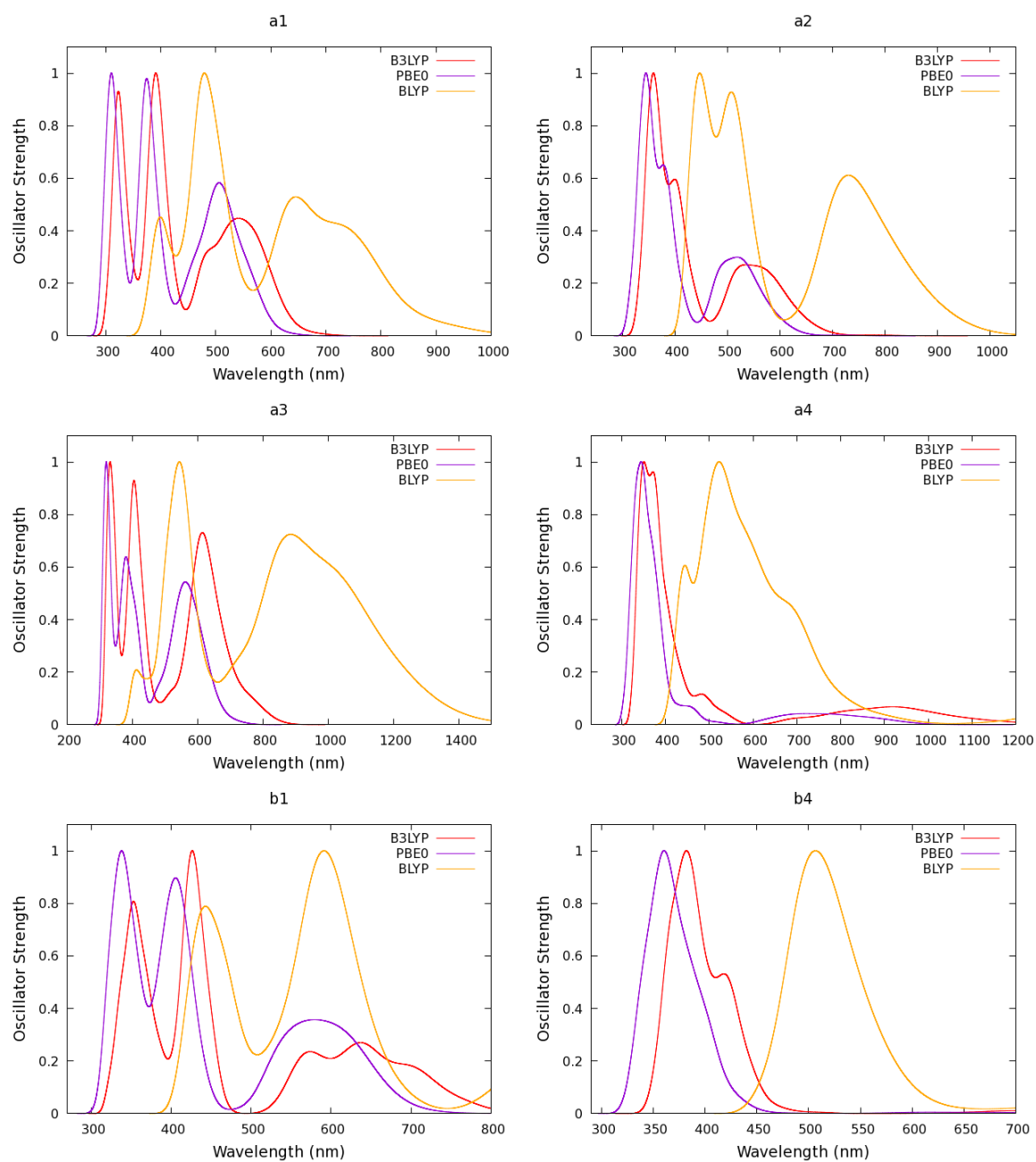


Figure 3.20. Absorption spectra of Group 3 emitters calculated with different functionals.

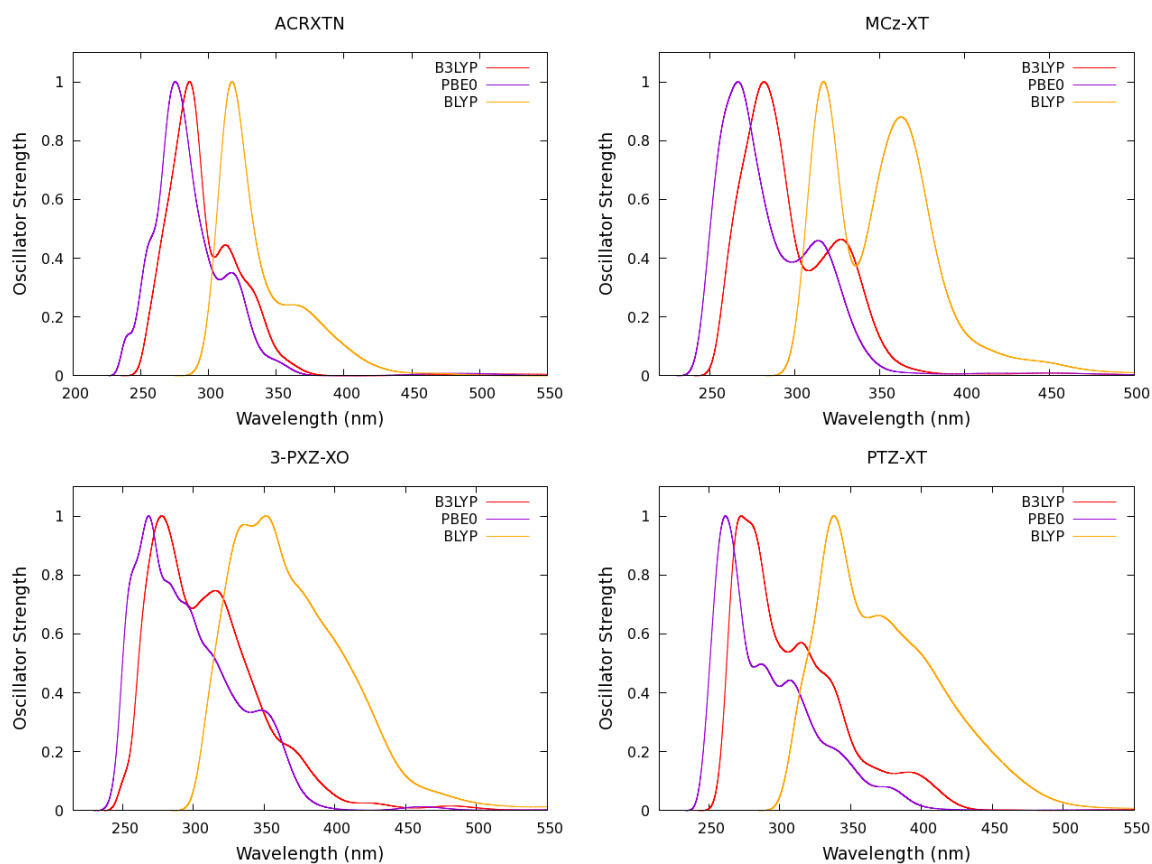


Figure 3.21. Absorption spectra of Group 4 emitters calculated with different functionals.

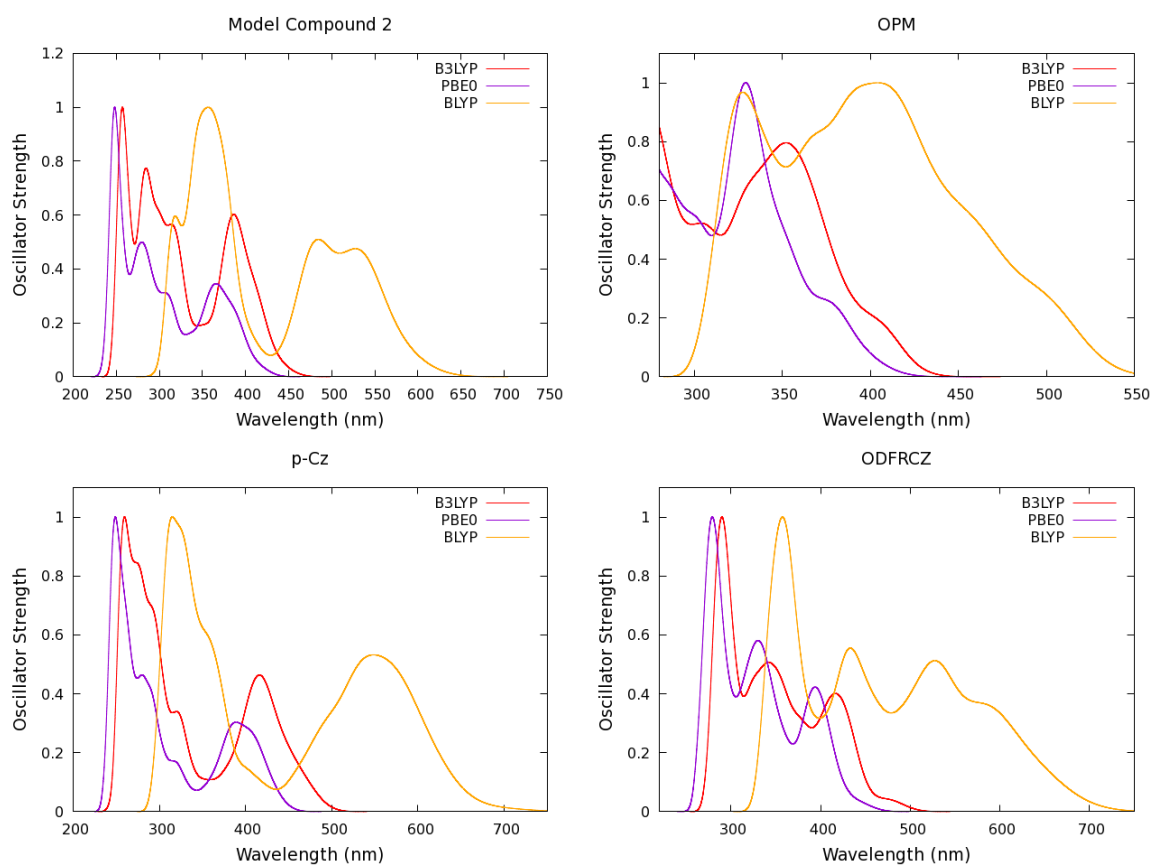


Figure 3.22. Absorption spectra of non-TADF emitters (Model Compound 2, OPM, *p*-Cz, ODFRCZ) calculated with different functionals.

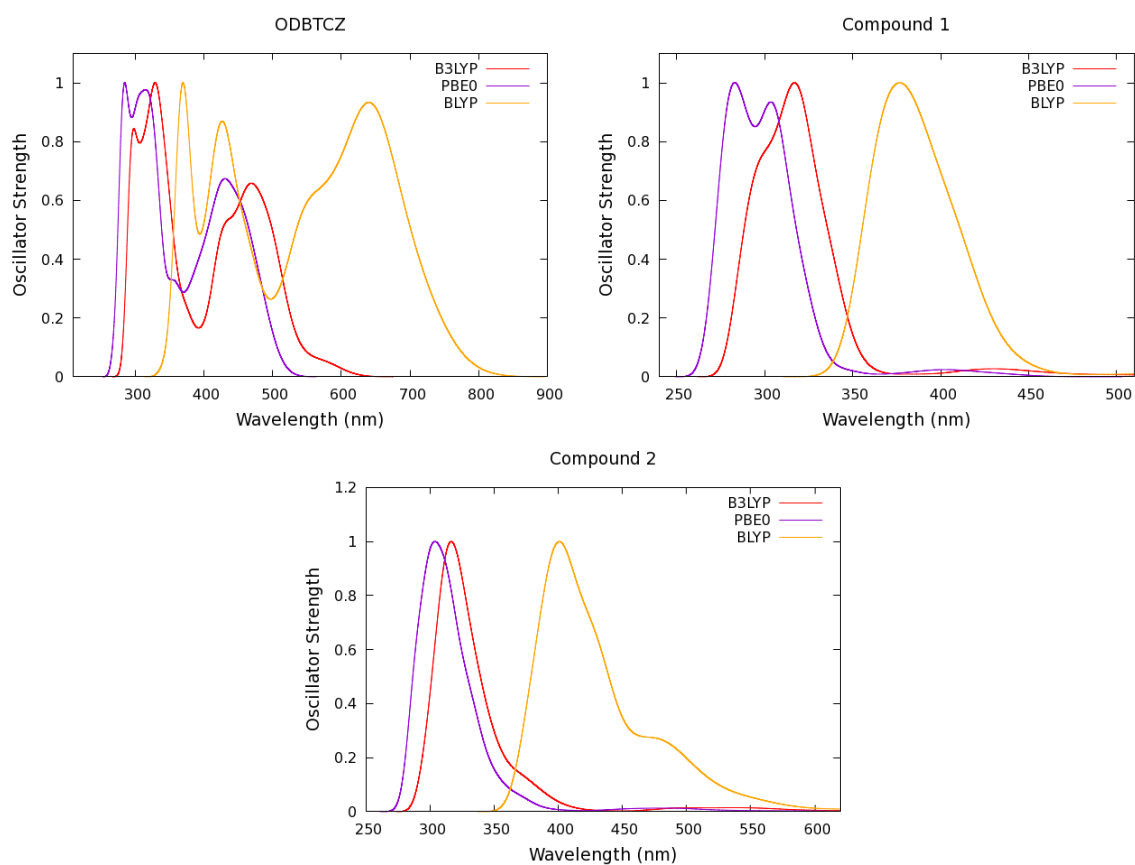


Figure 3.23. Absorption spectra of non-TADF emitters (ODBTCZ, Compound 1, Compound 2) calculated with different functionals.

Although the molecular structures of the Group 4 emitters are fairly rigid, the absorption spectra of them are prominently blue-shifted. This can be attributed to the D-A structure of the compounds where the presence of a single electron donating group might have an impact on the increased LE character. The decreased efficiency of the up-conversion from T_1 to S_1 in the D-A type emitters was reported previously by Chen *et al.* [125].

3.6. Descriptor Analysis

3.6.1. Torsion Angle

Torsion angle of a TADF emitter can be expressed as the dihedral angle between the donor and acceptor units. Twisted D-A structures are highly preferred in the design of TADF emitters since the increased orthogonality and rigidity of donor and acceptor groups interfere with the π -conjugation and gives rise to spatially separated HOMO and LUMO levels and reduced low-lying singlet triplet energy gaps [23,125]. Therefore, the structures and linkage positions of donor groups have a significant impact on TADF activities.

Torsion angles must be examined well since optical and photophysical properties of TADF compounds are determined by the structural attributes to a great extent. With this purpose, D-A torsion angles belonging to the S_0 and T_1 geometries of the investigated TADF and non-TADF compounds have been examined.

As depicted from Figure 3.24 to Figure 3.28, the molecules investigated in this study are given with their torsion angles, which are represented by the θ symbol. The values for the torsion angles are reported in Tables 3.3-3.7 for each group of emitters as well. Since D-A bonds in symmetrical D-A-D type emitters usually exhibit very close torsion angles, the torsion angle of only one of the D-A bonds has been included for each symmetrical emitter in the tables. However, for the unsymmetrical D-A-D emitters, the torsion angle of the donor group in which the HOMO level is localized has been taken into account by analyzing the NTOs. For instance, if the HOMO level

is localized on the other donor in the T_1 optimization due to structural changes, the torsion angle of that donor has been reported. Besides unsymmetrical emitters, two different torsion angles have been reported for the symmetrical TADF emitter b1 since its HOMO level becomes localized on the other donor group in the T_1 geometry. A comprehensive discussion on NTOs has been made in the following chapters as well. For the π -bridge containing b1 and b4, the torsion angles between the donor and π -bridge have been reported.

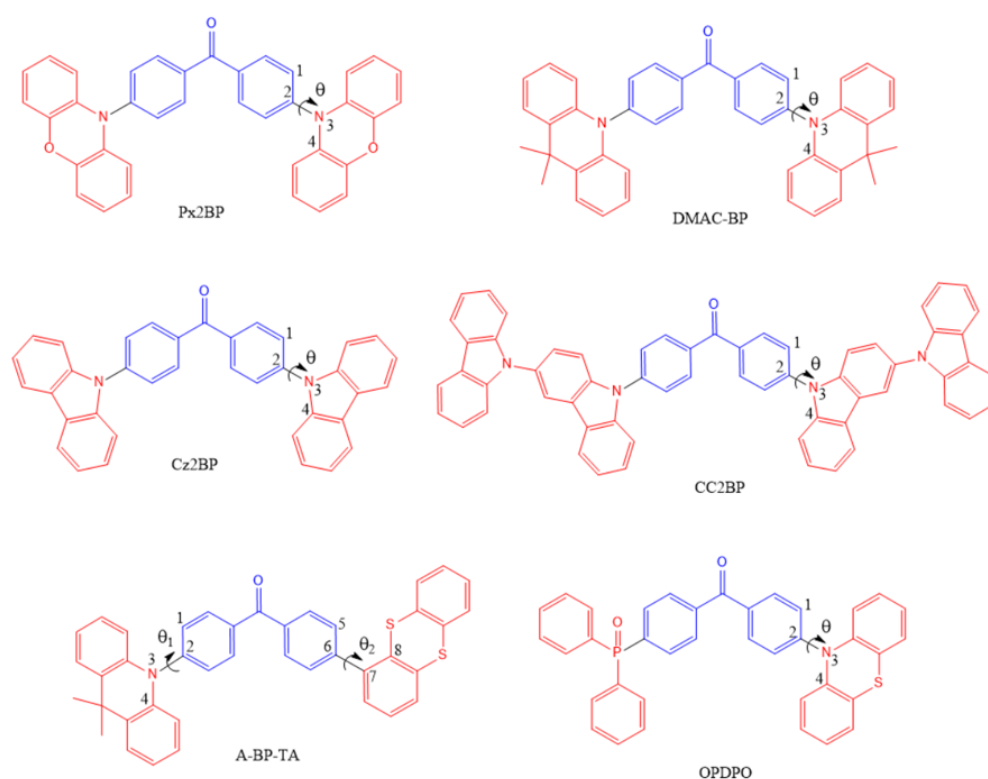


Figure 3.24. Group 1 emitters with their investigated torsion angles (For A-BP-TA, θ_1 has been taken for the S_0 geometry, while θ_2 has been taken for the T_1 geometry).

Table 3.3. Torsion angles (θ) for the Group 1 emitters measured from the S_0 and T_1 geometries (M06-2X/6-31+G(d,p)).

Compound	θ (S_0 Geometry)	θ (T_1 Geometry)
Px2BP	76.41	107.90
DMAC-BP	90.29	90.91
Cz2BP	51.43	48.19
CC2BP	54.35	43.33
A-BP-TA	89.41	38.90
OPDPO	76.93	90.06

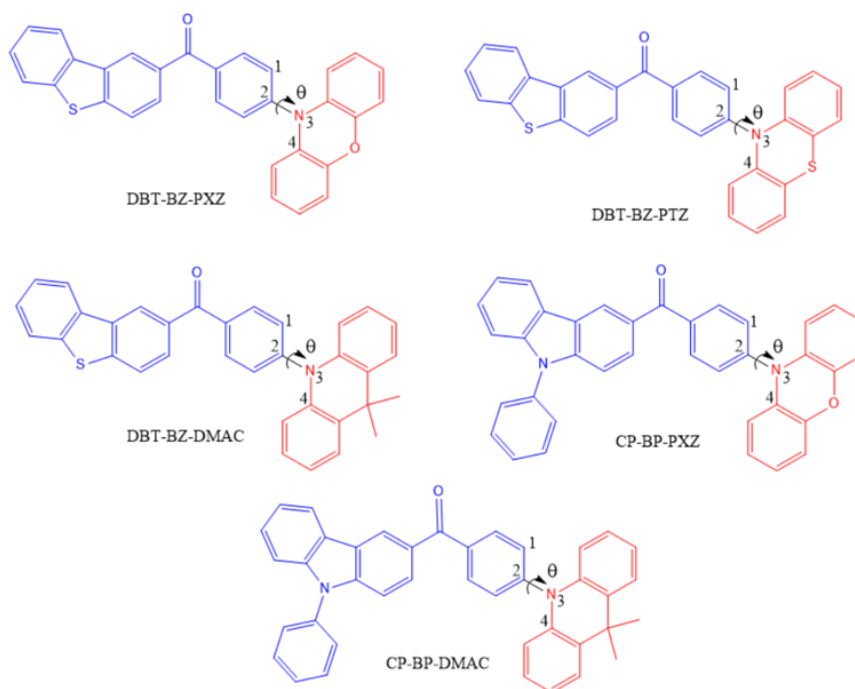


Figure 3.25. Group 2 emitters with their investigated torsion angles.

Table 3.4. Torsion angles (θ) for the Group 2 emitters measured from the S_0 and T_1 geometries (M06-2X/6-31+G(d,p)).

Compound	θ (S_0 Geometry)	θ (T_1 Geometry)
DBT-BZ-PXZ	76.10	83.84
DBT-BZ-PTZ	101.79	90.21
DBT-BZ-DMAC	90.14	90.11
CP-BP-PXZ	77.26	93.80
CP-BP-DMAC	89.82	88.90

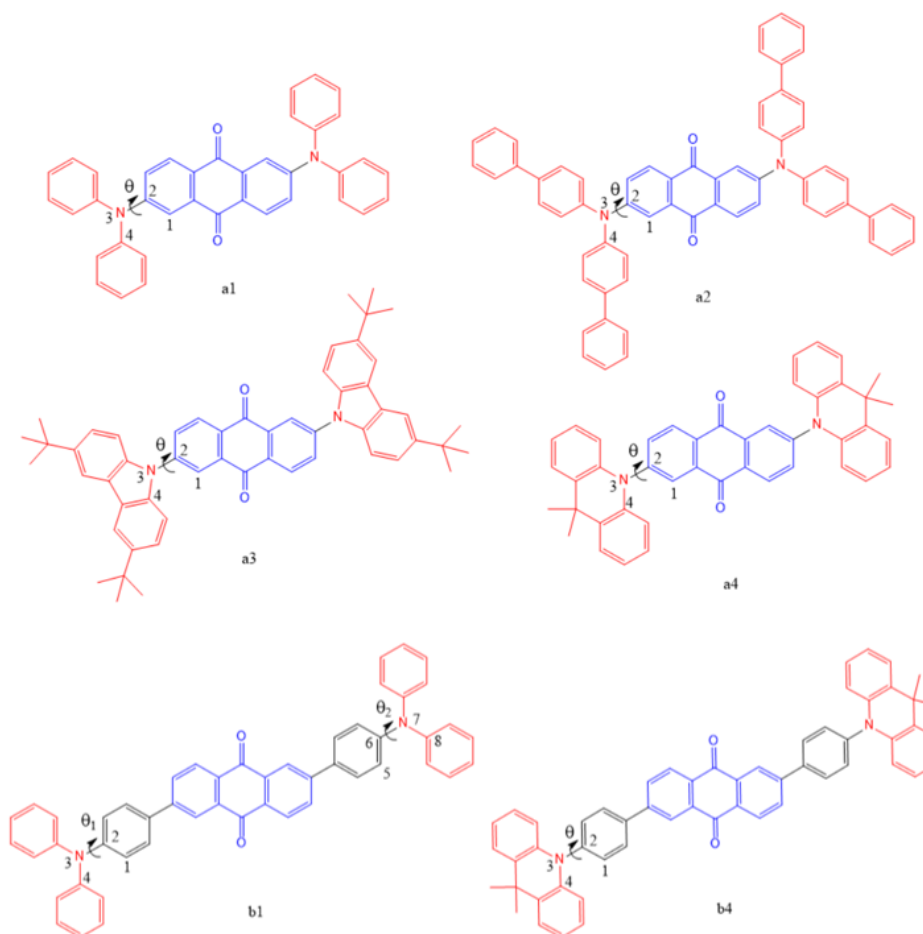


Figure 3.26. Group 3 emitters with their investigated torsion angles (For b1, θ_1 has been taken for the S_0 geometry, while θ_2 has been taken for the T_1 geometry).

Table 3.5. Torsion angles (θ) for the Group 3 emitters measured from the S_0 and T_1 geometries. (M06-2X/6-31+G(d,p))

Compound	θ (S_0 Geometry)	θ (T_1 Geometry)
a1	28.01	30.54
a2	28.81	33.32
a3	47.84	45.42
a4	90.95	90.67
b1	36.16	39.68
b2	89.40	91.00

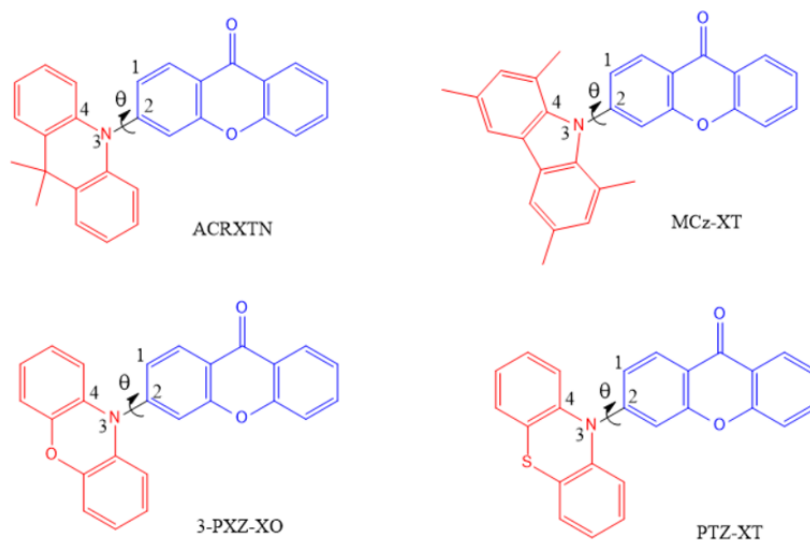


Figure 3.27. Group 4 emitters with their investigated torsion angles.

Table 3.6. Torsion angles (θ) for the Group 4 emitters measured from the S_0 and T_1 geometries (M06-2X/6-31+G(d,p)).

Compound	θ (S_0 Geometry)	θ (T_1 Geometry)
ACRXTN	87.79	90.21
MCz-XT	106.62	92.89
3-PXZ-XO	75.81	74.04
PTZ-XT	101.64	91.49

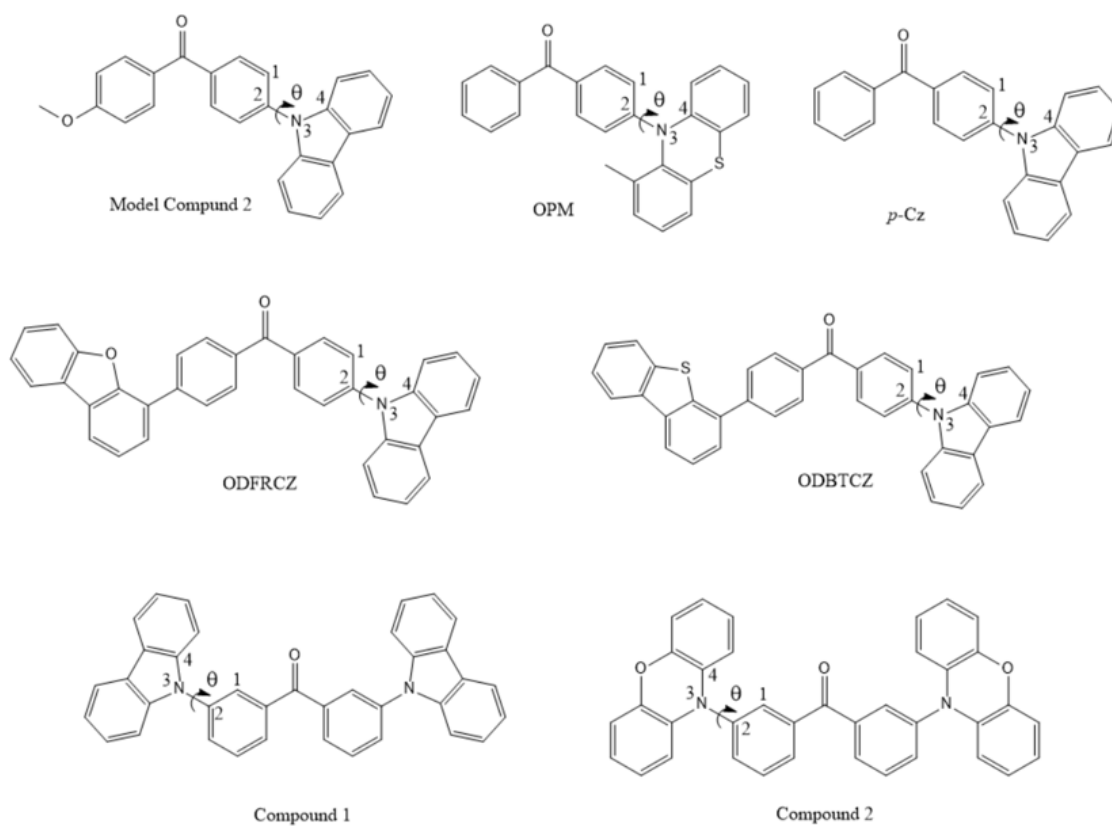


Figure 3.28. Non-TADF compounds with their investigated torsion angles.

Table 3.7. Torsion angles (θ) for non-TADF emitters measured from the S_0 and T_1 geometries (M06-2X/6-31+G(d,p)).

Compound	θ (S_0 Geometry)	θ (T_1 Geometry)
Model Compound 2	52.06	41.45
OPM	21.76	10.05
<i>p</i> -Cz	51.59	43.66
ODFRCZ	51.45	43.69
ODBTCZ	52.73	54.20
Compound 1	53.63	41.19
Compound 2	79.38	95.14

The reported torsion angles clearly indicate that the DMAC donors possess the largest torsion angles due to its dimethyl group which makes the structure of DMAC fairly rigid. Also the hydrogens on the DMAC donors interfere with the hydrogens on the phenyl rings of the benzophenone moiety, as depicted in Figure 3.29. This structural feature restricts the free rotation of DMAC and eliminates the inefficient conformations by locking the dihedral angle at around 90° [126]. Thus, compounds bearing DMAC electron donating units such as DMAC-BP, DBT-BZ-DMAC, CP-BP-DMAC, a4, b4 and ACRXTN, have highly twisted D-A torsion angles.

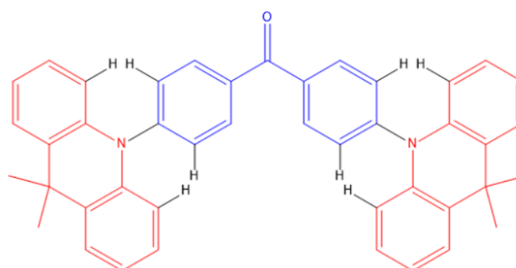


Figure 3.29. Molecular structure of DMAC-BP depicting the positions of the hydrogens which cause a highly twisted structure.

Donors PXZ and PTZ also possess high torsion angles around 75° in their ground state geometries. In their T_1 geometries, PXZ and PTZ donors become planar, and this leads to torsion angles around 90° , like in the cases of OPDPO, DBT-BZ-PXZ, DBT-BZ-PTZ, CP-BP-PXZ, PTZ-XT and non-TADF Compound 2. Px2BP and 3-PXZ-XO are exceptions where the torsion angles did not increase remarkably upon planarization.

Compounds bearing Cz donors and its derivatives usually exhibit smaller torsion angles when compared to the compounds with DMAC, PXZ or PTZ donor groups, because rotation of smaller Cz rings are less restricted. The examples include TADF emitters such as Cz2BP, CC2BP, a3, MCz-XT; and non-TADF emitters like Model Compound 2, *p*-Cz, ODFRCZ, ODBTCZ and Compound 1. Similar to DMAC, the structure of Cz does not change in T_1 optimizations, thus the torsion angles of the compounds bearing Cz donors are similar in the ground state and T_1 geometries.

The emitters with DPA donating groups display the smallest torsion angles in general. The examples include a1, a2 and b1. The unrestricted rotation of the phenyl rings of the DPA moiety leads to an uninterrupted π -conjugation and smaller torsion angles.

The non-TADF compound OPM exhibits the lowest torsion angle despite having a PTZ donor. The unexpected bending of the C-N bond between the D-A moieties of this compound accounts for the low torsion angle observed.

For a better comprehension, the torsion angles of the investigated compounds are shown in a chart given in Figure 3.30.

whereas values closer to 1 point out the presence of the local excitation.

In Tables 3.8-3.12, ϕ_S indices calculated with BLYP, B3LYP and PBE0 functionals and 6-31+G(d,p) basis set are reported for each group. Occupied and virtual NTOs are also depicted in Figures 3.31-3.41. Only the NTOs generated with B3LYP/6-31+G(d,p) method are shown since there was no visible difference in the NTOs generated with PBE0 and BLYP functionals.

The results of Group 1 TADF emitters clearly indicate the importance of the molecular rigidity for a satisfying HOMO-LUMO separation. As ϕ_S indices and NTO analysis suggest, HOMO-LUMO overlap is high in Cz2BP and CC2BP due to the Cz donor units in these compounds. Low rigidity in Cz donor units leads to lower D-A torsion angles which increase π -delocalization and HOMO-LUMO overlap in both S_0 and T_1 geometries.

In Px2BP, HOMO became localized only on the planarized PXZ donor in T_1 geometry, and the higher torsion angle of this geometry caused higher ϕ_S indices. However in S_0 geometry, where HOMO is localized on both of the PXZ donors, ϕ_S indices are significantly lower. A similar pattern is also present in DMAC-BP, where HOMO became localized only on one of the symmetrical DMAC donors in T_1 geometry. Nonetheless, calculated ϕ_S indices are low in both S_0 and T_1 geometries in this molecule thanks to the orthogonal D-A structures in both geometries.

In A-BP-TA, HOMO level is localized on the more rigid DMAC donor in S_0 geometry, however in T_1 geometry, it becomes localized on the planar thianthrene donating unit. The lower torsion angle induced by thianthrene donor caused an increase in the ϕ_S indices in T_1 geometry. In OPDPO, the molecular structure did not change drastically in T_1 optimization. Thus, HOMO is localized on the PTZ donor in both S_0 and T_1 geometries and the ϕ_S indices are sufficiently low in both cases.

Table 3.8. ϕ_S indices for Group 1 emitters in Lowdin (L) and Mulliken (M) charge distributions for the excitations from S_0 to S_1 .

Compound	Method	S_0 Geometry		T_1 Geometry	
		L	M	L	M
Px2BP	BLYP	0.2055	0.3682	0.3708	0.4718
	B3LYP	0.2191	0.3793	0.6097	0.7479
	PBE0	0.2594	0.4034	0.5827	0.7093
DMAC-BP	BLYP	0.2250	0.3392	0.1939	0.2765
	B3LYP	0.2488	0.3519	0.1991	0.2920
	PBE0	0.2515	0.3240	0.2169	0.2911
Cz2BP	BLYP	0.3584	0.4066	0.4085	0.4703
	B3LYP	0.4209	0.4763	0.4603	0.5073
	PBE0	0.4596	0.5099	0.4904	0.5269
CC2BP	BLYP	0.1807	0.2195	0.2586	0.2972
	B3LYP	0.3059	0.3566	0.5206	0.6021
	PBE0	0.3703	0.4126	0.5681	0.6363
A-BP-TA	BLYP	0.0642	0.1109	0.1226	0.1942
	B3LYP	0.0943	0.1396	0.4509	0.5170
	PBE0	0.1208	0.1489	0.4743	0.5342
OPDPO	BLYP	0.2336	0.2336	0.1213	0.1477
	B3LYP	0.2019	0.2609	0.1009	0.1265
	PBE0	0.2183	0.2777	0.1255	0.1427

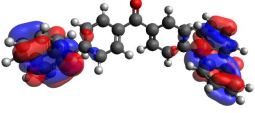
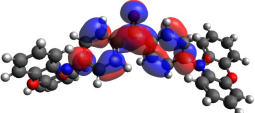
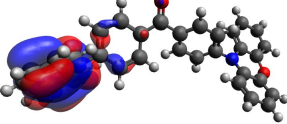
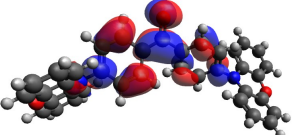
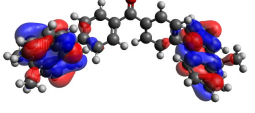
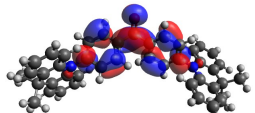
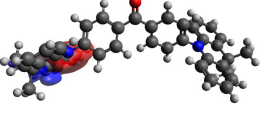
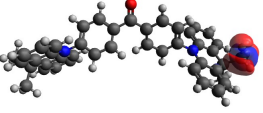
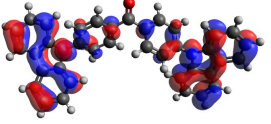
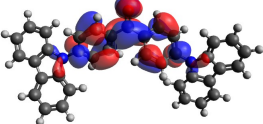
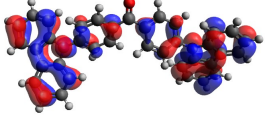
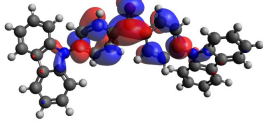
Compound	Geometry	Occupied	Virtual
Px2BP	S_0		
	T_1		
DMAC-BP	S_0		
	T_1		
Cz2BP	S_0		
	T_1		

Figure 3.31. Occupied and virtual NTOs for Px2BP, DMAC-BP and Cz2BP (TDA: B3LYP/6-31+G(d,p)).

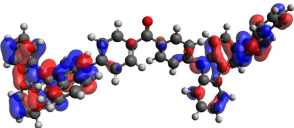
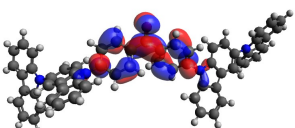
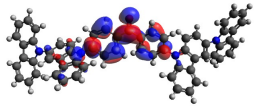
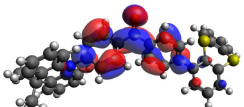
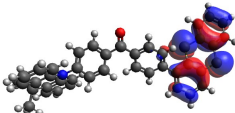
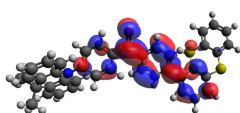
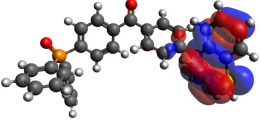
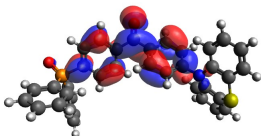
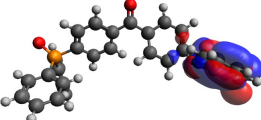
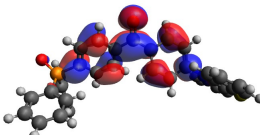
Compound	Geometry	Occupied	Virtual
CC2BP	S_0		
	T_1		
A-BP-TA	S_0		
	T_1		
OPDPO	S_0		
	T_1		

Figure 3.32. Occupied and virtual NTOs for CC2BP, A-BP-TA and OPDPO (TDA: B3LYP/6-31+G(d,p)).

Table 3.9. ϕ_S indices for Group 2 emitters in Lowdin (L) and Mulliken (M) charge distributions for the excitations from S_0 to S_1 .

Compound	Method	S_0 Geometry		T_1 Geometry	
		L	M	L	M
DBT-BZ-PXZ	BLYP	0.1763	0.2764	0.1633	0.2490
	B3LYP	0.1667	0.2660	0.1279	0.2146
	PBE0	0.1774	0.2641	0.1318	0.2060
DBT-BZ-PTZ	BLYP	0.1991	0.3187	0.1372	0.1827
	B3LYP	0.2825	0.4175	0.1480	0.2004
	PBE0	0.3762	0.4940	0.1531	0.1988
DBT-BZ-DMAC	BLYP	0.1057	0.1781	0.1359	0.1978
	B3LYP	0.1080	0.1814	0.1967	0.2656
	PBE0	0.1274	0.1767	0.1998	0.2473
CP-BP-PXZ	BLYP	0.1743	0.2630	0.1425	0.2189
	B3LYP	0.1994	0.2907	0.1494	0.2357
	PBE0	0.2185	0.2949	0.1695	0.2403
CP-BP-DMAC	BLYP	0.1162	0.1958	0.1163	0.1753
	B3LYP	0.1618	0.2473	0.1514	0.2138
	PBE0	0.1634	0.2198	0.1639	0.2136

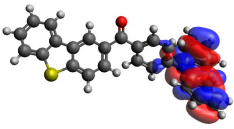
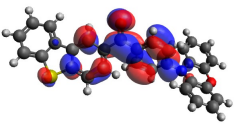
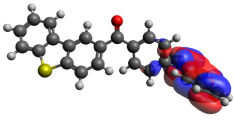
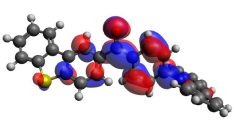
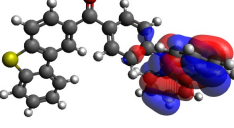
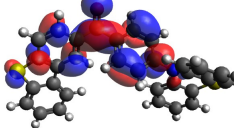
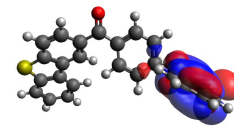
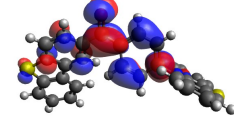
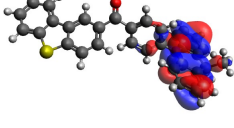
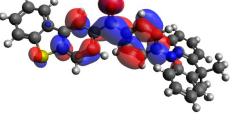
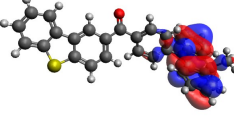
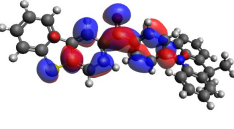
Compound	Geometry	Occupied	Virtual
DBT-BZ-PXZ	S_0		
	T_1		
DBT-BZ-PTZ	S_0		
	T_1		
DBT-BZ-DMAC	S_0		
	T_1		

Figure 3.33. Occupied and virtual NTOs for DBT-BZ-PXZ, DBT-BZ-PTZ and DBT-BZ-DMAC (TDA: B3LYP/6-31+G(d,p)).

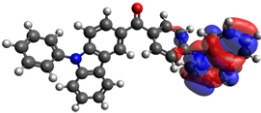
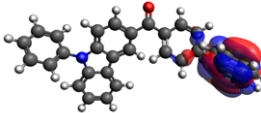
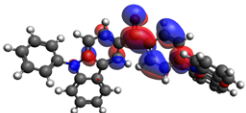
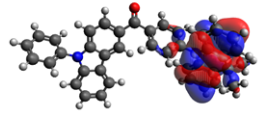
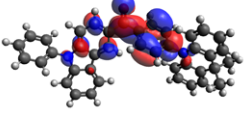
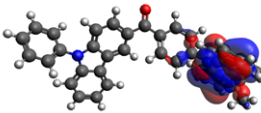
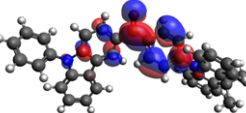
Compound	Geometry	Occupied	Virtual
CP-BP-PXZ	S_0		
	T_1		
CP-BP-DMAC	S_0		
	T_1		

Figure 3.34. Occupied and virtual NTOs for CP-BP-PXZ and CP-BP-DMAC (TDA: B3LYP/6-31+G(d,p)).

Group 2 emitters exhibited similar ϕ_S indices and NTO profiles in all compounds. The planar PXZ and PTZ donors caused a slight decrease in the ϕ_S indices in the T_1 geometries of DBT-BZ-PXZ, DBT-BZ-PTZ and CP-BP-PXZ. Nevertheless, HOMO-LUMO separation is at a sufficient level in both S_0 and T_1 geometries in these compounds. In DMAC containing DBT-BZ-DMAC and CP-BP-DMAC, similar and adequately low ϕ_S indices have been obtained in both S_0 and T_1 geometries.

Table 3.10. ϕ_S indices for Group 3 emitters in Lowdin (L) and Mulliken (M) charge distributions for the excitations from S_0 to S_1 .

Compound	Method	S_0 Geometry		T_1 Geometry	
		L	M	L	M
a1	BLYP	0.6604	0.7240	0.6843	0.7351
	B3LYP	0.6685	0.7327	0.6839	0.7329
	PBE0	0.6625	0.7143	0.6833	0.7260
a2	BLYP	0.6932	0.7263	0.6253	0.7404
	B3LYP	0.6704	0.7094	0.6992	0.7284
	PBE0	0.6780	0.7128	0.7124	0.7476
a3	BLYP	0.4419	0.4952	0.4780	0.5468
	B3LYP	0.5299	0.5520	0.5689	0.5896
	PBE0	0.5827	0.5973	0.6219	0.6335
a4	BLYP	0.0444	0.0475	0.0497	0.0552
	B3LYP	0.0607	0.0634	0.0546	0.0591
	PBE0	0.0611	0.0601	0.0597	0.0614
b1	BLYP	0.4099	0.4517	0.3369	0.3588
	B3LYP	0.3682	0.3996	0.3627	0.3784
	PBE0	0.4419	0.4656	0.5492	0.5688
b4	BLYP	0.0262	0.0549	0.0408	0.0730
	B3LYP	0.0929	0.1262	0.0544	0.0862
	PBE0	0.1075	0.1335	0.0817	0.1082

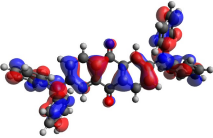
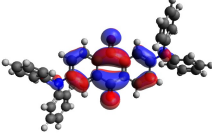
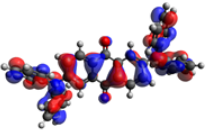
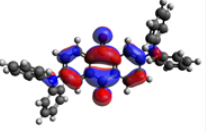
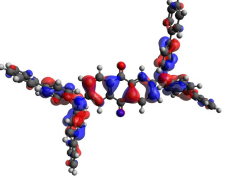
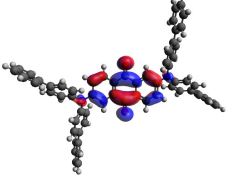
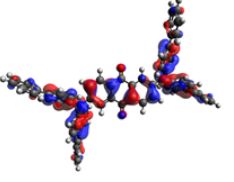
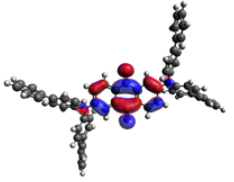
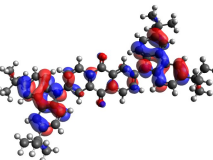
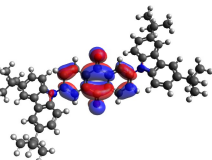
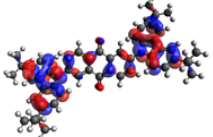
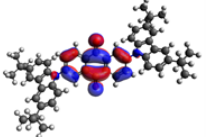
Compound	Geometry	Occupied	Virtual
a1	S_0		
	T_1		
a2	S_0		
	T_1		
a3	S_0		
	T_1		

Figure 3.35. Occupied and virtual NTOs for a1, a2 and a3 (TDA: B3LYP/6-31+G(d,p)).

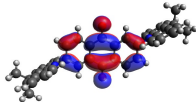
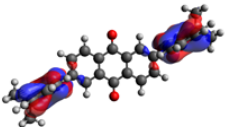
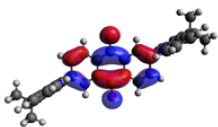
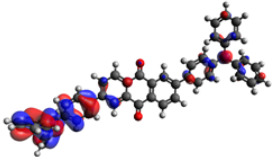
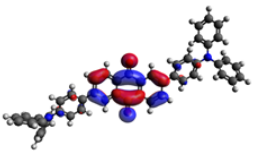
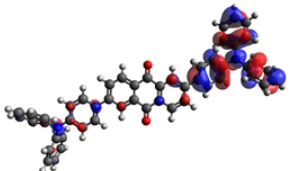
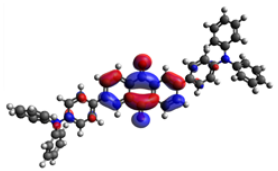
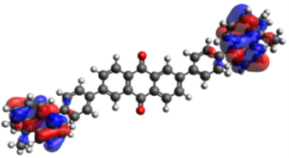
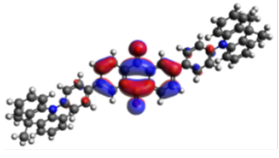
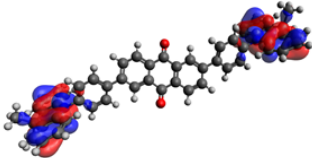
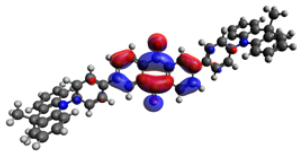
Compound	Geometry	Occupied	Virtual
a4	S_0		
	T_1		
b1	S_0		
	T_1		
b4	S_0		
	T_1		

Figure 3.36. Occupied and virtual NTOs for a4, b1 and b4 (TDA: B3LYP/6-31+G(d,p)).

Group 3 emitters exhibit relatively high ϕ_S indices and large HOMO-LUMO overlap except for the DMAC containing compounds a4 and b4. Freely rotating DPA donors in a1, a2 and π -bridge containing b1 induce low D-A torsion angles, which cause π -delocalization and HOMO-LUMO overlap. Similarly in a3, tert-butyl containing Cz donors exhibit low torsion angles, as in the cases of Cz2BP and CC2BP. Therefore, due to low rigidity introduced by the donor groups, HOMO-LUMO overlap and the ϕ_S indices are high in the compounds a1, a2, a3 and b1. In DMAC containing a4 and its π -bridge bearing analogue b4, the ϕ_S indices have been calculated to be lower because of the increased rigidity in these compounds.

Table 3.11. ϕ_S indices for Group 4 emitters in Lowdin (L) and Mulliken (M) charge distributions for the excitations from S_0 to S_1 .

Compound	S_0 Geometry		T_1 Geometry	
	L	M	L	M
ACRXTN	0.0460	0.0622	0.0516	0.0628
	0.0610	0.0820	0.0595	0.0711
	0.0803	0.1056	0.0665	0.0767
MCz-XT	0.0682	0.1062	0.1272	0.1371
	0.1038	0.1531	0.1199	0.1294
	0.1117	0.1402	0.1244	0.1323
3-PXZ-XO	0.0507	0.0885	0.3427	0.4065
	0.0767	0.1311	0.3243	0.3972
	0.0918	0.1535	0.2937	0.3537
PTZ-XT	0.0776	0.1619	0.0706	0.0757
	0.1028	0.1755	0.0721	0.0760
	0.1178	0.1796	0.0810	0.0841

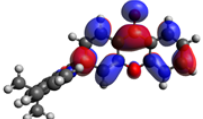
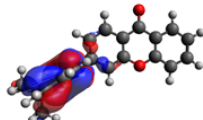
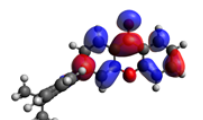
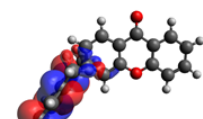
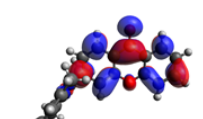
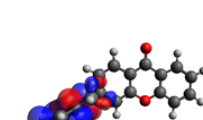
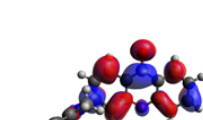
Compound	Geometry	Occupied	Virtual
ACRXTN	S_0		
	T_1		
MCz-XT	S_0		
	T_1		

Figure 3.37. Occupied and virtual NTOs for ACRXTN and MCz-XT (TDA: B3LYP/6-31+G(d,p)).

ϕ_S indices and HOMO-LUMO separations are satisfying for all of the compounds included in Group 4. This outcome might be related to the rigid xanthone acceptor core. Nevertheless, in the T_1 geometry of 3-PXZ-XO, an increase in the ϕ_S indices has been observed due to the slightly increased torsion angle in this geometry.

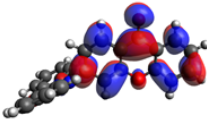
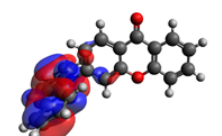
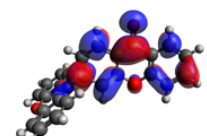
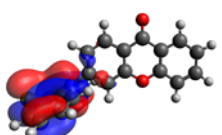
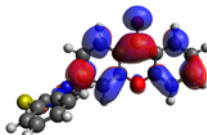
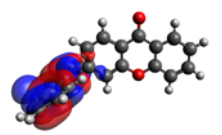
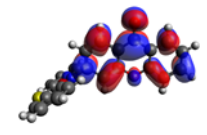
Compound	Geometry	Occupied	Virtual
3-PXZ-XO	S_0		
	T_1		
PTZ-XO	S_0		
	T_1		

Figure 3.38. Occupied and virtual NTOs for 3-PXZ-XO and PTZ-XO (TDA: B3LYP/6-31+G(d,p)).

Table 3.12. ϕ_S indices for non-TADF emitters in Lowdin (L) and Mulliken (M) charge distributions for the excitations from S_0 to S_1 .

Compound	Method	S_0 Geometry		T_1 Geometry	
		L	M	L	M
Model Compound 2	BLYP	0.4323	0.4719	0.5595	0.5967
	B3LYP	0.4643	0.5079	0.5879	0.6259
	PBE0	0.4913	0.5304	0.6026	0.6384
OPM	BLYP	0.4026	0.4926	0.4907	0.5580
	B3LYP	0.5535	0.6354	0.6566	0.7241
	PBE0	0.5611	0.6271	0.6043	0.6658
<i>p</i> -Cz	BLYP	0.3970	0.4344	0.5410	0.5907
	B3LYP	0.4389	0.4847	0.5675	0.6088
	PBE0	0.4885	0.5292	0.5923	0.6335
ODFRCZ	BLYP	0.3811	0.4128	0.5612	0.6112
	B3LYP	0.4664	0.5039	0.5936	0.6435
	PBE0	0.4965	0.5273	0.6101	0.6540
ODBTCZ	BLYP	0.4692	0.4929	0.4296	0.4722
	B3LYP	0.5648	0.5846	0.4911	0.5257
	PBE0	0.5989	0.6107	0.5548	0.5862
Compound 1	BLYP	0.3273	0.3846	0.2953	0.3449
	B3LYP	0.3624	0.4358	0.4369	0.5282
	PBE0	0.4214	0.4902	0.4764	0.5549
Compound 2	BLYP	0.5548	0.6764	0.3857	0.4607
	B3LYP	0.5380	0.6559	0.4208	0.5038
	PBE0	0.4828	0.5937	0.4114	0.4866

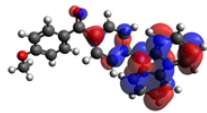
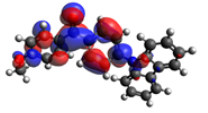
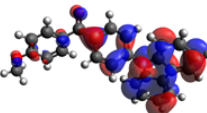
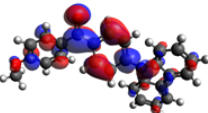
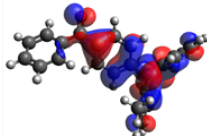
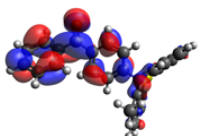
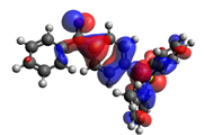
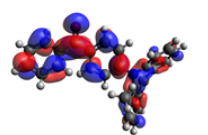
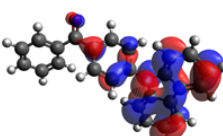
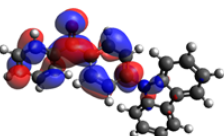
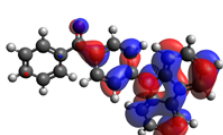
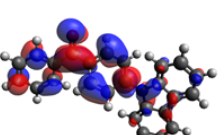
Compound	Geometry	Occupied	Virtual
Model Compound 2	S_0		
	T_1		
OPM	S_0		
	T_1		
<i>p</i> -Cz	S_0		
	T_1		

Figure 3.39. Occupied and virtual NTOs for Model Compound 2, OPM and *p*-Cz (TDA: B3LYP/6-31+G(d,p)).

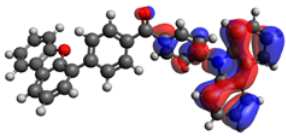
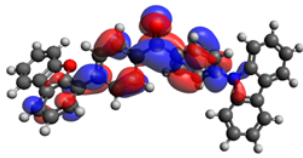
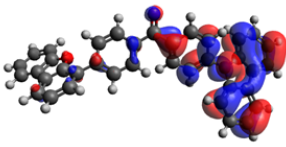
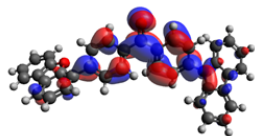
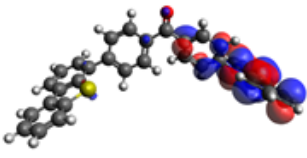
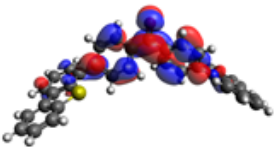
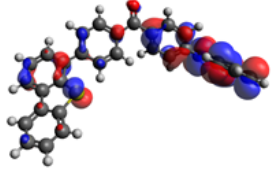
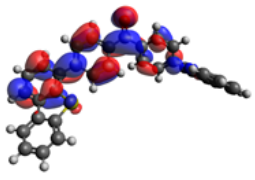
Compound	Geometry	Occupied	Virtual
ODFRCZ	S_0		
	T_1		
ODBTCZ	S_0		
	T_1		

Figure 3.40. Occupied and virtual NTOs for ODFRCZ and ODBTCZ (TDA: B3LYP/6-31+G(d,p)).

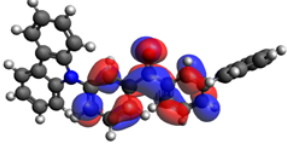
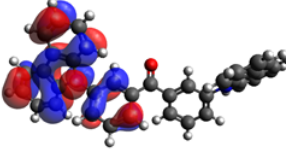
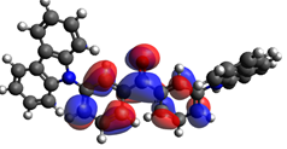
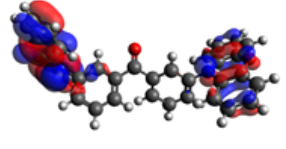
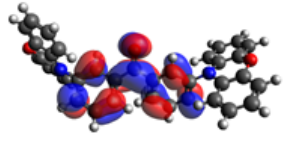
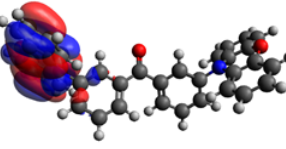
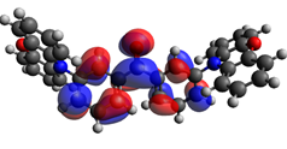
Compound	Geometry	Occupied	Virtual
Compound 1	S_0		
	T_1		
Compound 2	S_0		
	T_1		

Figure 3.41. Occupied and virtual NTOs for Compound 1 and Compound 2 (TDA: B3LYP/6-31+G(d,p)).

[illegible]

Figure 3.42. ϕ_S indices for the investigated emitters calculated from S_0 and T_1 geometries (TDA: B3LYP/6-31+G(d,p)).

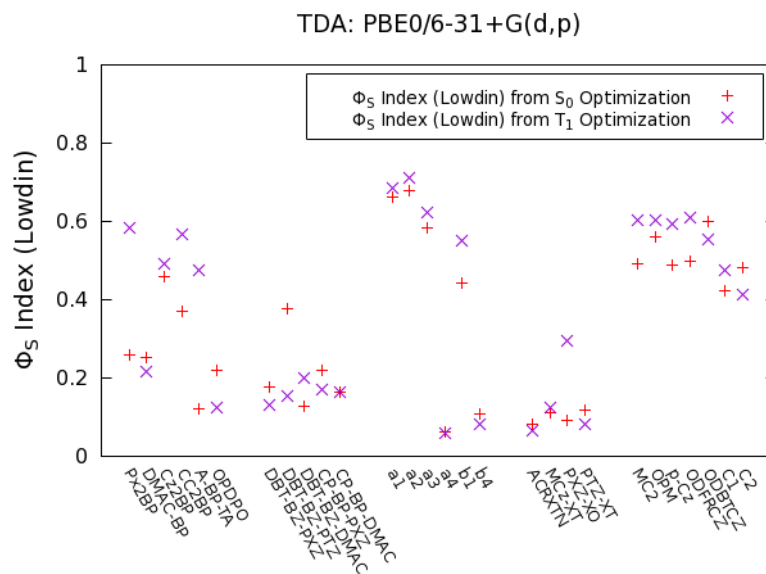


Figure 3.43. ϕ_S indices for the investigated emitters calculated from S_0 and T_1 geometries (TDA: PBE0/6-31+G(d,p)).

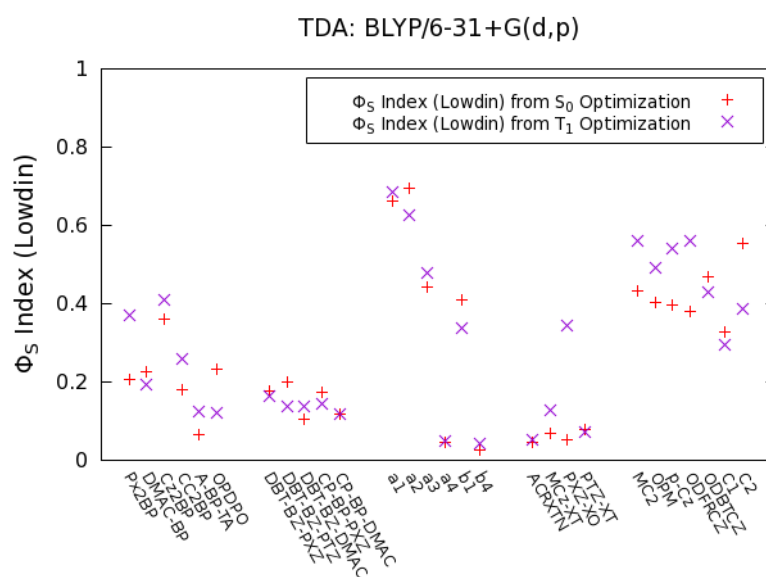


Figure 3.44. ϕ_S indices for the investigated emitters calculated from S_0 and T_1 geometries (TDA: BLYP/6-31+G(d,p)).

As it can be observed from the charts, ϕ_S indices calculated with BLYP are usually lower as compared to B3LYP and PBE0. The inclination of BLYP to produce excitations with more CT character has already been observed in the absorption spectra, since the spectra generated with BLYP were red-shifted.

3.6.3. Low Lying Singlet-Triplet Energy Gaps (ΔE_{ST})

An effective RISC process requires the up-conversion of the triplet excitons into the first singlet excited (S_1) state. Up-conversion of the triplet excitons can be achieved through a reduced singlet-triplet energy gap. Once in the S_1 state, the up-converted excitons can radiate back to the ground state in a delayed process.

A small low lying singlet-triplet gap can be realized by strong electron donating and accepting units aligned in an orthogonal position. The spatially separated donor and acceptor units disrupt π -conjugation and lead to separated HOMO and LUMO levels, resulting in the formation of intramolecular charge transfer (ICT). Consequently, ICT facilitates RISC process which is essential for an efficient TADF emission [129]. Usually, RISC process is less likely to occur if ΔE_{ST} is above 0.3 eV, while a ΔE_{ST} below 0.1 is ideal for an effective up-conversion of the triplet excitons [12].

As reported in the study of Huang *et al.* [130], if T_1 state and the upper lying triplet states are in close proximity, strong mixing between these triplet states through spin-vibronic coupling also enhances the coupling between S_1 and T_1 states. In other words, an enhanced internal conversion (IC) is closely associated with efficient ISC and RISC processes. Therefore, the energy gap between S_1 and T_2 states ($\Delta E_{S_1-T_2}$) should also be investigated since up-conversion may occur from the T_2 state as an alternate RISC path.

Hence, TDA calculations have been performed with BLYP, B3LYP and PBE0 functionals and 6-31+G(d,p) basis set for the investigated TADF and non-TADF emitters, in order to determine the $\Delta E_{S_1-T_1}$ and $\Delta E_{S_1-T_2}$ values. From Tables 3.13 to 3.17, the results calculated from the S_0 and T_1 geometries have been reported. From Figures

3.45 to 3.47, the charts presenting the ΔE_{ST} values of all compounds are given for each functional together with the experimental values. The missing $\Delta E_{S_1-T_2}$ values in some cases indicate that the T_2 state is higher in energy than the S_1 state, therefore they were not estimated.

Table 3.13. Low lying singlet-triplet energy gaps ($\Delta E_{S_1-T_1}$, $\Delta E_{S_1-T_2}$) in eV for Group 1 emitters.

Compound	Method	S_0 Geometry		T_1 Geometry	
		$\Delta E_{S_1-T_1}$	$\Delta E_{S_1-T_2}$	$\Delta E_{S_1-T_1}$	$\Delta E_{S_1-T_2}$
Px2BP	BLYP	0.004	0.002	0.165	-
	B3LYP	0.007	0.005	0.104	-
	PBE0	0.010	0.007	0.106	-
DMAC-BP	BLYP	0.004	0.001	0.014	-
	B3LYP	0.006	0.003	0.013	-
	PBE0	0.009	0.006	0.017	-
Cz2BP	BLYP	0.099	0.090	0.149	0.138
	B3LYP	0.232	0.165	0.278	0.224
	PBE0	0.321	0.216	0.366	0.271
CC2BP	BLYP	0.017	0.013	0.015	-
	B3LYP	0.085	0.069	0.284	0.013
	PBE0	0.165	0.114	0.406	0.025
A-BP-TA	BLYP	0.004	-	0.066	0.002
	B3LYP	0.006	-	0.225	-
	PBE0	0.008	-	0.275	-
OPDPO	BLYP	0.003	-	0.003	-
	B3LYP	0.006	-	0.004	-
	PBE0	0.010	-	0.005	-

ΔE_{ST} values for the Group 1 emitters are usually sufficiently low and in agreement with the high torsion angles and low ϕ_S indices of the compounds. Cz possess-

ing emitters Cz2BP and CC2BP exhibit higher ΔE_{ST} values as compared to Px2BP, DMAC-BP, A-BP-TA and OPDPO, due to the low torsion angles and high HOMO-LUMO overlaps in these compounds introduced by freely rotating Cz donors. Similarly, A-BP-TA displays increased ΔE_{ST} values in its T_1 optimized structure due to the increased overlap between the frontier orbitals in this geometry.

Table 3.14. Low lying singlet-triplet energy gaps ($\Delta E_{S_1-T_1}$) in eV for Group 2 emitters.

Compound	Method	S_0 Geometry	T_1 Geometry
		$\Delta E_{S_1-T_1}$	$\Delta E_{S_1-T_1}$
DBT-BZ-PXZ	BLYP	0.004	0.026
	B3LYP	0.008	0.018
	PBE0	0.011	0.020
DBT-BZ-PTZ	BLYP	0.004	0.004
	B3LYP	0.009	0.005
	PBE0	0.015	0.007
DBT-BZ-DMAC	BLYP	0.004	0.002
	B3LYP	0.006	0.004
	PBE0	0.009	0.009
CP-BP-PXZ	BLYP	0.005	0.011
	B3LYP	0.009	0.011
	PBE0	0.013	0.013
CP-BP-DMAC	BLYP	0.004	0.006
	B3LYP	0.007	0.008
	PBE0	0.010	0.011

Group 2 TADF compounds exhibit low ΔE_{ST} values in both S_0 and T_1 geometries. The compounds bearing DMAC donating groups such as DBT-BZ-DMAC and CP-BP-DMAC are observed to display even slightly smaller ΔE_{ST} values.

Table 3.15. Low lying singlet-triplet energy gaps ($\Delta E_{S_1-T_1}$, $\Delta E_{S_1-T_2}$) in eV for Group 3 emitters.

Compound	Method	S_0 Geometry		T_1 Geometry	
		$\Delta E_{S_1-T_1}$	$\Delta E_{S_1-T_2}$	$\Delta E_{S_1-T_1}$	$\Delta E_{S_1-T_2}$
a1	BLYP	0.375	0.254	0.440	0.309
	B3LYP	0.443	0.284	0.481	0.302
	PBE0	0.483	0.317	0.513	0.324
a2	BLYP	0.338	0.238	0.376	0.277
	B3LYP	0.398	0.258	0.428	0.280
	PBE0	0.435	0.286	0.455	0.295
a3	BLYP	0.182	0.138	0.239	0.183
	B3LYP	0.211	0.138	0.272	0.177
	PBE0	0.234	0.151	0.291	0.184
a4	BLYP	0.005	0.004	0.005	0.004
	B3LYP	0.008	0.004	0.007	0.004
	PBE0	0.010	0.005	0.008	0.004
b1	BLYP	0.107	0.085	0.127	0.088
	B3LYP	0.150	0.104	0.346	0.110
	PBE0	0.179	0.124	0.400	0.097
b4	BLYP	0.001	0.001	0.002	0.002
	B3LYP	0.001	0.001	0.001	0.001
	PBE0	0.001	0.001	0.001	0.001

Group 3 emitters exhibit remarkably high ΔE_{ST} values for the compounds a1, a2 and a3, because of the low rigidity in these compounds introduced by DPA and Cz donors. As mentioned previously, low rigidity causes increased overlap between HOMO and LUMO levels as π -conjugation becomes favourable. Despite having DPA donors, b1 exhibits slightly lower ΔE_{ST} values. The lowered singlet-triplet gap was probably acquired by the π -bridges in this compound which spatially separate donor

and acceptor units. As expected, a4 and b4 possess lower ΔE_{ST} due to the rigid DMAC donors and increased torsion angles.

Table 3.16. Low lying singlet-triplet energy gaps ($\Delta E_{S_1-T_1}$) in eV for Group 4 emitters.

Compound	Method	S_0 Geometry	T_1 Geometry
		$\Delta E_{S_1-T_1}$	$\Delta E_{S_1-T_1}$
ACRXTN	BLYP	0.006	0.006
	B3LYP	0.010	0.008
	PBE0	0.013	0.011
MCz-XT	BLYP	0.006	0.009
	B3LYP	0.009	0.011
	PBE0	0.012	0.014
3-PXZ-XO	BLYP	0.006	0.089
	B3LYP	0.011	0.066
	PBE0	0.015	0.070
PTZ-XT	BLYP	0.006	0.012
	B3LYP	0.013	0.018
	PBE0	0.020	0.022

The low ΔE_{ST} values for Group 4 emitters are also in line with the low ϕ_S indices and HOMO-LUMO overlaps observed in these compounds. The calculated ΔE_{ST} values are also compatible with the experimental ones.

Table 3.17. Low lying singlet-triplet energy gaps ($\Delta E_{S_1-T_1}$, $\Delta E_{S_1-T_2}$) in eV for non-TADF emitters.

Compound	Method	S_0 Geometry		T_1 Geometry	
		$\Delta E_{S_1-T_1}$	$\Delta E_{S_1-T_2}$	$\Delta E_{S_1-T_1}$	$\Delta E_{S_1-T_2}$
MC2	BLYP	0.152	-	0.445	0.118
	B3LYP	0.289	0.037	0.651	0.152
	PBE0	0.392	0.170	0.743	0.241
OPM	BLYP	0.338	-	0.595	0.220
	B3LYP	0.667	0.307	0.944	0.350
	PBE0	0.755	0.436	1.019	0.422
<i>p</i> -Cz	BLYP	0.164	-	0.443	-
	B3LYP	0.275	-	0.613	0.011
	PBE0	0.358	0.053	0.697	0.127
ODFRCZ	BLYP	0.131	-	0.372	-
	B3LYP	0.238	0.038	0.553	0.024
	PBE0	0.322	0.187	0.637	0.124
ODBTCZ	BLYP	0.124	-	0.059	-
	B3LYP	0.218	0.048	0.591	-
	PBE0	0.292	0.179	0.765	-
C1	BLYP	0.060	0.057	0.101	-
	B3LYP	0.123	0.118	0.283	-
	PBE0	0.161	0.156	0.343	-
C2	BLYP	0.012	-	0.011	-
	B3LYP	0.019	-	0.016	-
	PBE0	0.026	0.004	0.019	-

Non-TADF compounds possess relatively high singlet-triplet energy differences in general, which are in agreement with the available experimental findings. The high ΔE_{ST} values calculated for non-TADF compounds are consistent with the high π -delocalization and HOMO-LUMO overlap observed in these compounds, which might be explained by low torsion angles and molecular rigidity. However, Compound 2 is an exception. Despite having high ϕ_S indices, Compound 2 exhibits extremely low ΔE_{ST} values which is an unexpected result. Still, the notably high experimental ΔE_{ST} value of Compound 2 might be due to some side processes like oxygen quenching which causes non-radiative decay pathways especially for triplet excitons in solution [131].

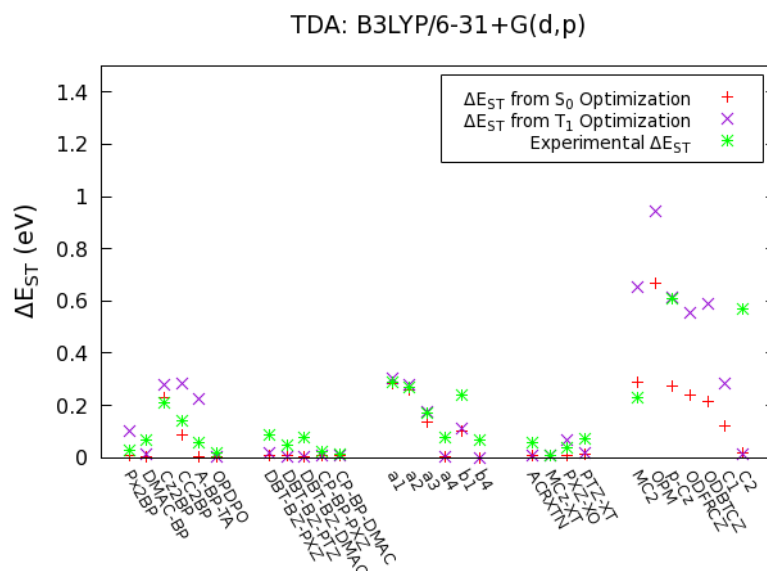


Figure 3.45. ΔE_{ST} values for the investigated TADF emitters calculated from S_0 and T_1 geometries together with the experimental values (TDA: B3LYP/6-31+G(d,p)).

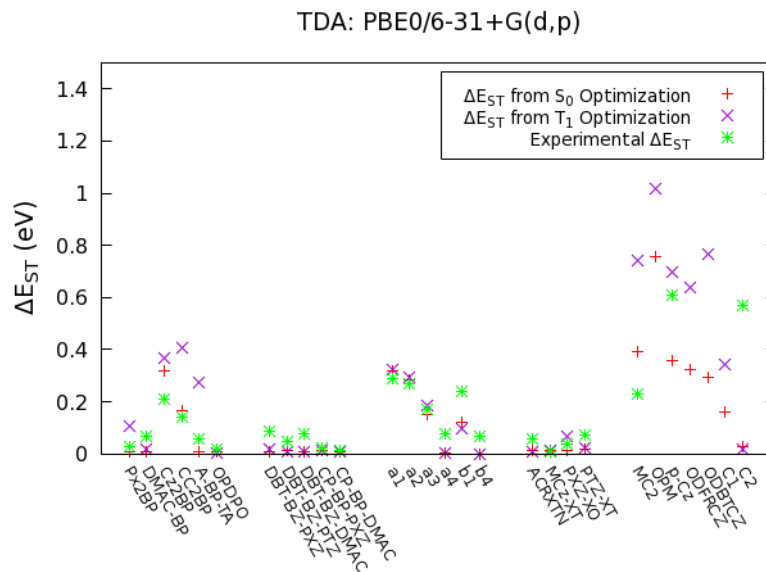


Figure 3.46. ΔE_{ST} values for the investigated TADF emitters calculated from S_0 and T_1 geometries together with the experimental values (TDA: PBE0/6-31+G(d,p)).

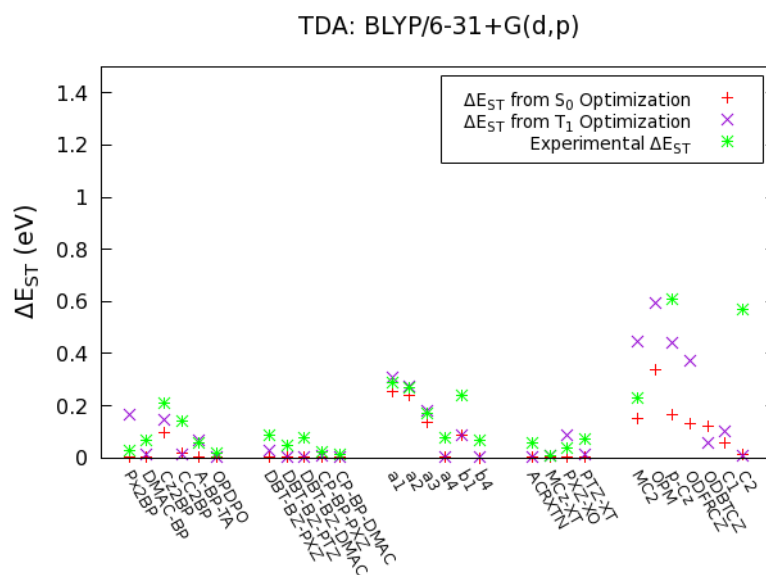


Figure 3.47. ΔE_{ST} values for the investigated TADF emitters calculated from S_0 and T_1 geometries together with the experimental values (TDA: BLYP/6-31+G(d,p)).

Except for the Group 3 emitters, the ΔE_{S1-T1} values were included in the charts depicted in Figures 3.45 to 3.47. Since the ΔE_{S1-T2} values of Group 3 emitters are much more closer to the experimental results, they were taken into account in the charts instead of the ΔE_{S1-T1} values.

To sum up, the computed singlet-triplet gaps are consistent with the estimated torsion angles and ϕ_S indices in almost each case. Low molecular rigidity, together with the torsion angles far below 90° , results in increased HOMO-LUMO overlap and singlet-triplet energy difference. The absence of the delayed fluorescence in most of the non-TADF compounds is closely related with the high singlet-triplet gaps observed in these compounds.

Also, ΔE_{ST} values calculated with BLYP are observed to be lower as compared with other two functionals. This finding is in agreement with the lower ϕ_S indices and higher $\lambda_{\max}$ values computed with BLYP.

3.6.4. Spin-Orbit Couplings (SOC)

ΔE_{ST} is not the sole factor determining the efficiency of RISC. Spin-orbit coupling (SOC) interaction provides information about the possibility of ISC or RISC processes since it contributes to the mixing of the wave functions of singlet and triplet states [132]. As it has been previously stated in Equation 1.2, SOC is directly related with RISC rate. Thus, an adequate amount of SOC matrix elements is crucial for a strong RISC process to obtain high TADF efficiency.

Nonetheless, SOC constants in pure organic chromophores are very small as compared to compounds containing transition metals, since SOC is directly correlated with atomic charges [133]. In addition to this, El-Sayed’s rule suggests that direct transitions between CT states possess negligible SOC constants and local excited triplet states are necessary to achieve an adequate RISC rate [132]. To overcome this issue, different mechanisms have been suggested. One of the most prominent suggested mechanisms was the introduction of a three-state degeneracy between S_{CT} , T_{CT} and T_{LE}

states [134].

Accordingly, low SOC values are expected for the compounds which exhibit orthogonal D-A arrangements and more efficient TADF characteristics.

Therefore, effects of the molecular modifications on SOC should be investigated as low SOC values are an indicator of the presence of charge transfer states. With this purpose, SOC values of the selected TADF and non-TADF compounds have been calculated with BLYP, B3LYP and PBE0 functionals and DZP basis set. The computations have been carried using the geometries optimized at T_1 state since SOC of the up-conversion of the triplet excitons is of interest.

The SOC interaction between the S_1 and T_2 states have also been taken into account along with the interaction between the S_1 and T_1 , if the T_2 state of the compound lies below the S_1 state. The results are reported in Tables 3.18-3.22 and the chart displaying the S_1 - T_1 SOC interactions for all compounds is given in Figure 3.48.

Table 3.18. Spin-orbit coupling (SOC) values between different energy states for Group 1 emitters.

Compound	Method	SOC	
		S_1-T_1	S_1-T_2
Px2BP	BLYP	0.060	-
	B3LYP	0.073	-
	PBE0	0.086	-
DMAC-BP	BLYP	0.020	-
	B3LYP	0.037	-
	PBE0	0.045	-
Cz2BP	BLYP	0.057	0.158
	B3LYP	0.465	0.105
	PBE0	0.565	0.117
CC2BP	BLYP	0.048	-
	B3LYP	0.942	0.868
	PBE0	1.231	2.142
A-BP-TA	BLYP	0.764	-
	B3LYP	0.999	-
	PBE0	1.068	0.291
OPDPO	BLYP	0.003	-
	B3LYP	0.004	-
	PBE0	0.004	-

Table 3.19. Spin-orbit coupling (SOC) values between S_1 and T_1 for Group 2 emitters.

Compound	Method	SOC
		S_1 - T_1
DBT-BZ-PXZ	BLYP	0.040
	B3LYP	0.042
	PBE0	0.046
DBT-BZ-PTZ	BLYP	0.002
	B3LYP	0.002
	PBE0	0.002
DBT-BZ-DMAC	BLYP	0.005
	B3LYP	0.026
	PBE0	0.446
CP-BP-PXZ	BLYP	0.022
	B3LYP	0.026
	PBE0	0.028
CP-BP-DMAC	BLYP	0.004
	B3LYP	0.009
	PBE0	0.013

Table 3.20. Spin-orbit coupling (SOC) values between different energy states for Group 3 emitters.

Compound	Method	SOC	
		S_1-T_1	S_1-T_2
a1	BLYP	0.216	0.000
	B3LYP	0.144	0.000
	PBE0	0.163	0.000
a2	BLYP	0.000	0.117
	B3LYP	0.120	0.000
	PBE0	0.109	0.000
a3	BLYP	0.000	0.079
	B3LYP	0.134	0.000
	PBE0	0.138	0.000
a4	BLYP	0.016	0.000
	B3LYP	0.025	0.000
	PBE0	0.031	0.000
b1	BLYP	0.057	0.023
	B3LYP	0.097	0.059
	PBE0	0.072	0.006
b4	BLYP	0.000	0.004
	B3LYP	0.000	0.004
	PBE0	0.000	0.005

Table 3.21. Spin-orbit coupling (SOC) values between S_1 and T_1 for Group 4 emitters.

Compound	Method	SOC
		S_1 - T_1
ACRXTN	BLYP	0.016
	B3LYP	0.025
	PBE0	0.029
MCz-XT	BLYP	0.018
	B3LYP	0.026
	PBE0	0.029
3-PXZ-XO	BLYP	0.047
	B3LYP	0.060
	PBE0	0.065
PTZ-XT	BLYP	0.005
	B3LYP	0.022
	PBE0	0.033

Table 3.22. Spin-orbit coupling (SOC) values between different energy states for non-TADF emitters.

Compound	Method	SOC	
		S_1-T_1	S_1-T_2
Model Compound 2	BLYP	1.390	2.878
	B3LYP	0.617	4.203
	PBE0	0.435	4.494
OPM	BLYP	1.581	4.635
	B3LYP	2.070	8.383
	PBE0	8.381	7.830
p-Cz	BLYP	0.335	-
	B3LYP	0.246	5.306
	PBE0	0.274	5.500
ODFRCZ	BLYP	0.321	-
	B3LYP	0.345	3.449
	PBE0	0.299	3.825
ODBTCZ	BLYP	0.314	-
	B3LYP	1.078	-
	PBE0	1.262	-
Compound 1	BLYP	0.121	-
	B3LYP	0.202	-
	PBE0	0.231	-
Compound 2	BLYP	0.011	-
	B3LYP	0.015	-
	PBE0	0.016	-

As expected, the emitters which exhibit low ΔE_{ST} values and ϕ_S indices, such as Px2BP, DMAC-BP, OPDPO, DBT-BZ-PXZ, DBT-BZ-PTZ, DBT-BZ-DMAC, CP-BP-PXZ, CP-BP-DMAC, a4, b4, ACRXTN, MCz-XT, 3-PXZ-XO and PTZ-XT, possess negligible SOC values due to high orthogonality and strong intramolecular charge transfer in these compounds.

Additionally, higher SOC interactions between the S_1 and T_2 states may indicate that RISC process might be occurring from the T_2 state instead of the T_1 state.

4. CONCLUSION

In this study, a series of experimentally investigated benzophenone based TADF and non-TADF emitters have been analyzed by computational methods in terms of their structural and photophysical properties. A set of descriptors have been determined to assess the TADF activities, such as torsion angles, singlet-triplet energy gaps (ΔE_{ST}), ϕ_S indices, NTO profiles, SOC constants and absorption spectra. The compounds have been divided into groups based on their molecular similarities and acceptor units to gain a better insight into the influence of the molecular backbone on the efficiency of TADF process.

A comprehensive conformational search has been applied to the ground states of all emitters investigated in this study. The ground state optimizations have been carried out at M06-2X/6-31+G(d,p) level. For the excited state calculations, different functionals have been tested, including BLYP, B3LYP, PBE0 and M06-2X, combined with 6-31+G(d,p) basis set. ΔE_{ST} values and absorption spectra computed with these functionals have been compared with the experimental data to determine the most promising TDA functionals. Also, effects of all possible conformations have been investigated by including them in the absorption spectra. Integral equation formalism polarizable continuum model (IEF-PCM) has been applied implicitly for solvation effects and all calculations have been performed with the experimentally used solvents. For the compounds containing phosphorus, 6-311++G(2d,2p) extrabasis set has been used, while for the compounds including sulphur, 6-311++G(3df,3pd) extra basis set has been implemented.

Comparison with the available experimental data have led us to conclude that M06-2X reproduces larger ΔE_{ST} values and also the absorption spectra generated with it exhibit hypsochromic shift, which is an indication of the LE states rather than CT states. Since BLYP, B3LYP and PBE0 performed satisfactorily with respect to experimental results, further excited state calculations have been carried out with them. Additionally, absorption spectra generated through Wigner distribution have shown

that all conformations display similar photophysical properties, therefore the rest of the calculations were done using the most energetically favourable conformations.

Optimizations at T_1 state have also been performed at M06-2X/6-31+G(d,p) level to examine the photophysical properties at this state, since excited state twisting causes conformational changes.

One of the most significant TADF descriptors is the torsion angle between donor and acceptor units. A torsion angle closer to 90° ensures the spatial separation of the donor and acceptor units, and therefore HOMO and LUMO levels. As shown in this study, more rigid donors such as DMAC, PXZ or PTZ induce higher torsion angles whereas the orthogonality becomes disrupted in the cases where the donors are freely rotating Cz or DPA.

Free rotation and flexibility in the molecular structure causes π -delocalization and HOMO-LUMO overlap. A high degree of HOMO-LUMO overlap has been observed by NTO analysis for the compounds bearing Cz or DPA donors, including Cz2BP, CC2BP, a1, a2, a3, b1 and most of the non-TADF compounds. ϕ_S index, which quantifies the degree of HOMO-LUMO overlap, was estimated to be high for these compounds as well. On the other hand, emitters bearing PXZ, PTZ or DMAC, such as Px2BP, DMAC-BP, OPDPO, a4, b4, ACRXTN, 3-PXZ-XO and PTZ-Xt, exhibit a better separation of HOMO-LUMO and lower ϕ_S indices due to the orthogonality introduced by more rigid donors. Acceptor structure also affects rigidity as in the cases of xanthone based Group 4 molecules. Irrespective of the type of the donor moiety, Group 4 compounds displayed negligible overlap between the frontier orbitals.

Singlet-triplet energy gap (ΔE_{ST}) is directly associated with HOMO-LUMO overlap, therefore in almost all cases, compounds exhibiting high ϕ_S indices and HOMO-LUMO overlap also possess high ΔE_{ST} values. The situation is reversed for the compounds with more orthogonal structures as expected. Despite possessing relatively high ϕ_S indices, non-TADF Compound 2 exhibit low ΔE_{ST} values, which is an exception.

SOC is also informative for determining the charge transfer character of the compounds, as compounds bearing high CT character usually exhibit low SOC constants. Thus, lower SOC values have been obtained for the compounds bearing reduced ΔE_{ST} values and ϕ_S indices.

Some compounds exhibit different photophysical properties at S_0 and T_1 geometries. A-BP-TA is the most prominent of them. Butterfly shaped donor structures such as PXZ, PTZ or thianthrene becomes planar in the T_1 geometries. In the ground state geometry of A-BP-TA, HOMO level was on the DMAC donor group, however in the T_1 geometry, it became localized on the thianthrene donor. This changed the photophysical properties of A-BP-TA in its T_1 geometry since thiantherene is more flexible than the rigid DMAC donor. Accordingly, different photophysical properties have been obtained in the geometries optimized at different energy states in some of the compounds.

To conclude, it has been observed that molecular structure governs the efficiency of TADF to a great extent. A stronger and more efficient RISC process can be achieved through more rigid molecular structures since rigidity supresses non-radiative processes and eventually increases internal quantum efficiency of the device. It has been shown that the analyzed descriptors and the implemented computational methodologies in this study predicted well the experimental results. These findings may shed light on the design modifications of more convenient novel TADF emitters to be utilized in OLEDs.

5. FUTURE WORK

This study has shown that high TADF efficiencies can be achieved by utilizing benzophenone-like acceptors in the molecular design. However, there are also other compounds widely used as electron acceptors in the design of efficient TADF emitters, as depicted in Figure 5.1. Hence, investigation and modeling of TADF materials containing acceptor units such as dicyanobenzene, benzonitrile, triazine, sulfone, boron, pyrazine and pyridine, is also crucial to gain a deeper insight into the structural influences on the photophysical processes. Examining the excited state behaviours of these compounds under the guidance of the computational descriptors used in this study may be helpful to propose new efficient TADF emitters.

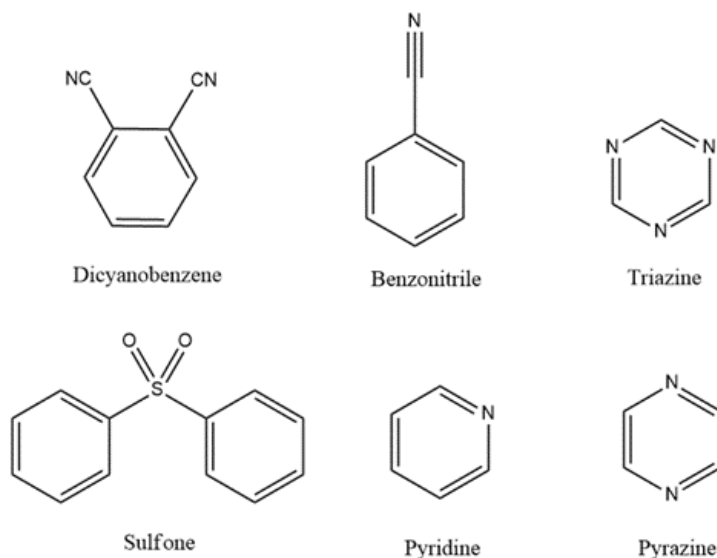


Figure 5.1. Commonly used electron acceptors other than benzophenone in the design of TADF materials.

TADF materials remarkably improve the performances of pure organic OLEDs, however they also exhibit device efficiency problems. The most important issues encountered in TADF based OLEDs include aggregation caused quenching (ACQ) and exciton annihilations which cause efficiency roll-off. In order to reduce concentration quenching and exciton annihilation, TADF based emitters are usually doped in a host

material. However, this host-guest system gives rise to challenges regarding the control of film composition. Moreover, vacuum deposition is more suitable for TADF materials in general. Therefore, solution based deposition must be taken into account to obtain controllable and efficient OLED materials [135].

According to the recent studies, aggregation-induced emission (AIE) mechanism is helpful to overcome ACQ problem [136,137]. To weaken intermolecular π - π interactions which cause non-radiative pathways in the aggregated form, AIE materials comprise highly twisted structures similar to TADF emitters, and they exhibit weak emissions in solutions. In solid state however, they display efficient emission and high quantum photoluminescence yields. Thus, AIE materials can be utilized in non-doped OLEDs due to their high electroluminescence efficiencies [135].

Nonetheless, the roll-off caused by non-emissive triplet excitons is still an issue in AIE materials, therefore AIE materials should also exhibit TADF properties for an effective up-conversion of the triplet excitons. To induce AIE properties, the materials can be in the form of dendrimers or polymers, where intramolecular rotations are more restricted [138]. Figure 5.2 displays the dendrimer CzTAZPO which exhibits excellent AIE properties according to the study of Wang *et al.* [135].

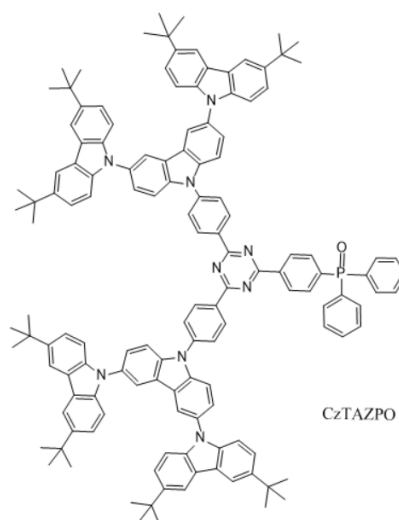


Figure 5.2. The structure of the dendrimer CzTAZPO which shows AIE emission.

The study of Wei *et al.* [110] also demonstrates the TADF efficiencies of polymeric materials. While the monomer unit Model Compound 2, which was also investigated in this study among the non-TADF compounds, does not exhibit TADF emission, its polymer form displays excellent TADF properties because of the conjugation induced reduction of the energy splitting between the S_1 and T_1 states and the destabilization of the π -conjugated HOMO level. The molecular structure of the polymer form of Model Compound 2 is depicted in Figure 5.3.

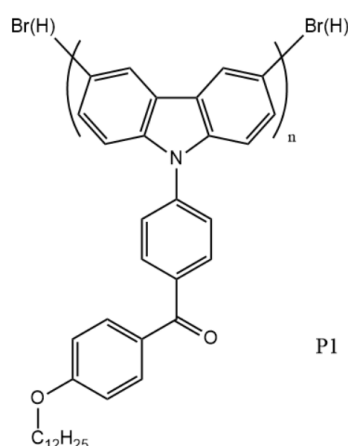


Figure 5.3. The structure of the polymeric TADF material P1.

Hence, the future work will be the modeling of the TADF and AIE materials which are in the form of polymers or dendrimers. In addition to the descriptors used in this study, RISC rates can also be computed as a novel approach to elucidate the plausibility of the exciton up-conversion mechanisms. Furthermore, the photophysical descriptors can be investigated at the S_1 optimized geometries as well, since fluorescence involves the radiative decay of singlet excitons.

In summary, there are many efficient design strategies to improve OLED performances. Thus, computational investigation of the factors that cause different photophysical and optical properties is essential to elucidate the mechanisms underlying device efficiencies of OLEDs. Novel and efficient TADF emitters can be proposed with the help of the computational methods utilized in this study.

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