A Novel Carbazolophane: A Comparison of the Performance of Two Planar Chiral CP-TADF Emitters

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The prototypical example of a (cyclo)phane, [2.2]paracyclophane (PCP), has proven to be a versatile stereogenic moiety within the design of circularly polarized thermally activated delayed fluorescence (CP-TADF) emitters; however, the exploration of other cyclophanes within CP-TADF emitter design has been largely neglected. Here, a comparative study of the photophysical and optoelectronic properties of two cyclophane emitters, (1,7)tBuCzpPhTrz and its isomer (1,4)tBuCzpPhTrz, is presented. The carbazolophane-triazine compound (1,7)tBuCzpPhTrz, obtained via an unprecedented intramolecular rearrangement, is the first example of a planar chiral TADF emitter deviating from the PCP scaffold. Significant geometrical change of the enclosed carbazole in (1,7)tBuCzp results in an attenuation of the donor strength, while the merits of rigidity and steric bulk remain. In particular, the full width at half maximum (FWHM) of the photoluminescence spectrum in toluene of (1,7)tBuCzpPhTrz is reduced by 34% and blue-shifted by 20 nm compared to that of (1,4)tBuCzpPhTrz. In doped films, the compounds reach high photoluminescence quantum yields ($\Phi_{PL}$) of 91 and 81%, respectively. The chiroptical properties reveal dissymmetry factors $|g_{PL}|$ of up to $5 \times 10^{-4}$. These results demonstrate the impact of the cyclophane for the development of CP-TADF materials and add to the currently limited scope of available planar chiral donors.

1. Introduction

Compounds exhibiting thermally activated delayed fluorescence (TADF) show a dual emission where a prompt fluorescence originates from rapid radiative decay of singlet excitons and a delayed fluorescence follows the endothermic up-conversion of non-emissive triplet excitons to singlets. This reverse intersystem crossing (RISC) is exploited in organic light-emitting diodes (OLEDs), which can then reach an internal quantum efficiency (IQE) of up to 100%, making organic TADF materials desired targets for electroluminescent device applications. TADF emitter design produces organic semiconductors that possess a suitably small energy gap, $\Delta E_{ST}$, between the first excited singlet ($S_1$) and triplet ($T_1$) excited states. The most prominent design are compounds that have a strongly twisted donor-acceptor (D-A) structure wherein the electron density in the highest occupied molecular orbital (HOMO) is mainly localized on the

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donor moiety while the lowest unoccupied molecular orbital (LUMO) is found on the electron-withdrawing acceptor, leading to a small exchange integral and thus a small $\Delta E_{ST}$ that is essential for TADF.\[14] OLEDS face a trade-off between high contrast ratios, achieved by reducing reflection of incident light, and brightness loss, when $\approx50\%$ of the produced light from the emissive layer is absorbed by anti-glare filters that are present in most of these devices. These filters convert unpolarized light into circularly polarized (CP) light (CPL). Upon reflection, the polarization of the CPL is reversed, preventing it from passing the filter; however, besides the suppression of the reflected incident light, the generated light of the OLED is also trapped. A strategy to circumvent this loss channel is to use a material with inherent CPL, thus making anti-glare filters redundant. A quantification of the degree of CPL is the photoluminescence dissymmetry factor $|\Phi g|$, which can have a maximum value of 2. Most closed-shell organic emitters, however, have very low $|\Phi g|$, on the order of $10^{-3}$.\[24] Thus, to achieve optimal results in a device requires employing an emitter that simultaneously can harvest both singlet and triplet excitons to produce light, is bright (i.e., has a high photoluminescence quantum yield, $\Phi PL$), and that the light emanating be CP.

One strategy to design CPL-active materials is to incorporate a planar chiral motif within the emitter design.\[8] Among such well-studied motifs are the (cyclo)phanes, a class of cyclic compounds featuring at least one bridged arene. The [2.2]paracyclophan (PCP), a prototypical example consisting of two closely stacked benzene rings, has been at the center of scientific attention, and has proven useful in catalysis,\[6] $\pi$-conjugated oligomers,\[7] porous frameworks,\[8] chemical vapour deposition (CVD) coatings,\[9] and other material applications.\[10] In 2018, we were the first to incorporate this three-dimensional scaffold within a CP-TADF emitter.\[11] Decorating the decks with donor (D) and acceptor (A) units produces a material that possessed low-lying charge transfer (CT) excited states whose electronic communication was mediated through the $\pi$-stacked core of the PCP. Both isomers, cis- and trans-Bz-PCP-TPA, showed blue TADF with photoluminescence maxima, $\lambda_{PL}$, at 480 nm and 465 nm, respectively in 15 wt% doped films in 1,3-bis(N-carbazolyl)benzene (mCP); however, their low $\Phi PL$ of 12% and 15% precluded their use as emitters in OLEDS (Figure 1).

Zhao and co-workers reported a similar through-space PCP-based emitter BNMe$_2$-CP that contained a bulky dimethylbenzanthracene-oracle intended to suppress concentration-induced quenching.\[15] A hypochromic shift was observed in toluene for the pseudo-meta derivative m-BNMe$_2$-CP ($\lambda_{PL}$ = 521 nm) that has the larger D-A distance compared to g-BNMe$_2$-CP ($\lambda_{PL}$ = 531 nm). This latter compound has a very short $\tau_g$ of 0.38 $\mu$s in toluene, a high $\Phi PL$ of 72% in cyclohexane and a $|\Phi g|$ value of 4.2 x $10^{-3}$ in toluene. Insertion of an ortho-functionalized phenyl moiety produced conformationally more rigid structures g-BPhNMe$_2$-CP, m-BPhNMe$_2$-CP and m-BPhNPh$_2$-CP, emitting at $\lambda_{PL}$ of 488, 461, and 455 nm and having high $\Phi PL$ of 83, 93, and 82%, respectively, in tetrahydrofuran (Figure 1).\[16] The $|\Phi g|$ values were high for organic emitters at 1.3 x $10^{-2}$, 1.7 x $10^{-2}$, and 1.7 x $10^{-2}$, respectively.

The dominant molecular designs for PCP-containing TADF emitters are those with PCP-fused N-heterocyclic donors. The [2]paracyclo[2](1,4)carbazolophane (Czp) was introduced as a sterically more demanding and stronger donor that produces emitters with smaller $\Delta E_{ST}$ compared to analogues using carbazole (Cz).\[12] Compounds CzpPhTrz, CNCzpPhTrz and CF$_3$CzpPhTrz emit at $\lambda_{PL}$ of 482, 458, and 456 nm and all have high $\Phi PL$ of up to 70% in 10 wt% doped films in bis-[2-(diphenylphosphino)phenyl] ether oxide (DPEPO) or 2,8-bis(diphenylphosphoryl)dibenzo[\ell]dithiophene (PPT). The enantiomers of CzpPhTrz emit CPL with $|\Phi g|$ of 1.3 x $10^{-3}$.\[12b,13] OLEDS with the latter two emitted at $\lambda_{EL}$ of around 460 nm and showed $\Phi_{max}$ of 7.4 and 12%, respectively. The devices suffered from severe efficiency roll-off resulting from the long $\tau_g$ of 135 and 158 $\mu$s, respectively, and possible degradation as a new emission band at longer wavelength was observed under electrical excitation. The device with CzpPhTrz emitted at $\lambda_{EL}$ of 480 nm and reached an $\Phi_{max}$ of 17%. The analogous phenazine-derived PCP, PXZp-Ph-Trz, has also been reported where the enantiomers emit CPL with $|\Phi g|$ of 3.3 x $10^{-3}$.\[14] The solution-processed CP-OLEDs emitted at $\lambda_{EL}$ of 560 nm, showed an $\Phi_{max}$ of 7.8% and an electroluminescence dissymmetry factor $|\Phi g|$ of 4.6 x $10^{-3}$. The structurally related emitter PXZ-PT contains a PCP that bridges a phenoxazine (PXZ) donor and a triazine acceptor on the same deck. The respective enantiomers emit CPL with $|\Phi g|$ of 1.9 x $10^{-3}$. The devices emitted at $\lambda_{EL}$ of 557 nm and showed an $\Phi_{max}$ of 20% and $|\Phi g|$ of 1.5 x $10^{-3}$.\[15] Recently, Czp-BuCzB and Czp-POAB have been reported as the first examples of planar chiral multi-resonance TADF (MR-TADF) emitters, where the Czp donor decorates two known MR-TADF cores. Sky-blue and green CP-TADF devices emitted at $\lambda_{EL}$ of 479 and 513 nm, and showed $\Phi_{max}$ of 32 and 29% and $|\Phi g|$ of 1.5 x $10^{-3}$ and 1.3 x $10^{-3}$.\[16] To the best of our knowledge, all planar chiral TADF emitters hitherto rely on the PCP scaffold, while the use of other phane-based moieties is scarce\[17] and limited only to larger macrocyclic assemblies, where planar chirality is not present.

Herein, we report the synthesis of a novel carbazolophane class ([2]paracyclo[2](1,7)carbazolophane) for the design of the carbazolophane donor-acceptor TADF emitter (1,7)BuCzpPhTrz. Anchored by two ethylene bridges at the 1- and 7-positions, the carbazole unit adopts a convex geometry that engages in $\pi$-stacking interactions with the benzene deck of the cyclophane. Its properties are compared to the PCP-fused carbazolophane analogue (1,4)BuCzpPhTrz. Compound (1,7)BuCzpPhTrz has a higher $\Phi PL$ of 91% in comparison to 84% for (1,4)BuCzpPhTrz. Blue OLEDS showed $\Phi_{max}$ of 14 and 17%, respectively, and enantiomerically pure samples of both compounds exhibit similar $|\Phi g|$ values around 5 x $10^{-4}$.

2. Results and Discussion

2.1. Structural Design and Synthesis

We revisited earlier works\[12,18] on the synthesis of planar chiral carbazole derivatives bearing PCP, and disclose the synthetic route towards (1,4)BuCzpPhTrz and (1,7)BuCzpPhTrz as outlined in Scheme 1. Both carbazolophane isomers, (1,7)BuCzp (3a) and (1,4)BuCz (4a), were
Figure 1. Summary of reported [2.2]paracyclophane-based TADF Emitters.
obtained by Pd-catalyzed oxidative cyclization of 4-N-(4-(tert-butyl)phenyl)amino[2.2]paracyclophane (2a) under aerobic conditions. In the presence of palladium(II) acetate and pivalic acid in acetic acid (1,4)Czp and (1,7)Czp were successfully formed in an overall yield of 39% in a ratio of 5:2. The latter implicates an unexpected migration of the ethylene bridge to the aniline arene, which was confirmed by X-ray diffraction analysis. In contrast to the planar geometry of the carbazole moiety in (1,4)Czp, an angle of 38° between the two benzene planes of the carbazole was measured in (1,7)carbazolophane (for more details see Figure S84, Supporting Information). On the basis of previous CH-activation studies,[19] we propose a mechanism for the oxidative cyclization/rearrangement sequence (Scheme S1, Supporting Information). For the initial ortho palladation step, we consider two intermediates, the relevant for (1,7)BuCzp formation being A (Scheme S2, Supporting Information). Consecutive CH insertion of both ortho palladation states followed by reductive elimination affords the expected carbazolophane (1,4)BuCzp. The alternative pathway from A, involves palladation of the distorted C(sp²) bridgehead atom and a [1,5]-alkyl shift, which should result in a release of ring strain. Reductive elimination of palladacycle C and [1,3]-H shift provides (1,7)BuCzp and reforms the active palladium catalyst. Such an alteration of the PCP skeleton through C–C bond breakage has rarely been documented in the literature.[20] Compared to the conventional route of photo-deselenation to afford mixed carbazolophanes,[21] this finding not only highlights an efficient alternative approach to synthesize this new class of carbazolophane derivatives, but also facilitates their use as building blocks of elaborated structures. For example, the amino group in 3 needs no protection and can serve as a reactive site for further functionalization.

In order to explore the compatibility of this protocol, we studied a series of phenylarnino[2.2]paracyclophanes of varying electronic and steric demand. As shown in Scheme 1b, the reaction proceeded in good-to-moderate yields for para-alkylated substrates (2a-c) with an overall yield of up to 52% and a ratio of 1:3 for the methylated cyclophanes 3c and 4c, respectively. The reaction yields of the (1,4)Czp derivatives (4b, 4c) are comparable to the previously reported studies; however, the formation of the (1,7)Czp derivatives (3b, 3c) have not as of yet been documented.[18] A decrease in yield was observed for meta-substituted amines (2d, 2e) due to the increase in steric hindrance. Consequently, only one selective regiosomer of 3d and 4d was formed. As determined by NMR spectroscopy analysis for both molecules, the carbazole C–C bond...
was formed at the less hindered position, confirming the observations of other Pd-catalyzed carbazole protocols based on CH-activation. Electron-withdrawing groups in the para position are tolerated although slightly longer reaction times were required to achieve full conversion. No consumption was observed during the reaction of 2k, bearing electron-deficient groups meta to the amine. However, oxidative cyclization of nitro-substituted 2g yields solely the respective (1,4)carbazolophane 4g in 42%. In general, highly reactive functionalities (2h–j) were found to be incompatible under the studied reaction conditions and led to decomposition.

To systematically explore the impact of these two cyclophane species in TADF materials, we selected (1,7)BuCzp (3a) and (1,4)BuCzp (4a) as examples to ensure high solubility of the donor-acceptor type molecules. The target materials (1,7)BuCzpPhTrz (6) and (1,4)BuCzpPhTrz (7) were prepared upon nucleophilic aromatic substitution with 2-(4-fluorophenyl)−4,6-diphenyl-1,3,5-triazine (5) and isolated in 85 and 56% yield, respectively. The two emitters were fully characterized by nuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectroscopy, melting point analysis (Mp), high resolution mass spectrometry (HRMS), high performance liquid chromatography (HPLC), and elemental analysis (EA) (details see ESI). Single crystals suitable for X-ray diffraction were collected during sublimation or by slow evaporation from n-hexane/CH2Cl2 solution and unambiguously confirmed the molecular structure of both target materials (Figure 2). For the following photophysical and optoelectronic characterization, the emitters were used in their racemic form. The chiroptical properties were studied with the resolved starting materials (Rp)/(Sp)-(1,4)BuCzp and (Rp)/(Sp)-(1,7)BuCzp, which were isolated by semi-preparative HPLC on a chiral stationary phase in high enantiomeric excess (ee) of >98% for each. Subsequent conversion yielded (Rp)/(Sp)-(1,4)BuCzpPhTrz and (Rp)/(Sp)-(1,7)BuCzpPhTrz in a purity of >99/98% ee and >92/98% ee, respectively (Scheme S3).

Crystallographic analysis revealed that the carbazole of (1,4)BuCzpPhTrz engages in π-stacking with the cyclophane deck in an analogous manner to the parent emitter, (1,4)CzpPhTrz (aka CzpPhTrz), previously reported by us.12b The carbazole moiety of (1,7)BuCzpPhTrz adopts a puckered conformation and the ethylene C–C bonds of the PCP are much shorter than those in (1,4)BuCzpPhTrz (1.56 Å vs 1.58 Å). This brings the carbazole and phenylene rings closer together (2.31–3.33 Å) than in (1,4)BuCzpPhTrz (2.76–3.09 Å). Due to the spatial orientation of the ethylene bridges in (1,7)BuCzpPhTrz, which are positioned perpendicular to the triazine axis, the torsion angle between the pyrrole core of the carbazole to the grafted phenylene of the triazine in (1,7)BuCzpPhTrz is shallower (33.4°) compared to (1,4)BuCzpPhTrz (51.7°) and (1,4)CzpPhTrz (51.8°), where the steric hindrance of the cyclophane bridge becomes more pronounced. The compounds pack through π–π stacking of the triazine moieties, with the neighboring triazines facing towards each other in an anti-parallel fashion (Figure 2b,c). The intermolecular distance of these π–π stacked planes in the two crystal structures of the two compounds is in a similar range of around 3.3 Å.

Figure 2. a) Molecular structures of (1,4)BuCzpPhTrz (CCDC 2305740) and (1,7)BuCzpPhTrz (CCDC 2261384). Displacement parameters are drawn at 50% probability level, hydrogen atoms are omitted for clarity. Schematic presentation of the π–π stacking along the triazine planes in b) (1,4)BuCzpPhTrz and c) (1,7)BuCzpPhTrz.
2.2. Theoretical Calculations

We undertook a theoretical study to understand the impact of the connectivity of the cyclophane on the optoelectronics of the emitters. The ground-state optoelectronic properties of (1,4)BuCzpPhTrz and (1,7)BuCzpPhTrz were calculated using density functional theory (DFT) at the PBE0/6-31G(d,p) level in the gas phase. As shown in Figure 3, the torsion angles between the donor and acceptor moieties are around 55.5° and 36.2° for (1,4)BuCzpPhTrz and (1,7)BuCzpPhTrz, which are in agreement to the angles found in the crystal structures (51.7° and 33.4°, respectively). The HOMO is mainly localized on the (1,4)BuCzp or (1,7)BuCzp donors with a small degree of electron density on the bridging phenylene, the HOMO energy levels are nearly identical at −5.46 and −5.42 eV, respectively. Similarly, the lowest unoccupied molecular orbital (LUMO) is located on the triazine acceptor and the bridge, with the LUMO of (1,7)BuCzpPhTrz being slightly destabilized at −1.76 eV compared to that of (1,4)BuCzpPhTrz at −1.86 eV. The HOMO-LUMO gap is thus essentially the same in the two compounds.

Time-dependent DFT (TD-DFT) calculations within the Tamm-Dancoff approximation (TDA-DFT), performed at the same level of theory, predict that both compounds have large ΔEST of 0.30 and 0.37 eV for (1,4)BuCzpPhTrz and (1,7)BuCzpPhTrz, respectively. Both compounds have similar predicted S1 levels to the parent (1,4)CzpPhTrz (S1 level of 3.11 eV) and the S1 state is predicted to show CT character with a high oscillator strength. However, their triplet levels are more stabilized compared to the T1 of (1,4)CzpPhTrz (2.81 eV), with predicted T1 levels are 2.77 and 2.75 eV for (1,4)BuCzpPhTrz and (1,7)BuCzpPhTrz. There is a large spin-orbital coupling constant between the S1 and T1 states at their optimized ground-state geometries (0.33 cm⁻¹ for (1,4)BuCzpPhTrz and 0.31 cm⁻¹ for (1,7)BuCzpPhTrz). The NTO analysis of both compounds based on the optimized S1 and T1 geometries were also calculated (Figure S100, Supporting Information). For both compounds the S1 and T1 states showed similar location of particles mainly on the triazine group and holes mainly on the donor groups, indicating that both states possess CT character. Thus, on balance and despite the large predicted ΔEST values, these two compounds are predicted to show TADF and emit in the blue.

2.3. Electrochemistry

The energies of the HOMO and LUMO were inferred from cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements in deaerated dichloromethane containing 0.1 M [Bu4N]PF6 as the supporting electrolyte (Figure S101, Supporting Information). The electrochemical data are summarized in Table 1. The Eonset values, determined from the DPV peaks, are 1.08 V/−1.72 V and 1.13 V/−1.74 V for (1,4)BuCzpPhTrz and (1,7)BuCzpPhTrz, respectively, versus SCE, with corresponding HOMO/LUMO values of −5.42 eV/−2.62 eV and −5.47 eV/−2.60 eV. The redox gaps of 2.80 V and 2.87 V for (1,4)BuCzpPhTrz and (1,7)BuCzpPhTrz largely mirror the calculated HOMO-LUMO gaps.

2.4. Photophysical Measurements

We next measured the photophysical properties of the two compounds in dilute (10⁻⁵ m) toluene solution at 298 K (Figure 4a...
and Table 2). The absorption spectra for both compounds have intense bands at around 385 nm, which are assigned by TDA-DFT calculations to the intramolecular charge transfer between the donor and the triazine acceptor. This assignment is also in line with that for (1,4)CzpPhTrz which has an ICT absorption band at 375 nm. The ICT band of (1,4)BuCzpPhTrz has a higher molar absorptivity value ($\varepsilon = 45 \times 10^3$ m$^{-1}$ cm$^{-1}$) than (1,4)BuCzpPhTrz ($\varepsilon = 29 \times 10^3$ m$^{-1}$ cm$^{-1}$), indicating a higher oscillator strength for the $S_0$ and $S_1$ transition, which is in line with the trend in predicted $S_1$ oscillator strengths. The steady-state photoluminescence (PL) spectra in toluene are broad and unstructured, as typically observed in donor-acceptor TADF compounds, with peak maxima, $\lambda_{PL}$, at 466 and 446 nm for (1,4)BuCzpPhTrz and (1,7)BuCzpPhTrz, respectively. Notably, the full width at half maxima (FWHMs) are different at 76 and 50 nm, respectively, suggesting that there is less geometric reorganization in the excited state of (1,7)BuCzpPhTrz than (1,4)BuCzpPhTrz. The emission of both compounds is blue-shifted compared to that of (1,4)CzpPhTrz ($\lambda_{PL}$ of 470 nm in toluene). There is an observed solvatochromism in the PL of both compounds (Figure S102, Supporting Information), which corroborates the assignment of the $S_1$ state as having CT character. The optical gap ($E_g$), determined from the intersection of the normalized absorption and emission spectra, are 2.94 eV and 2.99 eV for (1,4)BuCzpPhTrz and (1,7)BuCzpPhTrz, respectively. The $\Phi_{PL}$ values of (1,4)BuCzpPhTrz and (1,7)BuCzpPhTrz in degassed toluene solutions are 82 and 78%, respectively, which decrease to 68 and 72% upon exposure to oxygen. The time-resolved emission decays for both compounds have lifetimes, $\tau_{PL}$, of 8.2 and 4.2 ns, no obvious delayed emission was detected.

We next investigated their photophysical properties in both a wide bandgap polymer host, PMMA, and also a high triplet energy small molecule host, DPEPO ($\phi_T = 3$ eV$^{[23]}$), with a view to employing these compounds as emitters in OLEDs. The concentration of the doped films was chosen as 10 wt% as this is what was used for the previous study with (1,4)CzpPhTrz, (1,4)BuCzpPhTrz and (1,7)BuCzpPhTrz showed unstructured CT-based emission at $\lambda_{PL}$ of 470 and 457 nm as in 10 wt% doped films in PMMA, respectively (Figure 4b). The FWHMs are 83 and 66 nm, respectively, which are slightly broader than FWHMs measured in toluene of 76 and 50 nm. These emission spectra are red-shifted to 480 and 473 nm in 10 wt% doped films in DPEPO, with FWHMs of 87 and 69 nm, reflecting the higher polarity of this host compared to PMMA. These $\lambda_{PL}$ values are similar to that reported for (1,4)CzpPhTrz ($\lambda_{PL}$ = 482 nm in 10 wt% doped films in DPEPO). The $\Phi_{PL}$ values of the doped DPEPO films of (1,4)BuCzpPhTrz and (1,7)BuCzpPhTrz are 84 and 91%, respectively, which decrease to 78 and 81% under air, respectively. The $\Phi_{PL}$ values in 10 wt% doped films of (1,7)BuCzpPhTrz in DPEPO are similar to those of the 10 wt% doped films in mCP:PPT (1:1): the $\lambda_{PL}$ values of 473 and 463 nm in doped mCP:PPT (1:1) films mirror those in PMMA (Table S9, Supporting Information). In 10 wt% doped films in mCP:PPT, the $\Phi_{PL}$ of (1,4)BuCzpPhTrz is slightly lower at 77% under N$_2$ and 68% under air.

The $S_1$ and $T_1$ energies for both compounds were extracted from the onsets of the steady-state PL and delayed emission spectra (1–10 ms) at 77 K in both 2-MeTHF glass and the 10 wt% doped films in DPEPO (Figure 5). The $\Delta E_{ST}$ values of (1,4)BuCzpPhTrz and (1,7)BuCzpPhTrz are 0.11 and 0.23 eV in 2-MeTHF, while those in 10 wt% doped films in DPEPO are 0.18 and 0.25 eV, respectively. These are smaller than the calculated $\Delta E_{ST}$ values and reflect the impact of the host in modulating the energies of the excited states. The larger $\Delta E_{ST}$ for (1,7)BuCzpPhTrz results from the smaller D-A torsion angle,
Table 2. Photophysical properties of (1,4)\textit{t}BuCzpPhTrz and (1,7)\textit{t}BuCzpPhTrz.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\lambda_{\text{abs}}) [nm]</th>
<th>(\lambda_{\text{PL}}) a) [nm]</th>
<th>(\lambda_{\text{PL}}) b) [nm]</th>
<th>(\Phi_{\text{PL}}) a) [%]</th>
<th>(\Phi_{\text{PL}}) b) [%]</th>
<th>(E_{\text{g}}) c) [eV]</th>
<th>(\tau_{\text{p}}) a),d) [ns]</th>
<th>(\tau_{\text{d}}) b),d) [(\mu\text{s})]</th>
<th>(S_{1}/T_{1}) [eV]</th>
<th>(\Delta E_{\text{ST}}) e) [eV]</th>
</tr>
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<tr>
<td>(1,4)\textit{t}BuCzpPhTrz</td>
<td>384</td>
<td>466</td>
<td>480</td>
<td>82(68)</td>
<td>84(78)</td>
<td>2.94</td>
<td>8.2</td>
<td>8.9</td>
<td>315</td>
<td>2.97/2.79</td>
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<td>(1,7)\textit{t}BuCzpPhTrz</td>
<td>388</td>
<td>446</td>
<td>473</td>
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<td>91(81)</td>
<td>2.99</td>
<td>4.2</td>
<td>5.3</td>
<td>637</td>
<td>2.92/2.72</td>
</tr>
</tbody>
</table>

\(^{a)}\)In toluene at 298 K; \(^{b)}\)Thin films were prepared by vacuum depositing at 10 wt% doping in DPEPO (\(\lambda_{\text{exc}}=360\) nm); \(^{c)}\)The optical bandgaps were calculated from the intersection point of the normalized absorption and emission spectra; \(^{d)}\)Average lifetime (\(\tau_{\text{avg}}=\Sigma A_i\tau_i^2/\Sigma A_i\tau_i^2\), where \(A_i\) is the preexponential for lifetime \(\tau_i\)). Prompt and delayed emissions were measured by TCSPC and MCS, respectively (\(\lambda_{\text{exc}}=379\) nm); \(^{e)}\)Determined from the onset of prompt and delayed spectra in 2-MeTHF, measured at 77 K.

as determined in the crystal structure analysis, that leads to a larger exchange integral. The time-resolved PL decays of the 10 wt% doped films of (1,4)\textit{t}BuCzpPhTrz and (1,7)\textit{t}BuCzpPhTrz in DPEPO at room temperature show a prompt fluorescence lifetime, \(\tau_p\), of 8.9 and 5.3 ns, and an average delayed fluorescence lifetime, \(\tau_d\), of 315 and 637 \(\mu\text{s}\), respectively (Figure 6a,b). The delayed emission is significantly quenched in the presence of oxygen while the prompt emission is invariant. The temperature-dependent time-resolved PL decays (Figure 6c,d) reveal the expected increase in the intensity of the delayed emission with increasing temperature that is emblematic of TADF.

2.5. Chiroptical Properties

We next measured the chiroptical properties of both enantiomeric pairs. The electronic circular dichroism (ECD) spectra of both compound pairs display mirror image behavior in tetrahydrofuran (Figure 7). A pronounced band is observed for (1,4)\textit{t}BuCzpPhTrz at 219 nm (\(\Delta\varepsilon=+77.8\) m\(^{-1}\) cm\(^{-1}\) for \(R_p\)), while weaker responses are found at 261 nm (\(\Delta\varepsilon=-11\) m\(^{-1}\) cm\(^{-1}\) for \(R_p\)), 280 nm (\(\Delta\varepsilon=+16\) m\(^{-1}\) cm\(^{-1}\) for \(R_p\)) and 308 nm (\(\Delta\varepsilon=+78\) m\(^{-1}\) cm\(^{-1}\) for \(R_p\)). The CT absorption band at 380 nm (\(\Delta\varepsilon=+78\) m\(^{-1}\) cm\(^{-1}\) for \(R_p\)) is of similar wavelength to that reported for other (1,4)carbazolophane-based compounds.\(^{[12b,16]}\) An
absorption dissymmetry factor ($g_{\text{abs}}$) of $-6 \times 10^{-4}$ at 380 nm was determined for (R$_S$)-(1,4)BuCzpPhTrz. For (1,7)BuCzpPhTrz, three main bands are observed at 261 nm ($\Delta \varepsilon = +16 \text{ m}^{-1} \text{ cm}^{-1}$ for R$_S$), 314 nm ($\Delta \varepsilon = +15 \text{ m}^{-1} \text{ cm}^{-1}$ for R$_S$) and the CT band at 388 nm ($\Delta \varepsilon = -6.2 \text{ m}^{-1} \text{ cm}^{-1}$ for R$_S$). The $g_{\text{abs}}$ of $-4 \times 10^{-4}$ at 388 nm for (R$_S$)-(1,7)BuCzpPhTrz was found to be in the same order than the (1,4) isomer. The absolute configurations of the enantiomers were determined by comparison of the experimental data with predicted spectra based on TD-DFT calculations at the M06/6-311G(d,p) level with an implicit solvent field using the conductor-polarized continuum model (CPCM).\(^{26}\) The second enantiomer of (1,4)BuCzp was assigned to be (S$_S$), while for (1,7)BuCzp the first isolated enantiomer was assigned to be (R$_S$) (Figure S85, Supporting Information). The ECD spectra of the derived emitters (S$_S$)-(1,4)BuCzpPhTrz and (R$_S$)-(1,7)BuCzpPhTrz broadly match the predicted spectra (Figure 7a,b). The circularly polarized luminescence (CPL) spectra of both emitters in toluene displayed mirror-image and unstructured CPL in the region between 425 to 600 nm ($\lambda_{\text{exc}} = 350 \text{ nm}$) with peaks observed at 465 nm for (R$_S$)/(S$_S$)-(1,4)BuCzpPhTrz and 447 nm for (R$_S$)/(S$_S$)-(1,7)BuCzpPhTrz (Figure 7c,d). The corresponding $g_{\text{PL}}$ values are $-5 \times 10^{-4}$ with negative signals for the (R$_S$) enantiomers. Interestingly, as shown in Figure S99 (Supporting Information), the $g_{\text{PL}}$ spectra are shown throughout the whole emission band, affording further evidence of the nearly pure CT character of the emission for these chiral systems. Furthermore, the $g_{\text{abs}}/g_{\text{PL}}$ ratios of $+0.8$ and $+1.25$ for (1,4)BuCzpPhTrz and (1,7)BuCzpPhTrz, respectively, also indicate weak structural/electronic reorganization during excitation/emission processes. These dissymmetry factors are comparable to those of PCP-based compounds,\(^{13b}\) suggesting that the incorporation of cyclophanyl-based planar chirality is a promising strategy for generating CPL-active emitters.

2.6. Organic Light-Emitting Diodes

Having identified the potential of these compounds as emitters, vacuum-deposited OLEDs with (1,4)BuCzpPhTrz and (1,7)BuCzpPhTrz were fabricated. The first set of OLEDs was made using our previously reported stack,\(^{12b}\) with DPEPO as the host. Figure 8a,b shows the schematic of the device layout and the chemical structures of the organic materials. The device structure was: indium tin oxide (ITO)/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)/mCP (10 nm)/DPEPO (20 nm) with 10 wt% of (1,4)BuCzpPhTrz or (1,7)BuCzpPhTrz/DPEPO (10 nm)/1,3,5-tris(3-pyridyl-3-phenyl)benzene (TmPyPB, 40 nm)/lithium fluoride (LiF, 0.8 nm)/aluminum (Al, 100 nm). Here, NPB, TCTA and mCP served as hole injection, transport, and exciton blocking layers, respectively, while TmPyPB and DPEPO were used as electron transport, and hole blocking layers, respectively. The comparison of current density-voltage-luminescence (JVL) characteristics for both devices is shown in Figure 8c. The devices with (1,4)BuCzpPhTrz and (1,7)BuCzpPhTrz using DPEPO as the
host had high turn-on voltages of 3.7 and 4.3 V, respectively. This indicated that DPEPO was not a favorable host, likely causing charge trapping on the host or charge accumulation at the EML interfaces.\cite{27} Even though the devices with (1,4)tBuCzpPhTrz (Figure 8d) showed an EQE_{max} of 18.5%, the efficiency roll-off was severe as the EQE_{1000} (EQE at 100 cd m\(^{-2}\)) was 8% while the EQE_{100} decreased to 2.2%. The previously-reported device with (1,4)CzpPhTrz showed an EQE_{max} of 17% and a slightly improved efficiency roll-off, with the EQE_{100} of 12%.\cite{12b} The more pronounced efficiency roll-off in the devices with (1,4)tBuCzpPhTrz as compared to the reported device with (1,4)CzpPhTrz may in part be due to the longer \(t_d\) (315 \(\mu\)s) of the former as compared to the \(t_d\) (65 \(\mu\)s) of the latter. Emitters with longer \(t_d\) typically correlate with devices showing more severe efficiency roll-off.\cite{26} The device with (1,7)tBuCzpPhTrz achieved a comparable EQE_{max} of 18%, but the efficiency roll-off was even more pronounced with the EQE_{100}/EQE_{1000} dropping to 4.8/1.1%. The electroluminescence (EL) spectra for these two devices were similar with emission peaks, \(\lambda_{EL}\), at 486 and 490 nm for the devices with (1,4)tBuCzpPhTrz and (1,7)tBuCzpPhTrz, respectively (Figure 8e). The CIE coordinates for devices with both emitters were also similar at (0.19, 0.33) (Figure 8f).

In an effort to reduce the efficiency roll-off, a second set of devices was fabricated using a 1:1 mixture of mCP and PPT. The use of this ambipolar co-host system was expected to result in a wider recombinaton zone and improve the mobility of both charges. The device structure (Figure 8a) was thus modified to be: ITO/1,4,5,8,9,11-hexaaazatriphenylenehexacarbonitride (HATCN, 10 nm)/1,1-bis[di-4-tolylamino]phenyl)cyclohexane (TAPC, 25 nm)/TCTA (10 nm)/mCP (10 nm)/mCP:PPT (20 nm) with 10 wt% of (1,4)tBuCzpPhTrz or (1,7)tBuCzpPhTrz/PPT (10 nm)/TmPyPB (40 nm)/LiF (0.8 nm)/Al (100 nm). The thickness of the layers was optimized based on simulations for outcoupling efficiencies, and layer thicknesses were varied in increments of 5 nm to identify the best combination of optical and electrical properties (Figure S103, Supporting Information). Here, HATCN was used as the hole injection layer, TAPC as the hole transport layer, TCTA as electron blocking, mCP as the exciton blocking layer, PPT as the hole blocking layer, and TmPyPB for electron injection and transport.

The turn-on voltages were lower at 3.1 and 3.0 V for the devices with (1,4)tBuCzpPhTrz and (1,7)tBuCzpPhTrz, respectively, compared to those using DPEPO, indicating that the co-host system improved charge injection into the EML. This was also reflected in the higher current density and luminance as compared to the devices with DPEPO (Figure 8c). The EQE_{max} of the OLEDs with (1,4)tBuCzpPhTrz decreased slightly to 17%, but there was a modest improvement in the efficiency roll-off where the EQE_{100}/EQE_{1000} were maintained at 11.2/4.8%. Similarly, the device with (1,7)tBuCzpPhTrz showed a lower EQE_{max} of 13.5%; however, the EQE_{100} (3.2%) was slightly improved compared to the device using DPEPO. One factor that may contribute to the higher EQE for the device with (1,4)tBuCzpPhTrz compared to that with (1,7)tBuCzpPhTrz is the greater horizontal orientation of the transition dipole moment of the emitter in the former (Figure S104, Supporting Information). The \(\lambda_{EL}\) for the

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**Figure 7.** Experimental and calculated ECD spectra of a) \((R_p)/(S_p)-(1,4)tBuCzpPhTrz\) and b) \((R_p)/(S_p)-(1,7)tBuCzpPhTrz\) measured in tetrahydrofuran. Predicted spectra were calculated at the TD-DFT-M06/6-311++G(d,p) with an implicit tetrahydrofuran solvent field (ccpcm). CPL spectra of c) \((R_p)/(S_p)-(1,4)tBuCzpPhTrz\) and d) \((R_p)/(S_p)-(1,7)tBuCzpPhTrz\) in toluene (\(\lambda_{exc}=350\) nm).
Figure 8. a) Schematic of the OLED device structures. b) Chemical structures of the organic materials used in the devices. c) Current density-Voltage-Luminance (JVL) curves. d) External quantum efficiency (EQE) versus Luminance. e) Electroluminescence spectra from the fabricated devices. f) CIE coordinates of the devices with (1,4)BuCzpPhTrz and (1,7)BuCzpPhTrz using either DPEPO or 1:1 mCP:PPT as hosts. g) Photograph of the OLEDs with (1,7)BuCzpPhTrz in 1:1 mCP:PPT.
device with (1,4)tBuCzpPhTrz was 490 nm, which was similar to that of the device using DPEPO (486 nm). The $\lambda_{pl}$ for the device with (1,7)tBuCzpPhTrz was 475 nm, which was blue-shifted compared to the device using DPEPO (490 nm), but is close to the $\lambda_{pl}$ (467 nm in 1:1 mCP:PPT). These results point to a reduced propensity to aggregate in the co-host system compared to DPEPO for the vacuum-deposited films with (1,7)tBuCzpPhTrz. Indeed, aggregates were found to contribute to a red-shifting of the emission of (1,7)tBuCzpPhTrz in the 1:1 mCP:PPT co-host only at higher doping concentrations (Figure S105, Supporting Information). The CIE coordinates for the device with (1,4)tBuCzpPhTrz were (0.19, 0.38) while those for the device with (1,7)tBuCzpPhTrz were (0.16, 0.27) (Figure Sf,g) shows the photograph of the (1,7)tBuCzpPhTrz OLED in mCP:PPT co-host.

3. Conclusion

Here, we disclosed a new design concept to introduce planar chirality into TADF emitters by employing a novel cyclophane ([2]paracyclo[2]-3-tertbutyl(1,7)carbazolophane, (1,7)tBuCzp) as a donor unit. This building block is obtained through an oxidative cyclization method involving an atypical rearrangement process. Due to its puckered geometry, carbazolophane (1,7)tBuCzp is a weaker donor than (1,4)tBuCzp. Photophysical studies showed a sharper, slightly blue-shifted emission of (1,7)tBuCzpPhTrz with a $\lambda_{pl}$ of 446 nm and FWHM of 50 nm compared to (1,4)tBuCzpPhTrz ($\lambda_{pl}$ = 466 nm, FWHM = 76 nm). The TADF character of both compounds was verified. (1,7)tBuCzpPhTrz has a superior Ph of 91% ($\lambda_{pl}$ = 473 nm) versus 84% ($\lambda_{pl}$ = 480 nm) for (1,4)tBuCzpPhTrz. The enantiomeric pairs exhibited mirror image CPL behavior with $\delta_{500}$ of $5 \times 10^{-4}$. Blue OLEDs with (1,4)tBuCzpPhTrz and (1,7)tBuCzpPhTrz achieved comparable EQE values of 19 and 18%, respectively. The initial devices were found to suffer from high-efficiency roll-off, which was improved by changing the host from DPEPO to a 1:1 mCP:PPT co-host system. This led to an EQE of 17% for the device with (1,4)tBuCzpPhTrz and a lower EQE of 14% for the (1,7)tBuCzpPhTrz device. The efficiency roll-off at high luminance (100 to 1000 cd m$^{-2}$) was alleviated from 73% to 57% for the OLED with (1,4)tBuCzpPhTrz and from 77% to 35% for the OLED with (1,7)tBuCzpPhTrz. We believe that this report provides fundamental insights for the development of planar chiral TADF materials and the impact of the cyclophanic structure to achieve narrower emission.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available at https://doi.org/10.17630/ceaea778-414-a4e9-ad7-bdf2e4208 and in the repository Chemotion (https://www.chemotion-repository.net/). All DOIs minted for the data are linked to the specific experiments in the Supporting Information and a summary of all new data obtained in this study can be gained with the collection DOI https://dx.doi.org/10.14272/collection/JTS 2023-02-24 and https://dx.doi.org/10.14272/collection/JTS 2023-10-11.

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