Fluorinated dibenzo[a,c]-phenazine-based green to red thermally activated delayed fluorescent OLED emitters†

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Purely organic thermally activated delayed fluorescence (TADF) emitting materials for organic light-emitting diodes (OLEDs) enable a facile method to modulate the emission color through judicious choice of donor and acceptor units. Amongst purely organic TADF emitters, the development of TADF molecules that emit at longer wavelengths and produce high-efficiency devices that show low efficiency roll-off remains a challenge. We report a modular synthesis route that delivers three structurally related molecules that emit at longer wavelengths and produce high-efficiency devices that show low efficiency roll-off.

Introduction

Among the emitting materials for use in organic light-emitting diodes (OLEDs), purely organic thermally activated delayed fluorescence (TADF) emitters have drawn intense interest in recent years as they enable devices to reach a theoretical internal quantum efficiency (IQE) of 100%. This is possible through efficient harvesting of both singlet and triplet excitons to produce light, the latter of which are converted to the former via reverse intersystem crossing (RISC). Organic TADF emitters do not contain scarce, noble metals that are extracted through environmentally damaging mining operations. Swift progress has been reported in the development of purely organic TADF emitters and now there are numerous examples of TADF OLEDs showing comparable efficiencies to phosphorescent devices.¹²

RISC at ambient temperatures occurs in organic compounds that possess a small energy gap, ΔE_{ST}, between the lowest-lying singlet state S₁ and triplet state T₁, and show non-zero spin–orbit coupling (SOC).³ For this scenario to occur, there must be a spatial separation of the electron-donating unit accommodating the highest-occupied molecular orbital (HOMO) and the electron-accepting unit hosting the lowest-unoccupied molecular orbital (LUMO).⁴ The implementation of this donor–acceptor molecular design produces a strong charge-transfer (CT) character of the S₁ state.⁵

The design of TADF materials that emit at longer wavelengths poses some unique challenges for maintaining a high...
photoluminescence quantum yield ($\Phi_{\text{PL}}$). The $\Phi_{\text{PL}}$ is dependent on the rate constant of radiative decay processes such as fluorescence, but also nonradiative decay processes such as internal conversion (IC) and intersystem crossing (ISC). In large, aromatic molecules, where the electronic relaxation lies within the rule of a weak coupling limit as reported by Englman and Jortner, the rate constant of the nonradiative decay, $k_{\text{nr}}$, is inversely proportional to the exponential of the optical energy gap $\Delta E_{\text{opt}}$. In contrast, the rate constant of the radiative decay, $k_r$, is proportional to the cube of $\Delta E_{\text{opt}}$. As the energy of the emissive excited state decreases, the influence of nonradiative decay increases exponentially because the vibronic coupling between the excited state and ground state is facilitated. The challenge of reducing losses due to vibrational quenching and other nonradiative decay pathways in TADF molecules emitting at longer wavelengths can be partially addressed by introducing rigidity into the molecular structure of the donor and acceptor units. Common acceptors for purely organic TADF emitters are aromatic ketones such as anthraquinones, napthalimides, or heteroaromatic systems like quinoxaline and dibenz[a,c]phenazine (BP). These acceptors show deep LUMO levels of $-3.4 \text{ eV}$, $-2.99 \text{ eV}$, $-2.81 \text{ eV}$, and $-2.90 \text{ eV}$, respectively, that contribute to stabilizing the $S_1$ state and are therefore beneficial for use in the design of TADF emitters targeting longer wavelength regions.

Zhao and co-workers first reported TADF compounds bearing the BP acceptor, which exhibits a rigid, large $\pi$-conjugated system. These compounds contain one to three donor moieties in the donor-acceptor or poly(donor)-acceptor strategy, which are commonly applied for TADF molecule design. The greater number of 9,9-dimethyl-9,10-dihydroacridine (DMAC) donors was expected to strengthen the intramolecular charge transfer (ICT) and lead to color-tuning from green to orange-red emission with electroluminescence maxima, $\lambda_{\text{EL}}$, of 560 nm, 576 nm, and 606 nm for devices featuring 1DMAC-BP, 2DMAC-BP, and 3DMAC-BP, respectively (Fig. 1). A maximum external quantum efficiency (EQE max) of 22.0% was observed for the OLED device with 3DMAC-BP doped in mCBP (18 wt%) at 606 nm.
By employing the stronger donor 10H-phenazine (PXZ), the \( \lambda_{\text{ex}} \) for the devices with 1PXZ-BP, 2PXZ-BP, and 3PXZ-BP were red-shifted to 590 nm, 606 nm, and 634 nm, respectively. The most efficient device with 1PXZ-BP as the emitter showed an EQE\(_{\text{max}}\) of 26.3\% (7 wt\% doped in CBP).\(^{13}\) Both Lee and coworkers as well as Wang and coworkers, have reported fluorosubstituted BP acceptors intending to strengthen the acceptor with the presence of the strongly inductively electron-withdrawing fluorine substituent.\(^{15,16}\) Lee and coworkers reported the use of a fluorine substituent at the acceptor moieties in the ortho-position (FBPCNac, Fig. 1) to the donor moiety. FBPCNac is brightly luminescent in 1 wt\% doped poly styrene film with \( \lambda_{\text{PL}} = 607 \) nm, a \( \Phi_{\text{PL}} \) of 79\% and a delayed lifetime of \( \tau_d \) of 11.1 \( \mu s \). In the electroluminescence (EL) device, it showed an emission maximum of \( \lambda_{\text{el}} = 597 \) nm, an EQE\(_{\text{max}}\) of 23.8\% and low efficiency roll-off. Wang and coworkers on the other hand, attached two fluorine substituents in 11- and 12-position to the TAT-FDBPZ and 674 nm in toluene solution, respectively. Showing the largest \( \Phi_{\text{PL}} \) of 79\% and a delayed lifetime of \( \tau_d \) of 2.30 \( \mu s \). The device based on TAT-FDBPZ showed \( \lambda_{\text{el}} \) of 611 nm and an EQE\(_{\text{max}}\) of 9.2\%.

Building on these findings, we aimed to reduce the molecular weight of the emitter in the context of vacuum-deposited device fabrication. We investigated a compromise of the poly(donor)–acceptor strategy by installing two donor units and an electron-withdrawing fluorine substituent to strengthen the dibenzo[\( a,c \)]phenazine acceptor. We designed three new TADF emitters, shown in Fig. 1, based on 10-fluorodibenzo[\( a,c \)]phenazine (BP-F), each incorporating two donor moieties, namely 3,6-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)-10-fluorodibenzo[\( a,c \)]phenazine (2DTCz-BP-F), 3,6-bis(9,9-dimethylacridin-10(9H)-yl)-10-fluorodibenzo[\( a,c \)]phenazine (2DMAC-BP-F) and 10,10'-10-fluorodibenzo[\( a,c \)]phenazine-3,6-diyl]bis[10H-phenoxazine] (2PXZ-BP-F). We successfully applied a modular synthesis strategy that allowed for the facile synthesis of these TADF molecules. The compounds show color tuning based on the choice of donor, emitting from green to deep-red for 2DTCz-BP-F, 2DMAC-BP-F, and 2PXZ-BP-F at peak wavelengths, \( \lambda_{\text{PL}} \) of 505 nm, 589 nm, and 674 nm in toluene solution, respectively. 2DMAC-BP-F and 2PXZ-BP-F show small \( \Delta E\text{sc} \) of 0.11 eV and 0.02 eV while using the weakest DTCz donor resulted in a compound 2DTCz-BP-F showing the largest \( \Delta E\text{sc} \) of 0.30 eV in doped mCBP film (5 wt\% 2DTCz-BP-F, 10 wt\% 2DMAC-BP-F, and 1.5 wt\% 2PXZ-BP-F). The corresponding delayed lifetimes follow the trend in \( \Delta E_{\text{ST}} \) at 90.6 \( \mu s \), 1.83 \( \mu s \) and 10.152 ms, respectively, for 2DMAC-BP-F, 2PXZ-BP-F and 2DTCz-BP-F. The OLEDs fabricated with 2DMAC-BP-F, 2PXZ-BP-F and 2DTCz-BP-F exhibited EQE\(_{\text{max}}\) of 21.8\%, 12.4\% and 2.1\% at \( \lambda_{\text{el}} \) of 585 nm, 605 nm and 518 nm, respectively.

### Results and discussion

#### Molecular design and synthesis

The synthesis of the 2D-BP-F (D = PXZ, DMAC, DTCz) family of emitters is outlined in Scheme 1. Firstly, 3,6-dibromo-10-fluorodibenzo[\( a,c \)]phenazine 3 was synthesized through a condensation reaction of 3-fluorobenzene-1,2-diamine 1 and 3,6-dibromophenanthrene-9,10-dione 2 in acetic acid and ethanol at elevated temperatures. Proceeding from intermediate 3, the target compounds 2DTCz-BP-F, 2DMAC-BP-F and 2PXZ-BP-F were obtained through Pd-catalyzed Buchwald–Hartwig cross-coupling reactions in excellent yields. While the catalyst system Pd(OAc)\(_2\)/P(\( \text{Bu}\)\(_3\)) gave excellent yields for the synthesis of 2DTCz-BP-F and 2DMAC-BP-F, the catalyst system Pd(dba)\(_2\)/\( \text{P} \)\(_{\text{Bu}}\)\(_3\) gave higher yields for the synthesis of 2PXZ-BP-F.

The three emitters were purified further by gradient-temperature sublimation. The chemical structure and purity of the three compounds were confirmed using \(^1\)H, \(^{13}\)C, and \(^{19}\)F nuclear magnetic resonance (NMR) spectroscopy, high-resolution mass spectrometry (HRMS), infrared spectroscopy, melting point analysis, and elemental analysis (EA). A single crystal suitable for X-ray diffraction analysis was obtained for 2DMAC-BP-F by evaporating a solution in deuterated benzene in an NMR tube at room temperature (Fig. 2a). Analysis of the crystal structure of 2DMAC-BP-F showed that the fluorine atom is disordered about a mirror plane. The DMAC donor units are strongly twisted with a dihedral angle of 65° to the BP acceptor. The DMAC donors display an almost planar conformation with the quaternary carbon being pushed out of the plane by 0.11 Å while the two benzene rings of the DMAC are tilted towards each other by 4°. Crystals of 2DTCz-BP-F were obtained by evaporation of a solution in deuterated chloroform in an NMR tube at room temperature (Fig. 2b). Four crystallographically independent molecules were found with the fluorine atoms disordered about a mirror plane and the donor units strongly twisted with an average dihedral angle of 46.6°. Crystallographic data of both molecules are quoted in the ESI† (Table S1).

#### Theoretical calculations

The ground-state geometries of 2DTCz-BP-F, 2DMAC-BP-F, and 2PXZ-BP-F were optimized using density functional theory (DFT) at the PBE0/6-31G(d,p) level of theory in the gas phase.\(^{17,18}\) The excited state properties were calculated by time-dependent density functional theory (TD-DFT) within the Tamm–Dancoff approximation (TDA-DFT) based on the optimized ground-state geometries.\(^{19}\) The calculated energy levels of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) are presented in Fig. 3, and the results are summarized in Table S2 (ESI†). The dihedral angles between the donor and acceptor moieties were found to be around 48.6° and 47.6° for 2DTCz-BP-F, 87.9°, and 90.1° for 2DMAC-BP-F and 85.9° and 72.2° for 2PXZ-BP-F, respectively. In comparison with the value obtained from the crystal structure, the dihedral angle between the DMAC and the BP-F groups in 2DMAC-BP-F (65°) was found to be smaller than that...
theoretically calculated, while the average dihedral angle between the DTCz and the BP-F groups in 2DTCz-BP-F (46.6°) was in good accordance with the calculated value. Due to the almost orthogonal conformations of 2DMAC-BP-F and 2PXZ-BP-F, the HOMO and LUMO distributions are localized on the donor and acceptor moieties, respectively, in both molecules, which results in small ΔE_{opt}. The LUMOs of all three compounds are distributed over the BP-F acceptor core, while the HOMOs are...
versus
The values are reported for ammonium hexafluorophosphate as the supporting electrolyte.

Cyclic voltammetry (CV) was performed to determine the oxidation and reduction processes. The main oxidation waves occur at 0.80 V, 1.00 V, and 1.32 V for 2PXZ-BP-F, 2DMAC-BP-F, and 2DTCz-BP-F, respectively. These are each assigned to the oxidation of PXZ, DMAC, and DTCz, and reflect the relative strength of the donors. 2DMAC-BP-F shows an additional minor oxidation wave at 0.77 V, which is characteristic of the redox behavior of DMAC-containing compounds. The respective HOMO levels are −5.14 eV, −5.34 eV, and −5.66 eV for 2PXZ-BP-F, 2DMAC-BP-F, and 2DTCz-BP-F. The reduction waves occur at very similar potentials of −1.21 V, −1.19 V, −1.18 V for 2PXZ-BP-F, 2DMAC-BP-F, and 2DTCz-BP-F, respectively, and indicate that the electronic coupling between the donor and acceptor moieties is small.

The corresponding redox gaps, ΔE_{H-L}, decrease from 2.50 V to 2.20 V and 2.01 V for 2DTCz-BP-F, 2DMAC-BP-F, and 2PXZ-BP-F, respectively.

| Emitter         | E_{ox}^{a} [V vs. SCE] | E_{red}^{a} [V vs. SCE] | E_{HOMO}^{b} [eV] | E_{LUMO}^{b} [eV] | ΔE_{H-L}^{c} [eV] |
|-----------------|-------------------------|--------------------------|-------------------|-------------------|-------------------|
| 2PXZ-BP-F       | 0.80                    | −1.21                    | −5.14             | −5.33             | 2.01              |
| 2DMAC-BP-F      | 1.00                    | −1.19                    | −5.34             | −5.15             | 2.20              |
| 2DTCz-BP-F      | 1.32                    | −1.18                    | −5.66             | −5.18             | 2.50              |

|   | ΔE_{H-L} [eV] |
|---|--------------|
| a | In Ar-saturated DCM [0.1 M [nBu4N][PF6]] at a scan rate of 100 mV s\(^{-1}\). E_{ox}^{a} = E_{red}^{a} + 0.46. 21 The HOMO and LUMO energies were determined using E_{HOMO/LUMO} = (E_{ox}/E_{red} + 4.8) eV. 22 23 ΔE_{H-L} = |E_{HOMO} − E_{LUMO}|.

The UV-vis absorption spectra of the three emitters in dilute toluene are shown in Fig. 5a, and the photophysical properties are summarized in Table 2. All three compounds exhibit strong absorption bands around 310 nm, which can be attributed to locally excited (LE) π−π* transitions of the donors and BP-F...
moieties, respectively. Positive solvatochromism is observed for 2DTCz-BP-F, 2DMAC-BP-F, and 2PXZ-BP-F, respectively.}

The optical bandgaps, $E_g$, calculated from the normalized absorption and emission spectra intersection point, are 2.60 eV, 2.32 eV, and 2.13 eV for 2DTCz-BP-F, 2DMAC-BP-F, and 2PXZ-BP-F, respectively. Except for 2DTCz-BP-F ($E_g = 2.60$ eV vs. $E_{S1,\text{theory}} = 2.73$ eV), experimental $E_g$ for 2DMAC-BP-F ($E_g = 2.32$ eV vs. $E_{S1,\text{theory}} = 2.16$ eV) and 2PXZ-BP-F ($E_g = 2.13$ eV vs. $E_{S1,\text{theory}} = 1.89$ eV) were found to be larger than those calculated. The photoluminescence quantum yields, $\Phi_{\text{PL}}$, in degassed toluene solution of 2DTCz-BP-F, 2DMAC-BP-F, and 2PXZ-BP-F are 51%, 30%, and 8%, respectively. These dropped to 49%, 21%, and 6% upon exposure to oxygen (Table 2). The prompt fluorescence and phosphorescence spectra of all compounds in 2-MeTHF at 77 K were measured to determine the $S_1$ and $T_1$ energies from their respective onsets (Fig. 5b and Fig. S18b, ESI†). The S1 energies of 2DTCz-BP-F, 2DMAC-BP-F, and 2PXZ-BP-F are 2.64 eV, 2.47 eV, and 2.23 eV, and the $T_1$ energies are 2.21 eV, 2.27 eV, and 2.28 eV, respectively. The phosphorescence spectra of 2DTCz-BP-F and 2DMAC-BP-F are structured, and each is assigned from TDDFT calculations as a mixed locally excited triplet ($^3LE$) state of the acceptor (BP-F) and charge-transfer ($^3CT$) state (see Fig. S18a and Table S4, ESI†). The phosphorescence spectrum of 2PXZ-BP-F is structureless to a mainly charge-transfer ($^3CT$) state. The $\Delta E_{S1}$ of 2DTCz-BP-F, 2DMAC-BP-F is 0.43 eV and 0.20 eV, respectively. The phosphorescence spectrum of 2PXZ-BP-F in 2-MeTHF (Fig. 5 and Fig. S18b, ESI†) is slightly blue-shifted compared to the prompt fluorescence, leading to an apparent $\Delta E_{S1}$ of $\approx 0.05$ eV, indicating that the emission from these two states results from different conformers. To understand how the solvent polarity affects the energies of $S_1$ and $T_1$ for 2PXZ-BP-F, we measured the prompt fluorescence and phosphorescence spectra in hexane at 77 K, and the $\Delta E_{S1}$ is 0.05 eV for 2PXZ-BP-F (Fig. 5b bottom). We measured the PL decays of all molecules in toluene under degassed conditions using time-correlated single-photon counting (TCSPC, Fig. S19, ESI†). The ICT band of 2DMAC-BP-F and 2PXZ-BP-F decays with biexponential kinetics with prompt fluorescence lifetimes, $\tau_p$, of 27.7 ns and 16.9 ns, and delayed fluorescence lifetimes, $\tau_d$, of 19.0 µs and 0.2 µs, respectively (Fig. S19, ESI† and Table 2). The delayed emission is strongly quenched upon the exposure of oxygen, indicating accessible triplet states. The ICT band of 2DTCz-BP-F decays monoexponentially with $\tau_p$ of 6.6 ns, no delayed emission is observed for this compound.

To assess the emission properties of these emitters in the solid-state, their photophysical properties were first investigated in PMMA. The PL spectra are unstructured with $\lambda_{PL}$ at 524, 588, and 615 nm for 2DTCz-BP-F, 2DMAC-BP-F, and 2PXZ-BP-F, respectively (Fig. S20, ESI† and Table 2). The optimized $\Phi_{\text{PL}}$ in doped PMMA films under an N$_2$ atmosphere are 29%, 48%, and 28%, respectively, for 2DTCz-BP-F (5% in PMMA), 2DMAC-BP-F (10% in PMMA), and 2PXZ-BP-F (1.5% in PMMA). The $\Phi_{\text{PL}}$ values were reduced to 27%, 34%, and 17%, respectively, under air. Multietenotional decay kinetics were observed in the time-resolved decays with average $\tau_d$ values of 10.1 ms, 5.0 ms, and 2.99 µs for 2DTCz-BP-F, 2DMAC-BP-F, and 2PXZ-BP-F, respectively.
As a result, 2DMAC-BP-F (0.28 eV) and 2DTCz-BP-F (0.34 eV) have the smallest $\Delta E_{ST}$ while 2DMAC-BP-F (0.28 eV) and 2DTCz-BP-F (0.34 eV) show significantly larger singlet–triplet gaps.

We next measured the photophysical properties of all three compounds in an OLED-relevant host 3,3'-carbazol-9-yl)-biphenyl (mCBP) as this host matrix has sufficiently high triplet energy ($T_1 = 2.84$ eV) to confine the excitons onto the emitter.\(^{(28)}\) The dopant concentration was varied from 1–10 wt% in doped film to optimize the PL of 584 nm, and 1.5 wt% 2PXZ-BP-F in doped film is 78.0% at $T_1 = 2.56$ eV, respectively. The corresponding rate constants of reverse intersystem crossing ($k_{RISC}$) in mCBP films for 2PXZ-BP-F reached $2.41 \times 10^5$ s$^{-1}$, a value much faster than 2DTCz-BP-F of $5.14 \times 10^4$ s$^{-1}$, and 2DMAC-BP-F of $1.33 \times 10^4$ s$^{-1}$, respectively. The relative intensities of the delayed PL increased with increasing temperature from 100 K to 300 K, thereby corroborating the TADF nature of the emission of these three compounds in the mCBP films. The extremely long lifetime and sharp decrease of the emission intensity at low temperature for the 2DTCz-BP-F doped mCBP film can be explained by the large $\Delta E_{ST}$ (vide infra) and inefficient TADF.

There is an expectedly large $\Delta E_{ST}$ of 0.30 eV for 2DTCz-BP-F, while the $\Delta E_{ST}$ for 2DMAC-BP-F and 2PXZ-BP-F is much smaller than 0.11 eV, and 0.02 eV, respectively. The $S_1$ level of 2DTCz-BP-F in mCBP doped film ($S_1 = 2.54$ eV) is similar to the $S_1$ level of 2DTCz-BP-F in PMMA doped film ($S_1 = 2.56$ eV) and very close to the energy level of 2DTCz-BP-F in 2-MeTHF glass ($S_1 = 2.64$ eV), all of which indicates that the $S_1$ state in 2DTCz-BP-F is of mixed $^1LE$ and $^1CT$ character. The structured phosphorescence and triplet energy level of 2DTCz-BP-F does not change in different media such as PMMA ($S_1 = 2.22$ eV, Figs. S22d, ESI$^{1}$), mCBP ($T_1 = 2.24$ eV, Figs. S22a, ESI$^{1}$), and in 2-MeTHF glass ($T_1 = 2.21$ eV, Fig. 5b). Furthermore, these values match with the phosphorescence of the F-BP acceptor (2.26 eV) in 2-MeTHF glass (Fig. S18a, ESI$^{1}$) and imply that the $T_1$ level of 2DTCz-BP-F has $^3LE$ character. The calculated $\Delta E_{ST}$ value of 2DTCz-BP-F in PMMA is 0.34 eV and 0.30 eV in mCBP, values that render TADF inefficient. The weak emission band at 522 nm in the millisecond timescale spectra of 2DTCz-BP-F in mCBP and PMMA may be due to residual delayed fluorescence.

The $S_1$ levels of the other two emitters 2DMAC-BP-F and 2PXZ-BP-F in PMMA are 2.56 eV and 2.34 eV, which are significantly blue-shifted in comparison to those in mCBP doped films, for which the $S_1$ level for 2DMAC-BP-F is 2.40 eV, and for 2PXZ-BP-F is 2.22 eV. The $T_1$ level of 2DMAC-BP-F is
Table 2 Photophysical properties of 2DTCz-BP-F, 2DMAC-BP-F, and 2PXZ-BP-F

| Emitter          | λ_{PL} [nm] | τ_{p} [ns] | τ_{d} [µs] | S_{ST}/T_{1} | ΔE_{ST} [eV] | Φ_{PL} [%] |
|------------------|-------------|------------|------------|--------------|--------------|------------|
| In solution      |             |            |            |              |              |            |
| 2DTCz-BP-F       | 505a        | 6.6a       | —          | 2.64/2.21b   | 0.43b        | 51 (49)a   |
| 2DMAC-BP-F       | 589a        | 27.2a      | 19.0a      | 2.47/2.27b   | 0.20b        | 30 (21)a   |
| 2PXZ-BP-F        | 674a        | 16.9a      | 0.2a       | 2.23/2.28     | -0.05b       | 8 (6)a     |
| In PMMA®         |             |            |            |              |              |            |
| 2DTCz-BP-F (5 wt%) | 524 —       | 10105d     | 2.56/2.22  | 0.34         | 29 (27)d     |            |
| 2DMAC-BP-F (10 wt%) | 588 —      | 503d       | 2.56/2.28  | 0.28         | 48 (34)d     |            |
| 2PXZ-BP-F (1.5 wt%) | 615 —      | 2.99d       | 2.34/2.28  | 0.06         | 28 (17)d     |            |
| In mCBF®         |             |            |            |              |              |            |
| 2DTCz-BP-F (5 wt%) | 522 4.3d    | 10152d     | 2.54/2.24  | 0.30         | 60 (47)d     |            |
| 2DMAC-BP-F (10 wt%) | 584 19.6d   | 90.6d      | 2.40/2.29  | 0.11         | 78 (48)d     |            |
| 2PXZ-BP-F (1.5 wt%) | 611 30.1d   | 1.83d      | 2.22/2.20  | 0.02         | 58 (47)d     |            |

*At 298 K, values quoted are in degassed toluene solutions prepared by three freeze–pump–thaw cycles: for λ_{PL} the λ_{exc} = 343 nm for 2DTCz-BP-F, λ_{exc} = 391 nm for 2DMAC-BP-F and 2PXZ-BP-F. For lifetime τ_{exc} is 379 nm. Φ_{PL} values inside parenthesis quoted after aeration of a toluene solution. Obtained from the onset of the prompt fluorescence (time window: 1–100 ns) and phosphorescence spectra (time window: 1–8.5 ms) measured in 2-MeTHF glass at 77 K. λ_{exc} = 343 nm. Thin films of PMMA and mCBP were prepared by spin-coating. Steady-state and time-resolved emission spectra were recorded at 298 K under an O₂-free atmosphere (λ_{exc} = 343 nm for steady-state and λ_{exc} = 379 nm for time-resolved emission). Average lifetime (τ_{avg} = ∑A_{i}/A_{τi}, where A_{i} is the pre-exponential for lifetime τ_{i}). Prompt and delayed emissions were measured by TCSPC and MCS, respectively (λ_{exc} = 343 nm). Photoluminescence quantum yields of thin films were determined using an integrating sphere (λ_{exc} = 305 nm or 340 nm) under N₂ atmosphere at 298 K. Values quoted inside the parentheses are in the presence of O₂.

Device characterization

OLED devices based on 2PXZ-BP-F, 2DMAC-BP-F and 2DTCz-BP-F were fabricated by vacuum deposition following a typical bottom-emitting OLED device architecture (Fig. 7a) that consists of indium tin oxide (ITO)/1,4,5,8,9,11-hexaacrylthiophen-11-oxide [(HATCNC) (5 nm)/N,N-di[(1-naphthyl)-N,N'-diphenyl-[1,1′-biphenyl]-4,4'-diamine (NPB) (40 nm)/tris(4-carbazoyl-9-ylphenyl)amine (TCTA) (10 nm)/emissive layer (20 nm)/1,3,5-tri(3-pyridyl)-phen-3-ylbenzene (TmPyPB) (40 nm)/LiF (0.6 nm)/Al (100 nm), where HATCN, NPB and TCTA play the role of hole injection layer (HL), hole transportation layer (HTL) and electron block layer (EBL), respectively. TmPyPB acts both as electron transport layer (ETL) and hole blocking layer due to its deep HOMO (−6.7 eV), and LiF acts as an electron injection layer (EIL). The molecular structures of the materials used in these OLEDs are shown in Fig. 7b. The emission layer (EML) comprises 1.5 wt% of 2PXZ-BP-F, 10 wt% 2DMAC-BP-F, or 5 wt% of 2DTCz-BP-F doped into mCBP, based on the doping study discussed above (Table S5, ESI†). The performance of the OLEDs is summarized in Table 3. Current density–voltage–brightness (J–V–L) curves, EQE–luminance curves, and electroluminescence spectra (EL) are given in Fig. 7c. As shown in Fig. 7e, each EL spectrum is similar to that of the corresponding PL spectrum in the thin film with EL maxima, λ_{max} at 605 nm for 2PXZ-BP-F, 585 nm for 2DMAC-BP-F, and 518 nm for 2DTCz-BP-F. Similar to that observed by PL, the trend in emission energy follows that of increasing donor strength. The corresponding CIE coordinates are (0.55, 0.44), (0.51, 0.48) and (0.29, 0.58) for the devices with 2PXZ-BP-F, 2DMAC-BP-F and 2DTCz-BP-F, respectively. The turn-on voltage of the devices lies between 3.3 V to 3.7 V and is dependent on the energy gap between the HOMO of materials used in HTL and EML layers. The 2DMAC-BP-F-based device showed the best overall performance with the highest maximum external quantum efficiency (EQE_{max}) of 21.8%, a maximum current efficiency (CE_{max}) of 59.7 cd A⁻¹, and maximum power efficiency (PE_{max}) of 55.4 lm W⁻¹ (Table 3, Fig. 7d and Fig. S23 and S24, ESI†). The EQE_{max} of the 2PXZ-BP-F-based device is 12.4% with CE_{max} = 26.3 cd A⁻¹ and PE_{max} = 23.0 lm W⁻¹. The 2PXZ-BP-F-based device showed moderate roll-off efficiency, with the EQE at 100 cd m⁻² at 9.3% and the EQE at 1000 cd m⁻² at 6.3%. The 2DMAC-BP-F-based device, however, showed higher efficiency roll-off, with an EQE at 100 cd m⁻² of 8.7% and an...

![Fig. 6 Temperature-dependent time-resolved PL decay of (a) 5 wt% 2DTCz-BP-F doped mCBP film; (b) 10 wt% 2DMAC-BP-F doped mCBP film; (c) 1.5 wt% 2PXZ-BP-F doped mCBP film (λ_{exc} = 379 nm).](image-url)

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EQE of 1000 cd m\(^{-2}\) at 3.3%. The maximum brightness of the 2PXZ-BP-F-based device reached 12350 cd m\(^{-2}\) at an EQE of 2.3%. The relatively low efficiency roll-off in 2PXZ-BP-F originates in part from the low triplet exciton concentration due to the relatively short delayed lifetime (\(t_d = 1.83\) ms).\(^{30,31}\) Notably, the 2PXZ-BP-F-based device reached an EQE of 2.5% at 10000 cd m\(^{-2}\) with an emission wavelength beyond 600 nm. Although 2DTCz-BP-F shows a high \(\Phi_{PL}\) of ca. 60% in the 5 wt% doped in mCBP, the device exhibits a low \(\text{EQE}_{\text{max}}\) of 2.1%. As a result of the too high \(D_{ST}\), the harvesting of triplet excitons in the 2DTCz-BP-F-based device is very inefficient as reflected in the very long delayed lifetime, which causes more triplet-triplet annihilation and triplet-polaron annihilation. Devices fabricated using MoO\(_3\) as the HIL showed similar performance but reached lower luminance and lower current density than the devices using HATCN (Table S6 and Fig. S25, ESI\(^{†}\)).

Conclusions

This study reported a series of green-to-red-emitting fluorine-substituted dibenzo[a,c]phenazine-based (BP-F) TADF emitters, 2DTCz-BP-F, 2DMAC-BP-F, and 2PXZ-BP-F, which showed color tuning based on the choice of donor, emitting from green to deep-red. The rigid and planar constituent groups with large steric hindrance between donor and acceptor units endow these emitters with high \(\Phi_{PL}\) values and suitably small \(D_{ST}\). Among them, 2DMAC-BP-F exhibits the highest \(\Phi_{PL}\) at 78%, a relatively small \(D_{ST}\) of 0.11 eV at 584 nm in 10 wt% doped mCBP, whereas 2PXZ-BP-F shows the smallest \(D_{ST}\) of 0.02 eV with shortest delay lifetime of 1.83 ms at 611 nm in 1.5 wt% doped mCBP. OLED devices using these TADF materials showed excellent performance with an \(\text{EQE}_{\text{max}}\) of 21.8% in the case of 2DMAC-BP-F with \(\lambda_{\text{EL}}\) of 585 nm and 12.4% for 2PXZ-BP-F with \(\lambda_{\text{EL}}\) of 605 nm. The relatively low efficiency roll-off in 2PXZ-BP-F is due to the short delayed lifetime, making this material a very good TADF emitter for OLEDs in the family of devices that can reach brightness above 10000 cd m\(^{-2}\) with an emission wavelength beyond 600 nm. These results demonstrate that simple modification of the BP acceptor with a fluorine substituent is an effective approach to design orange-red/red TADF emitters with devices that show high \(\text{EQE}\) and low-efficiency roll-off.

Data availability

The research data supporting this publication can be accessed at https://doi.org/10.17630/2553f890-29d1-4fb8-a49c-0cf06404d856.
Conflicts of interest
The authors declare no conflict of interest.

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