Electron-withdrawing Group Modified Carbazolophane Donors for Deep Blue Thermally Activated Delayed Fluorescence OLEDs

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Abstract

We report two blue-emitting thermally activated delayed fluorescence (TADF) compounds employing a substituted carbazolophane (Czp) donor (indolo[2.2]paracyclophane). The compounds CNCzpPhTRZ and CF₃CzpPhTRZ show emission maxima of 426 nm and 432 nm, respectively, with high photoluminescence quantum yields (Φₚₐ) of 73% and 80%, respectively. The singlet-triplet energy gap (ΔEₛₜ) of both emitters is 0.22 eV, resulting in long-delayed lifetimes of 132 μs for CNCzpPhTRZ and 158 μs for CF₃CzpPhTRZ in PPT as the host matrix. Blue organic light-emitting diodes (OLEDs) showed maximum external quantum efficiencies (EQEs) of 7.4% for CNCzpPhTRZ and 11.6% for CF₃CzpPhTRZ with electroluminescence maxima of ca. 460 nm.

Keywords: TADF, OLEDs, deep blue, paracyclophane

Introduction
The development of purely organic thermally activated delayed fluorescence (TADF) emitters is considered as one of the most promising approaches to utilize singlet and triplet excitons to access highly efficient organic light-emitting diodes (OLEDs). The design principle of generating a structure with spatially separated donor and acceptor moieties to limit the exchange integral between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) thereby leading to a small singlet and triplet excited state energy difference, $\Delta E_{ST}$, has been a reliable and fruitful strategy to construct TADF emitters. To obtain a small $\Delta E_{ST}$, there are at present at least six design strategies, which are twisted donor-acceptor, multiresonance, spiro-conjugation, exciplex, excited-state intramolecular proton transfer (ESIPT), and through-space-conjugation. The most popular of these is to electronically decouple the donor and acceptor by ensuring a highly twisted conformation.

The [2.2]paracyclophane (PCP) is a rigid molecule containing two slightly bent benzene rings connected by ethylene bridges. Due to the spatial stacked configuration and a short distance of 2.78–3.09 Å between the two benzene decks, which is smaller than the van der Waals distance between the layers of graphite (3.35 Å), a strong transannular electronic communication can take place, as demonstrated by Bazan et al. Substituted PCPs can possess planar charity and emissive analogs can exhibit circularly polarized luminescence (CPL). The characteristics of rigid skeleton, chemical and photo stability, planar charity, and through-space electronic communication possessed by PCP core make it a potentially useful building block for organic semiconductor materials.
In 2018, we first demonstrated that the PCP moiety could be used to mediate weak electronic communication between donor and acceptor groups on different decks of the PCP.\textsuperscript{9} \textit{trans-Bz-PCP-TPA} and \textit{cis-Bz-PCP-TPA} showed photoluminescence maxima, $\lambda_{\text{PL}}$, at 455 nm, photoluminescence quantum yields, $\Phi_{\text{PL}}$, of 60\% (in toluene), $\Delta E_{\text{ST}} = 0.19$ eV and delayed lifetime, $\tau_d$, of 3.6 $\mu$s for \textit{trans-Bz-PCP-TPA} and $\lambda_{\text{PL}}$ of 492 nm, $\Phi_{\text{PL}}$ of 45\% (in toluene), $\Delta E_{\text{ST}} = 0.04$ eV and $\tau_d$ of 1.8 $\mu$s for \textit{cis-Bz-PCP-TPA} in 15 wt\% mCP doped film (Figure 1). Zhao \textit{et al.} also reported a series of structurally similar chiral green TADF molecules \textit{g-BNMe-Cp} and \textit{m-BNMe-Cp} containing a PCP, with emission at 531 nm ($\Phi_{\text{PL}} = 72\%$ in cyclohexane, $\Delta E_{\text{ST}} = 0.17$ eV and $\tau_d = 0.38$ $\mu$s in toluene) and 521 nm ($\Phi_{\text{PL}} = 39\%$ in cyclohexane, $\Delta E_{\text{ST}} = 0.12$ eV and $\tau_d = 0.22$ $\mu$s in toluene), respectively (Figure 1).\textsuperscript{16} Recently, the same group introduced a phenylene spacer between the PCP and the acceptor moiety to obtain sky-blue to green TADF emitters showing increased $\Phi_{\text{PL}}$ (in cyclohexane) to 83\% for \textit{g-BPhNMe$_2$-Cp}, 93\% for \textit{m-BPhNMe$_2$-Cp}, and 82\% for \textit{g-BPhNPh$_2$-Cp} (Figure 1).\textsuperscript{17} Besides using the PCP as a bridge motif to enable electronic coupling between donor and acceptor groups, we also demonstrated how the PCP skeleton could be incorporated within the carbazole donor unit. Carbazolophane (Czp, [2]paracyclo[2](1,4)carbazolophane) group is a stronger electron donor that adopts a more twisted conformation due to its greater steric bulk.\textsuperscript{9} We reported the chiral TADF emitter CzpPhTRZ, which showed a small $\Delta E_{\text{ST}}$ of 0.16 eV, and $\lambda_{\text{PL}}$ at 482 nm with $\Phi_{\text{PL}} = 69\%$ and a $\tau_d$ of 65 $\mu$s in 10 wt\% DPEPO doped film.\textsuperscript{18} Sky-blue OLEDs with CzpPhTRZ showed a maximum external quantum efficiency ($\text{EQE}_{\text{max}}$) of 17.0\% and CIE coordinates of (0.17, 0.25). Zheng and co-workers reported an analog of CzpPhTRZ, PXZp-Ph-TRZ, where the Czp donor was replaced with a phenoxazinephane (PXZp). PXZp-Ph-TRZ possesses a $\Delta E_{\text{ST}}$ of 0.03 eV and shows yellow emission with $\lambda_{\text{PL}}$ at 560 nm in 10 wt\% CBP doped film. The OLED showed an $\text{EQE}_{\text{max}}$ of 7.8\%
and CIE coordinates of (0.49, 0.50).\textsuperscript{19} As we can see from Figure 1 since our first report, a handful of emitters have been reported containing the PCP moiety; however none to date show pure blue emission.

Building on our prior work and with the goal to obtain a blue-shifted emission, we designed two new TADF emitters CNCzpPhTRZ and CF\textsubscript{3}CzpPhTRZ, by introducing electron-withdrawing groups on the Czp donor unit of the parent CzpPhTRZ emitter. We successfully blue-shifted the emission without adversely affecting the TADF efficiency. CNCzpPhTRZ emits at 426 nm, and CF\textsubscript{3}CzpPhTRZ emits at 432 nm in toluene, representing a ca. 40 nm blue-shift compared to that of CzpPhTRZ. The $\Phi_{PL}$ remained high at 73\% and 80\%, respectively. Further, we fabricated bluer OLEDs with electroluminescence maxima at ca. 460 nm. However, we observed the evolution of a red emission band at around 600 nm in the OLEDs, the origin of which we rationalized due to electromer formation upon the degradation of both blue emitters during the operation of the device.
Figure 1. Chemical structures and performance of PCP-based TADF molecules.
Results and Discussion

Synthesis

The synthesis is based on our previously reported route. Aniline derivatives were coupled to bromo[2.2]paracyclophane with yields of 63% for 1a, and 55% for 1b. The generated intermediates were used to form the functionalized carbazolophane donor units with yields of 44% for 2a and 62% for 2b via a Pd-catalyzed intramolecular oxidative cyclization process where the ortho-chlorine atoms act as the directing group. Lastly, the prepared donor 2 and triazine-based acceptor were linked together via a nucleophilic aromatic substitution with yields above 50% using tripotassium phosphate as a base in DMSO at 120 °C. The targeted compounds, CN_{CzpPhTRZ} and CF_{3}CzpPhTRZ, show strong blue luminescence under UV excitation. The identity and purity of CN_{CzpPhTRZ} and CF_{3}CzpPhTRZ were determined by a combination of NMR, MS, HRMS, Mp, and IR.

![Scheme 1. Synthetic route to CN_{CzpPhTRZ} and CF_{3}CzpPhTRZ.](image)

Theoretical calculations

Density functional theory (DFT) calculations were performed to investigate the frontier orbital densities and energy states of model compounds of the two emitters. The geometries in the ground state of the two emitters were optimized in the gas phase at the PBE0/6-31G(d,p) level of theory. Time-dependent DFT calculations using the Tamm–Dancoff approximation (TDA-DFT) in the
gas phase based on the optimized molecular structures provide insight into the energies and nature of the lowest-lying singlet and triplet excited states.\textsuperscript{20} The frontier orbitals and energy levels of these molecules are shown in Figure 2 and Table S1.

The torsion angles between the \textit{Czp} donors and the bridging phenylene are expected not unaffected by the substitution on the distal side of the donor. While for the previously reported \textit{CzpPhTRZ}, the torsion angle obtained from DFT calculations was 58°, the torsion angles for \textit{CF}_3\textit{CzpPhTRZ} and \textit{CNCzpPhTRZ} are 56° and 58°, respectively. The DFT calculations reveal that the frontier orbitals and states are effectively tuned \textit{via} the introduction of electron-withdrawing groups. The HOMO is located primarily on the carbazolophane donor moiety, while the LUMO is distributed across the triazine acceptor and phenylene bridge. The HOMO levels of the two derivatives are expectedly significantly stabilized at $-5.91$ eV (\textit{CNCzpPhTRZ}), and $-5.78$ eV (\textit{CF}_3\textit{CzpPhTRZ}) compared to that of the parent emitter \textit{CzpPhTRZ} ($-5.54$ eV) due to the presence of the electron-withdrawing cyano and trifluoromethyl groups, respectively. The more positive Hammett $\sigma_p$ value for cyano (0.66) versus trifluoromethyl (0.54) explains the 0.13 eV greater stabilization observed for the HOMO of \textit{CNCzpPhTRZ}. The LUMO levels are somewhat less affected by substituting the carbazolophane at $-2.08$ and $-2.00$ eV, respectively, for \textit{CNCzpPhTRZ} and \textit{CF}_3\textit{CzpPhTRZ} and deeper than that of \textit{CzpPhTRZ} ($-1.88$ eV). There is a corresponding increase in the energy of the $S_1$ state from 3.12 eV (\textit{CzpPhTRZ}) to 3.27 eV (\textit{CNCzpPhTRZ}) and 3.23 eV (\textit{CF}_3\textit{CzpPhTRZ}). The triplet energies are unaffected by the substituents with 2.81 eV (\textit{CzpPhTRZ}), 2.96 eV (\textit{CNCzpPhTRZ}) and 2.92 eV (\textit{CF}_3\textit{CzpPhTRZ}). The $\Delta E_{ST}$ values of \textit{CNCzpPhTRZ} (0.31 eV) and \textit{CF}_3\textit{CzpPhTRZ} (0.31 eV) are almost identical to that of \textit{CzpPhTRZ} (0.30 eV), which suggests that these three molecules will be equally promising TADF emitters. The oscillator strengths, $f$, for the transition to the $S_1$ state of \textit{CNCzpPhTRZ} ($f = 0.319$)
and CF\textsubscript{3}CzpPhTRZ \((f = 0.325)\) are slightly reduced compared to CzpPhTRZ \((f=0.418)\), indicating a slightly slower radiative decay rate.

**Figure 2.** DFT calculations of CNCzpPhTRZ and CF\textsubscript{3}CzpPhTRZ.

**Electrochemical studies**

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements in dichloromethane (DCM) with tetra-\(n\)-butylammonium hexafluorophosphate (TBAPF\textsubscript{6}) as the supporting electrolyte were used to infer the HOMO/LUMO levels of CF\textsubscript{3}CzpPhTRZ and CNCzpPhTRZ from the redox potentials. The resulting voltammograms are shown in Figure S1, and the data are summarized in Table 2. Both emitters possess similar quasi-reversible oxidation
potentials. The oxidation potential of $\text{CF}_3\text{CzpPhTRZ}$ is 1.30 V vs SCE, and that of $\text{CNCzpPhTRZ}$ is 1.34 V vs SCE (Figure S1), which are each assigned to the oxidation of the carbazolophane (Czp) donor moieties, values that are anodically shifted relative to that of $\text{CzpPhTRZ}$ (1.14 V). The estimated HOMO levels are -5.64 eV and -5.68 eV for $\text{CF}_3\text{CzpPhTRZ}$ and $\text{CNCzpPhTRZ}$, respectively. These two HOMO levels are very similar, suggesting that the CN and CF$_3$ have a similar electron-withdrawing ability in these compounds.

Further, the ionization potential was directly measured by UV ambient pressure photoemission spectroscopy (APS) and showed deeper levels of 6.05 eV for $\text{CF}_3\text{CzpPhTRZ}$ and 5.93 eV for $\text{CNCzpPhTRZ}$ than those determined from the solution-state electrochemistry, this due in part to the different measurement environments (neat film for APS and DCM for DPV). These values align much more closely to the DFT calculated values (vide supra), although we note the calculations are in vacuo whereas the measurements are on solid films. The reduction waves assigned to the reduction of the cycaphenine acceptor are quasi-reversible at -1.67 V vs SCE. The reduction potentials are slightly shifted anodically compared to $E_{\text{red}}$ of -1.78 V for $\text{CzpPhTRZ}$. The corresponding LUMO levels are -2.68 V and -2.67 V for $\text{CF}_3\text{CzpPhTRZ}$ and $\text{CNCzpPhTRZ}$, respectively.

**Table 2.** Electrochemical, HOMO-LUMO and $\Delta E_{\text{ST}}$ of $\text{CF}_3\text{CzpPhTRZ}$ and $\text{CNCzpPhTRZ}$.

| Emitters    | $E_{\text{ox}}$ / V | $E_{\text{red}}$ / V | $E_{\text{HOMO}}$ / eV | $E_{\text{LUMO}}$ / eV | $E_{\text{S}}/E_{\text{T}}^\#$ / eV | $\Delta E_{\text{ST}}$ / eV |
|-------------|---------------------|----------------------|------------------------|------------------------|----------------------------------|-------------------------|
| $\text{CF}_3\text{CzpPhTRZ}$ | 1.30                | -1.66                | -5.64 (6.05)           | -2.68                  | 2.91/2.69                        | 0.22                    |
| $\text{CNCzpPhTRZ}$    | 1.34                | -1.67                | -5.68 (5.93)           | -2.67                  | 2.92/2.69                        | 0.23                    |

$E_{\text{ox}}$ and $E_{\text{red}}$ are anodic and cathodic peak potentials, respectively, obtained from DPV using $\text{F}_2/\text{F}_2^+$ as the internal reference and referenced versus SCE (0.46 V vs SCE) in DCM with 0.1 M $[\text{iBu}_4\text{N}]\text{PF}_6$ as the supporting electrolyte.$^{21}$ $^\#E_{\text{HOMO/LUMO}} = -(E_{\text{ox}}/E_{\text{red}} + 4.8)\text{eV}$, where $E_{\text{ox}}$ is anodic peak potential and $E_{\text{red}}$ is cathodic peak potential calculated from DPV relative to $F_2/F_2^+$. $^\dagger$ Obtained from the onset of the prompt fluorescence (time window: 1 ns – 100 ns) and phosphorescence spectra (time window: 1 ms – 10 ms) of 10 wt% samples doped in PPT at 77 K. $^\ddagger\Delta E_{\text{ST}} = E_{\text{S}} - E_{\text{T}}$. 


Solution-state photophysical studies

**Figure 3.** Molar absorptivity and photoluminescence spectra of CF$_3$CzpPhTRZ and CNCzpPhTRZ in toluene at 298 K ($\lambda_{\text{exc}} = 360$ nm). Inset: Photos of photoexcited solutions in toluene.

Both molecules show similar absorption and photoexcitation spectra in dilute toluene (Figure 3 and Figure S2). The absorption bands of CF$_3$CzpPhTRZ at 363 nm and CNCzpPhTRZ at 365 nm are of similar intensities ($\varepsilon = 1.6 \times 10^4$ vs $1.4 \times 10^4$ M$^{-1}$cm$^{-1}$) and are assigned to an intramolecular charge transfer (ICT) from the carbazolophane donor to the triazine acceptor. These CT bands are ca. 10 nm hypsochromically shifted compared to the CT band of the reference compound CzpPhTRZ.$^{18}$

The photoluminescence (PL) spectra of both emitters in toluene are shown in Figure 3. The PL maxima of CF$_3$CzpPhTRZ at 432 nm and CNCzpPhTRZ at 426 nm are significantly blue-shifted compared to that of the reference CzpPhTRZ emitter ($\lambda_{\text{PL}} = 470$ nm). The emission spectra are unstructured, indicative of an excited state with a strong ICT character. The full-width-at-half maximum (FWHM) for CNCzpPhTRZ (0.36 eV) is slightly smaller than that of CF$_3$CzpPhTRZ (0.41 eV). The PL quantum yield ($\Phi_{\text{PL}}$) values in degassed toluene are 80% for CF$_3$CzpPhTRZ...
and 73% for CNCzpPhTRZ, which decreased upon exposure to oxygen to 69% for CF₃CzpPhTRZ and 61% for CNCzpPhTRZ. The φₚL of both emitters in toluene is higher than that of the parent emitter (70% in degassed toluene and 55% after exposure to oxygen).¹⁸ Triplets are sensitive to quenching by oxygen and so the lower φₚL after exposure to oxygen shows that triplets play a role in the light emission process.²³,²⁴ The time-resolved PL decays of both compounds exhibited mono-exponential decay kinetics with PL lifetimes, τ, of 5.47 ns and 4.87 ns for CF₃CzpPhTRZ and CNCzpPhTRZ, respectively (Figure S3); no delayed emission in toluene was detected despite the oxygen sensitivity noted for the φₚL. Thus, the delayed fluorescence in CzpPhTRZ, CF₃CzpPhTRZ, and CNCzpPhTRZ in toluene is smaller than we can reliably detect.

Figure 4. Photoluminescence spectra of CF₃CzpPhTRZ and CNCzpPhTRZ dispersed at 10 wt% in PPT matrix at 295 K (λₑₓc = 360 nm).
Table 3. Photophysical properties of CF₃CzpPhTRZ and CNCzpPhTRZ.a

| Emitters         | λPL / nm | ΦP / ns | τP / μs | ΦPL / % |
|------------------|---------|--------|--------|--------|
|                  | In toluene\(^b\) |        |        |        |
| CF₃CzpPhTRZ      | 432     | 5.47   | -      | 80 (69) |
| CNCzpPhTRZ       | 426     | 4.87   | -      | 73 (61) |
|                  | 10 wt% doped in PMMA\(^c\) |        |        |        |
| CF₃CzpPhTRZ      | 436     | 6.84   | 151.4  | 63 (61) |
| CNCzpPhTRZ       | 435     | 7.32   | 132.1  | 62 (59) |
|                  | 10 wt% doped in PPT\(^c\) |        |        |        |
| CF₃CzpPhTRZ      | 456     | 6.63   | 158.3  | 70 (65) |
| CNCzpPhTRZ       | 458     | 6.75   | 135.0  | 65 (60) |

\(^a\)At 298 K. \(^b\)Quinine sulfate (0.5 M) in H₂SO₄ (aq) was used as the reference (ΦFL: 54.6%, λexc = 360 nm). Values quoted are in degassed solutions, which were prepared by three freeze-pump-thaw cycles. The values in parentheses are in the presence of O₂. \(^c\)Thin films were prepared by spin-coating 10 wt% doped samples in PMMA and PPT. Steady-state and time-resolved emission spectra were recorded at 298 K under an O₂-free atmosphere (λexc = 360 nm for steady-state and λexc = 379 nm for time-resolved emission). Photoluminescence quantum yields of thin films were determined using an integrating sphere (λexc = 300 nm or 360 nm) under N₂ atmosphere at 298 K. The values in parentheses are in the presence of O₂.

Photophysical properties in thin films

Recognizing examples where there is little evidence for TADF in solution but that TADF is prevalent in the solid-state for compounds with relatively large calculated ΔEST values,\(^{24,26}\) we next focused our attention on the photophysical properties of CF₃CzpPhTRZ and CNCzpPhTRZ in doped thin films. Initially, a photophysical investigation was conducted on spin-coated 10 wt% doped films in poly(methyl methacrylate) (PMMA) as the polarity of this host closely mimics that of toluene (PhMe). The absorption bands are of similar energy to those in PhMe, with the CT band observed at about 363 nm (Figure S4). Both compounds showed the unstructured ICT-based emission at around 435 nm, similar to that observed in PhMe (Figure S4). The PL spectra are blue-shifted by ca. 30 nm compared to that of the parent emitter CzpPhTRZ. The ΦPL values are modestly decreased relative to those in solution at 63% and 62% for CF₃CzpPhTRZ and CNCzpPhTRZ, respectively, under N₂ atmosphere, likely reflective of some aggregation-caused quenching. Biexponential decay kinetics were observed in the time-resolved decays with τP values
of 6.84 ns and 7.32 ns and \( \tau_d \) values of 151.4 and 132.1 \( \mu \)s for CF\(_3\)CzpPhTRZ and CNCzpPhTRZ, respectively (Figure S5). We measured prompt fluorescence and phosphorescence spectra of both emitters in PMMA films at 77 K. The energy difference, taken from the onsets of these spectra, provides \( \Delta E_{ST} \) values of 0.27 and 0.30 eV for CF\(_3\)CzpPhTRZ and CNCzpPhTRZ, respectively. These data are consistent with TADF being operative for the emitters in PMMA films. We then investigated the photophysical behavior of the both compounds in suitably high triplet energy and deep HOMO level OLED-relevant hosts such as bis[2-(diphenylphosphino)phenyl]ether oxide (DPEPO, \( E_T = 3.0 \) eV, \( E_{HOMO} = -6.3 \) eV\)\(^{27,28} \) and 2,8-bis(diphenyl-phosphoryl)-dibenzo[b,d]thiophene (PPT, \( E_T = 3.1 \) eV, \( E_{HOMO} = -6.7 \) eV).\(^{29} \) A concentration study of both emitters revealed that the \( \Phi_{PL} \) was highest in 10 wt% doped films in PPT (Table S2). The \( \Phi_{PL} \) of 10 wt% CF\(_3\)CzpPhTRZ doped in PPT is 70%, while in DPEPO at the same doping concentration, it is 53%. Similarly, the \( \Phi_{PL} \) of 10 wt% CNCzpPhTRZ doped in PPT is 65%, and in the corresponding DPEPO film, it is 52%. By contrast, the parent emitter CzpPhTRZ showed \( \Phi_{PL} \) of 69% in the 10 wt% doped DPEPO film and only 55% in the 10wt% doped PPT film.\(^{18} \) The absorption spectra in these host matrices are very similar to those in PMMA (Figure S6). However, \( \lambda_{PL} \) of both emitters are about 20 nm red-shifted at around 456 nm in these two host matrices, suggesting stronger aggregation\(^{30,31} \) (Figure 4 and Figure S7 and Table 3). The emission of both emitters is expectedly blue-shifted (~25 nm) in comparison to parent emitter CzpPhTRZ (\( \lambda_{PL} = 482 \) nm in 10 wt% doped films in DPEPO)\(^{18} \). The time-resolved PL decays in PPT show a nanosecond prompt emission and microsecond delayed emission at room temperature with comparable values to those measured in PMMA. The \( \tau_d \) values of the 10 wt% doped PPT films are 158.3 \( \mu \)s for CF\(_3\)CzpPhTRZ and 135.0 \( \mu \)s for CNCzpPhTRZ, which is significantly longer than that measured for parent emitter CzpPhTRZ in the 10 wt% DPEPO film (\( \tau_d = 65 \) \( \mu \)s).
The temperature-dependent time-resolved PL decays in PPT are shown in Figure 5. The prompt emission is insensitive to temperature, while the delayed emission is thermally activated, a behavior consistent with TADF.

Figure 5. Temperature-dependent time-resolved photoluminescence lifetime of 10 wt% doped films of a) CF$_3$CzpPhTRZ and b) CNCzpPhTRZ in PPT ($\lambda_{exc} = 379$ nm).

We next prepared 10 wt% doped films of each emitter in PPT as a host matrix. As shown in Figure 7, the $S_1$ levels of CF$_3$CzpPhTRZ ($S_1 = 2.92$ eV) and CNCzpPhTRZ ($S_1 = 2.91$) are very similar and at higher energy than that of the parent emitter CzpPhTRZ ($S_1 = 2.77$ eV); interestingly, the $S_1$ level of CzpPhTRZ in DPEPO is 2.89 eV. The $S_1$ energies in PPT are only slightly lower in energy than those determined in PMMA ($S_1 = 3.0$ eV), Figure S8. The $T_1$ levels remain largely the same, regardless of the nature of the host medium or the structure of the emitter, and are of similar magnitude to their corresponding triphenyl triazine acceptor segments in toluene,\textsuperscript{32} indicating that the $T_1$ state is locally excited ($^3$LE) character. The $T_1$ levels for CF$_3$CzpPhTRZ, CNCzpPhTRZ and CzpPhTRZ are all around 2.69 eV in PPT (Figure 6) and closely resembles those measured in PMMA at 2.73 eV (Figure S8) and the reported triplet energy of CzpPhTRZ in DPEPO (2.73 eV).\textsuperscript{18} The corresponding $\Delta E_{ST}$ values are 0.22 eV for CF$_3$CzpPhTRZ, 0.23 eV for
CNCzpPhTRZ, and 0.09 eV for CzpPhTRZ in PPT (Figure 6 and Table 2); the reported $\Delta E_{ST}$ of 10 wt% CzpPhTRZ doped in DPEPO is 0.16 eV.\textsuperscript{18} The larger $\Delta E_{ST}$ values for CF\textsubscript{3}CzpPhTRZ and CNCzpPhTRZ explain the longer delayed lifetimes and less efficient RISC, which can be rationalized due to the weaker electron-donor leading to a larger overlap integral.

![Figure 6](image_url)

**Figure 6.** 77 K prompt PL and phosphorescence spectra measurement of 10 wt% a) CzpPhTRZ b) CF\textsubscript{3}CzpPhTRZ and c) CNCzpPhTRZ doped in PPT host ($\lambda_{exc} = 343$ nm), the $\Delta E_{ST}$ value is taken from the onset value difference between the 77 K prompt fluorescence and phosphorescence spectra.
Device characterization

**Figure 7.** (a) Energy level diagram of materials employed in the devices; (b) Molecular structure of materials used in the devices; (c) Current density and luminescence versus voltage characteristics for the devices; (d) External quantum efficiency versus luminescence curves for the devices; (e) Electroluminescence spectra of the device of CF<sub>3</sub>CzpPhTRZ and CNCzpPhTRZ, the inset is the electroluminescence of CF<sub>3</sub>CzpPhTRZ.

Based on the promising photophysical properties of CF<sub>3</sub>CzpPhTRZ and CNCzpPhTRZ in PPT films, we fabricated thermally-evaporated multilayer bottom-emitting OLEDs. The OLED stack architecture is shown in Figure 7a and consisted of: indium tin oxide (ITO)/1,4,5,8,9,11-hexaaazatriphenylenehexacarbonitrile (HATCN) (5 nm)/N,N'-di(1-naphthyl)-N,N'′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (NPB) (30 nm)/tris(4-carbazoyl-9-ylphenyl)amine (TCTA) (20 nm)/1,3-bis(N-carbazolyl)benzene (mCP) (10 nm)/emissive layer (20 nm)/1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) (40 nm)/LiF (0.5 nm)/Al (100 nm), where HATCN plays the role
of hole-injection layer (HIL), NPB and TCTA were employed as hole-transport layer (HTL), mCP acts as an electron/exciton-blocker layer (EBL) and TmPyPB plays the role of an electron-transport layer (ETL) and hole-blocking layer (HBL) due to its deep HOMO (-6.7 eV); LiF acts as electron-injection layer (EIL) by modifying the work function of the aluminum cathode. The molecular structures of the materials used in these OLEDs are shown in Figure 7b. The emission layer (EML) comprises 10 wt% of CF3CzpPhTRZ or 10 wt% CNCzpPhTRZ doped into PPT. The electroluminescence properties of the OLEDs are summarized in Table 4, and current density–voltage–brightness (J–V–L) curves, EQE–luminance curves and electroluminescence spectra (EL) are given in Figures 7e-e. The turn-on voltage of the devices is ca. 3.7 V at 1 cd/m². The maximum external quantum efficiency (EQEmax) of the CF3CzpPhTRZ and CNCzpPhTRZ based devices at 1 cd/m² and is 11.6% and 7.4%, respectively, with a current efficiency (CE) = 16.8 cd/A and 9.08 cd/A and a power efficiency (PE) = 13.7 lm/W and 7.5 lm/W, respectively (Figure S9 and S10). The devices with both emitters show high-efficiency roll-off with EQEs at 100 cd/m² at only 2.7%, due in part to inefficient harvesting triplet exciton because of the high triplet lifetime of both emitters. As expected, the optimized CF3CzpPhTRZ and CNCzpPhTRZ based devices display a blue-shifted emission at around 460 nm compared to the previously reported OLED with CzpPhTRZ (λEL = 480 nm), consistent with the trend of their film PL emission (Figure 7e). The corresponding CIE coordinates are (0.186, 0.200), and (0.194, 0.182) for CF3CzpPhTRZ and CNCzpPhTRZ, respectively.
Surprisingly, we observed spectral changes of the electroluminescence in both devices with an emission band in the region of 600 nm developing as the device was run whereas upon photoexcitation, we did not observe any emission around 600 nm. We ascribe this new feature in the EL spectrum to degradation of the emitter during device operation. We also observed emission at around 600 nm from the decomposed residue isolated from the sample boat after gradient sublimation under vacuum, which is very similar to the EL feature above 600 nm (Figure S11) and may be attributed to aggregate formation.

**Conclusions**

We developed two new TADF emitters containing a substituted carbazolophane (Czp) donor unit (indolo[2.2]paracyclophane) containing the electron-withdrawing groups cyano (CN) and trifluoromethyl (CF₃) to obtain the deep and pure blue emission. Both emitters show high photoluminescence quantum yield. The $\Delta E_{ST}$ is 0.23 eV for CF₃CzpPhTRZ and 0.22 eV for CNCzpPhTRZ with long-delayed lifetime of 158.3 µs for CF₃CzpPhTRZ and 135.0 µs for CNCzpPhTRZ in PPT host shows TADF behavior. Blue OLEDs were fabricated with these new TADF emitters showing an EQE$_{max}$ of 7.4% for CNCzpPhTRZ and 11.6% for CF₃CzpPhTRZ at electroluminescence wavelength around 460 nm with CIE coordinates of (0.194, 0.182) for the device with CF₃CzpPhTRZ and (0.186, 0.200) for the device with CF₃CzpPhTRZ. We observed

| Emitter       | Host | $V_{on}$ / V | $\lambda_{EL}$ / nm | $CE$ / cd A$^{-1}$ | $PE_{max}$ / lm W$^{-1}$ | EQE$^c$ / % | CIE$^d$ / x,y |
|---------------|------|--------------|---------------------|-------------------|--------------------------|------------|----------------|
| CF₃CzpPhTRZ (10 wt%) | PPT  | 3.7          | 460                 | 16.8              | 13.7                     | 11.6/2.7   | 0.186, 0.200  |
| CNCzpPhTRZ (10 wt%)  | PPT  | 3.7          | 456                 | 9.1               | 7.5                      | 7.4/2.7    | 0.194, 0.182  |

*a The turn-on voltage at a brightness 1 cd m$^{-2}$. b The electroluminescence maximum recorded at 6 V. c EQE$_{max}$ at 1 cd m$^{-2}$ and EQE at 100 cd m$^{-2}$. d The CIE coordinates were recorded at 7 V.
an unexpected emission band around 600 nm in OLEDs upon electrical excitation, which we attributed to degradation of the emitter.

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