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# Systematic investigation *via* controlling the energy gap of the local and charge-transfer triplet state for enabling high efficiency thermally activated delayed fluorescence emitters†

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Thermally activated delayed fluorescence (TADF) emitters have evolved as a certified candidate in light generation technologies for producing efficient organic light-emitting diodes (OLEDs) on account of their 100% internal quantum efficiency (IQE) *via* reverse intersystem crossing (RISC) and toxic metal-free design. The fast rate of RISC ( $k_{\text{RISC}}$ ) is the ultimate requirement of an efficient TADF emitter, which can be achieved by minimizing the singlet–triplet energy gap ( $\Delta E_{\text{ST}}$ ). Here, four donor–acceptor type TADF emitters namely **3BPpy-mDCz**, **3BPpy-mDTA**, **3BPpy-mDMAC**, and **3BPpy-mDPT** were synthesized based on benzoyl pyridine (3BPpy) as an unaltered acceptor and varying the donor strength ranging from carbazole to phenothiazine. These emitters show low  $\Delta E_{\text{ST}}$  values forecasting their TADF nature. The  $\Delta E_{\text{ST}}$  values decreased from 0.22 to 0.14 eV upon increasing the donor strength. The maximum external quantum efficiency (EQE) of 18.7% for **3BPpy-mDCz**, 22.5% for **3BPpy-mDTA**, 13.8% for **3BPpy-mDMAC** and 2.1% for **3BPpy-mDPT** was obtained. These drastic differences in the performances of **3BPpy-mDTA** and **3BPpy-mDPT** are due to the locally excited  $^3\text{LE}(\text{T}_2)$  intermediate state between the lowest singlet ( $\text{S}_1$ ) and triplet ( $\text{T}_1$ ). Among **3BPpy-mDMAC** and **3BPpy-mDPT**, the efficiency of **3BPpy-mDMAC** is superior due to less CT character and high photoluminescence quantum yield (PLQY). This work paves a new direction for efficient TADF molecular design by indicating the role of the intermediate triplet state ( $^3\text{LE}$ ) despite possessing high  $\Delta E_{\text{ST}}$  values.

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## 1. Introduction

Light-emitting materials with thermally activated delayed fluorescence (TADF) have attracted a great deal of interest owing to the utilization of their potential features in next-generation organic light-emitting diodes (OLEDs).<sup>1,2</sup> TADF emitters have emerged as a promising technology and prospective alternative to phosphorescent emitters for OLEDs due to their ability to reach 100% internal quantum efficiency (IQE) without the use of rare-earth metals.<sup>3–8</sup> Efficient up-conversion *via* reverse intersystem crossing (RISC) is needed in TADF emitters to achieve a reduction in triplet–triplet annihilation (TTA), which is the primary cause of degradation in phosphorescent emitters.<sup>9,10</sup> Hence, fast RISC is required to acquire high-performance TADF OLEDs over phosphorescent OLEDs. Therefore, a small energy gap between the lowest singlet ( $\text{S}_1$ )

and triplet ( $\text{T}_1$ ) excited states ( $\Delta E_{\text{ST}} < 0.2$  eV) is required to facilitate efficient exciton up-conversion from  $\text{T}_1 \rightarrow \text{S}_1$  *via* reverse intersystem crossing.<sup>11,12</sup> A commonly used TADF molecular design strategy is constructing a twisted molecular conformation with various donor and acceptor units in order to separate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and achieve small  $\Delta E_{\text{ST}}$ .<sup>13–15</sup> Furthermore, increasing the steric hindrance and highly twisted conformation and breaking conjugation in the molecular geometry are also the most effective pathways to fulfill the above criterion *via* minimizing electron exchange energy splitting  $\text{S}_1$  from  $\text{T}_1$ .<sup>16–19</sup>

According to the Franck–Condon transition principle and Fermi's golden rule, high oscillator strength is needed for high photoluminescence quantum yield ( $\Phi_{\text{PL}}$ ), which can be achieved by a large overlap degree of the frontier molecular orbital.<sup>2,18,20</sup> Upon increasing the donor strength we can get low  $\Delta E_{\text{ST}}$  but it suffers from low  $\Phi_{\text{PL}}$  due to which efficient TADF can't be obtained. The main reason behind this is the weak spin–orbit coupling (SOC) between  $\text{S}_1$  and  $\text{T}_1$  due to the charge transfer (CT) character of states leading to inefficient RISC.<sup>21–23</sup> Hence, low

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$\Delta E_{ST}$  is not the sole criteria to achieve efficient TADF emitters. There are several requirements for efficient TADF materials but the core parameter is still the fast rate of RISC ( $k_{RISC}$ ) as well as radiative de-activation ( $k_r$ ). For efficient TADF, both small  $\Delta E_{ST}$  and considerable  $k_{RISC}$  have to be realized simultaneously.

SOC in purely organic emitters has drawn considerable attention due to its tendency to facilitate RISC. According to the El-Sayed rule, SOC increases with the difference in nature of the excited states (charge transfer excited state, CT *vs.* localized excited state, LE).<sup>24</sup> In most of the cases,  $S_1$  displays predominantly CT character ( $^1CT$ ) and therefore the vicinity of the localized triplet state ( $^3LE$ ) will increase SOC.<sup>25,26</sup> RISC proceeds *via* vibronic coupling between  $^3CT(T_1)$  and  $^3LE(T_2)$  states followed by SOC between  $^1CT(S_1)$  and  $^3LE(T_2)$ .<sup>23,27,28</sup> Although there are a range of theoretical reports explaining the role of intermediate states in enhancing SOC, it is less explored experimentally in purely organic emitters without any heavy atom. To overcome this bottleneck, the optimum molecular design for efficient TADF emitters should be well understood and proper guidelines for rational molecular design are highly desired for the practical application of TADF-based OLEDs.

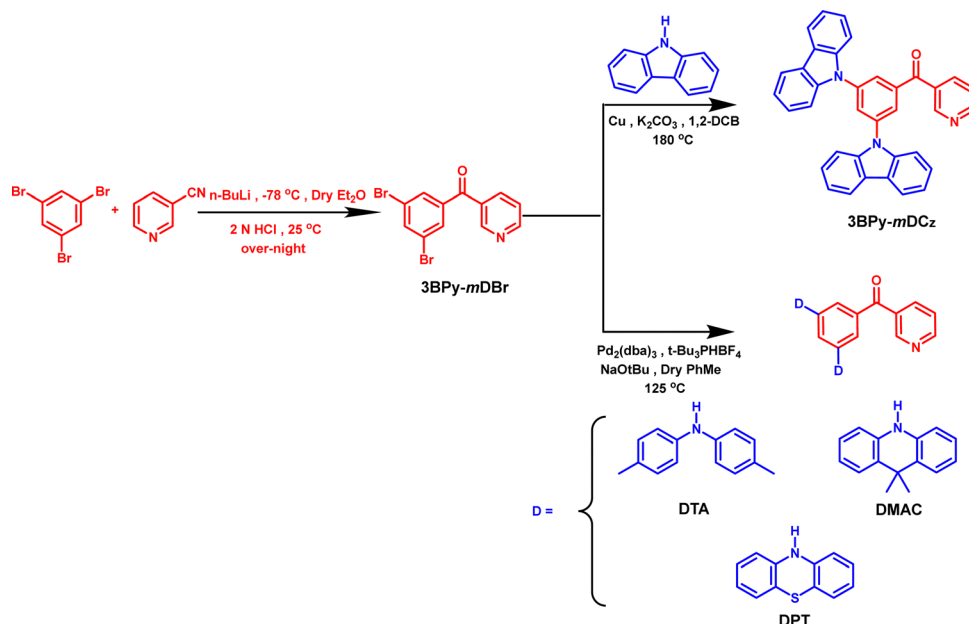
In this study, we designed and synthesized four donor-acceptor based TADF molecules **3BPy-mDCz**, **3BPy-mDTA**, **3BPy-mDMAC** and **3BPy-mDPT** (Scheme 1). Benzoyl pyridine (3BPy) acts as an unaltered acceptor moiety while the donor moiety varies from carbazole to phenothiazine. The  $\Delta E_{ST}$  values also decreased from 0.22 to 0.14 eV, and hence improved performance was expected. By adopting the above emitters as dopants, we acquire blue to yellow TADF OLEDs. However, the maximum EQEs of 18.7% for **3BPy-mDCz**, 22.5% for **3BPy-mDTA**, 13.8% for **3BPy-mDMAC** and 2.1% for **3BPy-mDPT** were obtained. **3BPy-mDCz** and **3BPy-mDTA** possess an intermediate  $^3LE(T_2)$  state between  $S_1$  and  $T_1$  which facilitates both  $k_{RISC}$  and  $k_r$  and hence these emitters

show high efficiency as compared to other emitters. High performance can be achieved in spite of having a relatively large  $\Delta E_{ST}$  value *via* systematically optimising the number and nature of intermediate states between  $S_1$  and  $T_1$ . This work highlights that increasing the donor strength or reducing the  $\Delta E_{ST}$  is not the only desired criteria to get efficient TADF while the position/nature of the additional triplet state ( $^3LE/{}^3CT$ ) state is equally important in enhancing the efficiency of TADF emitters.<sup>29,30</sup>

## 2. Results and discussion

### 2.1. Theoretical calculation

To understand the effect of variation of the donor moieties, density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed using the B3LYP/6-31G(d,p) method. The atomic delocalization of the  $S_0$  geometry and excited-state energy levels of the four designed molecules was then conducted. Fig. 1 shows the optimized molecular structure along with the molecular orbital distribution of the HOMO and the LUMO of these molecules. The LUMOs were mainly residing on the acceptor unit (3BPy) due to its electron withdrawing nature while the HOMOs were widely localized on the donor groups and extended to the phenyl ring based on their descending order of donor strengths, which are crucial for the occurrence of delayed fluorescence. The calculated excitation energies and HOMO/LUMO energy levels of the  $S_1$  and  $T_1$  excited states are shown in Table S1, ESI† The FMO distributions resulted in reduced  $\Delta E_{ST}$  values as 0.19, 0.24, 0.03 and 0.02 eV for **3BPy-mDCz**, **3BPy-mDTA**, **3BPy-mDMAC** and **3BPy-mDPT**, respectively. The small  $\Delta E_{ST}$  values suggest that molecules can exhibit TADF properties. Overlap between the HOMO and LUMO retains high oscillator strength ( $f$ ) in



Scheme 1 Synthesis of **3BPy-mDCz**, **3BPy-mDTA**, **3BPy-mDMAC** and **3BPy-mDPT**.

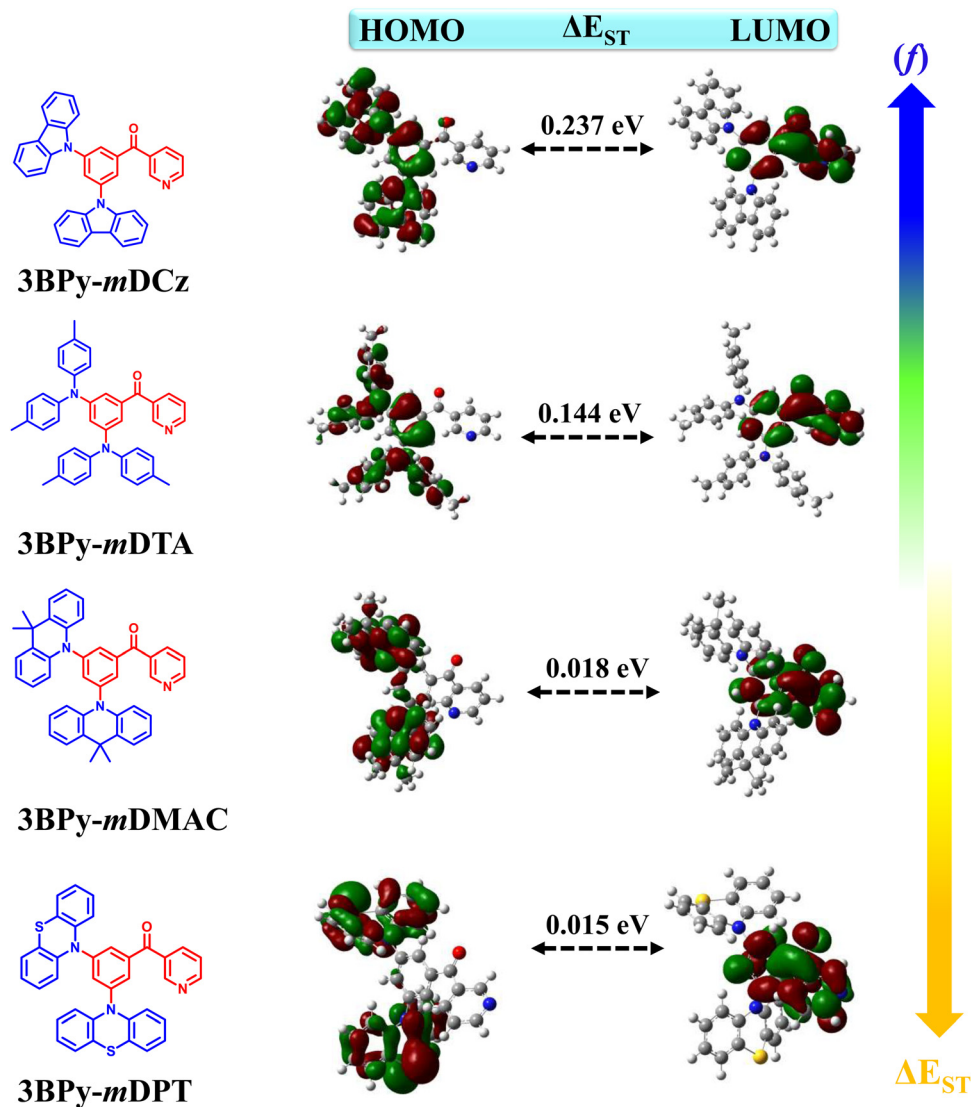


Fig. 1 The distribution of the molecular orbital of the HOMO and LUMO with a calculated  $S_1$  and  $T_1$  energy gap ( $\Delta E_{ST}$ ). The right side top and bottom of the arrow marks indicate the enhancement of oscillator strengths ( $f$ ) and reduction of  $\Delta E_{ST}$  when increasing the donor strength.

3BPY-mDCz and 3BPY-mDTA as compared to other derivatives, which is helpful to maintain a high radiative decay rate ( $k_r$ ).<sup>31</sup>

## 2.2. Synthesis and characterization

The designed compounds were synthesized in high yields *via* the Ullmann coupling reaction and Buchwald-Hartwig amination of (3-bromobenzoyl)pyridine with various donor moieties. The synthetic routes are displayed in Scheme 1 while the detailed synthetic procedures and characterization data are given in the ESI.† All the compounds were further purified by temperature-gradient vacuum sublimation and chemical structures are confirmed by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and high-resolution mass spectrometry (HRMS) (Fig. S9–S18, ESI†).

## 2.3. Thermal and electrochemical properties

All four materials (3BPY-mDCz, 3BPY-mDTA, 3BPY-mDMAC and 3BPY-mDPT) show good thermal stability with decomposition

temperatures ( $T_d$ ) corresponding to 5 wt% loss in the range of 331–422 °C (Fig. S1, ESI† and Table 1). The glass transition was not obtained during differential scanning calorimetry (DSC) analysis. These high stabilities are important for stable film formation.

The energy band gap ( $E_g$ ) that is being calculated from the absorption onset for all emitters is listed in Table S2, ESI.† The electrochemical properties of all the four emitters were examined by cyclic voltammetry (CV) as shown in Fig. S2, ESI.†<sup>32</sup> All emitters exhibited two reversible oxidation waves confirming the oxidation of both the donor moieties. The HOMO energy level came out to be −5.26, −5.14, −4.95 and −5.03 eV for 3BPY-mDCz, 3BPY-mDTA, 3BPY-mDMAC and 3BPY-mDPT, respectively, as listed in Table S2, ESI.† Upon increasing the donor strength, the HOMO level increases due to the increase in the electron donating ability and this trend matches with theoretical values. The calculated LUMO energy

Table 1 Photophysical properties of **3BPy-mDCz**, **3BPy-mDTA**, **3BPy-mDMAC** and **3BPy-mDPT**

Compound	$\lambda_{\text{abs}}^a$ (nm)	$\lambda_{\text{PL}}^b$ (nm) (sol/film)	$\lambda_{\text{ph}}^c$ (nm) (sol/film)	$\Delta E_{\text{ST}}^d$ (eV) (sol/film)	$\phi_{\text{PL}}^e$ (air/vac)	$\tau_{\text{P}}^f$ (ns)	$\tau_{\text{D}}^g$ ( $\mu$ s) (air/vac)	$T_{\text{d}}^h$ ( $^{\circ}$ C)
<b>3BPy-mDCz</b>	338, 372	456/463	472/493	0.13/0.22	56/59	10.3	118.8/340.3	381
<b>3BPy-mDTA</b>	300, 424	522/532	551/576	0.18/0.20	16/48	6.8	119.7/785.7	350
<b>3BPy-mDMAC</b>	287, 401	534/528	547/535	0.15/0.11	34/53	30.9	6.6/9.2	331
<b>3BPy-mDPT</b>	319, 425	—/551	—/565	—/0.14	7/12	16.1	13.8/41.4	422

<sup>a</sup> Absorbance peaks. <sup>b</sup> Steady state emission maxima at room temperature. <sup>c</sup> Phosphorescence emission maxima in solution measured in toluene (Tol) ( $1 \times 10^{-5}$  M) and doped film (7 wt% of emitter:host) at 77 K. <sup>d</sup> Singlet-triplet energy gap. <sup>e</sup> Absolute PLQY in doped films using an integrating sphere under air and vacuum atmosphere. <sup>f</sup> Prompt lifetime. <sup>g</sup> Delayed lifetime at room temperature under air and vacuum. <sup>h</sup> Thermal decomposition temperature under a  $\text{N}_2$  atmosphere.

levels were  $-2.26$ ,  $-2.54$ ,  $-2.25$  and  $-2.65$  eV, respectively, by taking into account the HOMO and  $E_{\text{g}}$  values.

#### 2.4. Photophysical properties

Photophysical properties of **3BPy-mDCz**, **3BPy-mDTA**, **3BPy-mDMAC** and **3BPy-mDPT** in  $10 \mu\text{M}$  toluene solution are shown in Fig. 2 and Fig. S3, ESI.† All the compounds display similar absorption spectral profiles with a strong absorption band observed before  $350$  nm associated with the  $\pi$ - $\pi$  and  $n$ - $\pi^*$  transitions<sup>33</sup> and relatively weak and structureless broadband absorption peaks observed at  $372$ ,  $425$ ,  $394$  and  $423$  nm for **3BPy-mDCz**, **3BPy-mDTA**, **3BPy-mDMAC** and **3BPy-mDPT**, respectively, which is associated with the intra-molecular charge transfer (ICT) from the donor moieties to the acceptor moiety.<sup>34</sup> The PL spectra were measured in toluene ( $10 \mu\text{M}$ ) at room temperature (RT) and **3BPy-mDCz**, **3BPy-mDTA** and **3BPy-mDMAC** show slightly broad and structureless emission. **3BPy-mDPT** is not emissive in the solution state, and hence the emission spectra couldn't be studied in the solution state. The summary of the photophysical properties is depicted in Table 1. It is noteworthy that the emission maximum peaks of **3BPy-mDCz**, **3BPy-mDTA** and **3BPy-mDMAC** have been observed at  $456$ ,  $522$  and  $534$  nm, respectively. Furthermore, the  $S_1$  energies were calculated to be  $3.08$ ,  $2.71$  and  $2.76$  eV, respectively from the onset of the fluorescence spectra. The phosphorescence spectra of these systems were measured at  $77$  K in toluene ( $10 \mu\text{M}$ ) with peaks centered at  $472$ ,  $551$  and  $547$  nm, respectively, as shown in Fig. 2. The phosphorescence spectra of these emitters showed broad structureless emission, which indicates that their phosphorescence emission originates from the CT triplet state of these molecules. Furthermore, the  $T_1$  energies were calculated to be  $2.95$ ,  $2.53$  and  $2.61$  eV, respectively from the onset of their phosphorescence spectra. Therefore, the  $\Delta E_{\text{ST}}$  was estimated in the range of  $0.13$ ,  $0.18$  and  $0.15$  eV, respectively, as shown in Table 1. The small  $\Delta E_{\text{ST}}$  of these molecules suggests that these emitters may have TADF properties. The solvatochromic study was done by taking emission spectra in various solvent polarities as shown in Fig. S4, ESI.† Significantly, their PL spectra are concomitantly red-shifted and slightly broadened with the increase of the solvent polarity, which clearly indicates that these molecules are CT in nature and the  $S_1$  state is stabilized upon increasing solvent polarity.

In order to get an overview of the optical properties in the thin film, a photophysical study was carried out in doped thin film. DPEPO (triplet energy of  $3.0$  eV) host was taken for



Fig. 2 UV-Vis absorption, fluorescence (RT), and phosphorescence (77 K) spectra of **3BPy-mDCz**, **3BPy-mDTA**, and **3BPy-mDMAC** respectively in toluene (Tol) ( $1 \times 10^{-5}$  M).

**3BPy-mDCz** while *m*CBP (triplet energy of  $2.8$  eV) host was taken for the remaining three emitters, which confine triplet excitons and efficiently suppress backward energy transfer from the guest to the host materials. The doped films with  $7$  wt% doping concentration give blue to yellow emission with an emission peak of  $463$  nm for **3BPy-mDCz**,  $532$  nm for **3BPy-mDTA**,  $528$  nm for **3BPy-mDMAC** and  $551$  nm for **3BPy-mDPT**. The fluorescence and phosphorescence spectra of the co-doped films were measured and presented in Fig. 3 and Table 1. The  $\Delta E_{\text{ST}}$  values measured from the onset of the PL spectra at RT and phosphorescence spectra at  $77$  K are  $0.22$ ,  $0.20$ ,  $0.11$  and  $0.14$  eV for **3BPy-mDCz**, **3BPy-mDTA**, **3BPy-mDMAC** and **3BPy-mDPT**, respectively. The  $\Delta E_{\text{ST}}$  gradually decreased upon increasing the donor strength. These values are low enough to have efficient up-conversion of  $T_1$  excitons to the  $S_1$  state.<sup>35</sup>

Furthermore, the PLQY of the doped films was measured using an integrating sphere under the air and a  $\text{N}_2$  atmosphere. Under air, the PLQYs of the doped films came out to be  $56\%$  for





Fig. 3 Fluorescence (FI) and phosphorescence (Ph) spectra of 7 wt% **3BPY-mDCz**:DPEO, **3BPY-mDTA**:mCBP, **3BPY-mDMAC**:mCBP and **3BPY-mDPT**:mCBP doped film.

**3BPY-mDCz**, 16% for **3BPY-mDTA**, 34% for **3BPY-mDMAC** and 7% for **3BPY-mDPT** while under a  $N_2$  atmosphere, the PLQY increased to 59% for **3BPY-mDCz**, 48% for **3BPY-mDTA**, 53% for **3BPY-mDMAC** and 12% for **3BPY-mDPT**. The PLQY enhancement in a  $N_2$  atmosphere compared to air is likely due to the suppression of triplet exciton quenching by atmospheric oxygen.<sup>36,37</sup> The corresponding PLQY values decreased as the donor strength increased on account of the increase in CT character.<sup>22</sup> The decrease of PLQY in the presence of oxygen supports that these materials possess unambiguous TADF properties and suggests that the  $T_1$  states of these molecules are readily quenched by the triplet ground state oxygen molecules. The quenching of  $T_1$  by oxygen leads to the quenching of the delayed fluorescence and a decrease in the emission intensity.

To further reveal the effect of donor strength on the TADF properties of the emitters, we studied transient photoluminescence decay (TRPL) of the doped films (7 wt% **3BPY-mDCz**, **3BPY-mDTA**, **3BPY-mDMAC** and **3BPY-mDPT**) which were fabricated by vacuum deposition. As shown in Fig. 4, the transient

decay curves show two components. The first one is the prompt fluorescence decay from  $S_1$  to  $S_0$  with a lifetime  $\tau_p$  and the second one is delayed emission with a lifetime  $\tau_d$ , which can be rationalized as the thermal up-conversion of  $T_1$  to  $S_1$  through RISC followed by fluorescence to the  $S_0$ . **3BPY-mDCz** and **3BPY-mDTA** possess a shorter excited state prompt lifetime as compared to other derivatives. Furthermore, to confirm the TADF characteristics of these emitters, the temperature-dependent TRPL decay was measured. As shown in Fig. S5, ESI,† a temperature sweep between 200 to 298 K under vacuum was carried out. The delayed component increases with an increase of temperature from 200 K to 298 K (RT), which has concomitantly disclosed that the efficient exciton up-conversion occurred from  $T_1$  to  $S_1$  via RISC.

## 2.5. Electroluminescence performance

Devices were fabricated to investigate the electroluminescence (EL) properties using an optimized structure of ITO/NPB (30 nm)/TAPC (20 nm)/host:emitter (7 wt%) (30 nm)/PPT (10 nm)/TmPyPb (60 nm)/LiF (1 nm)/Al (100 nm), where the emitters are **3BPY-mDCz**, **3BPY-mDTA**, **3BPY-mDMAC** and **3BPY-mDPT**. The device architecture along with the molecular structure of all the entities is shown in Fig. S6, ESI.† In these devices,  $N,N'$ -bis(1-naphthyl)- $N,N'$ -diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) acts as the hole injection material, 1,1-bis[4-[ $N,N'$ -di(*p*-tolyl)amino]phenyl] cyclohexane (TAPC) acts as the hole transporting material as well as an exciton blocker and 1,3,5-tri(*m*-pyrid-3-yl-phenyl)benzene (TmPyPb) is the electron-transporting material.<sup>38</sup> Additionally, 2,8-bis(diphenyl-phosphoryl)-dibenzo[*b,d*]thiophene (PPT) has been used as an electron transport as well as hole blocking layer. Bis[2-(diphenylphosphino)phenyl]ether oxide (DPEPO) was taken as the host for **3BPY-mDCz**, 3,3'-bis(9*H*-carbazol-9-yl)-1,1'-biphenyl (mCBP) for **3BPY-mDTA** and 4,4'-bis(9*H*-carbazol-9-yl)-1,1'-biphenyl (CBP) for the remaining two emitters. Finally, lithium fluoride (LiF) was used as an electron injection layer and aluminium (Al) as the cathode. The EL characteristics of these four material-based OLED devices are displayed in Fig. 5 and the data are summarized in Table 2.

Fig. 5(a) shows normalised EL spectra of the four optimized OLEDs. On gradually enhancing the electron-donating capabilities,



Fig. 4 Transient PL decays of DPEO and mCBP host films doped with 7 wt% of emitter (a) prompt and (b) delayed component at 298 K.



Fig. 5 (a) EL spectra; (b) EQE versus luminance characteristics (c) luminance–voltage–current density characteristics. (d) Transient EL spectra; inset is an EL illumination image of **3BPpy-mDTA** (green emission) and **3BPpy-mDPT** (yellow emission).

the emission peaks drastically shifted from blue emission for **3BPpy-mDCz** with an EL  $\lambda_{\text{max}}$  of 473 nm, to green emission for **3BPpy-mDTA** with an EL  $\lambda_{\text{max}}$  of 525 nm, green emission for **3BPpy-mDMAC** with an EL  $\lambda_{\text{max}}$  of 523 nm and yellow emission for **3BPpy-mDPT** with an EL  $\lambda_{\text{max}}$  of 566 nm showing resemblance to the PL spectra, as shown in Fig. S7, ESI.† As the donor strength is increased, charge transfer nature increases subsequently increasing the full width at half maximum (FWHM) value (as evident from the DFT also). The **3BPpy-mDTA** based device shows higher FWHM value as compared to **3BPpy-mDMAC** due to the flexibility of the DTA donor (Table 2). However, the EQE vs. luminance plot indicates that on increasing the donor strength, EQE decreases from 18.7% to 2.1% except for **3BPpy-mDTA** which interestingly shows the highest EQE of 22.5% despite possessing larger  $\Delta E_{\text{ST}}$ , as shown in Fig. 5(b). However, **3BPpy-mDTA** possesses relatively higher efficiency roll-off as compared to other emitters on account of higher  $k_{\text{ISC}}$ , and hence longer excited lifetime leading to various exciton annihilation processes at high operating voltage.

To confirm their TADF properties in the device under electrical excitation, the transient EL decay was measured for devices at RT, as shown in Fig. 5(d). The EL delayed component lasts for several tens of  $\mu\text{s}$  and this result strongly supports the existence of the TADF under electrical excitation.

In order to get deeper insights into the relative performance of all the emitters, Natural Transition Orbital (NTO) calculations for hole and electron distributions were obtained using the Multiwfn program package, as shown in Fig. S8, ESI.† In the case of **3BPpy-mDCz** and **3BPpy-mDTA**, there is the presence of an additional intermediate state ( $^3\text{LE}$ ) between  $S_1$  and  $T_1$  while in the case of **3BPpy-mDMAC** and **3BPpy-mDPT** there is no additional intermediate state, as shown in Fig. 6. It is interesting to notice that the  $S_1$  state of each emitter is predominantly CT in nature but in the case of **3BPpy-mDTA**, it shows CT as well as LE nature. According to the NTO calculation, the nature of  $S_1$  and  $T_1$  excited states along with h/e overlap of **3BPpy-mDTA** has a large distribution on the phenyl bridge as compared to other

Table 2 Electroluminescence properties of **3BPpy-mDCz**, **3BPpy-mDTA**, **3BPpy-mDMAC** and **3BPpy-mDPT**

Device <sup>a</sup>	$\lambda_{\text{EL}}^b$ (nm)	FWHM <sup>c</sup> (nm)	$V_{\text{on}}^d$ (V)	$L_{\text{max}}^e$ (cd m <sup>-2</sup> )	PE <sup>f</sup> (lm W <sup>-1</sup> )	CE <sup>g</sup> (cd A <sup>-1</sup> )	EQE <sup>h</sup> (%) (max/100/500)	CIE <sup>i</sup> (x, y)
<b>3BPpy-mDCz</b>	473	68	4.0	635	21.9	31.5	18.7/8.4/2.8	(0.15, 0.21)
<b>3BPpy-mDTA</b>	525	91	2.8	13 139	70.4	78.7	22.5/11.9/4.8	(0.29, 0.58)
<b>3BPpy-mDMAC</b>	523	88	3.0	33 066	40.0	44.7	13.8/12.3/11.3	(0.31, 0.54)
<b>3BPpy-mDPT</b>	566	102	3.3	13 685	6.0	6.8	2.1/1.9/1.8	(0.44, 0.51)

<sup>a</sup> Device configuration: ITO/NPB (30 nm)/TAPC (20 nm)/Emitter: host (7 wt%) (30 nm)/PPT (10 nm)/TmPyPb (60 nm)/LiF (1 nm)/Al (100 nm) where DPEO was taken as the host for **3BPpy-mDCz**, mCBP for **3BPpy-mDTA**, and CBP for the remaining two emitters. <sup>b</sup> Electroluminescence maxima. <sup>c</sup> Full width at half maxima value. <sup>d</sup> Operating voltage at a brightness of 1 cd m<sup>-2</sup>. <sup>e</sup> Maximum luminance. <sup>f</sup> Maximum power efficiency. <sup>g</sup> Maximum current efficiency. <sup>h</sup> External quantum efficiency at Max/100/500 cd m<sup>-2</sup>. <sup>i</sup> Color coordinates (CIE 1931).



Fig. 6 Energy level diagram of excited states ( $S_1$ ,  $T_1$  and  $T_2$ ) for **3BPpy-mDCz**, **3BPpy-mDTA**, **3BPpy-mDMAC** and **3BPpy-mDPT** where the value in brackets indicates the hole–electron overlap for the specified level.

emitters, as shown in Fig. 7. Therefore, it possesses the  $S_1$  excited state with hybrid characteristics of local and charge-transfer excitations (CT/LE) for this particular molecular engineering.<sup>39</sup>

According to El-Sayed's rule, spin–orbit coupling (SOC) is forbidden between the same nature of states while it is allowed when the states have different nature.<sup>29</sup> **3BPpy-mDCz** possesses a h–e overlap of  $\sim 0.53$  (more LE character) and  $\sim 0.41$  (less LE character), respectively, for the  $T_2$  and  $T_1$  states enabling more mixing between these states. On the other hand, **3BPpy-mDTA** possesses a h–e overlap of  $\sim 0.58$  (more LE character) and  $\sim 0.51$  (more LE character) for the  $T_2$  and  $T_1$  state enabling less mixing. Since the  $S_1$  state of **3BPpy-mDTA** has more LE nature ( $\sim 0.41$ ) as compared to **3BPpy-mDCz** (0.30), a higher prompt efficiency is expected for **3BPpy-mDTA**. Similarly, the h–e overlap for **3BPpy-mDMAC** and **3BPpy-mDPT** is  $\sim 0.22$  and  $\sim 0.20$ , respectively for the  $T_1$  state. Due to less CT character of  $T_1$  in **3BPpy-mDMAC** as compared to **3BPpy-mDPT**, higher efficiency is expected for **3BPpy-mDMAC**. The combination of

the above factors feasibly allows the **3BPpy-mDTA** to maintain the highest  $f$  values and exhibit maximum efficiency irrespective of the large  $\Delta E_{ST}$  value. These findings highlight that randomly choosing a combination of D and A moieties will not be beneficial but the nature and number of intermediate states should also be considered in enhancing up-conversion and hence efficiency.

In order to validate this experimentally, the main kinetic parameters including the rate constants of fluorescence radiative decay ( $k_r$ ), non-radiative internal conversion ( $k_{IC}$ ), ISC ( $k_{ISC}$ ) and RISC ( $k_{RISC}$ ) are calculated according to eqn (S1)–(S5), ESI† which is summarised in Table 3. A higher value of  $k_r$  and  $k_{RISC}$  is needed to achieve high performance. **3BPpy-mDCz** shows the highest value of  $k_r$  but  $k_{RISC}$  is relatively slow. Similarly, for **3BPpy-mDMAC**  $k_{RISC}$  is the highest but  $k_r$  is small. In addition, the presence of the  $T_2$  state in between  $T_1$  and  $S_1$  helps to get the optimum value of  $k_{RISC}$  and simultaneously higher h–e overlap leads to higher prompt efficiencies for TADF emitters.<sup>40</sup>

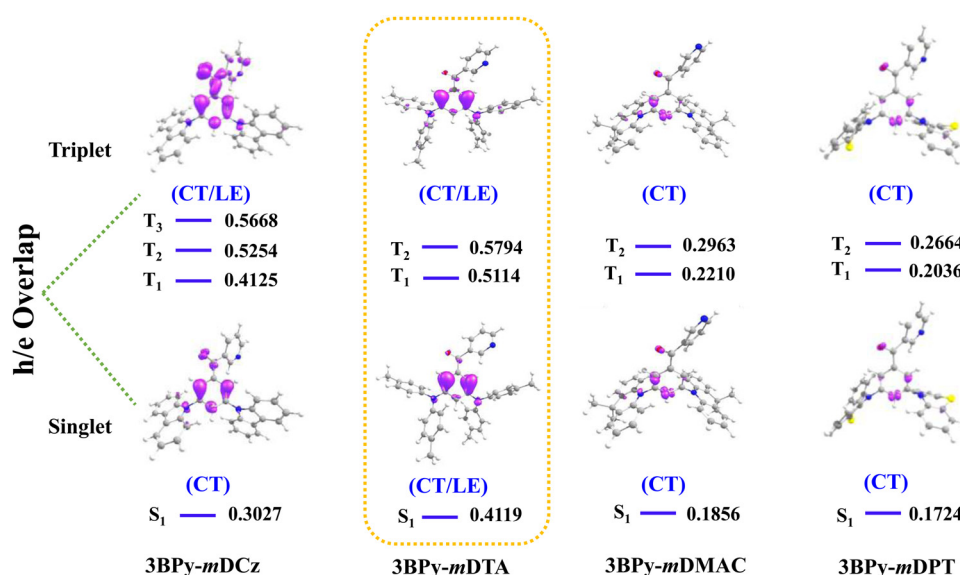


Fig. 7 Hole and electron overlap (h/e) in the singlet and triplet excited state of **3BPpy-mDCz**, **3BPpy-mDTA**, **3BPpy-mDMAC** and **3BPpy-mDPT**, respectively, with the corresponding obtained energy state.

Doped film <sup>a</sup>	$k_{\text{p}(\text{total})}^b$ ( $10^7 \text{ s}^{-1}$ )	$k_{\text{r}}^b$ ( $10^7 \text{ s}^{-1}$ )	$k_{\text{IC}}^b$ ( $10^7 \text{ s}^{-1}$ )	$k_{\text{ISC}}^b$ ( $10^7 \text{ s}^{-1}$ )	$k_{\text{RISC}}^b$ ( $10^3 \text{ s}^{-1}$ )
<b>3BPpy-mDCz</b>	9.64	5.43	3.71	0.50	3.09
<b>3BPpy-mDTA</b>	14.61	2.28	2.44	9.88	3.93
<b>3BPpy-mDMAC</b>	3.23	1.10	0.96	1.16	169.17
<b>3BPpy-mDPT</b>	6.19	0.44	3.28	2.46	40.04

**3BPpy-*m*DTA** has the optimum value of both the rate constants; hence it shows the highest performance. The experimental result further validates the superiority of **3BPpy-*m*DTA** molecular design. Therefore, the computational as well as experimental results strongly indicate that the influence of number and nature of intermediate states between  $S_1$  and  $T_1$  is very crucial to get high EQE.

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