Exploring the possibility of using fluorine-involved non-conjugated electron-withdrawing groups for thermally activated delayed fluorescence emitters by TD-DFT calculation

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Abstract

The trifluoromethyl group has been previously explored as a non-conjugated electron-withdrawing group in donor–acceptor thermally activated delayed fluorescence (TADF) emitters. In the present study, we investigate computationally the potential of other fluorine-containing acceptors, trifluoromethoxy (OCF$_3$), trifluoromethylthio (SCF$_3$), and pentafluorosulfanyl (SF$_5$), within two families of donor–acceptor TADF emitters. Time-dependent density functional theory calculations indicate that when only two ortho-disposed carbazole donors are used (Type I molecules), the lowest-lying triplet state possesses locally excited (LE) character while the lowest-lying singlet state possesses charge-transfer character. When five carbazole donors are present in the emitter design (Type II molecules), now both $S_1$ and $T_1$ states possess CT character. For molecules $2CzOCF_3$ and $5CzOCF_3$, the singlet energies are predicted to be 3.92 eV and 3.45 eV; however, the singlet-triplet energy gaps, $\Delta E_{ST}$s, are predicted to be large at 0.46 eV and 0.37 eV, respectively. The compounds $2CzCF_3$, $2CzSCF_3$, and $2CzSF_5$, from Type I molecules, show significant promise as deep blue TADF emitters, possessing high calculated singlet energies in the gas phase (3.62 eV, 3.66 eV, and 3.51 eV, respectively) and small, $\Delta E_{ST}$s, of 0.17 eV, 0.22 eV, and 0.07 eV, respectively. For compounds $5CzSCF_3$ and $5CzSF_5$, from Type II molecules, the singlet energies are stabilized to 3.24 eV and 3.00 eV, respectively, while $\Delta E_{ST}$s are 0.27 eV and 0.12 eV, respectively, thus both show promise as blue or sky-blue TADF emitters. All these six molecules possess a dense number of intermediate excited states between $S_1$ and $T_1$, thus likely leading to a very efficient reverse intersystem crossing in these compounds.
Introduction

Organic thermally activated delayed fluorescence (TADF) materials have generated significant attention recently, particularly for their use as emitters in organic light-emitting diodes (OLEDs). This is due to their ability to utilize both singlet excitons and triplet excitons, thereby increasing the theoretical internal quantum efficiency (IQE) to 100% from 25% for fluorescent compounds [1–4]. For TADF materials, a small energy gap between the lowest singlet and triplet excited states (ΔE_{ST}) is essential to permit the efficient up-conversion of triplet excitons to singlet excitons via reverse intersystem crossing (rISC) [5–7]. The rISC process can happen by hyperfine coupling when the ΔE_{ST} is sufficiently small (<10 meV) or spin orbit coupling (SOC), which requires different symmetry between the two states coupled with a relatively small singlet–triplet energy gap, ΔE_{ST}, (<300 meV) [8,9]. The ΔE_{ST} is directly dependent on the magnitude of the electron exchange energy J (Equation 1), which itself is dependent on the electron density overlap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) (Equation 2) [10,11]. Compounds possessing a donor–acceptor (D–A) structure could satisfy the requirements for efficient TADF if the donor and acceptor moieties are poorly conjugated with each other in order to minimize J. The HOMO/LUMO separation that controls J can be modulated by introducing strong and bulky electron donors and electron acceptors to produce large torsi ons between the donor and acceptor groups so as to localize the HOMO on the electron-donating moiety and to confine the LUMO on the electron-withdrawing moiety [12,13].

\[ ΔE_{ST} = E^S_{\text{orb}} + K + J - (E^T_{\text{orb}} + K - J) = 2J + (E^S_{\text{orb}} - E^T_{\text{orb}}) \]  
\[ J = \frac{\int \Phi_{\text{LUMO}}(r_2)\Phi_{\text{HOMO}}(r_1)\left(\frac{e^2}{r_1 - r_2}\right) dr_1 dr_2}{\langle \eta^2 \rangle} \]  

According to the Fermi’s golden rule, the reversed intersystem crossing rate (k_{rISC}) can be expressed as [14,15]:

\[ k_{rISC} = \frac{2\pi}{\hbar} |V_{\text{SOC}}|^2 \times \rho_{\text{FCWD}} \]  

Where |V_{SOC}|^2 is the spin-orbit coupling matrix element between S1 and T1 and ρ_{FCWD} is the Franck–Condon-weighted density of states, which can be expressed as [16]:

\[ \rho_{\text{FCWD}} = \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp \left( -\frac{(\Delta E_{ST} + \lambda)^2}{4\lambda k_B T} \right) \]

where λ is the Marcus reorganization energy associated with the intermolecular and intramolecular low-frequency vibrations; k_B is Boltzmann’s constant; and T is temperature. Combining Equation 3 and Equation 4, it is evident that k_{rISC} is proportional to |V_{SOC}|^2 × exp[−(ΔE_{ST}^2)]. Further, judicious molecular design in terms of the identity, position, and number of donor to acceptor moieties can also contribute to the modulation of ΔE_{ST}, leading to faster rISC. Typical donors include a small group of structurally related N-heterocycles such as carbazole [5], dimethylacridine [13], phenoxazine [17], and phenothiazine [18].

Prior studies have shown that placing the donor groups ortho to the acceptor can lead to more limited conjugation between the two, resulting in emitters with relatively smaller ΔE_{ST} compared to analogous compounds where the donor is positioned para to the acceptor [19,20]. Duan et al. have investigated the properties of D–A TADF benzonitrile-based emitters containing two carbazole donors disposed at different positions about the phenylene bridge [19]. The results showed that when the carbazoles were both located ortho to the cyano acceptor the molecule (2,6-2CzBN) possessed a highly twisted structure and a corresponding small ΔE_{ST} (0.27 eV in toluene). The ΔE_{ST}s increased to 0.41 (2,4-2CzBN) and 0.40 eV (3,5-2CzBN) in toluene when at least one of the carbazoles was disposed meta or para to the cyano acceptor [19]. OLEDs fabricated using 2,6-2CzBN as the emitter exhibited deep blue emission with λ_{EL} = 418 nm and CIE coordinate of (0.15, 0.05); however, due to the low photoluminescence quantum yields (Φ_{PL}) (28% in 10 wt % DPEPO films) and relatively slow k_{rISC} (0.86 × 10^5 s⁻¹) in the DPEPO host, the EQE_{max} was only 2.5%, and showed significant efficiency roll-off, reducing to 0.1% at 50 cd·m⁻² [21]. A similar study by Monkman, Lee and co-workers investigated the compound 2,6-2CzTRZ, which possessed the smallest ΔE_{ST} (0.02 eV) amongst the family of dicyanovinylene when at least one of the carbazoles was disposed meta or para to the cyano acceptor [19]. The single crystal structure of 2,6-2CzTRZ revealed a highly twisted structure with large torsions (81.0° and 0.29 eV for 3,4-2CzBN) in toluene. The ΔE_{ST}s increased to 0.10 eV for 2,4-2CzTRZ and 0.29 eV for 3,4-2CzTRZ. The small crystal structure of 2,6-2CzTRZ revealed a highly twisted structure with large torsions (81.0° and 76.3°) between the carbazole moieties and the central benzene ring; the same torsions are appreciably smaller at 45.6° and 69.6° for the molecule 2,4-2CzTRZ where one of the carbazole donors is situated at the para position and another one situated at the ortho position [20]. Compound 2,6-2CzTRZ possessed a very small ΔE_{ST} (0.02 eV) and short delayed fluorescence lifetime (τ_d = 16.4 μs) in zezonex [20]. These two studies illustrate that ortho-substituted D–A molecules possess highly twisted geometries, leading to spatially separated HOMO/LUMO distributions and, thus, small ΔE_{ST}s, while maintaining high energy excited states.
The presence of intermediate triplet states lying above T1 and below S1 have been shown to facilitate rISC and render TADF more efficient by opening up a reverse internal conversion (RIC) pathway that is mediated by spin-vibronic coupling between T1 and one or more of the intermediate states, followed by rISC [22]. This situation typically occurs when there are multiple donors about a single acceptor as exists in the molecules 5CzBN and 5CzTRZ. For 5CzBN, time-dependent density functional theory (TD-DFT) calculation revealed the existence of three intermediate triplet states [22]. The presence of these states helped to explain the short τd of 3.7 μs and the high EQE_max of 17% and good device stability with a T50 of 176 hours for the OLED [CIE coordinate (0.22, 0.40)] [23]. In an analogous manner, TD-DFT calculations predicted 5CzTRZ to possess a small ΔEST (0.02 eV) as well as a small energy gap (≈0.24 eV) between T2 and T1 [24]. In an analogous manner, 5CzTRZ showed very fast k_rISC of ≈1.5 × 10^7 s^{-1} in toluene, and the device based on 5CzTRZ exhibited superior EQE_max = 29% with λ_EL = 486 nm and very low efficiency roll-off with the EQE at 5,000 cd·m^{-2} remaining high at 27% [24]. Huang et al. also adopted a multiple donor strategy in concert with the weak trifluoromethyl (CF3) acceptor group in their TADF emitter design. The blue-emitting TADF emitter 5CzCF3 possessed a miniscule measured ΔEST of 0.02 eV and Φ_PL of 43% in oxygen-free toluene [25]. The solution-processed device based on 5CzCF3 exhibited sky-blue emission with CIE coordinates of (0.21, 0.33) and an EQE_max of 5.2% at 1 cd·m^{-2} [25].

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The promising performance of emitters possessing a CF3 acceptor group prompted us to investigate other fluorinated weakly-conjugated acceptor units in order to assess their potential within TADF emitter design (Figure 1) [25-27]. In the present study, we report on the impact of incorporating other fluorine-containing electron-withdrawing groups beyond trifluoromethyl (CF3), including trifluoromethoxy (OCF3), trifluoromethylthio (SCF3), and pentafluorosulfanyl (SF5) groups, and explore their potential computationally within TADF emitter design. We cross-compare their optoelectronic properties with analog materials using well-studied conjugated elec-
tron-withdrawing groups (cyano, benzophenone, and triazine). We investigated two families of structures. The first family consists of D–A–D (Type I) molecules containing two carbazole donors disposed each ortho to the acceptor group, while the second family consists of five carbazole donors substituted about a central benzene ring and the sixth position occupied by the acceptor moiety (Type II). Adachi et al. have shown that compounds that fall within the Type I family can simultaneously show high singlet and triplet energies and small $\Delta E_{ST}$ while compounds that are a part of Type II family possess a more dense number of low-lying excited states [22], the presence of which has been shown to assist in the rISC process through spin-vibronic coupling [23,24,27]. The energy levels and electronic configurations of S₁ and T₁ in these molecules were analysed and we found that compounds possessing either SCF₃ and SF₅ groups as acceptors (2CzSCF₃/2CzSF₅ in Type I, 5CzSCF₃/5CzSF₅ in Type II), possessed LUMOs that are mainly located on the central benzene ring and the acceptor group while the HOMOs are mainly localized on the carbazoles, thereby leading to small $\Delta E_{ST}$. The calculated $\Delta E_{ST}$s for 2CzSCF₃/2CzSF₅ are 0.22 eV and 0.07 eV, respectively, which are comparable to the calculated results for 2CzBN (0.18 eV) and 2CzTRZ (0.08 eV); likewise, the calculated $\Delta E_{ST}$s for 5CzSCF₃/5CzSF₅ are 0.27 eV and 0.12 eV, respectively, which are close to the calculated results of 5CzBN (0.20 eV) and 5CzTRZ (0.17 eV). The molecules incorporating an OCF₃ acceptor (2CzOCF₃ in Type I, 5CzOCF₃ in Type II), however, exhibited relatively larger $\Delta E_{ST}$ (0.46 eV for 2CzOCF₃, 0.37 eV for 5CzOCF₃). The calculated S₁ energies of 2CzSCF₃ (3.92 eV), 2CzSCF₃ (3.62 eV), 2CzSF₅ (3.51 eV), and 5CzOCF₃ (3.45 eV) demonstrate that these molecules show potential as deep blue emitters as their S₁ states are higher in energy than that of 2CzBN (3.34 eV calculated in gas phase in this work), which was reported as deep blue emitter with $\lambda_{EL} = 418$ nm and CIE coordinate of (0.15, 0.05) when doped in DPEPO [21]. DFT calculations for 5CzOCF₃, 5CzSCF₃, and 5CzSF₅ predicted dense populations of excited states between T₁ and S₁, which should assist in rISC process [28,29].

Results and Discussion

We employed density functional theory (DFT) and TD-DFT calculations to predict the photophysical properties of these emitters in order to assess their potential as TADF emitters for OLEDs. All ground-state calculations were performed using PBE0/6-31G(d,p) in the gas phase [30,31]. The lowest energy structures from these DFT calculations were used as input geometries for excited-state calculations using the Tamm–Dancoff approximation (TDA) to TD-DFT, which provide computed energies of the excited singlet and triplet states [32,33]. The nature of the lowest singlet and triplet states were ascertained by an analysis of the natural transition orbitals (NTO) obtained from the TDA-DFT calculations [34].

We first investigated the strength of the acceptor groups by modelling phenyl-substituted acceptors and compared their LUMO energies as well as the energies of the S₁ and T₁ states (Figure 2). Among the fluorinated electron-withdrawing groups in the study, PhOCF₃ possesses the shallowest LUMO at −0.22 eV while PhSF₅ possess the deepest LUMO at −0.90 eV, with PhSCF₃ (−0.78 eV) and PhCF₃ (−0.57 eV) possessing intermediate values. The LUMO energies of these four acceptors correlate linearly to the Hammett substituent constant, $\sigma_p$, (Figure 2c) [35]. All of these fluorinated acceptors are much weaker than the more commonly investigated benzonitrile (BN, −1.30 eV), triphenyltriazine (TRZ, −1.72 eV) and benzophenone (BP, −1.58 eV) acceptors. These results indicate that the use of the fluorinated acceptor groups in donor–acceptor TADF emitters should lead to a pronounced blue-shift in the emission, as reflected in the higher-energy singlet states of the model systems in Figure 2.

We next modelled the Type I emitters (Figure 3 and Figure 4). The DFT-calculated geometries indicate that the carbazoles adopt a significantly twisted conformation (dihedral angles > 50°) in order to minimize their interaction with the acceptor group. Specifically, for 2CzCF₃ the carbazoles are twisted to 60.2° and 70.5° with respect to the bridging phenyl ring while for 2CzSF₅, due to the increased bulkiness of the SF₅ group, the corresponding twist angle increased to 78.5° and 78.7°. These highly twisted conformations contribute to the spatial separation of the HOMO and LUMO.

Figure 3 shows the energies of the HOMOs and LUMOs and the S₁ and T₁ states for the fluorinated acceptor-containing emitters 2CzCF₃, 2CzOCF₃, 2CzSCF₃, and 2CzSF₅. The HOMOs in these compounds are mainly located on the two carbazole moieties and a small part on the bridging central benzene ring. The LUMOs of 2CzCF₃, 2CzSCF₃, and 2CzSF₅ are mainly located on the benzene ring and a small distribution onto the electron-withdrawing group, whereas the LUMO of 2CzOCF₃ is localized essentially only on the central benzene. Emitters 2CzCF₃, 2CzOCF₃, and 2CzSCF₃ show similarly deep HOMO values at around −5.80 eV, while the HOMO level of 2CzSF₅ is more stabilized at −5.89 eV. The trend in LUMO energies matches that observed for the model acceptors (Figure 2) where 2CzOCF₃ possesses the shallowest LUMO of −0.95 eV while 2CzSF₅ possesses the deepest LUMO level of −1.46 eV. 2CzOCF₃ possesses the largest energy gap ($\Delta E_g$) at 4.83 eV while the $\Delta E_f$ for 2CzSF₅ is the smallest at 4.43 eV amongst these four compounds. Figure 4 shows the correspond-

Figure 2: a) Calculated HOMO, LUMO, S\textsubscript{1} and T\textsubscript{1} energies, as well as HOMO and LUMO topologies of PhCF\textsubscript{3}, PhOCF\textsubscript{3}, PhOSCF\textsubscript{3}, and PhSF\textsubscript{5}. b) Calculated HOMO, LUMO, S\textsubscript{1} and T\textsubscript{1} energies, as well as HOMO and LUMO topologies of BN, TRZ and BP (isovalue = 0.02). c) Hammett para substituent values (σ\textsubscript{p}) relationship with the calculated LUMO energies for fluorine-containing acceptors PhCF\textsubscript{3}, PhOCF\textsubscript{3}, PhOSCF\textsubscript{3}, and PhSF\textsubscript{5}.

Table 1: Calculations of HOMO, LUMO, S\textsubscript{1} and T\textsubscript{1} energies, as well as HOMO and LUMO topologies of PhCF\textsubscript{3}, PhOCF\textsubscript{3}, PhOSCF\textsubscript{3}, and PhSF\textsubscript{5}. The emissive S\textsubscript{1} state for the seven Type I molecules is characterized mainly by a HOMO to LUMO transition, while the distribution of highest occupied natural transition orbitals (HONTOs) and the lowest unoccupied natural transition orbitals (LUNTOs) show good agreement with the HOMOs and LUMOs (Figure 5 and Figure 6). As the HOMOs and LUMOs of the seven molecules are sufficiently separated, the nature of the S\textsubscript{1} is charge-transfer (CT) in character. The S\textsubscript{1} energies of 2CzCF\textsubscript{3}, 2CzOCF\textsubscript{3}, 2CzSCF\textsubscript{3}, and 2CzSF\textsubscript{5} are much higher than those of 2CzBN, 2CzTRZ, and 2CzBP. 2CzOCF\textsubscript{3} possesses the highest S\textsubscript{1} at 3.92 eV followed by 2CzSCF\textsubscript{3}(3.66 eV) and 2CzCF\textsubscript{3}(3.62 eV). The S\textsubscript{1} of 2CzSF\textsubscript{5} at 3.51 eV is relatively more stabilized due to the stronger electron-withdrawing ability of the SF\textsubscript{5} group. The S\textsubscript{1} states of 2CzBN, 2CzTRZ, and 2CzBP are 3.34 eV, 3.22 eV, and 3.09 eV, respectively. The calculated S\textsubscript{1} values are slightly destabilized relative to the literature reported values for 2CzBN (3.27 eV in toluene [19]) and 2CzTRZ (3.12 eV in zeonex [20]).
Figure 3: Calculated HOMO, LUMO, S₁ and T₁ energies, as well as HOMO and LUMO topologies of 2CzCF₃, 2CzOCF₃, 2CzSCF₃, and 2CzSF₅ (isovalue = 0.02).

Figure 4: Calculated HOMO, LUMO, S₁ and T₁ energies, as well as HOMO and LUMO topologies of 2CzBN, 2CzTRZ, and 2CzBP (isovalue = 0.02).
The nature of the $T_1$ state of $2CzCF_3$, $2CzOCF_3$, and $2CzSF_5$ is of locally excited (LE) character on the carbazole, while for $2CzSCF_3$ the $T_1$ state is also LE, but also involving the bridging benzene ring. These assignments are reflected in very similar $T_1$ energies of around 3.45 eV. The corresponding $\Delta E_{ST}$ values are 0.17 eV for $2CzCF_3$, 0.46 eV for $2CzOCF_3$, 0.22 eV for $2CzSCF_3$ and 0.07 eV for $2CzSF_5$; thus, with the exception of $2CzOCF_3$, the small singlet-triplet energy gaps coupled with the large difference in symmetry between $S_1$ and $T_1$ augers well for efficient deep blue TADF emitters. By contrast, the triplet states of $2CzBN$, $2CzTRZ$, and $2CzBP$ are best characterized by HOMO to LUMO CT-type transition. The calculated $T_1$ values for $2CzBN$, $2CzTRZ$, and $2CzBP$ are 3.16 eV, 3.14 eV, and 3.00 eV, respectively. These values are slightly destabilized compared to the literature reported values for $2CzBN$ (3.03 eV in toluene [19]) and $2CzTRZ$ (3.05 eV in zeonex [20]). The corresponding $\Delta E_{ST}$ values are generally smaller than those of the Type I fluorinated compounds with values of 0.08 eV for $2CzTRZ$, 0.09 eV for $2CzBP$ and 0.18 eV for $2CzBN$; however, the similar orbital symmetries between $S_1$ and $T_1$ would render rISC between these two states less efficient. The calculated $\Delta E_{ST}$ values are close to the literature reported values for $2CzBN$ (0.27 eV in toluene [19]) and $2CzTRZ$ (0.07 eV in zeonex [20]).

Inspired by these results, we next extended our theoretical study to Type II compounds where we increased the number of carbazole donor groups from two to five. We expect this design
to lead to improved spatial separation of the electron density distributions between the HOMO and LUMO, thereby strengthening the CT character of the $S_1$ state and leading to smaller $\Delta E_{\text{ST}}$ values, and thus more efficient TADF. The HOMO and LUMO distributions and energies for the Type II emitters are shown in Figure 7 and Figure 8. The HOMOs of 5CzCF$_3$,
5CzOCF$_3$, and 5CzSCF$_3$ are mainly located on the carbazole moieties located ortho and meta to the acceptor group, with only a small distribution on the para-carbazole. For 5CzSF$_5$, the HOMO is evenly distributed over the five carbazole moieties. The LUMOs of 5CzCF$_3$, 5CzSCF$_3$, and 5CzSF$_5$ are mainly located on the bridging benzene ring and the electron-withdrawing groups along with a small contribution from the para-disposed carbazole, whereas the LUMO of 5CzOCF$_3$ is located only on the central benzene ring, a similar behavior to 2CzOCF$_3$. Compounds 5CzCF$_3$, 5CzSCF$_3$, and 5CzSF$_5$ showed similarly deep HOMO values of around $-5.65$ eV, while the HOMO value of 5CzOSF$_3$ is more stabilized at $-5.73$ eV. The 5CzOCF$_3$ possesses the most destabilized LUMO level at $-1.41$ eV, while 5CzSF$_5$ possesses the deepest LUMO level at $-1.80$ eV. The LUMO values for 5CzCF$_3$ and 5CzSCF$_3$ are $-1.61$ eV and $-1.63$ eV, respectively. 5CzOCF$_3$ has, therefore, the largest energy gap ($\Delta E_g$) at 4.32 eV while 5CzSF$_5$ has the smallest at 3.85 eV; both 5CzCF$_3$ and 5CzOCF$_3$ possess $\Delta E_g$ of 4.03 eV. The trends for the HOMO and LUMO energies for these five Type II emitters mirror those observed for their Type I analogues; however, the HOMO and LUMO values in the Type II emitters are more stabilized and the energy gaps are reduced.

The HOMO of 5CzBN is symmetrically distributed across the ortho- and meta-disposed carbazoles while the HOMO of 5CzTRZ is located mostly on the meta- and para-carbazoles. For 5CzBP, due to the asymmetric structure, the HOMO is located on one side of ortho- and meta-disposed carbazoles while the pseudo-degenerate HOMO=1 is located on the other ortho- and meta-disposed carbazoles. The LUMOs of 5CzBN, 5CzBP, and 5CzTRZ are each located on the central benzene ring and extending onto the electron-withdrawing group. The HOMO of 5CzBN is deepest at $-5.74$ eV, similar to that calculated for 5CzOCF$_3$, while the HOMOs of 5CzBP and 5CzTRZ are $-5.59$ and $-5.60$ eV, respectively. The LUMO values of 5CzBN, and 5CzBP are $-1.98$ eV, and $-1.89$ eV, respectively, which are significantly more stabilized than the fluorinated Type II emitters while the LUMO of 5CzTRZ at $-1.67$ eV is similar to those predicted for 5CzCF$_3$ ($-1.61$ eV) and 5CzSCF$_3$ ($-1.63$ eV). The $\Delta E_g$ values of 5CzBN (3.76 eV), 5CzTRZ (3.93 eV), and 5CzBP (3.70 eV) are all slightly smaller than those of the fluorinated Type II emitters.

The HONTOs and LUNTOs for the Type II emitters are shown in Figure 9 and Figure 10. These generally reflect the HOMO and LUMO distributions, save for 5CzTRZ where the HONTO of S$_1$ is located on the ortho-carbazoles. Due to the sufficiently large separation of the electron densities between the HOMO and LUMO of each of the seven Type II emitters, the S$_1$ state for each of these possesses CT character, analogously to those calculated for the Type I compounds. 5CzOCF$_3$ possesses the highest S$_1$ energy (3.45 eV) among Type II molecules, followed by 5CzSCF$_3$ (3.24 eV) and 5CzCF$_3$ (3.20 eV). The S$_1$ of 5CzSF$_5$ is 3.00 eV, which is close to the values of 5CzBN (2.98 eV), 5CzTRZ (3.08 eV) and 5CzBP (2.91 eV). The
calculated $S_1$ values are more destabilized than the literature reported values of 5CzBN (2.90 eV in toluene [23]), 5CzTRZ (2.85 eV in toluene [24]) and 5CzCF$_3$ (2.82 eV in toluene [25]). The nature of the $T_1$ state for each of these compounds is CT where the HONTOs of $T_1$ are mainly located on the carbazole moieties (and sometimes the central benzene) while the LUNTOs of $T_1$ are mainly located on the benzene ring and electron-withdrawing groups, except for 5CzOCF$_3$ where the LUNTO is located only on the benzene. 5CzOCF$_3$ possesses the highest $T_1$ energy (3.08 eV), while the $T_1$ energies of 5CzCF$_3$, 5CzSCF$_3$, and 5CzSF$_3$ are stabilized at 2.99 eV, 2.96 eV, and 2.88 eV, respectively. The $T_1$ energy of 5CzTRZ is 2.91 eV while those of 5CzBN and 5CzBP are more stabilized at 2.78 eV and 2.80 eV, respectively. The calculated $T_1$ energies match the literature reported value of 5CzBN (2.78 eV in toluene [23]) and are slightly destabilized relative to the literature reported value of 5CzTRZ (2.79 eV in toluene [24]) and 5CzCF$_3$ (2.82 eV in toluene [25]). The corresponding $\Delta E_{ST}$ value of 5CzOCF$_3$ is 0.37 eV, which is reduced by 0.11 eV compared to 2CzOCF$_3$ (0.46 eV). This reduction results from the greater CT character in both $S_1$ and $T_1$. However, as the HOMO/LUMO overlap includes a small distribution on para-disposed carbazole in the Type II emitters with the exception of 5CzOCF$_3$, the $\Delta E_{ST}$ values of Type II emitters are generally slightly larger compared to their Type I congeners. The $\Delta E_{ST}$s of 5CzCF$_3$, 5CzSCF$_3$ and 5CzSF$_3$ are 0.21 eV, 0.27 eV, and 0.12 eV, respectively, which are 0.04 eV, 0.05 eV, and 0.05 eV, respectively larger compared to 2CzCF$_3$ (0.17 eV), 2CzSCF$_3$ (0.22 eV), and 2CzSF$_3$ (0.07 eV). The $\Delta E_{ST}$s of 5CzBN and 5CzBP are 0.20 eV and 0.11 eV, which are only 0.02 eV larger compared to 2CzBN (0.18 eV) and 2CzBP (0.09 eV), while the $\Delta E_{ST}$ for 5CzTRZ is 0.17 eV, which is 0.09 eV larger than that of 2CzTRZ (0.08 eV). The calculated $\Delta E_{ST}$ values are slightly larger than the literature reported values for 5CzBN (0.12 eV in toluene [23]) and 5CzTRZ (0.06 eV in toluene [24]).

The spin-orbit coupling (SOC) values between excited singlet and triplet states were calculated by considering the three $T_1$ substates ($m = 0, \pm 1$) are degenerate and the $|V_{SOC}|^2$ as the average of the three spin-orbit coupling matrix elements (SOCME) between singlet and the triplet states [36]. The results are summarized in Table 1. Among the Type I molecules, 2CzSCF$_3$ possesses the highest $|V_{SOC}|^2$ value as 0.148 cm$^{-2}$, followed by 2CzBP (0.070 cm$^{-2}$) and 2CzSF$_3$ (0.053 cm$^{-2}$). The $|V_{SOC}|^2$ values for 2CzCF$_3$ and 2CzOCF$_3$ are 0.011 cm$^{-2}$ and 0.019 cm$^{-2}$, respectively, which are still much higher than 2CzBN (0.002 cm$^{-2}$) and 2CzTRZ (3 × 10$^{-2}$ cm$^{-2}$). The Type II molecules show an increase in $|V_{SOC}|^2$ values compared to their Type I counterparts. 5CzSCF$_3$ possesses the highest $|V_{SOC}|^2$ value at 0.750 cm$^{-2}$ which is five times higher than 2CzSF$_3$, and 5CzSF$_3$ possesses the second highest $|V_{SOC}|^2$ value as 0.718 cm$^{-2}$, which is more than thirteen times higher than 2CzSF$_3$. The higher $|V_{SOC}|^2$ values of 2CzSCF$_3$/5CzSCF$_3$ and 2CzSF$_3$/5CzSF$_3$ can be ascribed to the presence of the relatively heavier chalcogen, which has also been attributed by Duan et al. to much higher SOCME values in a sulfur-containing emitter than in analogs without the sulfur atom present [37]. The $|V_{SOC}|^2$ values of 5CzBN and 5CzBP increased to 0.298 cm$^{-2}$ and 0.267 cm$^{-2}$, respectively, which are more than one hundred times higher than 2CzBN and four times higher than 2CzBP. The $|V_{SOC}|^2$ values of 5CzCF$_3$ and 5CzOCF$_3$ are also higher at 0.090 cm$^{-2}$ and 0.060 cm$^{-2}$, respectively. The
We analysed the higher excited states of the fluorinated acceptor-containing emitters in both Type I and Type II structures. For 2CzCF$_3$, the $T_1$ is locally excited; further, $T_2$ (3.46 eV) to $T_6$ (3.58 eV) all exhibited significant LE character. The lowest triplet state that exhibits charge transfer characteristics is $T_7$ at 3.72 eV (Figure 11). By contrast, the $T_1$ of 5CzCF$_3$ exhibited CT character and the higher triplet states from $T_2$ to $T_6$ also exhibited CT character, which is a similar picture to the literature reported calculated electronic structure of 5CzBN using TD-DFT/ωB97XD [22] (Figure 12). This change from mostly low-lying LE triplet states in Type I emitters to mostly low-lying CT states in Type II emitters is prevalent in 2CzOCF$_3$/5CzOCF$_3$, 2CzSCF$_3$/5CzSCF$_3$, and 2CzSF$_3$/5CzSF$_3$ (Figures S1–S6, Supporting Information File 1). Both Type I and Type II molecules are predicted to possess multiple intermediate excited states between $S_1$ and $T_1$. For example, for 2CzCF$_3$, $T_2$ to $T_6$ lie between $S_1$ and $T_1$ and the energy gap between $T_4$ and $S_1$ ($\Delta E_{S_{1}T_{4}}$) is 0.04 eV while for 5CzCF$_3$ the $T_2$ to $T_4$ are intermediate states with energies below $S_1$ and the energy gap between $T_4$ and $S_1$ ($\Delta E_{S_{1}T_{4}}$) is 0.02 eV. This phenomenon is also observed in 2CzOCF$_3$ ($\Delta E_{S_{1}T_{6}}$ = 0.08 eV)/5CzOCF$_3$ ($\Delta E_{S_{1}T_{8}}$ = 0.02 eV), and 2CzSCF$_3$ ($\Delta E_{S_{1}T_{6}}$ = 0.09 eV)/5CzSCF$_3$ ($\Delta E_{S_{1}T_{4}}$ = 0.00 eV), 2CzSF$_3$ ($\Delta E_{S_{1}T_{3}}$ = 0.01 eV)/5CzCF$_3$ ($\Delta E_{S_{1}T_{4}}$ = 0.00 eV). We thus contend that the intermediate excited states present in the fluorinated acceptor-containing emitters will assist in the rISC process, and improve the TADF characteristics, mitigating the somewhat larger $\Delta E_{S_{1}}$ values in these compounds.

### Conclusion

This computational study demonstrates the high potential of fluorinated acceptors in TADF emitter design. In particular, we
Figure 11: HONTOs and LUNTOs of 2CzCF$_3$ in higher excited states (isovalue = 0.02).

Figure 12: HONTOs and LUNTOs of 5CzCF$_3$ in higher excited states (isovalue = 0.02).
showed that OCF$_3$, SCF$_3$ and SF$_5$ groups should all be considered when designing deep blue TADF emitters. Type II emitters, with five carbazole donors, showed the most promise in terms of suitable small $\Delta E_{ST}$ values, high spin-orbit coupling values coupled with a relatively large density of intermediate excited triplet states that can be recruited to render TADF more efficient. Present efforts are ongoing to synthesize promising candidates from this theoretical study.

**Supporting Information**

The research data underpinning this publication can be accessed at [https://doi.org/10.17630/bbf9f445-60a0-4c0a-808e-ce27cfcbf48a](https://doi.org/10.17630/bbf9f445-60a0-4c0a-808e-ce27cfcbf48a)

**Supporting Information File 1**
Calculation details, Cartesian coordinates of all the molecules, SOCME calculation result, and HONTOs and LUNTOs of 2CzCF$_3$5CzCF$_3$, 2CzOCF$_3$5CzOCF$_3$, 2CzSCF$_3$5CzSCF$_3$, and 2CzSF$_5$5CzSF$_5$ in higher-lying excited states are available in supporting information. [https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-17-21-S1.pdf](https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-17-21-S1.pdf)

**Acknowledgements**

We thank Oliver Lee for help with the SOCME calculations.

**Funding**

Dongyang Chen thanks the China Scholarship Council (201603780001). We acknowledge support from the Engineering and Physical Sciences Research Council of the United Kingdom (grant EP/P010482/1).

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The definitive version of this article is the electronic one which can be found at: https://doi.org/10.3762/bjoc.17.21