

Enhancing Thermally Activated Delayed Fluorescence by Fine-Tuning the Dendron Donor Strength

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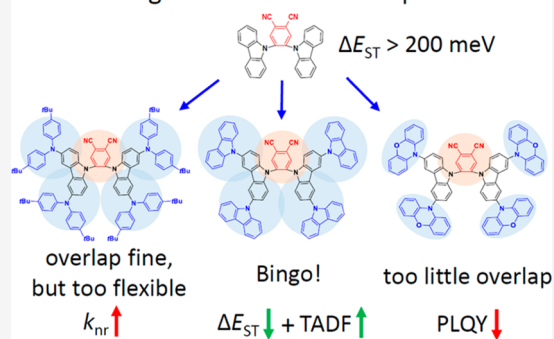
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ABSTRACT: Thermally activated delayed fluorescence (TADF) relies on a small energy gap between the emissive singlet and the nonemissive triplet state, obtained by reducing the wave function overlap between donor and acceptor moieties. Efficient emission, however, requires maintaining a good oscillator strength, which is itself based on sufficient overlap of the wave functions between donor and acceptor moieties. We demonstrate an approach to subtly fine-tune the required wave function overlap by employing donor dendrons of changing functionality. We use a carbazolyl-phthalonitrile based donor–acceptor core (2CzPN) as a reference emitter and progressively localize the hole density through substitution at the 3,6-positions of the carbazole donors (Cz) with further carbazole, (4-*tert*-butylphenyl)amine (^tBuDPA), and phenoxazine (PXZ). Using detailed photoluminescence studies, complemented with density functional theory (DFT) calculations, we show that this approach permits a gradual decrease of the singlet–triplet gap, ΔE_{ST} , from 300 to around 10 meV in toluene, yet we also demonstrate why a small ΔE_{ST} alone is not enough. While sufficient oscillator strength is maintained with the Cz- and ^tBuDPA-based donor dendrons, this is not the case for the PXZ-based donor dendron, where the wave function overlap is reduced too strongly. Overall, we find the donor dendron extension approach allows successful fine-tuning of the emitter photoluminescence properties.

Fine-tuning hole-electron overlap for TADF



INTRODUCTION

Emitters showing thermally activated delayed fluorescence (TADF) can achieve comparable internal quantum efficiencies to those of commercialized phosphorescent emitters, but without the need to employ scarce heavy metals within an organic light emitting diode (OLED).^{1–3} TADF allows noncoherent endothermic triplet exciton upconversion to the singlet state, mediated by the small singlet–triplet splitting. This is particularly useful when employing these materials for OLED applications, since in this way all electrically generated excitons in the OLED may be used toward light emission. The energy gap between the lowest singlet and triplet states, ΔE_{ST} , that governs in part the efficiency of the TADF process depends on the magnitude of the wave function overlap in the exchange integral.^{4,5} The singlet–triplet gap can therefore be reduced by localizing hole and electron wave functions onto different parts of the molecule, and this is commonly achieved by employing, respectively, donor and acceptor moieties that adopt a highly twisted conformation in the emitter structure.¹ Nevertheless, there needs to be sufficient wave function overlap to still allow for a reasonable transition dipole moment, and thus a good radiative decay rate.^{4,5} The balance of these

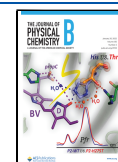
two factors is required to obtain a high-performance TADF emitter.

One way to adjust wave function overlap is by modulating the torsion between the donor and the acceptor moieties, which controls the extent of the conjugation between these two fragments.^{6–9} An alternative way is to increase the delocalization of the hole over the donor unit, which effectively localizes the hole density on this fragment.¹⁰ Implementation of this strategy is illustrated in dendrimers, which frequently contain dendritic donors surrounding an electron acceptor.^{5,11–14} It has been shown that the more moderate D–A torsions in the dendrimers would ensure sufficient overlap between HOMO and LUMO wave functions to achieve the paradox of a small ΔE_{ST} and a large oscillator strength.⁷ A further advantage of employing a dendritic structure for the emitter is to potentially obviate the need for a host matrix in

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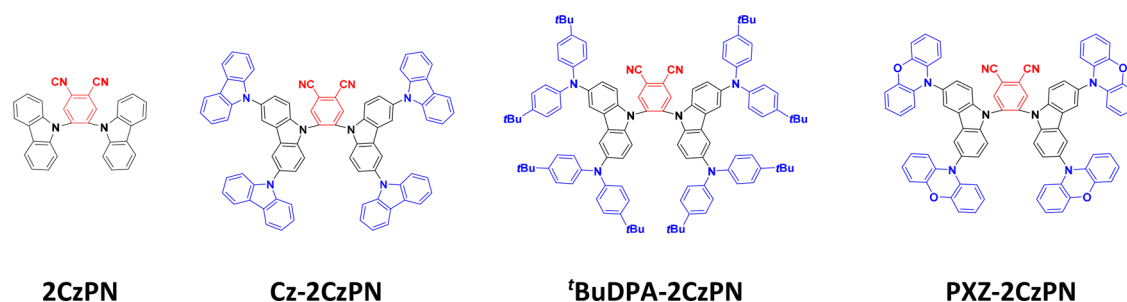


Figure 1. Chemical structures of the investigated compounds. The parent 2CzPN is extended using carbazole (Cz), di(4-*tert*-butylphenyl)amine (*t*BuDPA), and phenoxazine (PXZ).

the emitter layer of an OLED.^{2,15} Commonly, TADF emitters are dispersed in a host matrix to reduce concentration quenching. The dendritic structure itself is often sufficiently sterically crowded to mitigate concentration quenching of the vulnerable triplet states. Concentration quenching can be synergistically further suppressed by the use of sterically bulky groups decorating the donor dendrons. This facilitates the device fabrication and avoids issues associated with host–guest interactions such as exciplex formation and undesirable energy shifts.¹⁶ There are, however, few variants of donor dendrons that have been explored. An appreciation of the effect of structure modulation on the optoelectronic properties, particularly on the efficiency of the TADF process, is thus currently missing. A toolbox-like approach is desirable, where different donor units can be connected with ease to gently and gradually modify the properties.¹⁷

Here we demonstrate such a modular fine-tuning approach by changing the nature of the peripheral donor groups in donor dendrons, which affects hole localization, while maintaining the central carbazole donor unit and its connection to the common phthalonitrile acceptor. This strategy avoids reoptimizing the entire molecular design. We are not aware of detailed and systematic studies on the impact of the nature of the donor dendrons on the singlet–triplet gap and TADF properties. An overview of literature-reported emitters containing donor dendrons, including dendrimers, is given in the Supporting Information (SI) (Table S1, Figure S1). We address whether such a strategy can significantly improve the efficiency of the TADF process in an emitter that already shows TADF in thin films.

We implement our approach by changing the peripheral donor groups on the TADF-active sky-blue emitter 2CzPN (Figure 1).^{18–20} 2CzPN consists of an electron-accepting phthalonitrile core connected to two carbazole donor moieties at the 4- and 5-positions. These donors can be substituted comparatively easily at the 3,6-positions of the carbazole, allowing for the extension of the conjugated π -system. The compound is thus well-suited to study the impact of hole wave function delocalization on the singlet–triplet gap and the TADF performance. 2CzPN shows a desirable set of photophysical properties in terms of its high reported photoluminescence quantum yield (PLQY) of 89% and the reported presence of TADF in an mCP matrix,^{19,20} although we find a surprisingly high ΔE_{ST} gap of 230 meV in our measurements in a film with mCP as host matrix, increasing to 300 meV in toluene solution. To gradually reduce electron–hole overlap we progressively altered the electronic structure of the donor dendron by decorating the central carbazole with

either peripheral carbazole (Cz), di(4-*tert*-butylphenyl)amine (*t*BuDPA), or phenoxazine (PXZ) groups.

We find that our approach allows for an enhancement of the intramolecular charge transfer (CT) character of the emitter and a progressively smaller ΔE_{ST} , from 300 meV for the parent compound 2CzPN to 160 meV for Cz-2CzPN and 10 meV for the other two compounds in toluene. Consistent with this, the optical spectroscopy, as well as density functional theory (DFT) calculations, suggest that the overlap of electron and hole density reduces along the series, until for PXZ-2CzPN the hole density is localized only on the PXZ units, thus limiting the overlap with the electron density localized on the phthalonitrile unit. We also find that nonradiative losses are present in the case of Cz-2CzPN and *t*BuDPA-2CzPN, suppressing their full TADF potential. Nevertheless, overall we find that the donor-dendron extension approach allows for the optimization of the hole delocalization and, thus, for Cz-2CzPN to show an increase in PLQY over the parent compound. This improvement in ΔE_{ST} comes, however, at the expense of a red-shift in the emission color.

METHODS

We prepared solutions of 0.05 mg/mL in toluene (corresponding to 10^{-4} – 10^{-5} M depending on molecular weight) as well as spin-coated 10 wt % films in mCP and measured them at different temperatures in steady-state mode using a Jasco FP-8600 spectrofluorometer. In time-resolved mode they were measured using an iCCD camera (Andor iStar A-DH334T-18F-03) by exponentially increasing delay and gating times where the gating time is kept lower by 10 times compared to the delay time. For the steady-state mode, variable excitation wavelengths were used (see figure captions), while for the iCCD measurements, samples were excited at 355 nm. The quantum chemical calculations were performed using the Gaussian 09 (revision D.0184) suite for the DFT.²¹ Molecular structures were optimized in the ground-state geometry using PBE0²² functionals each employing the 6-31G(d,p) basis set with dispersion effects included.²³ Excited state calculations were performed within the Tamm–Dancoff approximation (TDA) at the same level of theory.²⁴ Full experimental and computational details as well as the information on the synthesis and chemical characterization are provided in the SI.

RESULTS

Theoretical Calculations. DFT calculations were undertaken to elucidate the effect of changing the donor in the 2CzPN derivatives on the distribution of electron and hole densities, the magnitude of the oscillator strengths for the vertical transition between the ground state and the singlet

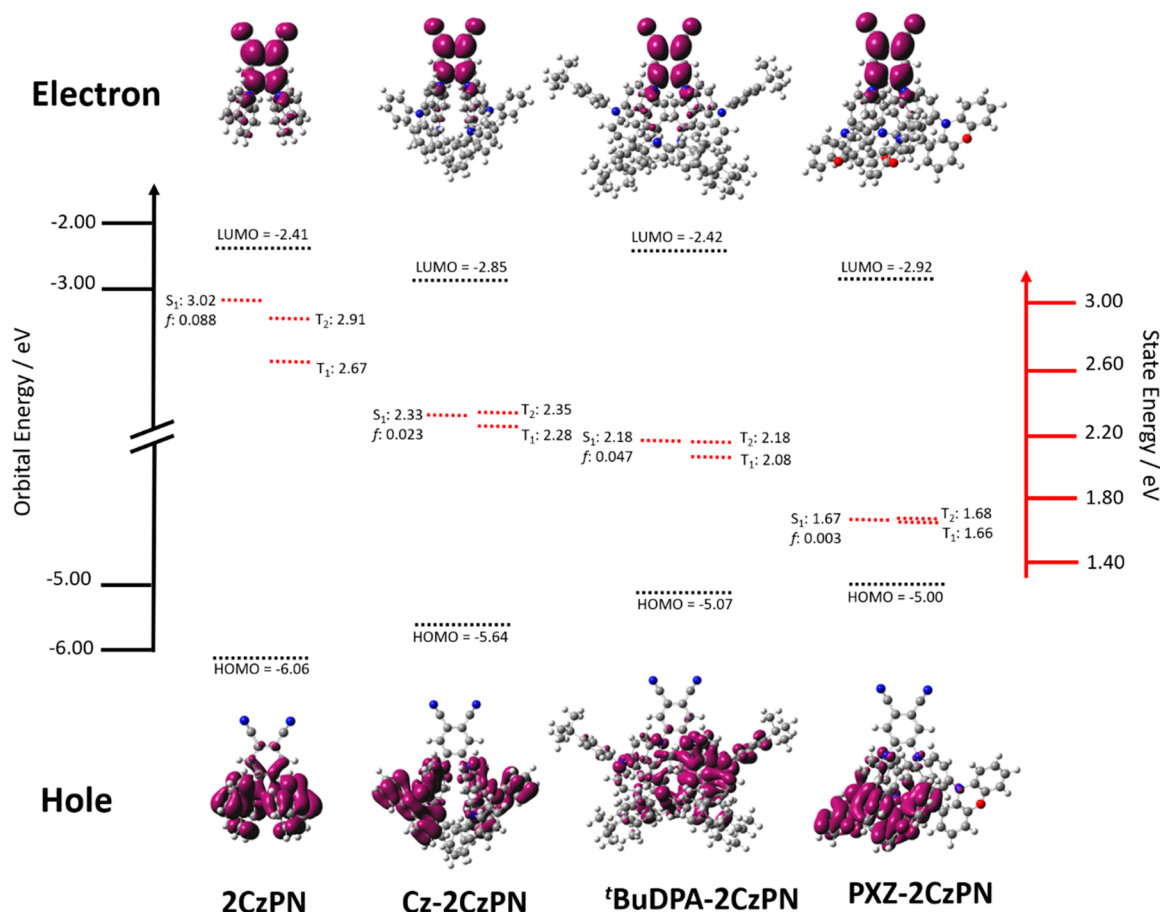


Figure 2. Left axis (black): HOMO and LUMO energies calculated for the ground-state geometry at the PBE0/6-31G(d,p) level. Right axis (red): vertical transition energies for S₁, T₁, and T₂ computed at the TDA-DFT using the PBE0 functional together with the 6-31G(d,p) basis set. Also shown are the electron (top) and hole densities (bottom) for the for S₁ state, where *f* is the oscillator strength.

excited states, and the orbital and state energies. Figure 2 presents the hole and electron densities for the lowest-lying excited singlet state calculated within the attachment/detachment formalism and the orbital and state energies from the ground-state geometry.²⁵ The lowest-lying triplet state electron and hole densities can be found in Figure S2 (SI).²⁶ This approach provides information about the reorganization of the electron density upon excitation of the molecule.

For all compounds, the electron density is localized on the phthalonitrile acceptor. By contrast, the localization of the hole density varies across the different emitters. For 2CzPN, the hole density is mainly localized on the carbazole donors with some delocalization onto the phthalonitrile phenyl ring. When extending the donor as in Cz-2CzPN and ^tBuDPA-2CzPN, however, the hole density is distributed across the now larger donor dendron moieties, with a reduced contribution on the phthalonitrile unit. For PXZ-2CzPN the hole density is mostly localized on the distal phenoxazine donors, with only a slight contribution from the inner carbazole. Close inspection reveals that the hole density on the phthalonitrile accepting unit decreases when moving from ^tBuDPA-2CzPN to Cz-2CzPN and PXZ-2CzPN. As discussed further below, this is related to changes in donor strength and the donor–acceptor torsion. The clear separation between electron and hole densities in each compound indicates that the singlet excited state possesses a dominant charge-transfer (CT) character. The degree of CT character can be quantified using the parameter

ϕ_S , where a value of 1 is indicative of a state of purely locally excited (LE) character and a value of 0 is a state of purely CT character, with the former signifying complete overlap and the latter no overlap. The ϕ_S value decreased from 0.42 for 2CzPN to 0.29, 0.20, and 0.11 for ^tBuDPA-2CzPN, Cz-2CzPN, and PXZ-2CzPN, respectively, for the S₁ state, suggesting an increase in CT character and supporting the decrease of the oscillator strength, *f* (see Figure 2). The electron and hole densities for the first triplet excited state closely resemble those of the S₁ state and are given in Figure S2 (SI). For each compound, we also calculated the energy of the T₂ state and characterized its nature. The presence of the intermediate triplet states energetically close to T₁ and S₁ states is essential for efficient TADF to take place. Indeed, El Sayed's rules essentially forbid the direct T₁ and S₁ conversion in cases where the states have the same nature, as would be the case when both are pure CT states, due to the predicted vanishing spin–orbit coupling. We consider that for our compounds the upconversion process from T₁ to S₁ involves reverse internal conversion from T₁ to T₂ driven by vibronic coupling, followed by efficient reverse intersystem crossing (RISC) to S₁ in the case where T₂ is of a different nature than S₁. Such a mechanism supports the high *k*_{RISC} rates observed even in the case of ΔE_{ST} values exceeding 200 meV.^{27,28} For 2CzPN, the T₂ state lies between the T₁ and S₁, while in each of the other three compounds it is either the same energy or slightly higher in energy than that of the S₁ state. Owing to the similar energy

Table 1. Electrochemical Data

compd	electrochemistry					DFT		
	E^{oxa} (V)	E^{reda} (V)	HOMO ^b (eV)	LUMO ^b (eV)	$\Delta E_{\text{H-L}}$ ^c (eV)	HOMO (eV)	LUMO (eV)	$\Delta E_{\text{H-L}}$ (eV)
2CzPN	1.54	-1.46	-5.87	-2.88	2.99	-6.06	-2.41	3.65
Cz-2CzPN	1.28	-1.36	-5.62	-2.98	2.64	-5.63	-2.85	2.78
^t BuDPA-2CzPN	0.72	-1.43	-5.04	-2.92	2.12	-5.07	-2.42	2.65
PXZ-2CzPN	0.80	-1.30	-5.14	-3.03	2.11	-5.00	-2.92	2.08

^aReported versus SCE in degassed DCM with 0.1 M [*n*Bu₄N]PF₆ as the supporting electrolyte and Fc/Fc⁺ as the internal reference (0.46 V vs SCE)³⁶ obtained from DPV. ^bThe HOMO and LUMO energies were determined using the equation $E_{\text{HOMO/LUMO}} = -(E^{\text{ox}}/E^{\text{red}} + 4.8)$ eV,³⁷ where E^{ox} and E^{red} are the anodic and cathodic peak potentials, respectively, measured from DPV relative to Fc/Fc⁺. ^c $E_{\text{H-L}} = |E_{\text{HOMO}} - E_{\text{LUMO}}|$.

Table 2. Energetic Positions and Transition Intensities for the CT and S₁ state, Derived from Optical Spectroscopy in Toluene Solution and from Computational Outputs at TDA-PBE0/6-31G(d,p)

compd	λ_{abs} ^a (eV, 300 K)	ϵ_{CT} ^b (10 ⁴ M ⁻¹ cm ⁻¹)	λ_{PL} ^c (eV, 300 K)	f^{d}	S ₁ (eV) ^e	ϕ_s^{f}
2CzPN	3.30 (376 nm)	1.49	2.56 (484 nm)	0.088	3.02	0.34
Cz-2CzPN	3.14 (395 nm)	0.90	2.32 (534 nm)	0.023	2.33	0.20
^t BuDPA-2CzPN	2.72 (456 nm)	0.85	1.88 (660 nm)	0.047	2.18	0.28
PXZ-2CzPN	2.72 (456 nm)	0.18	1.88 (660 nm)	0.003	1.67	0.11

^aPeak maximum of CT absorption. ^bMolar extinction coefficient of the lowest lying CT band for the compounds. ^cPeak maximum of CT photoluminescence. ^dOscillator strength. ^eCalculated vertical transition energy of S₁. ^fIndication of wave function overlap, with a value of 1 implying a locally excited (LE) nature and a value of 0 suggesting a charge transfer (CT) nature.

levels of S₁ and T₂ it is likely that these states exhibit nonvanishing intersystem crossing. Further, T₁ and T₂ are energetically close and could show efficient vibronic coupling.

The calculated HOMO energy progressively destabilizes, indicative of both the increasing strength of the donors as well as the delocalization of the HOMO orbital, across the series (Table 1). An unexpected trend is observed with the calculated LUMO energy. Both 2CzPN and ^tBuDPA-2CzPN have similar energies at -2.41 and -2.42 eV, respectively. By contrast, a significant stabilization is observed for Cz-2CzPN and PXZ-2CzPN, with LUMO energies of -2.85 and -2.92 eV, respectively. The change in behavior is likely related to the calculated torsional angles between the carbazole donor and phthalonitrile acceptor, with the torsions being greatest for PXZ-2CzPN and Cz-2CzPN, with average angles between the respective planes of 60° and 67–70°, respectively, compared to 53° and 56° for both 2CzPN and ^tBuDPA-2CzPN. The smaller torsion in the latter ensures a larger delocalization of the LUMO orbital onto the electron-donating Cz groups. These trends were also observed by X-ray crystallography (vide infra). The HOMO–LUMO gap is strongly affected by the changes in HOMO and LUMO energies, with values ranging from 2.08 eV for PXZ-2CzPN to 3.65 eV for 2CzPN. The trend in the HOMO–LUMO gap (Table 1) aligns also with the trend observed for the S₁ energies (Table 2) because this excited state is mainly described (>90%) by a HOMO to LUMO transition. The increasing CT character along the series is associated with a smaller calculated ΔE_{ST} , with the values decreasing from 0.34 eV in 2CzPN to 0.01 eV in PXZ-2CzPN (Table S2, SI). This is consistent with the values measured by photoluminescence spectroscopy (Table 3). When M062X is employed as the functional in lieu of PBE0 in the DFT calculations, identical trends are observed; however, the magnitude of the CT character changes slightly, owing to the changing HF content (54%²⁹ for M062X and 25%³⁰ for PBE0). This increased HF contribution helps to alleviate overstabilization of the CT states,³¹ however, as the S₁ and T₁ states are CT in nature in these compounds, the differences between the two methods are minimal. Data from the M062X

Table 3. Singlet and Triplet Energies in Toluene Solution and mCP Film (10 wt %)

compd	toluene			mCP		
	S ₁ (eV)	T ₁ (eV)	ΔE_{ST} (eV)	S ₁ (eV)	T ₁ (eV)	ΔE_{ST} (eV)
2CzPN ^a	3.03	2.73	0.30	2.85	2.62	0.23
Cz-2CzPN ^a	2.85	2.69	0.16	2.69	2.62	0.07
^t BuDPA-2CzPN ^b	2.37	2.36	0.01	2.34	2.33	0.01
PXZ-2CzPN ^a	2.57	2.56	0.01	2.40	2.37	0.03

^aValues determined using the onset at 77 K. ^bValues determined using the onset at 5 K.

calculations, including oscillator strength, ϕ_s , ΔE_{ST} , and calculated HOMO and LUMO energies, can be found in Table S3 (SI). Overall, the DFT data suggest that the design concept of reducing the singlet–triplet gap by increasing the strength of the peripheral donors of the donor dendrons is reasonable.

Synthesis and Chemical and Electrochemical Characterization. The synthesis of the emitters is outlined in Figure 3a. The identity and purity of all compounds were determined from a combination of NMR spectroscopy, high-resolution mass spectrometry, elemental analysis, and melting point determination. In addition, single crystals of Cz-2CzPN, DPA-2CzPN, and PXZ-2CzPN were each obtained either from the layering of a saturated solution of toluene with hexane (Cz-2CzPN, PXZ-2CzPN) or from the slow evaporation of a toluene solution (DPA-2CzPN, PXZ-2CzPN). Two structures of PXZ-2CzPN, showing different solvation and slightly different conformations, were obtained, designated PXZ-2CzPN(A) and PXZ-2CzPN(B). Owing to the insolubility of DPA-2CzPN, ^tBuDPA-2CzPN was also synthesized and we hypothesize that the addition of ^tBu groups should have a minimal impact on the photophysics while addressing the issues of solubility. This is corroborated by DFT calculations that predict nearly identical S₁ (2.19 and 2.18 eV for DPA-2CzPN and ^tBuDPA-2CzPN, respectively) and ΔE_{ST} (0.10 for

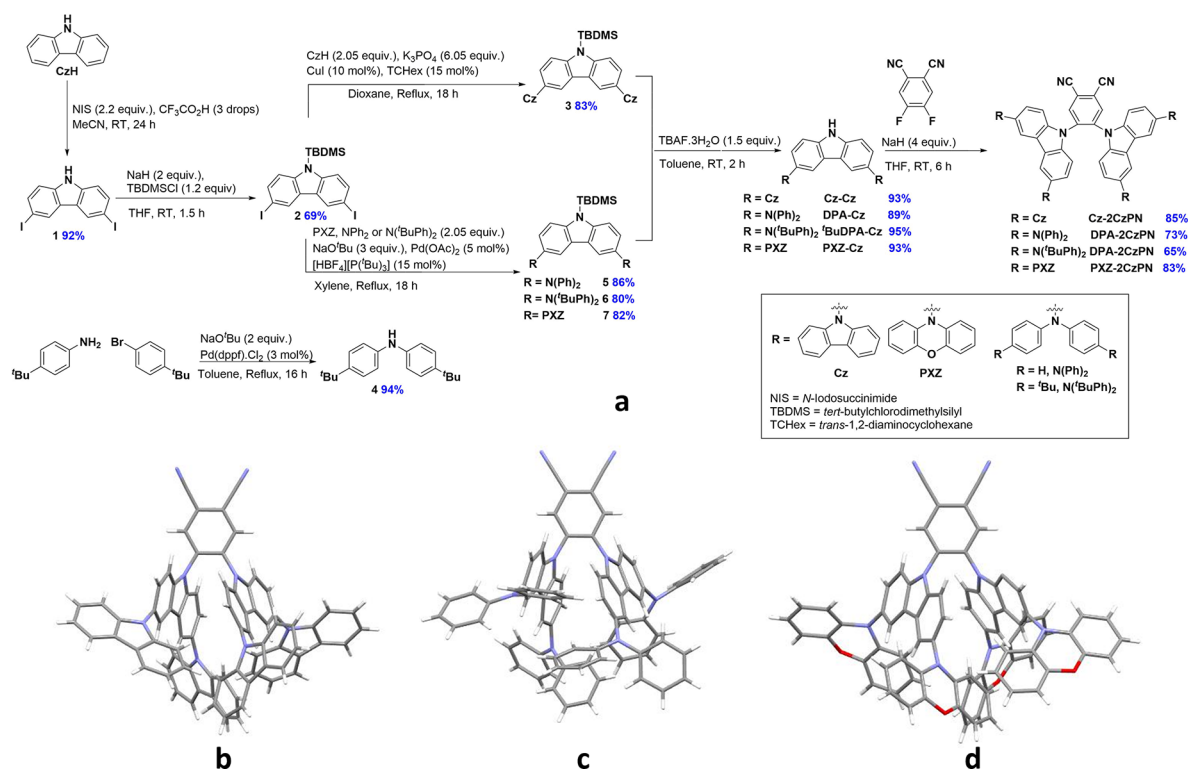


Figure 3. (a) Synthesis of the target emitters and single-crystal structures of (b) Cz-2CzPN, (c) DPA-2CzPN, and (d) PXZ-2CzPN.

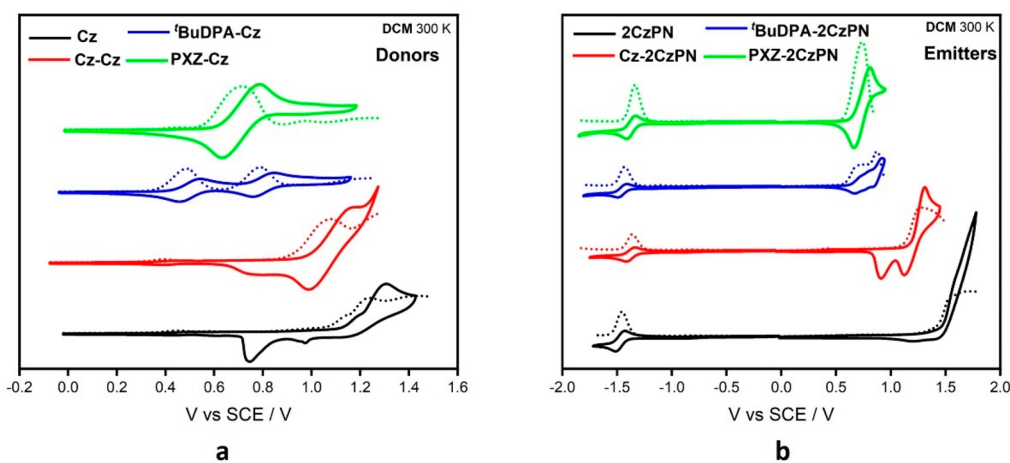


Figure 4. Cyclic voltammetry (solid trace) and differential pulsed voltammetry (dashed trace) in DCM of (a) the isolated donor groups and (b) the emitters.

both) values for the two compounds (Figure S3, Tables S2 and S3, SI). No further photophysical analysis was undertaken for DPA-2CzPN owing to its insolubility. Despite several crystallization conditions, crystals of ^tBuDPA-2CzPN could not be obtained owing to its improved solubility. Comparisons were made with DPA-2CzPN with similar conformations predicted by DFT (Table S5, SI).

Cz-2CzPN, DPA-2CzPN, and PXZ-2CzPN display generally similar torsion angles between the inner carbazole donor and the adjacent phthalonitrile acceptor, although greater variation is seen both between the two forms of PXZ-2CzPN and also between the torsion angles in PXZ-2CzPN(A) [average torsion for each carbazole: Cz-2CzPN, 61.5° and 63.1°, DPA-2CzPN, 54.5° and 59.1°; PXZ-2CzPN(A), 49.4° and 57.3°; and PXZ-2CzPN(B), 60.0° and 65.0°]. The DFT-calculated inner

dihedral angles, 53.8° (2CzPN), 60.2° and 60.3° (Cz-2CzPN), 53.4° (DPA-2CzPN), and 66.5° and 70.2° (PXZ-2CzPN), agree well with those from the crystal structures. The torsions calculated from DFT and measured from the crystal structures are summarized in Table S5 (SI). The differences between the two structures of PXZ-2CzPN include differences in torsions between rings, such as those mentioned above, as well as differences in the extent of puckering of the PXZ groups (Figure S4, SI). The PXZ groups adopt varying degrees of puckered conformation between the two structures, similar to that observed previously in structurally similar phenothiazine-containing compounds.³² In PXZ-2CzPN(A), two PXZ groups are near-planar (PXZ pucker angles of 1.4° and 4.9°) while two adopt a moderate pucker (angles of 13.8° and 17.3°), whereas in PXZ-2CzPN(B), two PXZ groups show slight pucker

(angles of 8.7° and 10.0°) while the other two show a greater pucker than any other PXZ in either structure (angles of 20.6° and 23.6°). The compounds have D–A torsions generally larger than those reported for 2CzPN, which ranged between 49.3° and 59.8° and which can be attributed to the increased steric bulk of the dendrons. The donor–donor torsions vary within individual compounds but show broad trends across the series. For Cz-2CzPN, the torsions of the peripheral carbazoles to the central carbazole range between 59.0° and 78.5°. Due to the larger size of the PXZ groups, there is a slightly larger set of PXZ-carbazole torsions [PXZ-2CzPN(A), 70.0°–78.6°; PXZ-2CzPN(B), 70.6°–79.2°] observed in the two structures. Smaller torsions (44.3°–65.8°) were observed between the DPA groups and the central carbazole in DPA-2CzPN. These smaller dihedral angles should result in an increased conjugation across the dendron, increasing the effective donor strength (vide infra).

To experimentally determine the HOMO and LUMO levels, cyclic voltammetry (CV) and differential pulsed voltammetry (DPV) were performed on each of the four emitters as well as on the isolated donors (and donor groups) in dichloromethane (DCM) [Figures 4 and S5–S9 (SI)]. A summary of the electrochemical data is found in Table 1 for the emitters and in Table S6 (SI) for the donor moieties.

We first investigated the electrochemical behavior of the isolated donors in DCM. As expected, the oxidation of carbazole is not reversible and the compound degrades upon successive scans (Figure S6, SI), via a putative electropolymerization.³³ The E^{ox} from the DPV of 1.15 V versus SCE matches that previously reported ($E^{\text{ox}} = 1.16$ V in MeCN).³⁴ Both ^tBuDPA and PXZ display quasi-reversible oxidation waves centered at 0.84 and 0.66 V (Figure S5, SI), respectively, indicating that PXZ is the strongest donor. The E^{ox} of Cz-Cz is cathodically shifted with respect to Cz at 1.08 V, in agreement with a similar derivative (wherein the N–H of Cz-Cz was replaced by N–C₆H₁₃) with E^{ox} also at 1.08 V in DCM.^{33,35} Only a single oxidation wave is observed, suggesting that the radical cation is delocalized over the Cz-Cz molecule. Cz-Cz is electrochemically unstable, as evidenced by the evolution of the CVs over multiple scans, where a second oxidation wave appears (Figure S6, SI), attributed to polymerization of the carbazole species. For ^tBuDPA-Cz, there are two observed reversible oxidation waves (Figure S7, SI) assigned to the oxidation of carbazole and then ^tBuDPA (Figure 4a). These are both cathodically shifted compared those of Cz (1.16 V) and ^tBuDPA (0.84 V), the E^{ox} of the first wave being 0.49 V. For PXZ-Cz, there is a single reversible oxidation wave at 0.71 V assigned to oxidation of PXZ (E^{ox} of PXZ = 0.66 V, Figure S7, SI). Although PXZ is a stronger donor than ^tBuDPA based on its cathodically shifted oxidation potential, the ability for ^tBuDPA to effectively conjugate to carbazole ensures that ^tBuDPA-Cz (E^{ox} of 0.49 V) is a stronger donor than PXZ-Cz (E^{ox} of 0.71 V).

We next investigated the electrochemistry of the emitters. The CV of 2CzPN shows an irreversible oxidation wave (Figure S5, SI) with E^{ox} at 1.54 V. The calculated HOMO at –5.87 eV reproduces that previously reported ($E_{\text{HOMO}} = -5.88$ eV).²⁰ The irreversible oxidation wave (Figure S5, SI) for Cz-2CzPN is cathodically shifted at $E^{\text{ox}} = 1.28$ V due to the stronger donor. There are two observed oxidation processes in the DPV for ^tBuDPA-2CzPN (Figure 4b). The first oxidation peak potential is significantly cathodically shifted at 0.72 V compared to that of Cz-2CzPN, reflecting the much stronger

donor character of the ^tBuDPA-Cz donor dendron. The E^{ox} for ^tBuDPA-2CzPN is anodically shifted compared to that of ^tBuDPA-Cz due to the conjugation with the electron-accepting phthalonitrile. The reversible oxidation (Figure S7, SI) of PXZ-2CzPN occurs almost exclusively on the PXZ moieties, with an E^{ox} of 0.80 V, which is slightly anodically shifted compared to the oxidation potential of PXZ-Cz (E^{ox} of 0.71 V). This assignment is supported by DFT calculations that reveal that the HOMO density resides on the PXZ units (Figure 2). The increasing donor strength is largely reflected in the oxidation potentials, with E^{ox} of 1.54, 1.28, 0.72, and 0.80 V for 2CzPN, Cz-2CzPN, ^tBuDPA-2CzPN, and PXZ-2CzPN, respectively. The relative order of the oxidation potentials reflects the interplay between the degree of conjugation between the peripheral donors and the central carbazole and the strength of the peripheral donors.

Reversible reduction waves are observed for all four emitters, assigned to the reduction of the phthalonitrile acceptor (Figure S9, SI). The reduction potentials are more cathodically shifted for 2CzPN and ^tBuDPA-2CzPN with E^{red} of –1.46 and –1.43 V, compared to those of Cz-2CzPN and PXZ-2CzPN (E^{red} of –1.36 V and –1.30 V, respectively, Figure S9, SI). This trend is corroborated by DFT calculations (Figure 2). We attribute these trends to an increased electronic interaction between the donors and the acceptor in 2CzPN and ^tBuDPA-2CzPN owing to the less twisted conformation present in these two compounds. Increased electron density on the electron-accepting unit destabilizes the LUMO with respect to the more twisted conformers. Indeed, the calculated D–A torsions of 54° for both compounds, with associated larger ϕ_s values of 0.34 and 0.28, respectively, indicate greater LE character in these two compounds, whereas in Cz-2CzPN and PXZ-2CzPN the larger respective D–A torsions of 60° and 67°–70° are linked with ϕ_s of 0.20 and 0.11, pointing to greater CT character. Overall, there is good agreement between experimentally determined and calculated HOMO and LUMO values. The HOMO–LUMO gaps are 3.0, 2.6, 2.1, and 2.1 eV for 2CzPN, Cz-2CzPN, ^tBuDPA-2CzPN, and PXZ-2CzPN, respectively. Although ^tBuDPA-2CzPN and PXZ-2CzPN have differing conjugation lengths and donor strengths, they nevertheless show similar ΔE .

Photophysics in Solution and Film. The photophysical data is collated in Table 2. We first consider the compounds in dilute toluene solution (0.05 mg/mL, corresponding to 10^{–4}–10^{–5} M, depending on compound), where intermolecular interactions can be expected to be suppressed. This should provide a clear photophysical understanding related to monomolecular processes.

All compounds show a broad, unstructured, low-intensity absorption peak at the low-energy side of the absorption band, with the peak positions indicated in Table 2. Along the series, the absorption maxima shift to lower energy, consistent with the trends observed for the HOMO–LUMO gap found from electrochemistry, and they reduce in intensity (Table 2). We assign these bands to a transition with a predominant CT character between the electron-rich donors and the electron-poor phthalonitrile, as predicted by time-dependent DFT calculations carried out within the Tamm–Dancoff approximation (TDA-DFT) calculations. The trend of the progressive decrease of the molar extinction coefficients of this low-energy band reflects the increasing strength of the CT transition and is largely consistent with the trend in the theoretically calculated oscillator strengths (Table 2). The observation of extinction

coefficients in the range of $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for the first three compounds in the series suggests that the excited states involved have a mixed CT-LE character with a dominant CT character, in agreement with the calculated electron–hole distributions shown in Figure 2 and the calculated ϕ_s listed in Table 2.

At higher energies ($E \geq 3.6 \text{ eV}$) in the absorption spectra, transitions localized on the conjugated donors are evident. For example, in the absorption spectrum of 2CzPN, there is a feature at 3.75 eV (331 nm). We attribute this feature to a transition localized on the carbazole moiety, since *N*-phenylcarbazole has an absorption peak at 3.65 eV³⁸ and the shift to the blue side of the carbazole absorption in 2CzPN by 10 meV will result from the acceptor unit withdrawing the electron density from the carbazole. Adding four further carbazole units to the compound to obtain Cz-2CzPN results in the appearance of an additional absorption peak at 3.65 eV (340 nm). We contend that the peak at 3.65 eV can be attributed to transitions localized on the inner carbazoles while the peak at 3.75 eV results from those on the outer carbazoles, on the basis that the outer carbazoles donate some of their electron density to the inner carbazoles, thus restoring the “normal” electron density of carbazoles there, while the outer carbazoles become electron deficient. In the case of ^tBuDPA-2CzPN and PXZ-2CzPN, there is a sharp increase in absorption with a peak at 4.10 eV (302 nm) and 3.88 eV (320 nm) (both off-scale in Figure 5, presented in full in

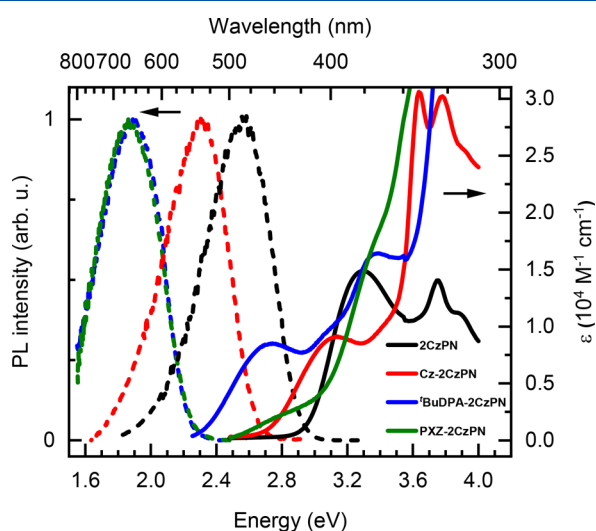


Figure 5. Absorption (solid line) and steady-state emission (dashed line) spectra of 2CzPN, Cz-2CzPN, ^tBuDPA-2CzPN, and PXZ-2CzPN in toluene at 300 K ($\lambda_{\text{exc}} = 300 \text{ nm}$).

Figure S10, SI), representing locally excited (LE) transitions from diarylamine and phenoxazine³⁹ units, respectively (see also Figure S10, SI). The absorption band associated with the phthalonitrile acceptor is located at even higher energies, with peaks from 4.6 eV (270 nm) onward.⁴⁰

Regarding the emission in toluene, all steady-state spectra are broad and structureless, characteristic of emission from a state with a dominant CT character. The photoluminescence maxima shift to lower energies across the family of derivatives, analogous to the shifts in the absorption maxima of the low-energy CT bands and in alignment with the TDA-DFT-predicted S_1 energies. ΔE_{ST} was determined from the measurements of fluorescence and phosphorescence spectra

taken at the same temperature, namely 77 K, to exclude different temperature-dependent energy shifts of the two emissions. This is shown in Figure 6a, with the room-temperature steady-state emission added for comparison. The steady-state emission at 77 K contains contributions from the prompt emission and delayed emission, which is mostly phosphorescence and, except for ^tBuDPA-2CzPN, a negligible contribution of delayed fluorescence (cf. Figure 6c). For ^tBuDPA-2CzPN, the delayed fluorescence was found to be still competing in intensity with phosphorescence at 77 K, so that ΔE_{ST} was determined from the 5 K measurements. The decrease in temperature leads to a blue-shift of the steady-state emission compared to its room-temperature spectrum. We attribute this to the freezing of the solvation shell at low temperatures that prevents reorganization of the solvent molecules after photoexcitation of the emitter molecules.⁴¹ To obtain the phosphorescence spectrum without contribution from fluorescence, we recorded the emission with detection in the millisecond range (see the SI for details). Table 3 below summarizes the energies obtained for the onsets of the singlet and triplet states along with the singlet–triplet gaps that are determined from them.

To address the CT or LE nature of the phosphorescence, we compared the position of the phosphorescence of the donor–acceptor compounds with the phosphorescence of the isolated donor and acceptor moieties themselves. For 2CzPN, the phosphorescence maximum is much lower in energy than both the phosphorescence peaks of carbazole and of phthalonitrile [with peaks at 2.64 vs 3.0³⁸ and 3.2 eV⁴² (470 vs 410 and 390 nm) respectively]. Thus, the spectroscopic data clearly identify the phosphorescence in 2CzPN as a predominant CT transition with some LE contributions, as evident from the vibrational structure. This is in agreement and supported by the quantum chemical calculations (Figure S2, Table S2, SI) and the work by Wong et al.²⁰ The same reasoning assigns the phosphorescence in the three derivatives as predominantly CT transitions. The ΔE_{ST} values in solution decrease along the series from 0.30 eV for the parent compound 2CzPN to 0.01 eV for ^tBuDPA-2CzPN and PXZ-2CzPN. This decrease reflects the increasing hole localization on the donor dendron, which is consistent with the DFT calculations. Thus, the concept underlying the chemical design is confirmed.

To understand how the photophysical properties in solution transfer into film, we next investigated the compounds in 10 wt % mCP film [mCP = 1,3-bis(*N*-carbazolyl)benzene], where mCP is a host matrix with sufficiently high triplet energy (2.90 eV) to ensure confinement of the triplet excitons on the emitter.⁴³ Figure 6b shows the thin-film PL emission for the series at 300 and 77 K (5 K for ^tBuDPA-2CzPN). We find the same trend in the singlet–triplet gap as in solution, with ΔE_{ST} decreasing along the series (within the experimental error margin of 10 meV, Table 3). In contrast to solution, the room-temperature steady-state spectra almost coincide with the low-temperature steady-state spectra. We attribute this to the absence of solvent reorganization after excitation in the solid matrix.⁴¹ It implies that the spectra and energy gaps obtained at low-temperature represent the room-temperature situation well.

For pronounced TADF, a small ΔE_{ST} value is a necessary but not a sufficient condition. To evaluate the potential of a molecule as a TADF emitter, we also need to consider the relevant rates of radiative and nonradiative decay, as reflected in the PLQY, delayed emission lifetimes, and the contribution

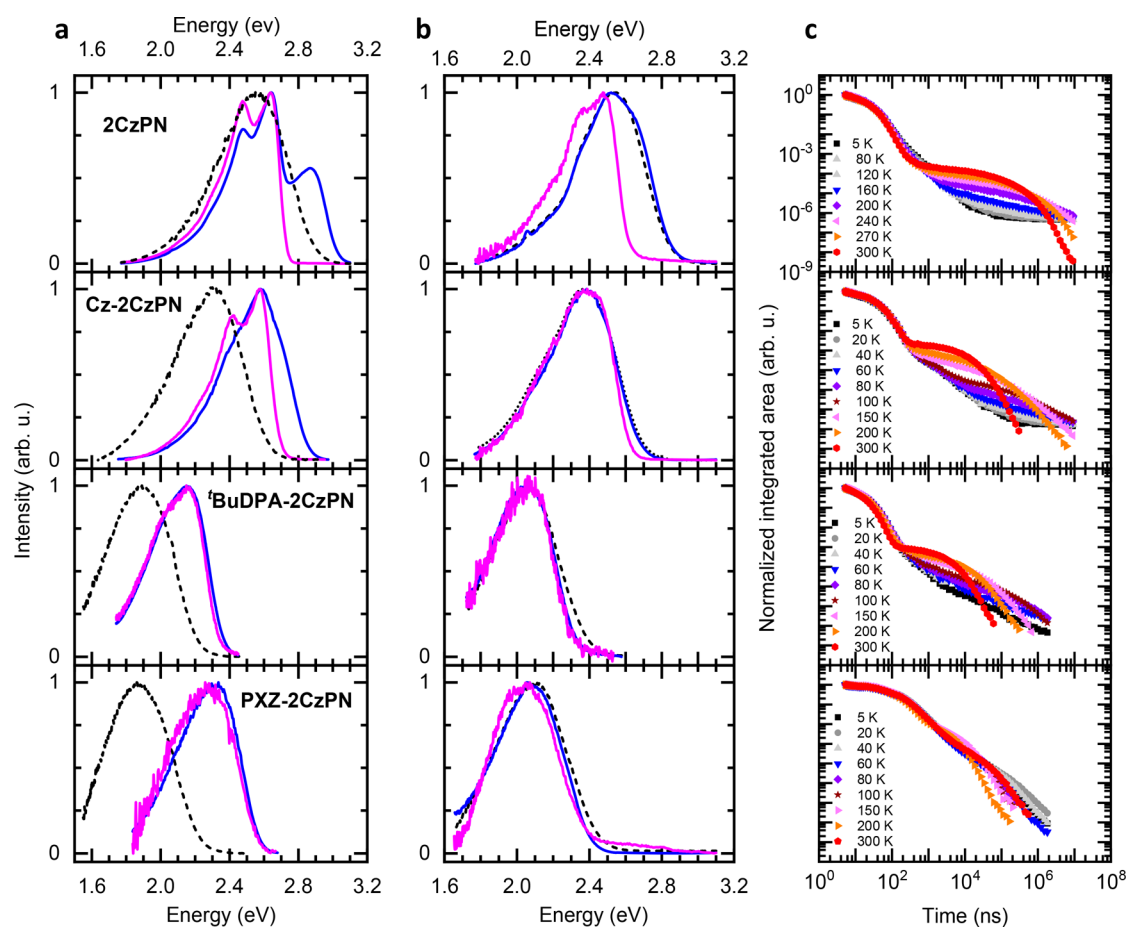


Figure 6. PL emission and transient decay of 2CzPN, Cz-2CzPN, ^tBuDPA-2CzPN, and PXZ-2CzPN. Black dashed lines denote the steady-state PL at 300 K. Blue lines denote the steady-state emission at 77 K. Magenta lines denote the PL with detection in the millisecond range (see the SI) at 77 K. [For ^tBuDPA-2CzPN, the steady-state emission and PL with the detection in the millisecond range is obtained at 5 K ($\lambda_{\text{exc}} = 355$ nm).] (a) PL emission in toluene for excitation at the maximum of the CT absorption band. (b) PL emission in 10 wt % mCP film ($\lambda_{\text{exc}} = 300$ nm). (c) Transient PL decay in 10 wt % mCP film at 300 K ($\lambda_{\text{exc}} = 355$ nm).

Table 4. Quantum Yields (Φ), Lifetimes (τ), and Rates (k) for the Compounds in Toluene

compd	ΔE_{ST}^a (meV)	Φ_{PL}^b (%)	$\Phi_{\text{DF}}/\Phi_{\text{PF}}^c$	τ_{PF}^d (ns)	τ_{DF}^e (μs)	k_r^f ($\times 10^7$ s ⁻¹)	k_{nr}^g ($\times 10^7$ s ⁻¹)
2CzPN	300 \pm 10	38	0.01	27	6.0	1.4	2.3
Cz-2CzPN	160 \pm 10	63	0.43	42	4.5	1.1	1.4
^t BuDPA-2CzPN	10 \pm 10	2	0.01	2	1.2	1.0	49.0
PXZ-2CzPN	10 \pm 10	3	0.02	23	2.3	0.1	4.3

^a $\Delta E_{\text{ST}} = S_1 - T_1$. Estimated from the onsets at 77 K (5 K for ^tBuDPA-2CzPN) as in Table 3. ^bTotal PLQY at 300 K measured in the integrating sphere under N₂. $\lambda_{\text{exc}} = 355$ nm. ^cRatio between the integrated area under the delayed and prompt emission at 300 K. ^dPrompt emission lifetime at 300 K extracted from a monoexponential fitting (Figure S11, SI). ^eDelayed emission lifetime at 300 K extracted from a monoexponential fitting (Figure S11, SI). ^fConstant of radiative decay rate extracted using $k_r^f = \Phi_{\text{DF}}/\tau_{\text{DF}}$. ^gConstant of nonradiative decay rate extracted using $\tau_{\text{PF}} = 1/(k_r^f + k_{\text{nr}}^g)$.

of the TADF to the total emission. With a view to their use as emitters in OLEDs, we focus the discussion on the TADF-related parameters in film, comparing with the solution data wherever relevant. Figure 6c shows the transient PL decays for the compounds in 10 wt % mCP film. The analogous data for solution are given in the SI, along with a complete list of parameters used in the monoexponential fittings for transient decay profiles in solution and film (Figure S11, Table S7, SI). The photophysical parameters obtained are summarized in Table 4 for solution and Table 5 for films.

For both solution and film, we can identify two regimes in the PL decay, that is, a prompt decay in the nanosecond range and a delayed emission that takes place in the microsecond

range. We can safely attribute the delayed emission to TADF, based on the small ΔE_{ST} gap and the increase of the emission in the microsecond range with increasing temperature. From the temperature dependence of the delayed fluorescence (DF) in the film, we derive the activation energy for TADF [Table 5, Figure S12 (SI)]. As with the singlet–triplet gap, the activation energy also decreases along the series. The lower or comparable activation energy than the ΔE_{ST} measured from the steady-state emission spectra, together with the prediction from TDA-DFT calculations of closely lying T_1 , T_2 , and S_1 , points to the involvement of higher-lying triplet states (Table S2, SI). We note that the difference between ΔE_{ST} and the measured activation energy is strongest for 2CzPN, which is

Table 5. Quantum Yields (Φ), Activation Energies (E_{act}), Lifetimes (τ), and Rates (k) for the Compounds in mCP Films

compd	ΔE_{ST}^a (meV)	E_{act} (meV)	Φ_{PL}^b (%)	$\Phi_{\text{DF}}/\Phi_{\text{PF}}^c$	τ_{PF}^d (ns)	τ_{DF}^e (μs)	k_r^{Sf} ($\times 10^7 \text{ s}^{-1}$)	$k_{\text{nr}}^{\text{Sg}}$ ($\times 10^7 \text{ s}^{-1}$)	τ_{Ph}^h (ms)	
									5 K	80 K
2CzPN	230 \pm 10	75 \pm 5	93	1.0	16	42.6	2.9	3.4	170	110
Cz-2CzPN	70 \pm 10	39 \pm 3	78	0.6	25	7.0	1.9	2.1	150	60
^t BuDPA-2CzPN	10 \pm 10	21 \pm 1	14	0.1	10	2.3	1.2	8.8	3.5	
PXZ-2CzPN	30 \pm 10		23	0.3	95	2.5	0.2	0.9	0.2	

^a $\Delta E_{\text{ST}} = S_1 - T_1$. Estimated from the onsets as in Table 3. ^bTotal PLQY at 300 K measured in the integrating sphere under N_2 . $\lambda_{\text{exc}} = 355 \text{ nm}$. ^cRatio between the integrated area under the delayed and prompt emission. ^dPrompt emission lifetime at 300 K extracted from a monoexponential fitting (Figure S11, SI). ^eDelayed emission lifetime at 300 K extracted from a monoexponential fitting (Figure S11, SI). ^fConstant of radiative decay rate extracted using $k_r^{\text{Sf}} = \Phi_{\text{PF}}/\tau_{\text{DF}}$. ^gConstant of nonradiative decay rate extracted using $\tau_{\text{PF}} = 1/(k_r^{\text{Sf}} + k_{\text{nr}}^{\text{Sg}})$. ^hPhosphorescence lifetime extracted from a monoexponential fitting (Figure S13, SI).

the compound with the highest LE contribution in T_2 , which is expected to lead to the highest spin–orbit coupling with the S_1 CT state.

We note that for Cz-2CzPN and ^tBuDPA-2CzPN the radiative decay rate from the singlet state k_r^{S} is only slightly reduced relative to that of the parent compound, while it is significantly reduced for PXZ-2CzPN, indicating a too strong decoupling of the hole and electron wave functions for this compound. This is consistent with both the low calculated oscillator strength and the low PLQY in PXZ-2CzPN. For ^tBuDPA-2CzPN, the ΔE_{ST} is small and a high radiative rate from the CT singlet is maintained, yet a high nonradiative CT singlet decay rate precludes a high photoluminescence quantum yield. This finding is consistent with the work of Yang and co-workers,^{44,45} who reported a diphenylsulfone core linked to acridine-based donor dendrons. When they attached diphenylamine or carbazole as peripheral donor groups they also found a smaller gap and lower PLQY in toluene for the former (40 meV, 12%) than for the latter (90 meV, 68%).^{44,45}

Despite the small ΔE_{ST} , we observe very little TADF in solution except for Cz-2CzPN [cf. column 3 in Table 4 and Table S8 (SI)]. A low TADF yield in solution at room temperature has been observed previously in compounds otherwise predicted to show TADF.^{20,46} We attribute this to enhanced quenching of the triplet state in solution compared to film, which can occur, for example, by collisions with solvent molecules. The fact that quenching does not occur for Cz-2CzPN hints that its triplet may be localized somewhat more on the inner carbazole of the donor dendrons, where it is more shielded from intermolecular quenching. Thus, in solution, the emission characteristics are dominated by the prompt singlet-state emission.

In the film, the rigid matrix removes this collisional quenching mechanism, so that TADF has a stronger contribution to the overall PLQY. Nevertheless, the ratio between the integrated emission intensities of delayed and prompt fluorescence is less than 4 for all compounds, including the parent 2CzPN, so that the commonly used approximation forwarded by Dias et al. to calculate the RISC rate does not apply.⁴⁷ An assessment of the efficiency of RISC is still possible by considering the DF/PF ratio (PF = prompt fluorescence) and the DF lifetime together. As summarized in Table 5, the three 2CzPN derivatives show a shorter DF lifetime than the parent compound. While this by itself could indicate a faster RISC rate, the lower DF/PF ratios in the extended compounds indicate that there must be an additional dominant process present. We conclude that the shorter lifetime of the DF is thus rather associated with a quenching channel for the triplet states from which the DF is fed. We confirmed this by measuring the

phosphorescence lifetimes. The triplet lifetime of ^tBuDPA-2CzPN and PXZ-2CzPN at 5 K is about 50 and 1000 times shorter than that for the parent 2CzPN. For Cz-2CzPN, it is comparable with 2CzPN at 5 K, yet decreases more strongly upon heating, for example, to 80 K, thus also indicating thermally activated nonradiative decay channels [Table 5, and Figure S13 (SI)]. The nearly identical triplet energy of 2CzPN and Cz-2CzPN excludes the energy-gap law as the origin. Most likely, the shorter triplet lifetime results from the higher conformational degrees of freedom in the three 2CzPN derivatives, so that deactivation by torsional modes is facilitated. Overall, we find that employing donor dendrons indeed reduces the singlet–triplet gap and concomitantly the activation energy for TADF. However, in the film this advantage is compromised by an increased nonradiative decay from the triplet state, which occurs in different degrees for the different extensions.

CONCLUDING DISCUSSION

While employing donor dendrons has been explored before as a means to increase the TADF yield, often with the same donor units used throughout the dendron, there are few investigations into the relationship between the nature of the donor dendron and the reduction in the singlet–triplet gap.⁴⁸ In our work, we synthesized a series of molecules based on the TADF-active 2CzPN where we increased the hole-localization through suitable decoration of the carbazole donors. Our results show that the singlet–triplet gap can be reduced while maintaining a sufficiently high oscillator strength for efficient emission. Indeed, Cz-2CzPN demonstrates the most suitable balance in charge distribution, where in solution this compound significantly exceeds the PLQY and TADF properties of the parent 2CzPN. However, we also find that, in the film, a high nonradiative rate of the triplet state prohibits a stronger role of TADF in the extended donor molecules, despite a reduced gap between the singlet and triplet state. Our results imply that the approach of fine-tuning the donor dendron strength indeed can improve the TADF emission, yet for implementation, this still requires more control over the nonradiative decay of the triplet state in the film by, for instance, ensuring that the donor dendrons are sufficiently rigid.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.1c05749>.

Literature survey, DFT calculations, X-ray crystallography, electrochemical and photophysical characterization, and synthesis and chemical characterization of compounds (PDF). The research data supporting this publication can be accessed at <https://doi.org/10.17630/960264e9-239a-4e31-870d-15da5067256a>.

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Notes

The authors declare no competing financial interest.

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