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## Deep-red to NIR solution-processed OLEDs of donor-decorated quinoxaline-based TADF aggregates†

Abhishek Kumar Gupta, \*<sup>ab</sup> David B. Cordes, <sup>a</sup> Joydip De, <sup>a</sup> Alexandra M. Z. Slawin, <sup>a</sup> Stuart Warriner, <sup>c</sup> Ifor D. W. Samuel \*<sup>b</sup> and Eli Zysman-Colman \*<sup>a</sup>

We report the use of an extended  $\pi$ -conjugated electron-deficient "pyrazino[2,3-*g*]quinoxaline (**PQ**)" as a strong, planar acceptor in a donor–acceptor thermally activated delayed fluorescence (TADF) emitter design to achieve deep-red to NIR emission. A pair of multi-donor–acceptor (multi-D–A) emitters, **4DMAC-TPPQ** and **4PXZ-TPPQ**, using **PQ** as the strong acceptor and dimethylacridine (DMAC) and phenoxazine (PXZ) as strong donors, respectively, emit at 650 and 762 nm in toluene, which is significantly red-shifted in comparison to the parent compound **TPPQ** ( $\lambda_{PL}$  = 456 nm). Both compounds show aggregation-induced emission enhancement in THF:water mixtures. Both compounds exhibit TADF as doped films in 4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl (CBP) and as neat films. The emission of the neat film is similar to that in toluene with  $\lambda_{PL}$  of 654 and 770 nm for **4DMAC-TPPQ** and **4PXZ-TPPQ**, respectively. Solution-processed organic light-emitting diodes (SP-OLEDs) of neat **4DMAC-TPPQ** showed electroluminescence ( $\lambda_{EL}$ ) at 685 nm and an  $EQE_{max}$  of 0.3%, while the device with **4PXZ-TPPQ** emitted at an  $\lambda_{EL}$  of 780 nm and showed an  $EQE_{max}$  of 0.04%. The OLEDs with **4PXZ-TPPQ** showed the most red-shifted emission amongst those employing TADF emitters containing a quinoxaline-type acceptor.

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## Introduction

Materials that emit in the deep-red (650–700 nm) to near-infrared (NIR) (700–1400 nm) wavelength range are used in numerous applications, including biomedical imaging,<sup>1–3</sup> forensic science,<sup>4,5</sup> chemical sensors,<sup>6,7</sup> dyes in photovoltaic cells,<sup>8</sup> fibre optic telecommunications,<sup>9–11</sup> and electroluminescent devices.<sup>12</sup> Both transition metal complexes<sup>11–13</sup> and conjugated polymers<sup>1,14</sup> can be considered rather mature classes of red emitters; however, the development of purely organic emitters in the deep-red to NIR region is challenging because of three main issues. Firstly, red emitters are not as emissive as higher energy analogues due to the energy gap law, which states that

radiative decay decreases and nonradiative decay accelerates as the emission wavelength shifts to the red. This is due to vibrational coupling between the excited state and the ground state.<sup>15,16</sup> Secondly, the use of large  $\pi$ -systems, particularly in terms of the electron acceptor in donor–acceptor emitter design, leads to aggregation-caused quenching (ACQ) of the emission.<sup>16,17</sup> Thirdly, most organic compounds are fluorescent and so only the electrogenerated singlet excitons are available to produce light in organic light emitting diodes (OLEDs), which limits the efficiency of these devices.<sup>15,16</sup>

One strategy to overcome these design limitations is to use thermally activated delayed fluorescence (TADF) emitters as these can harvest both singlet and dark triplet excitons to produce light in OLEDs.<sup>18,19</sup> To design an efficient NIR TADF emitter, the compound needs to possess a small singlet-triplet energy gap ( $\Delta E_{ST}$ ), which will enable a fast reverse intersystem (RISC) that should outcompete nonradiative decay pathways involving triplet excitons. This requires the use of rigid, planar and strong donor and acceptor motifs that are reasonably weakly coupled to each other to extend  $\pi$ -conjugation.<sup>15,16</sup> A second plausible strategy is to develop an emitter showing simultaneous TADF and aggregation-induced emission (AIE).<sup>20,21</sup> Our emitter design adheres to this latter paradigm. We envisioned having a strong acceptor motif (*i.e.*,  $E_{LUMO} < -2.50$  eV); however, the choice of acceptor moieties

<sup>a</sup> Organic Semiconductor Centre, EaStCHEM School of Chemistry, University of St Andrews, Fife KY16 9ST, UK. E-mail: eli.zysman-colman@st-andrews.ac.uk

<sup>b</sup> Organic Semiconductor Centre, SUPA. School of Physics and Astronomy, University of St Andrews, North Haugh, St Andrews, Fife KY16 9SS, UK

<sup>c</sup> School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, UK

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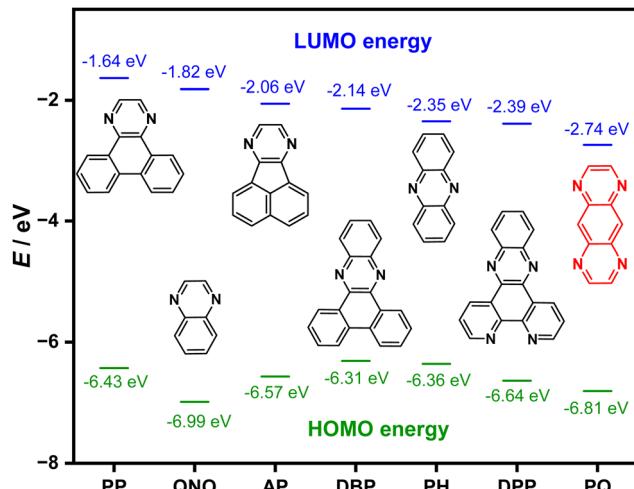


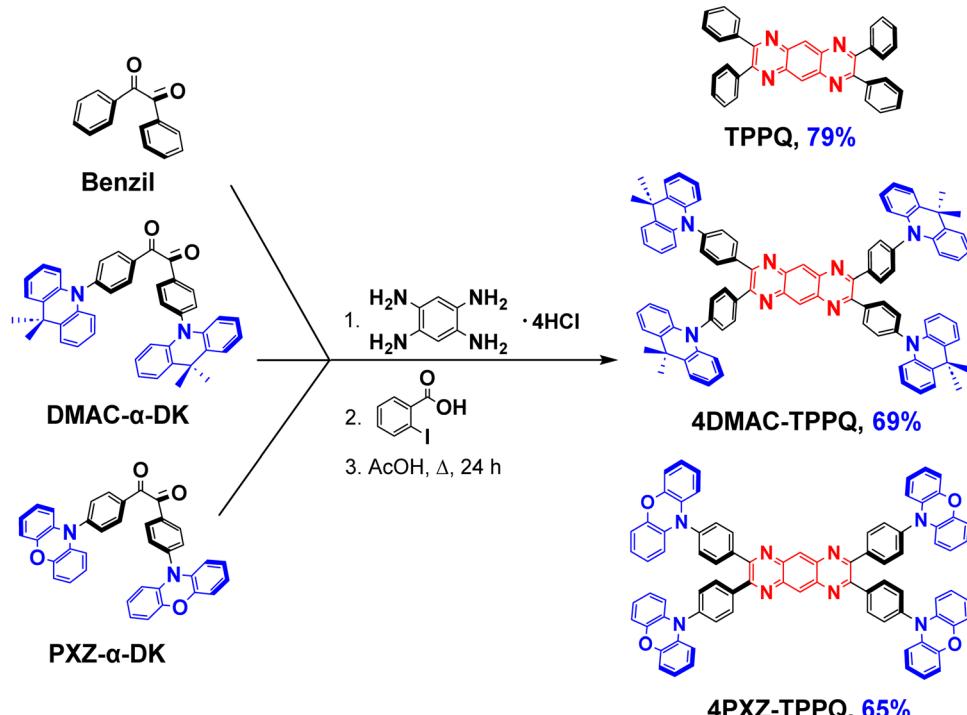
Fig. 1 Common pyrazine-based acceptor moieties and their corresponding highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies, calculated at the PBE0/6-31G(d,p) level in a vacuum.

is somewhat limited, and most NIR TADF emitters ( $\lambda_{PL} > 650$  nm) contain one of benzothiadiazole (BT),<sup>22,23</sup> pyridal[2,1,3]thiadiazole (PT),<sup>24</sup> naphtho[2,3-*c*][1,2,5]thiadiazole (NZP)<sup>25</sup> and pyrazine derivatives.<sup>7,26,27</sup> Out of these acceptor motifs, the most common pyrazine derivatives are phenanthropyrazine (PP), quinoxaline (QNO), acenaphthopyrazine (AP), dibenzophenazine (DBP), phenazine (PH), and dipyridophenazine (DPP), and their acceptor strengths are shown in Fig. 1.

With the goal of pushing the emission further into the NIR, our acceptor design contains a dipyrazine embedded within an

extended  $\pi$ -conjugative framework in the form of a pyrazine-quinoxaline (PQ). This motif can also be thought of as a fused tetraazaanthracene. Consequently, the presence of four nitrogen atoms makes the system quite electron deficient, reflected in a LUMO energy of  $-2.74$  eV (Fig. 1). Because of their strong accepting nature, PQ-based materials have been explored as fluorescent sensors,<sup>28</sup> as motifs in organic liquid-crystalline semiconductors,<sup>29–31</sup> and as components in OLEDs<sup>23</sup> and organic photovoltaics (OPVs).<sup>29</sup> Chen *et al.* reported an AIE active fluorescent donor-acceptor system based on PQ derivatives that exhibited green and red emission from their aggregates, and utilized these in bio-imaging applications.<sup>32</sup> Vishwakarma *et al.* reported a PQ based columnar liquid crystalline material (PQ10) and its use as a fluorescent emitter for green OLEDs.<sup>30</sup> Due to the impressive hole transporting mobility of PQ10, it was also used as a hole transporting material for photovoltaic applications.<sup>29</sup>

In our bid to design NIR emitters, we decorated the PQ moiety with four electron-donating groups, either dimethylacridane (DMAC) or phenoxazine (PXZ),<sup>33–35</sup> each separated by a phenylene bridge to the central PQ acceptor. We cross-compare the optoelectronic properties of 4DMAC-TPPQ, and 4PXZ-TPPQ with that of the electron-acceptor TPPQ (Scheme 1), including assessing whether each of these compounds shows aggregation-induced emission enhancement (AIE). TPPQ emits in the blue ( $\lambda_{PL} = 456$  nm) in toluene, while 4DMAC-TPPQ and 4PXZ-TPPQ emit at 650 and 762 nm, respectively (Fig. 4). Their corresponding  $\Delta E_{ST}$  values, obtained in glassy 2-MeTHF at 77 K, are 0.97, 0.41 and 0.24 eV. All these compounds show AIE in THF:H<sub>2</sub>O mixtures; indeed, upon increasing the water fraction in THF solution, the blue PL band peaking at 490 nm intensified,



Scheme 1 Synthetic scheme of TPPQ, 4DMAC-TPPQ, and 4PXZ-TPPQ.



which is associated with locally-excited emissions from **TPPQ**. Additionally, for **4DMAC-TPPQ**, there is the appearance of a deep-red band at 650 nm and for **4PXZ-TPPQ** a band at 790 nm emerges, both of which are associated with aggregate formation (Fig. 5). **4DMAC-TPPQ** shows emission from 627 to 654 nm and **4PXZ-TPPQ** shows emission from 682 to 770 nm by varying the doping concentration from 5 to 50 wt% in CBP and in neat film with lowering the  $\Delta E_{ST}$  to 0.29 and 0.04 eV, respectively (Fig. S34, ESI<sup>†</sup> and Table 2). Finally, we fabricated doped (in CBP) and neat film solution-processed OLEDs (SP-OLEDs) of **4DMAC-TPPQ** and **4PXZ-TPPQ**. The neat film SP-OLEDs with **4DMAC-TPPQ** emitted with an electroluminescence maximum,  $\lambda_{EL}$ , of 685 nm, while neat film SP-OLEDs with **4PXZ-TPPQ** emitted at an  $\lambda_{EL}$  of 780 nm. Notably, the PL spectrum of **4PXZ-TPPQ** and the EL spectrum of the OLED with this emitter were the most red-shifted among those of the 19 other TADF emitters containing a quinoxaline-type acceptor (Fig. S43 and Table S11, ESI<sup>†</sup>). Remarkably, we also enabled the TADF phenomena in **TPPQ** containing emitters, which was absent in previously reported compounds containing the **TPPQ** moiety.<sup>30,32</sup>

## Results and discussion

The  $\alpha$ -diketone derivatives of benzil-containing 9,9-dimethyl-9,10-dihydroacridine (**DMAC- $\alpha$ -DK**) and 10H-phenoxazine (**PXZ- $\alpha$ -DK**) moieties were synthesized through a palladium-catalysed Buchwald–Hartwig cross-coupling between 4,4'-dibromobenzil and DMAC or PXZ according to our previously reported procedure.<sup>34</sup> Benzil, **DMAC- $\alpha$ -DK** and **PXZ- $\alpha$ -DK** were condensed with 1,2,4,5-tetraaminobenzene tetrahydrochloride to afford pyrazinyl[2,3-g]quinoxaline derivatives **TPPQ**, **4DMAC-TPPQ** and **4PXZ-TPPQ**, respectively, in good yield (Scheme 1). Their identity and purity were determined by a combination of <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, high-pressure liquid chromatography (HPLC), high-resolution mass spectrometry (HRMS), elemental analysis, and single crystal X-ray diffraction (SC XRD) (Fig. 1 and Fig. S1–S15, ESI<sup>†</sup>). The decomposition temperature ( $T_d$ ), defined as the 5% weight loss of the material, is 356 °C for **TPPQ**, 445 °C for **4DMAC-TPPQ** and 495 °C for **4PXZ-TPPQ** (Fig. S16, ESI<sup>†</sup>). Thus, all three compounds show high thermal stability. DSC measurements reveal very high glass transition temperatures ( $T_g$ ) of 292 °C, 432 °C, and 450 °C for **TPPQ**, **4DMAC-TPPQ** and **4PXZ-TPPQ**, respectively.

Single crystals of **TPPQ**, **4DMAC-TPPQ** and **4PXZ-TPPQ** suitable for X-ray diffraction were grown by slow evaporation from either a mixture of dichloromethane and hexane, or chloroform and THF. The structures of **TPPQ**, **4DMAC-TPPQ** and **4PXZ-TPPQ** are found in the centrosymmetric space groups  $P2_1/c$  (**TPPQ**) and  $P2_1/n$  (both other structures). For **TPPQ** and **4DMAC-TPPQ** the asymmetric unit contains one half of an emitter molecule, as well as one or two molecules of dichloromethane, respectively, while the asymmetric unit of the structure of **4PXZ-TPPQ** contains a complete emitter molecule. The four phenyl rings attached to the central core of **PQ** in **TPPQ** are somewhat twisted, with dihedral angles between phenyl rings and the planes of **PQ** of 34.32(14) and 57.55(14)° (Fig. 2). The corresponding

dihedral angles are 34.74(16) and 49.47(6)° in **4DMAC-TPPQ**, and 47.81(12), 47.84(12), 48.60(5) and 58.02(15)° in **4PXZ-TPPQ**, while the dihedral angles between the bridging phenylene rings and the mean plane of the central six-membered heterocycle of the donor moieties show more twist at 69.95(6) and 78.23(7)° for **4DMAC-TPPQ**, and 59.27(13), 62.24(13), 68.40(6) and 73.17(18)° for **4PXZ-TPPQ** (Fig. 2a). This leads to the donor and acceptor groups being closer to co-planar in **4PXZ-TPPQ** than in **4DMAC-TPPQ**, the angles between the **PQ** plane and the central ring of the DMAC are 29.54(6) and 33.37(6)° in **4DMAC-TPPQ**, while in **4PXZ-TPPQ** the equivalent angles are decreased to 12.12(14), 15.25(13), 16.26(16) and 20.8(4)°. The **DMAC** groups show bowed conformations, with angles between phenyl ring planes of 23.23(8) and 33.19(8)°, while in **4PXZ-TPPQ** three of the **PXZ** donor groups show slightly bowed conformations (angle between phenyl ring planes 14.1(6), 14.68(16), 15.87(15)°) while one is closer to planar (angle between phenyl ring planes 5.8(2)°). The structure of **TPPQ** is a DCM solvate form of the previously reported structure, showing a very similar molecular conformation, but with molecules packed in a herringbone fashion (Fig. S17a, ESI<sup>†</sup>), rather than the previously encountered parallel sheet structure.<sup>32</sup> There are two sets of C–H···π intermolecular interactions between adjacent **TPPQ** molecules. One of these arises between a peripheral phenyl hydrogen and the central ring of the **PQ** group (H···centroid distance of 2.81 Å, C···centroid distance of 3.472(4) Å), which leads to chains of **TPPQ** molecules along the [0 1 0] axis. These are linked into two-dimensional sheets in the (1 0 0) plane (Fig. 2b) by the second set of C–H···π interactions, arising between symmetry-related phenyl rings (H···centroid distance of 2.94 Å, C···centroid distance of 3.608(5) Å). The crystal structure of **4DMAC-TPPQ** shows a combination of weak π···π and C–H···π intermolecular interactions, leading to a brickwork packing (Fig. S17b, ESI<sup>†</sup>). There are two sets of C–H···π intermolecular interactions between adjacent molecules. One of these arises between a bridging phenyl hydrogen and a phenyl of a **DMAC** group (H···centroid distance of 3.00 Å, C···centroid distance of 3.729(2) Å), the second between methyl hydrogen and a pyrazine ring of the **PQ** group (H···centroid distance of 2.99 Å, C···centroid distance of 3.537(3) Å). The CH···π interactions result in the formation of sheets in the (−1 0 1) plane (Fig. 2b), which are further supported by the π···π interactions between one pyrazine ring and another phenyl of a **DMAC** (centroid···centroid distance 3.8477(11)). In the structure of **4PXZ-TPPQ**, molecules show undulating layered packing, with channels for solvent (Fig. S17c, ESI<sup>†</sup>). This complex shows a more significant and more complex arrangement of supramolecular interactions. This comprises two-dimensional sheets in the (0 0 1) plane, built up of a combination of nine sets of interactions (Fig. 2b). These include two sets of π···π interactions from the central benzene ring of the **PQ** group to two peripheral phenyls, forming a three-layered π-stack (centroid···centroid distances of 3.570(2) and 3.616(2) Å), four sets of weak hydrogen bonds between four different aromatic CH groups of the bridging phenyls and two pyrazine nitrogen and two oxygen atoms of the **PXZ** groups (H···N distances of 2.47 and 2.60 Å, corresponding C···N



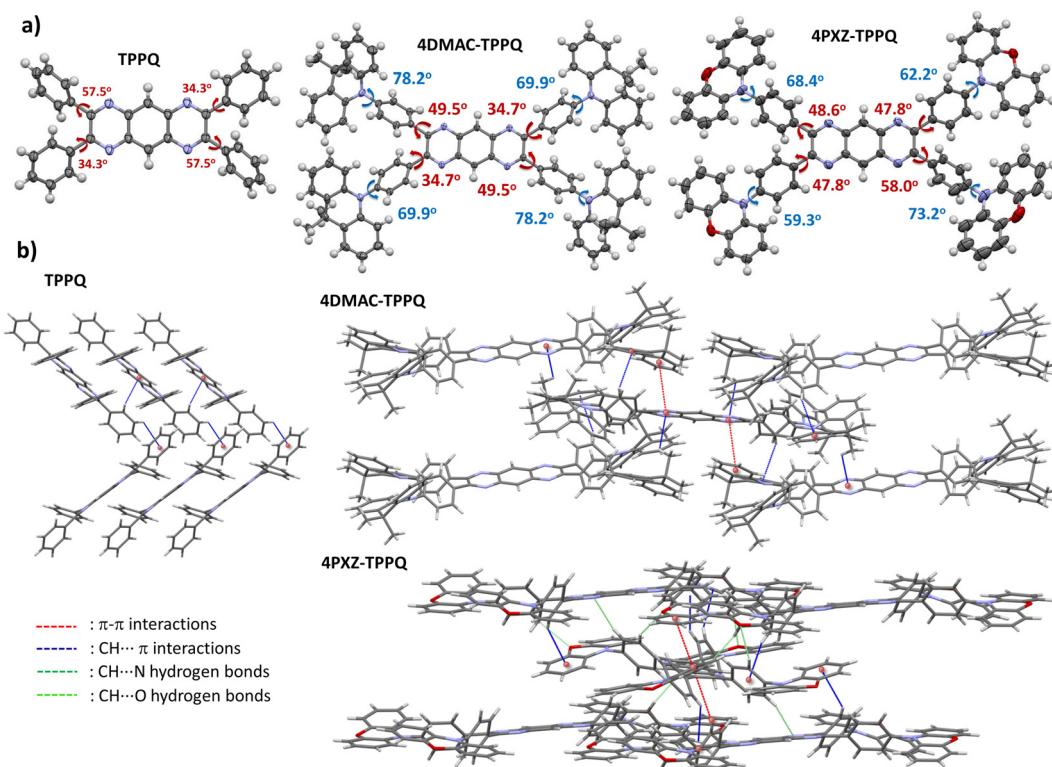


Fig. 2 (a) Thermal ellipsoid plots of the crystal structures with dihedral angles between the bridging phenylene ring and both donor and acceptor moieties of **TPPQ**, **4DMAC-TPPQ** and **4PXZ-TPPQ**. Ellipsoids are shown at the 50% probability level. (b) Views of the structure of **TPPQ**, **4DMAC-TPPQ** and **4PXZ-TPPQ** showing the intermolecular interactions leading to the formation of two-dimensional sheets. Solvent molecules and minor components of disorder are omitted.

distances of 3.302(4) and 3.439(4) Å;  $\text{H}\cdots\text{O}$  distances of 2.59 Å, with  $\text{C}\cdots\text{O}$  distances of 3.414(5) and 3.448(6) Å, and three sets of  $\text{CH}\cdots\pi$  interactions between three different aromatic CH groups of the bridging phenyls and one other bridging phenyl and two proximal phenyl groups of **PXZ** ( $\text{H}\cdots\text{C}$  centroid distances of 2.93 to 3.00 Å,  $\text{C}\cdots\text{C}$  centroid distances of 3.753(4) to 3.901(3) Å). These sheets are in turn weakly connected into a three-dimensional supramolecular structure *via* two further sets of dimer-forming  $\pi\cdots\pi$  interactions between two phenyl groups of **PXZ** and their symmetry-related neighbours (centroid $\cdots$ centroid distances of 3.726(10) and 3.947(3) Å) at the close points of approach of the undulations (Fig. S17c, ESI $\dagger$ ).

### Theoretical studies

Density functional theory (DFT) and time-dependent DFT calculations within the Tamm–Dancoff approximation (TDA-DFT) were performed to provide insight into the geometries and energies of the ground and the excited states of **TPPQ**, **4DMAC-TPPQ** and **4PXZ-TPPQ**. The ground-state geometries were optimized at the PBE0/6-31G(d,p) level of theory in the gas phase starting from the geometries obtained from the single crystal structures (Fig. 3). The central **PQ** moiety is almost planar in all three molecules, with dihedral angles between the planes of both pyrazine nitrogen in symmetrical pyrazine rings of  $3.88^\circ$  in **TPPQ**,  $3.74^\circ$  in **4DMAC-TPPQ** and  $3.79^\circ$  in **4PXZ-TPPQ**. In **TPPQ**, all four phenyl rings are equally twisted to the **PQ** with an angle

of  $39.68^\circ$ , whereas the dihedral angles between the phenylene rings and **PQ** in **4DMAC-TPPQ** are  $41.97$  and  $45.88^\circ$  and in **4PXZ-TPPQ** are  $43.31$  and  $43.49^\circ$ . In **4DMAC-TPPQ**, the DMAC moieties are strongly twisted with respect to the phenylene bridge ( $76.56$  and  $76.24^\circ$ ), while in **4PXZ-TPPQ** the PXZ moieties are slightly less twisted ( $70.64$  and  $71.37^\circ$ , Fig. S18, ESI $\dagger$ ). Moreover, the DMAC units retained their puckered/bowed conformations, with dihedral angles between the phenyl ring planes of  $31.72^\circ$  and  $28.96^\circ$ . Their conformation is well matched with that in the corresponding crystal structure; however, the PXZ units exhibited more planar conformations than seen in the crystal structure, with dihedral angles between their phenyl ring planes of  $2.07^\circ$  and  $2.32^\circ$ . The electron density of the highly occupied molecular orbital (HOMO) is delocalized over the whole **TPPQ** molecule, while the lowest unoccupied molecular orbital (LUMO) is somewhat more concentrated on the pyrazino[2,3-*g*]quinoxaline. The HOMO/LUMO levels are  $-6.23$ – $-2.56$  eV. A similar electron density distribution pattern of the orbitals of **TPPQ** has been previously reported, though those calculations diverge from those reported here as they included a THF environment and were carried out at the lower B3LYP/6-31G(d) level.<sup>32</sup> However, the literature calculated HOMO level was slightly shallower at  $-6.15$  eV, whilst the LUMO level was deeper at  $-2.80$  eV. Both **4DMAC-TPPQ** and **4PXZ-TPPQ** exhibit a similar pattern in the distribution of the electron densities to **TPPQ**, with the HOMO distributed across



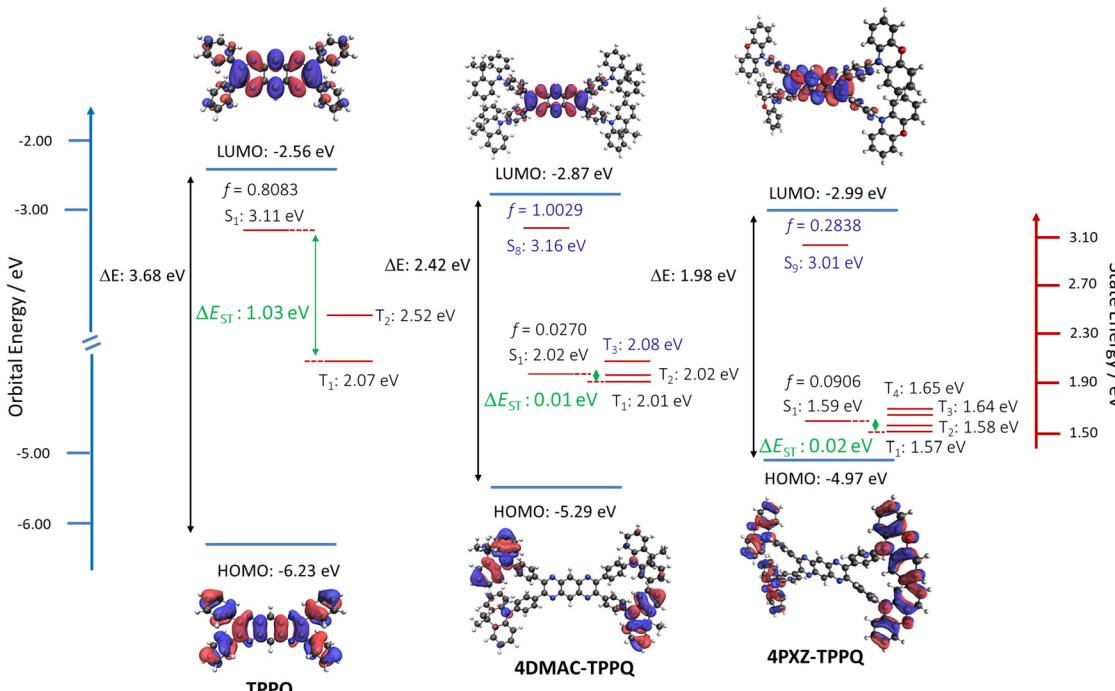


Fig. 3 The HOMO and LUMO distributions (isovalue = 0.02) of **TPPQ**, **4DMAC-TPPQ** and **4PXZ-TPPQ**, together with the transition energies for the relevant lowest singlet and triplet states calculated at the PBE0/6-31G(d,p) level in the gas phase.

the four donors and the LUMO localized mainly on the **PQ** acceptor (Fig. 3). Consequently, the HOMO levels are shallower compared to **TPPQ** at  $-5.29\text{ eV}$  for **4DMAC-TPPQ** and  $-4.79\text{ eV}$  for **4PXZ-TPPQ**, in line with their increasing donor strength, and the LUMO levels are stabilized compared to **TPPQ**, at  $-2.87\text{ eV}$  for **4DMAC-TPPQ** and  $-2.99\text{ eV}$  for **4PXZ-TPPQ**. The HOMO-LUMO gap,  $\Delta E_{\text{HOMO-LUMO}}$ , thus decreases from  $3.67\text{ eV}$  for **TPPQ** to  $2.42\text{ eV}$  for **4DMAC-TPPQ** and  $1.80\text{ eV}$  for **4PXZ-TPPQ**.

The excited-state properties were calculated using time-dependent density functional theory (TD-DFT) within the Tamm-Danoff approximation (TDA-DFT) based on the optimized ground-state geometries. The oscillator strength,  $f$ , of the  $S_0 \rightarrow S_1$  transition in **TPPQ** is high at 0.808, indicating a significant overlap of the electron density between the HOMO and LUMO (Fig. S19 and Table S3, ESI<sup>†</sup>). However, the  $f$  for the  $S_0 \rightarrow S_1$  transition of **4DMAC-TPPQ** and **4PXZ-TPPQ** is much lower at 0.027 and 0.091, respectively, reflecting the charge-transfer (CT) nature of this transition in these two compounds (Fig. S19 and Tables S4, S5, ESI<sup>†</sup>). The  $S_1$  energy of **TPPQ** is  $3.11\text{ eV}$ , while those of **4DMAC-TPPQ** ( $2.03\text{ eV}$ ) and **4PXZ-TPPQ** ( $1.59\text{ eV}$ ) are significantly stabilized (Fig. 3 and Tables S2–S5, ESI<sup>†</sup>). This trend in  $S_1$  energies mirrors the trend in the HOMO-LUMO gaps. The  $T_1$  state of **TPPQ**, mainly located on the pyrazine rings, is  $2.07\text{ eV}$  and, like the  $S_1$  state, also has a locally-excited (LE) character. The  $T_1$  state of **4DMAC-TPPQ** at  $2.01\text{ eV}$  is slightly lower in energy, while the  $T_1$  state of **4PXZ-TPPQ** at  $1.57\text{ eV}$  is significantly stabilized, reflecting their CT character (Fig. 3 and Table S6, ESI<sup>†</sup>). The corresponding calculated singlet-triplet energy gaps ( $\Delta E_{\text{ST}}$ ) of **4DMAC-TPPQ** ( $0.01\text{ eV}$ ) and **4PXZ-TPPQ** ( $0.02\text{ eV}$ ) are much smaller than that

of **TPPQ** ( $1.03\text{ eV}$ ) (Fig. 3). There are multiple high-lying triplet states in **4DMAC-TPPQ** and **4PXZ-TPPQ**, some of which have a different orbital type to  $S_1$ , and may participate in the TADF process in these two compounds (Fig. 3 and Table S7, ESI<sup>†</sup>). Additionally, at an excited  $T_1$  geometry, there is a decrease in the  $S_1-T_1$  spin-orbit coupling matrix element (SOCME) from  $3.99\text{ cm}^{-1}$  in **TPPQ** to  $0.01\text{ cm}^{-1}$  in **4DMAC-TPPQ** and  $0.02\text{ cm}^{-1}$  in **4PXZ-TPPQ** (Table S6, ESI<sup>†</sup>). It should be noted that the SOCME of  $S_1-T_n$  ( $n > 1$ ) in **4DMAC-TPPQ** ( $\langle S_1 | H_{\text{SO}} | T_3 \rangle$   $0.03\text{ cm}^{-1}$ ) and in **4PXZ-TPPQ** ( $\langle S_1 | H_{\text{SO}} | T_3 \rangle$   $0.06\text{ cm}^{-1}$ ) is larger because of the large changes in orbital character between these two states (Table S6, ESI<sup>†</sup>). All these studies support a RISC process could proceed *via* the  $T_3$  to  $S_1$  in **4DMAC-TPPQ** and the  $T_3$  to  $S_1$  in **4PXZ-TPPQ** as  $T_3$  lies just  $0.06\text{ eV}$  above  $S_1$  for **4DMAC-TPPQ** and  $0.05\text{ eV}$  above  $S_1$  for **4PXZ-TPPQ**, so is readily accessible because of their relatively large SOCME between these states.

### Electrochemistry

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were used to infer the HOMO/LUMO levels of **TPPQ**, **4DMAC-TPPQ**, and **4PXZ-TPPQ** in DCM. The voltammograms are shown in Fig. 4a and the data are summarized in Table 1. As expected, there is no observable oxidation wave for **TPPQ**, while there are two 1-electron reversible reduction waves at  $E_{\text{red1}} = -1.00\text{ V}$  and  $E_{\text{red2}} = -1.49\text{ V}$  vs. SCE in DCM, in line with the literature-reported electrochemistry.<sup>32</sup> The corresponding orbital energies are LUMO =  $-3.34\text{ eV}$  and LUMO+1 =  $-2.85\text{ eV}$ . **4DMAC-TPPQ** possesses a quasi-reversible oxidation wave at  $E_{\text{ox}}$  at  $1.00\text{ V}$  vs. SCE, which is assigned to the



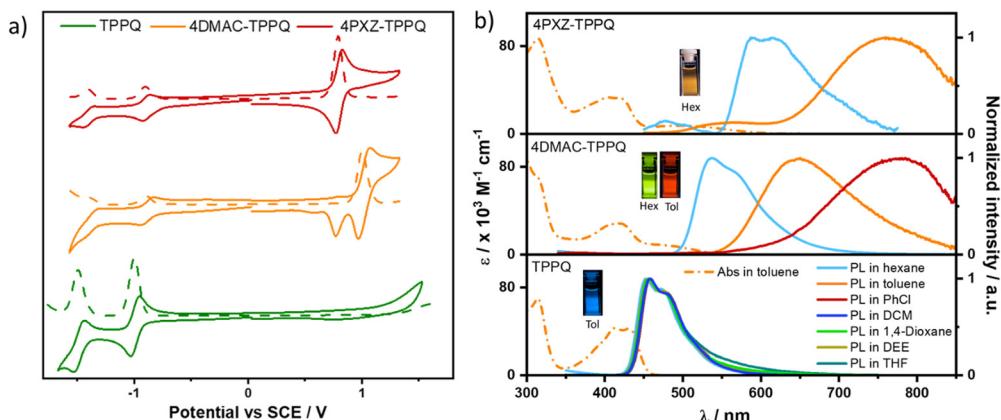


Fig. 4 (a) Cyclic and differential pulse voltammograms of TPPQ, 4DMAC-TPPQ and 4PXZ-TPPQ in degassed DCM (scan rate = 100 mV s<sup>-1</sup>). (b) Absorption in toluene and photoluminescence spectra of 5 × 10<sup>-5</sup> M TPPQ, 4DMAC-TPPQ and 4PXZ-TPPQ in various solvents ( $\lambda_{\text{exc}} = 315$  nm).

Table 1 Electrochemical data and HOMO–LUMO levels for TPPQ, 4DMAC-TPPQ and 4PXZ-TPPQ

| Emitters   | $E_{\text{ox}}^a$ /V | $E_{\text{red}}^a$ /V | HOMO <sup>b</sup> /eV | LUMO <sup>b</sup> /eV | $E_{\text{opt}}$ /eV |
|------------|----------------------|-----------------------|-----------------------|-----------------------|----------------------|
| TPPQ       | —                    | -1.00                 | -6.12 <sup>c</sup>    | -3.34                 | 2.78                 |
| 4DMAC-TPPQ | 1.00                 | -0.89                 | -5.34                 | -3.45                 | 2.32                 |
| 4PXZ-TPPQ  | 0.79                 | -0.90                 | -5.13                 | -3.44                 | 2.08                 |

<sup>a</sup>  $E_{\text{ox}}$  and  $E_{\text{red}}$  are anodic and cathodic peak potentials, respectively, obtained from DPV using  $\text{F}_c/\text{F}_c^+$  as the internal reference and referenced versus SCE (0.46 V vs. SCE) in DCM with 0.1 M [<sup>7</sup>Bu<sub>4</sub>N]PF<sub>6</sub> as the supporting electrolyte.<sup>36</sup> <sup>b</sup>  $E_{\text{HOMO/LUMO}} = -(E_{\text{ox}}^{\text{red}} + 4.8)$  eV,<sup>37</sup> where  $E_{\text{ox}}^{\text{red}}$  is the anodic peak potential and  $E_{\text{red}}^{\text{red}}$  is the cathodic peak potential calculated from DPV relative to  $\text{F}_c/\text{F}_c^+$ . <sup>c</sup>  $E_{\text{HOMO}} = |E_{\text{LUMO}} - E_{\text{opt}}|$  where  $E_{\text{opt}}$  is the optical band gap obtained from the intersection of the normalized absorption and emission spectra in toluene (Fig. S25, ESI).

oxidation of the DMAC donor moieties as this value aligns with the previously reported  $E_{\text{ox}}$  of 1.04 V for the DMAC-containing compound **DMAC- $\alpha$ -DK**.<sup>34</sup> The reversible oxidation wave of **4PXZ-TPPQ** is shifted cathodically at 0.79 V vs. SCE and is attributed to the oxidation of the PXZ donor moieties; indeed, the  $E_{\text{ox}}$  of **4PXZ-TPPQ** is similar to that of a related PXZ-containing compound, PXZ PDO ( $E_{\text{ox}} = 0.83$  V).<sup>33</sup> The HOMO levels thus are -5.34 and -5.13 eV for **4DMAC-TPPQ** and **4PXZ-TPPQ**, respectively, which are in line with the values and trends calculated using DFT (*vide supra*). The reduction waves are assigned to the reduction of the TPPQ acceptor, at around -1.00 V vs. SCE for both emitters. The corresponding LUMO energy levels are very similar, at -3.45 and -3.44 eV for **4DMAC-TPPQ** and **4PXZ-TPPQ**, respectively; the LUMO+1 for **4DMAC-TPPQ** is -2.94 eV and for **4PXZ-TPPQ** is -2.93 eV, quite close to the LUMO+1 energy of **TPPQ**. The estimated HOMO level of **TPPQ** is inferred to be -6.12 eV from the difference between the LUMO level and the optical gap ( $\Delta E_g = 2.78$  eV) of **TPPQ** (Table 1). The HOMO–LUMO energy gap of **TPPQ** (2.78 eV) is much larger than that of **4DMAC-TPPQ** (1.89 eV) and **4PXZ-TPPQ** (1.69 eV).

### Solution-state photophysical studies

The photophysical properties of all three molecules were first studied in toluene solution (Fig. 4b and Table S8, ESI<sup>†</sup>). There

are three distinct absorption bands in the UV-vis absorption spectra of **4DMAC-TPPQ** and **4PXZ-TPPQ**, while there are only two bands in the spectrum of **TPPQ**. The strong absorption band at 314 nm present in all three spectra corresponds to a LE  $\pi$ – $\pi^*$  transition of the TPPQ moiety ( $\varepsilon = 69.9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  for **TPPQ**,  $\varepsilon = 70.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  for **4DMAC-TPPQ** and  $\varepsilon = 86.9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  for **4PXZ-TPPQ**); the intensity of this band is influenced by the decoration about the acceptor (Fig. 4b). The absorption band located at 413 nm ( $\varepsilon = 42.9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  for **TPPQ**,  $\varepsilon = 28.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  for **4DMAC-TPPQ** and  $\varepsilon = 32.9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  for **4PXZ-TPPQ**) is of mixed LE/CT character, based on an analysis of the TD-DFT calculations, where the LE transition is centred on the acceptor and the CT transition occurs from the phenylene groups to the PQ (Fig. S19, ESI<sup>†</sup>). The weakly absorptive CT band of **4PXZ-TPPQ** ( $\varepsilon = 7.57 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  at  $\lambda_{\text{abs}} = 506$  nm) and **4DMAC-TPPQ** ( $\varepsilon = 8.75 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  at  $\lambda_{\text{abs}} = 475$  nm) reflects the poor orbital overlap between the donor and the PQ acceptor (Fig. 4); notably, the red-shifted band in **4PXZ-TPPQ** is consistent with its smaller HOMO–LUMO gap compared to that of **4DMAC-TPPQ**, as observed in the electrochemistry study. The photoluminescence (PL) of **TPPQ** does not change as a function of solvent, with a peak maximum,  $\lambda_{\text{PL}}$ , of around 456 nm, and a shoulder band at around 476 nm (Fig. 4b). This, coupled with the reasonably narrow FWHM (56 nm), indicates that the emission emanates from a LE state. In contrast, **4DMAC-TPPQ** and **4PXZ-TPPQ** show unstructured and broad emission that is sensitive to solvent polarity and thus is assigned to originating from a CT state. In toluene, **4DMAC-TPPQ** emits at a  $\lambda_{\text{PL}}$  of 650 nm, while **4PXZ-TPPQ** emits at a  $\lambda_{\text{PL}}$  of 762 nm (Fig. 4b and Table S8, ESI<sup>†</sup>).

Unexpectedly, we observed that **TPPQ** showed photochromic behaviour in ethereal solvents. On exposure to UV light (365 nm) at room temperature in THF solution, over 6 minutes the blue band at 456 nm decreased in intensity while a broad, green band at 556 nm appeared, with a corresponding iso-emissive point at 504 nm (Fig. S21, ESI<sup>†</sup>). At 77 K in glassy 2-MeTHF, there is no appearance of the green emission band and only the narrow blue emission band at 448 nm is observed (Fig. S22, ESI<sup>†</sup>). There were no changes in the <sup>1</sup>H NMR



spectrum of **TPPQ** in THF-*d*<sup>8</sup> before and after exposure to UV light (Fig. S23, ESI†), which confirms that there is no photodegradation of **TPPQ**. From these experiments, the appearance of the new green emission band at 556 nm in **TPPQ** is attributed to excimer formation. To corroborate these conclusions, we modelled a **TPPQ** dimer, which has a more stable  $S_1$  energy of 2.86 eV compared to the  $S_1$  energy of the **TPPQ** monomer of 3.11 eV (Fig. S20, ESI†). Both **4DMAC-TPPQ** and **4PXZ-TPPQ** also showed a similar but weak photochromic behaviour in ethereal solvents (Fig. S24, ESI†).

The photoluminescence quantum yield ( $\Phi_{PL}$ ) in degassed toluene of **4DMAC-TPPQ** is 13.7%, higher than those of **TPPQ** (2.1%) and **4PXZ-TPPQ** (0.8%). Upon exposure to air, the  $\Phi_{PL}$  for **TPPQ**, **4DMAC-TPPQ** and **4PXZ-TPPQ** decreases to 1.9, 7.3, and 0.6%, respectively. The PL decays of the three emitters in toluene under degassed and aerated conditions are shown in Fig. S26 (ESI†). There is only a single decay component observed for all three compounds, with lifetimes,  $\tau_{PL}$ , of 7.9 ns for **TPPQ**, 20.2 ns for **4DMAC-TPPQ** and 1.98 ns for **4PXZ-TPPQ**.

The steady-state PL and phosphorescence spectra of **4DMAC-TPPQ** and **4PXZ-TPPQ** in 2-MeTHF glass at 77 K were measured to ascertain the  $S_1$  and  $T_1$  levels from their respective onsets; the  $S_1$  and  $T_1$  levels of **TPPQ** were measured in methylcyclohexane (MCH) at 77 K to mitigate against possible photochromism in 2-MeTHF (Fig. S27, ESI†). In glassy MCH, the  $\lambda_{PL}$  of **TPPQ** is around 456 nm, while the delayed emission spectrum of **TPPQ**, attributed to phosphorescence, peaks at 766 nm. Notably, there is a weak residual prompt emission at around 460 nm. The corresponding  $S_1$  and  $T_1$  energies are 2.82 and 1.85 eV, and thus the  $\Delta E_{ST}$  is 0.97 eV. The  $S_1$  and  $T_1$  energies of **4DMAC-TPPQ** are 2.26 and 1.85 eV, while for **4PXZ-TPPQ** they are 2.08 and 1.84 eV (Fig. S27, ESI†). Thus, in these two compounds the  $S_1$  energies follow the trend calculated by DFT and the observed HOMO-LUMO gaps determined by electrochemistry, while the  $T_1$  energies, which are effectively the same as that of **TPPQ**, reflect the same  $^3LE$  state. The corresponding  $\Delta E_{ST}$  values of **4DMAC-TPPQ** and **4PXZ-TPPQ** are 0.41 and 0.24 eV, respectively.

### Aggregation-induced emission (AIE)

**TPPQ** has previously been reported as an AIE-active moiety.<sup>32</sup> Aware of this, we assessed whether **4DMAC-TPPQ** and **4PXZ-TPPQ** would also show AIE and thus explored their PL spectra in THF/H<sub>2</sub>O mixtures (Fig. 5a-c). Firstly, we re-confirmed the AIE behaviour of **TPPQ** in THF/H<sub>2</sub>O mixtures. The emission peaking at 456 and 476 nm of **TPPQ** in THF slightly red-shifts and increases in intensity by 1.8-fold upon increasing the water fraction ( $f_w$ ) to 60% (Fig. 5c and Fig. S28a, ESI†). On further increasing the  $f_w$  beyond 80%, the emission intensity then decreases and red-shifts further to 492 nm. We confirmed the formation of crystalline aggregates by powder XRD (Fig. S29, ESI†). Comparison of the powder XRD patterns to those simulated from the SC XRD data indicates structural differences, particularly in the cases of **TPPQ** and **4DMAC-TPPQ**, likely arising from the influence of solvent and its ordering on the structures. However, in the case of **4PXZ-TPPQ**, which lacks ordered solvent in its structure, a stronger similarity is seen between calculated and determined PXRD patterns. In comparison to **TPPQ**, **4DMAC-TPPQ** shows very weak emission at  $\lambda_{PL}$  of 568 nm, while **4PXZ-TPPQ** does not show any emission in THF, which points to non-radiative decay being significant in THF. Upon increasing  $f_w$  to 80%, the  $\lambda_{PL}$  of **4DMAC-TPPQ** red-shifts to 656 nm and becomes as much as 20-fold more intense (Fig. 5b and Fig. S28b, ESI†). Upon increasing the  $f_w$  from 80 to 95%, the emission intensity slightly decreases and further red-shifts to 690 nm. In the case of **4PXZ-TPPQ**, upon increasing the  $f_w$  to 40%, a new emission band at  $\lambda_{PL}$  of 790 nm appears, the intensity of which increases 23-fold at  $f_w = 80\%$  (Fig. 5c and Fig. S28c, ESI†). When the  $f_w > 80\%$ , the PL intensity decreases and slightly blue-shifts to 770 nm. In both molecules, the observed AIE is attributed to the formation of aggregates, as found in their crystal structures. The red-shifted emission observed from the aggregates formed in the 80% H<sub>2</sub>O/THF mixture in both molecules likely occurs because of stronger intermolecular interactions between adjacent donor and acceptor moieties that modulate the energy of intermolecular CT states. To understand the emissive behaviour of the

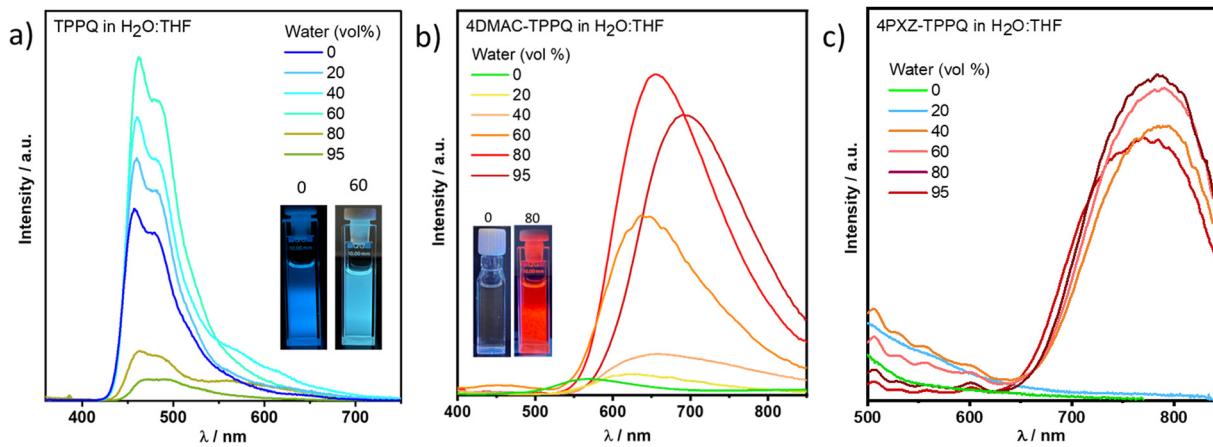


Fig. 5 (a) PL spectra of **TPPQ** ( $5 \times 10^{-5}$  M), (b) **4DMAC-TPPQ** ( $5 \times 10^{-5}$  M) and (c) **4PXZ-TPPQ** ( $5 \times 10^{-5}$  M) in THF–water mixtures with different water fractions in THF:H<sub>2</sub>O at 298 K ( $\lambda_{exc} = 315$  nm). Inset: photos of photoexcited solutions in different solvent systems as mentioned in the figures.



crystalline aggregates in THF/H<sub>2</sub>O solution ( $f_w = 80\%$ ), we measured the PL spectra of the dried aggregates isolated from the THF/H<sub>2</sub>O solution. These spectra closely resemble those of the neat films of **TPPQ**, **4DMAC-TPPQ** and **4PXZ-TPPQ** (Fig. S30, ESI<sup>†</sup>), indicating that the excited-state species are likely the same for both types of samples.

### Photophysical studies in thin films

We next focused our attention on the photophysical properties of **TPPQ**, **4DMAC-TPPQ** and **4PXZ-TPPQ** doped in poly(methylmethacrylate) (PMMA) and in 4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl (CBP) and in neat thin films. Initially, we measured the photophysical properties of the three emitters as 10 wt% doped films in PMMA as the polarity of this host closely mimics that of toluene. The absorption bands of all three compounds are of similar energy to those in toluene, with the weak CT band observed in the range of 451–650 nm for **4DMAC-TPPQ** while it is more red-shifted for **4PXZ-TPPQ** (Fig. S31a, ESI<sup>†</sup>). Upon photoexcitation at 315 nm, **TPPQ** shows a structured emission profile at 466 nm ( $\Phi_{PL} = 4.7\%$ ), similar to that measured in toluene, while the CT-based unstructured emission is at 635 nm for **4DMAC-TPPQ** ( $\Phi_{PL} = 14.3\%$ ) and at 681 nm for **4PXZ-TPPQ** ( $\Phi_{PL} = 3.0\%$ ), emission that is blue-shifted by 15 and 81 nm, respectively, compared to the  $\lambda_{PL}$  in toluene (Fig. S31b, ESI<sup>†</sup>). The emission of **TPPQ** decays with bi-exponential kinetics, with an average lifetime,  $\tau_{PL}$ , of 2.1 ns. The time-resolved PL of **4DMAC-TPPQ** and **4PXZ-TPPQ** shows multiexponential decay

kinetics, with average prompt lifetimes,  $\tau_p$ , of 25.2 and 15.8 ns, respectively (Fig. S32, ESI<sup>†</sup>), and average delayed lifetimes,  $\tau_d$ , of 390.9 and 342.5  $\mu$ s, respectively (Fig. S33 and Table S8, ESI<sup>†</sup>). The contribution from the delayed emission increases with increasing temperature, indicating that its origin is TADF.

To best evaluate whether these compounds could act as promising emitters in red-to-NIR OLEDs, we next turned our attention to assessing the photophysics of these three compounds in an OLED-relevant host, CBP, as this host matrix has a sufficiently high triplet energy ( $T_1 = 2.6$  eV) to confine excitons onto the emitters.<sup>38</sup> The  $\lambda_{PL}$  of the 10 wt% doped film of **TPPQ** in CBP is 548 nm and the PL spectrum is much broader (FWHM = 100 nm) and around 80 nm bathochromically shifted compared to that in PMMA ( $\lambda_{PL} = 466$  nm) and in solutions ( $\lambda_{PL} = 456$  nm) (Fig. 6). There is only a small red-shift (only 10 nm) of the  $\lambda_{PL}$  and moderate decrease in the  $\Phi_{PL}$  upon increasing the doping concentration of **TPPQ** from 5 to 30 wt% in CBP (Fig. S34a and Table S10, ESI<sup>†</sup>). To understand the large red-shift in the emission band of **TPPQ** in CBP in comparison to both in solution and in PMMA, we checked the PL spectrum of **TPPQ** in another host, 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1*H*-benzimidazole) (TPBi), Fig. S34a (ESI<sup>†</sup>). The 5 wt% doped films of **TPPQ** in TPBi emits at  $\lambda_{PL}$  of 470 nm and has a  $\Phi_{PL}$  of 4.8%, which is very similar to the properties in toluene and in the 10 wt% doped film in PMMA. Notably, the remarkably red-shifted emission of the 10 wt% doped film of **TPPQ** in CBP is reminiscent of the emission profile after UV exposure in

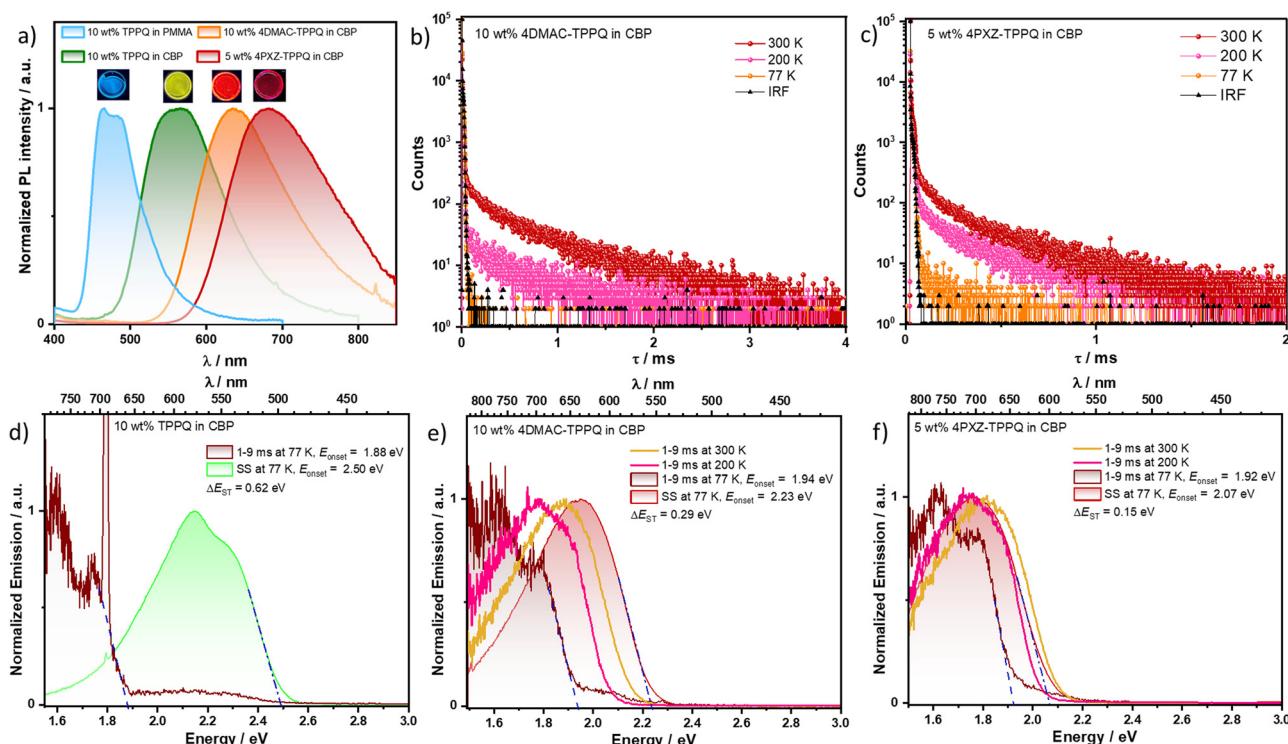


Fig. 6 (a) Photoluminescence spectra of the 10 wt% doped film of **TPPQ** in PMMA and the 10 wt% **4DMAC-TPPQ** and 5 wt% **4PXZ-TPPQ** doped films in CBP at 295 K ( $\lambda_{exc} = 340$  nm). Inset: photos of photoexcited thin films; (b) and (c) temperature-dependent time-resolved PL decay ( $\lambda_{exc} = 340$  nm) of 10 wt% **4DMAC-TPPQ** and 5 wt% **4PXZ-TPPQ** doped films in CBP; (d)–(f) steady-state fluorescence and phosphorescence spectra (acquisition time range of 1–9 ms) at 300, 200, and 77 K of 10 wt% **TPPQ**, 10 wt% **4DMAC-TPPQ** and 5 wt% **4PXZ-TPPQ** doped films in CBP ( $\lambda_{exc} = 340$  nm).



etheral solvents (*vide supra*). This may imply that there is an exciplex between CBP and **TPPQ** that emits at a similar energy to the **TPPQ** excimer. The photophysical properties of the doped films (5–50 wt%) of **4DMAC-TPPQ** and **4PXZ-TPPQ** in CBP and the neat films are shown in Fig. S34b, c and S35–S40 (ESI†) and Table 2. Of these films, the highest  $\Phi_{PL}$  was found to be 21.0% for **4DMAC-TPPQ** and 10.0% for **4PXZ-TPPQ** as 10 and 5 wt% doped films in CBP, respectively. The  $\lambda_{PL}$  of the 10 wt% doped film of **4DMAC-TPPQ** in CBP is 635 nm, which is very similar to that of the 10 wt% doped film in PMMA (Fig. 6 and Fig. S31, ESI†). The emission for this compound does not significantly change across a doping range from 5–50 wt% and even as the neat film ( $\lambda_{PL}$  ranging from 627 to 654 nm, Fig. S34b, ESI† and Table 2). The  $\lambda_{PL}$  of **4PXZ-TPPQ** is significantly shifted to the NIR region compared to that of **4DMAC-TPPQ**, at 682 nm for the 5 wt% doped film, at 713 nm for the 50 wt% doped film, and 770 nm for the neat film (Fig. S34c, ESI†). The substantially red-shifted emission as a function of doping concentration of **4PXZ-TPPQ** in comparison to **4DMAC-TPPQ** may be attributed to the formation of aggregates in the former resulting in strong interactions between adjacent chromophores. The emission profile of the neat films of **4DMAC-TPPQ** and **4PXZ-TPPQ** match well those in THF:H<sub>2</sub>O ( $f_w$  = 80%), indicating that the species responsible for the emission in each is the excimer.

At 77 K, the  $\lambda_{PL}$  of the steady-state PL spectrum of the 10 wt% doped film of **TPPQ** in CBP is 578 nm, while the delayed emission spectrum peaks at a  $\lambda_{ph}$  of 775 nm (Fig. 6). The corresponding  $S_1$  and  $T_1$  energies are 2.50 and 1.88 eV, thus the  $\Delta E_{ST}$  is 0.62 eV. The phosphorescence of **TPPQ** in CBP closely resembles that in glassy MCH, indicating that it occurs from the same <sup>3</sup>LE state. The  $S_1$  and  $T_1$  energies of the 10 wt% doped film of **4DMAC-TPPQ** in CBP are 2.23 and 1.94 eV, while those of the 5 wt% doped film of **4PXZ-TPPQ** in CBP are 2.07 and 1.92 eV (Fig. 6). The corresponding  $\Delta E_{ST}$  for **4DMAC-TPPQ** is 0.29 eV, and 0.15 eV for **4PXZ-TPPQ**. Given that the  $T_1$  state energy remains effectively the same for the same LE state, the

smaller  $\Delta E_{ST}$  values for the three emitters in CBP are due to the stabilization of the  $S_1$  state. In comparison to the doped film (5 wt%), the  $S_1$  energy of the neat film of **4PXZ-TPPQ** is significantly red shifted at 1.85 eV ( $\Delta S_1$  = 0.25 eV), while the neat film of **4DMAC-TPPQ** showed a small red-shift at 2.12 eV ( $\Delta S_1$  = 0.11 eV) in comparison to the doped film of 10 wt% **4DMAC-TPPQ** in CBP, however, the  $T_1$  energies of the neat films of both emitters are similarly red-shifted. The  $\Delta E_{ST}$  of neat **4PXZ-TPPQ** is significantly smaller at 0.04 eV, while  $\Delta E_{ST}$  of neat **4DMAC-TPPQ** is the same as the doped film, at 0.29 eV (Fig. S38, S40, ESI† and Table 2). These large declines in  $S_1$  energy and  $\Delta E_{ST}$  of the neat film **4PXZ-TPPQ** in comparison to doped films could be explained by the synergistic effect of the transformation of exciton states due to the formation of aggregates and shortening intermolecular distance because of planar phenoxazine motifs, which induce  $\pi$ – $\pi$  interactions between adjacent molecules in neat film **4PXZ-TPPQ** compared with the doped film.<sup>21</sup>

As expected, no delayed emission was observed in the 10 wt% doped film of **TPPQ** in CBP and the emission decays with biexponential kinetics, with an average lifetime,  $\tau_{PL}$  of 42.8 ns at 300 K. In contrast, the 10 wt% doped film of **4DMAC-TPPQ** and 5 wt% doped film of **4PXZ-TPPQ** in CBP show multi-exponential decay kinetics, with an average prompt lifetime,  $\tau_p$  of 25.2 and 17.6 ns, while the average delayed lifetime ( $\tau_d$ ) is 564.5 and 303.9  $\mu$ s at a  $\lambda_{PL}$  of 635 and 680 nm, respectively at 300 K (Fig. 6b and c). The corresponding estimated  $k_{RISC}$  and  $k_{ISC}$  of the 10 wt% **4DMAC-TPPQ** in CBP is  $1.32 \times 10^3$  and  $2.00 \times 10^7$  s<sup>-1</sup> which slightly increase to  $2.48 \times 10^3$  and  $3.17 \times 10^7$  s<sup>-1</sup> for the 5 wt% doped **4PXZ-TPPQ** in CBP, respectively (Table 2). On the other hand, the  $\tau_p$  of the neat film of **4DMAC-TPPQ** is 27.2 ns and the  $\tau_d$  is 109.4  $\mu$ s, while the  $\tau_p$  and  $\tau_d$  for the neat film of **4PXZ-TPPQ** are much shorter at 3.7 ns and 2.05  $\mu$ s, respectively. Therefore, the  $k_{RISC}$  of the neat film of **4PXZ-TPPQ** significantly increased ( $4.9 \times 10^5$  s<sup>-1</sup>) in comparison to the neat film of **4DMAC-TPPQ** ( $5.03 \times 10^3$  s<sup>-1</sup>) which is strongly aligned with the reduced  $\Delta E_{ST}$  of neat **4PXZ-TPPQ**.

Table 2 Photophysical properties of **TPPQ**, **4DMAC-TPPQ** and **4PXZ-TPPQ** in the CBP host

| Doping/wt%        | $\lambda_{PL}^c$ /nm | $\Phi_{PL}^d$ /% | $E_{S_1}^e$ /eV | $E_{T_1}^e$ /eV | $\Delta E_{ST}^f$ /eV | $\tau_p^g$ /ns | $\tau_d^h$ / $\mu$ s | $k_{RISC}^i$ /s <sup>-1</sup><br>( $\times 10^3$ ) | $k_{ISC}^i$ /s <sup>-1</sup><br>( $\times 10^7$ ) | $k_{S_{nr}}^i$ /s <sup>-1</sup><br>( $\times 10^7$ ) | $k_{S_r}^i$ /s <sup>-1</sup><br>( $\times 10^6$ ) |
|-------------------|----------------------|------------------|-----------------|-----------------|-----------------------|----------------|----------------------|--|---|--|---|
| <b>TPPQ</b>       |                      |                  |                 |                 |                       |                |                      |  |   |  |   |
| 10 <sup>a</sup>   | 548                  | 8.8 (8.5)        | 2.50            | 1.88            | 0.62                  | 42.8           | —                    | —  | —   | —  | —   |
| <b>4DMAC-TPPQ</b> |                      |                  |                 |                 |                       |                |                      |  |   |  |   |
| 10 <sup>a</sup>   | 635                  | 21.0 (17.2)      | 2.23            | 1.94            | 0.29                  | 25.2           | 564.5                | $1.32 \pm 0.8$                                     | $2.00 \pm 1.3$                                    | 2.6  | 6.8   |
| 100 <sup>a</sup>  | 654                  | 4.3 (4.1)        | 2.12            | 1.83            | 0.29                  | 27.2           | 109.4                | $5.03 \pm 4.5$                                     | $1.85 \pm 1.7$                                    | 3.3  | 1.5   |
| <b>4PXZ-TPPQ</b>  |                      |                  |                 |                 |                       |                |                      |  |   |  |   |
| 5 <sup>a</sup>    | 682                  | 10.2 (8.2)       | 2.09            | 1.94            | 0.15                  | 17.6           | 303.9                | $2.48 \pm 1.6$                                     | $3.17 \pm 2.1$                                    | 4.1  | 4.7   |
| 100 <sup>b</sup>  | 770                  | 1.5 (1.0)        | 1.85            | 1.81            | 0.04                  | 3.7            | 2.05 <sup>g</sup>    | $489 \pm 243$                                      | $17.7 \pm 8.8$                                    | 17.6   | 2.7   |

<sup>a</sup> Spin-coated film and annealed at 55 °C for 1 minute. <sup>b</sup> Drop-cast film and annealed at 70 °C for 1 minute. <sup>c</sup> PL measured under vacuum,  $\lambda_{exc}$  = 340 nm for all films except 100 wt% **4PXZ-TPPQ**, which has  $\lambda_{exc}$  = 465 nm. <sup>d</sup> Photoluminescence quantum yield ( $\Phi_{PL}$ ) of thin films determined using an integrating sphere ( $\lambda_{exc}$  = 305 nm or 340 nm) under a N<sub>2</sub> atmosphere at 298 K. The values in parentheses are in the presence of O<sub>2</sub> at 298 K. <sup>e</sup>  $E_{S_1}$  and  $E_{T_1}$  were obtained from the onset of the steady-state and phosphorescence spectra (time window: 1–9 ms), respectively, of doped films in CBP at 77 K,  $\lambda_{exc}$  = 340 nm, and for 100 wt% **4PXZ-TPPQ**,  $\lambda_{exc}$  = 465 nm. <sup>f</sup>  $\Delta E_{ST} = E_{S_1} - E_{T_1}$ . <sup>g</sup> Prompt lifetime was measured by TCSPC,  $\lambda_{exc}$  = 375 nm, the average lifetimes were calculated by using the equation  $\tau_{avg} = \sum A_i \tau_i^2 / \sum A_i \tau_i$ , (where  $A_i$  is the pre-exponential for lifetime  $\tau_i$ ). <sup>h</sup> Delayed emission was measured by MCS, using a microsecond flash lamp as an excitation source,  $\lambda_{exc}$  = 340 nm. <sup>i</sup>  $k_{S_{nr}}$ ,  $k_{S_r}$ ,  $k_{RISC}$  and  $k_{ISC}$  were calculated according to the method given in ref. 39 and 40.

The temperature-dependent time-resolved PL decay studies of both emitters indicate that these compounds are TADF active not only in doped films but also as their aggregates (Fig. S38 and S40, ESI<sup>†</sup>).

We next measured the delayed emission spectrum as a function of temperature of the respective 10 and 5 wt% films of **4DMAC-TPPQ** and **4PXZ-TPPQ** in CBP (Fig. 6e, f and Table S10, ESI<sup>†</sup>). There is an apparent shifting of the delayed emission, attributed to phosphorescence, as a function of temperature. The  $T_1$  state of **4DMAC-TPPQ** red-shifts from 2.15 eV at 300 K to 2.06 eV at 200 K to 1.94 eV at 77 K (Fig. 6e and Table S10, ESI<sup>†</sup>). Similarly, the  $T_1$  state of **4PXZ-TPPQ** red-shifts from 2.10 eV at 300 K to 2.02 eV at 200 K and

1.92 eV at 77 K (Fig. 6f and Table S10, ESI<sup>†</sup>). The apparent blue-shift of triplet states from 77 to 300 K in both molecules could be due to the fact that at 300 K the delayed emission originates from the monomer while at 77 K the delayed emission comes from the aggregate. This is supported by the TDA-DFT calculations (*vide supra*).

### OLED characterization

Having identified CBP as a viable host, we next proceeded to fabricate solution-processed OLEDs (SP-OLEDs) with **4DMAC-TPPQ** and **4PXZ-TPPQ**; furthermore, recognizing the AIE properties of these emitters, we also explored SP-OLEDs using neat films of both emitters. We employed a bottom-emitting OLED

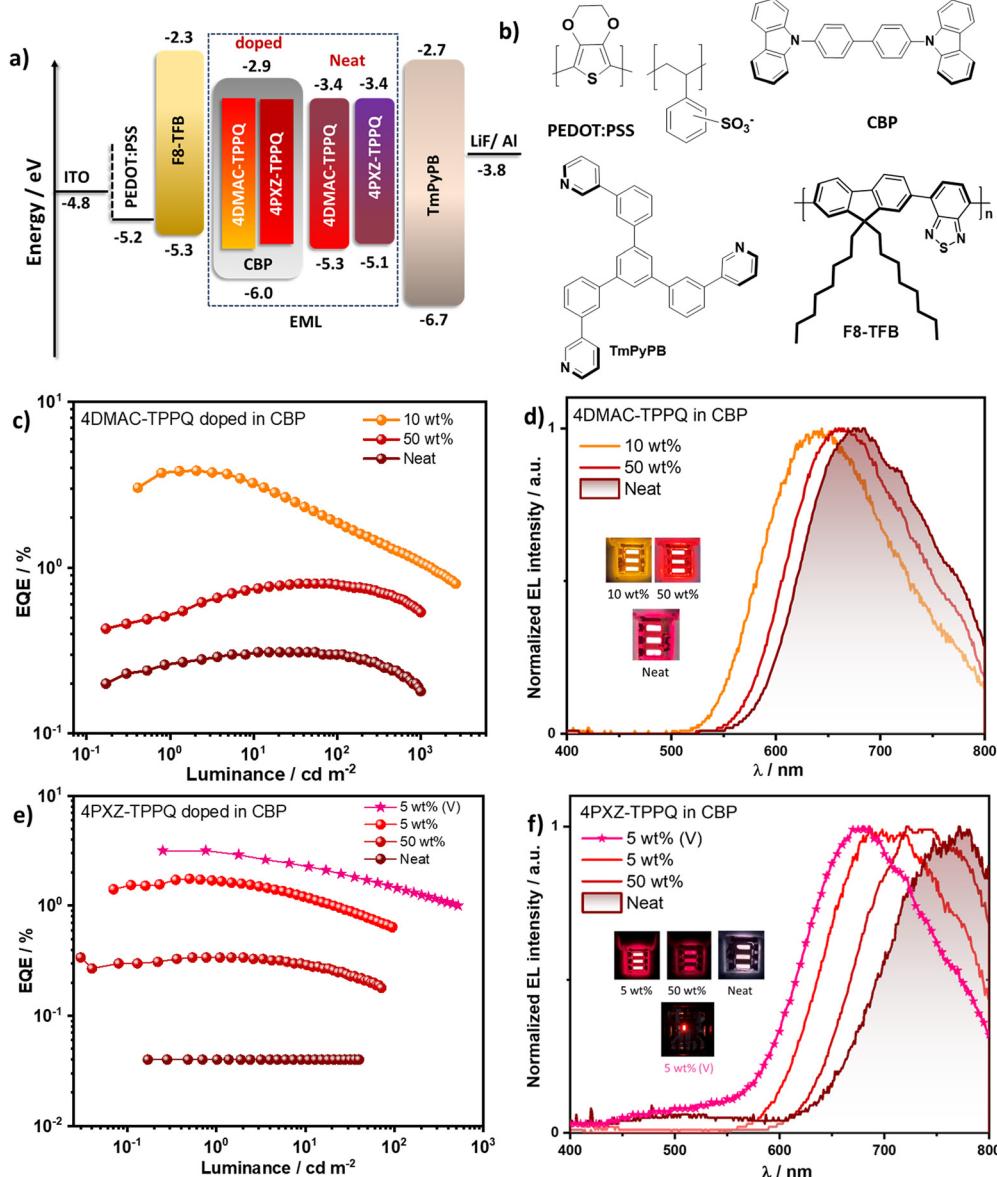


Fig. 7 (a) Energy level diagram of materials employed in the devices; (b) molecular structure of materials used in the devices; (c) external quantum efficiency versus luminance curves and (d) electroluminescence spectra of the SP-OLEDs of **4DMAC-TPPQ** (10 and 50 wt% doped in CBP and neat film); (e) external quantum efficiency versus luminance curves and (f) electroluminescence spectra of the SP-OLEDs of **4PXZ-TPPQ** [(10 and 50 wt% doped in CBP and neat film) and (5 wt% doped in CBP: vacuum-deposited OLEDs, V-OLEDs)].



Table 3 Electroluminescence data for the devices

| Doping/wt%        | V <sub>on</sub> <sup>a</sup> /V | λ <sub>EL</sub> <sup>b</sup> /nm | EQE <sup>c</sup> /% | EUE <sup>e</sup> /% |
|-------------------|---------------------------------|----------------------------------|---------------------|---------------------|
| <b>4DMAC-TPPQ</b> |                                 |                                  |                     |                     |
| 10                | 4.2 (5.6)                       | 640                              | 3.9/3.2/1.9         | 74.2                |
| 50                | 4.4 (6.1)                       | 670                              | 0.8/0.7/0.8         | 30.2                |
| 100               | 4.0 (5.6)                       | 685                              | 0.3/0.3/—           | 27.9                |
| <b>4PXZ-TPPQ</b>  |                                 |                                  |                     |                     |
| 5                 | 5.2 (8.8)                       | 686                              | 1.7/1.2/0.6         | 66.7                |
| 50                | 4.4 (8.2)                       | 735                              | 0.3/0.3/0.2         | 34.3                |
| 100               | 4.6 (7.3)                       | 780                              | 0.04/0.04/—         | 10.7                |
| 5 <sup>d</sup>    | 3.8 (4.8)                       | 681                              | 3.2/2.3/1.4         | —                   |

<sup>a</sup> The turn-on voltage at lowest luminance and 10 cd m<sup>-2</sup> in parenthesis. <sup>b</sup> The electroluminescence maximum recorded at 7 or 8 V.

<sup>c</sup> EQE<sub>max</sub>/EQE<sub>10</sub>/EQE<sub>100</sub>. <sup>d</sup> Device was fabricated by vacuum deposition.

<sup>e</sup> EUE = exciton utilization efficiency, calculated according to the equation: EQE =  $\eta_{\text{ext}} \times \Phi_{\text{PL}}$  of film  $\times \text{EUE} \times \gamma$ , in which  $\eta_{\text{ext}}$  = optical outcoupling efficiency, assumed to be 25% for an isotropic film, and  $\gamma$  = charge-balance factor, assumed to be 100%.

device architecture consisting of: indium tin oxide (ITO)/poly(3,4-ethylenedioxy-thiophene):poly(styrenesulfonate) (PEDOT:PSS) (40 nm)/F8-TFB (25 nm)/EML (25 nm for doped and 30 nm for neat film EMLs)/2,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) (70 nm)/LiF (1 nm)/Al (100 nm) (Fig. S41, ESI†). ITO and Al serve as the anode and cathode, respectively, PEDOT:PSS acts as the hole-transporting layer, F8-TFB acts as the electron-blocking layer (EBL) and hole-transporting layer (HTL), TmPyPB acts as the electron-transporting layer (ETL), and LiF acts as the electron-injection layer by modifying the work function of the aluminum cathode (Fig. 7b). The EQE-luminance curves and electroluminescence spectra (EL) are shown in Fig. 7 and the current density and luminance *versus* voltage are shown in Fig. S42 (ESI†) and the performance of the OLEDs is summarized in Table 3. The EL spectra mirror the corresponding PL spectra. The λ<sub>EL</sub> of the SP-OLEDs with **4DMAC-TPPQ** ranged from 640 to 670 nm for the 10 and 50 wt% doped film in CBP EMLs, while the neat film SP-OLEDs emitted at an λ<sub>EL</sub> of 683 nm. As expected, the SP-OLEDs with **4PXZ-TPPQ** emitted further into the NIR, with an λ<sub>EL</sub> of 686 nm (5 wt% in CBP), 735 nm (50 wt% in CBP), and 780 nm (for neat film devices) (Table 3). Of the devices fabricated with **4DMAC-TPPQ**, the highest EQE<sub>max</sub> was achieved with 10 wt% doping at 3.9%; the efficiency decreased to 1.9% at 100 cd m<sup>-2</sup>. The 50 wt% and neat film devices generally exhibited relatively low EQE, with EQE<sub>max</sub> of 0.8 and 0.3%, respectively (Table 3). The EQE<sub>max</sub> for the device with 5 wt% **4PXZ-TPPQ** in CBP was 1.7%; the EQE<sub>max</sub> was 0.3% for the 50 wt% doped device and 0.04% for the neat film OLEDs, values that are consistent with their lower Φ<sub>PL</sub>. For comparison, we fabricated vacuum-deposited devices (VD-OLEDs) with 5 wt% **4PXZ-TPPQ** in CBP, using the device structure shown in Fig. S41 (ESI†) and Table 3. Notably, the VD-OLEDs performance improved, reflected in the higher EQE<sub>max</sub> of 3.2% at λ<sub>EL</sub> at 681 nm, a similar EL spectrum to that observed for the 5 wt% SP-OLEDs. The fabrication of VD-OLEDs was not possible for **4DMAC-TPPQ** because its molecular weight was too high. The turn-on voltages for the SP-OLEDs range from 4.0 to 5.2 V, while

that for the VD-OLEDs is decreased at 3.8 V. Furthermore, the exciton utilization efficiency (EUE) of the SP-OLEDs with **4DMAC-TPPQ** and **4PXZ-TPPQ** is high as 74 and 67%, respectively, indicating that there is significant triplet exciton harvesting in these devices. The EL spectrum of the neat film SP-OLED with **4PXZ-TPPQ** mirrors the PL spectrum (λ<sub>PL</sub> = 770 nm). These devices are, to the best of our knowledge, the reddest of those based on emitters containing quinoxaline acceptors (Fig. S43 and Table S11, ESI†).

## Conclusion

We have developed deep-red and NIR TADF emitters containing an extended π-conjugated pyrazine-quinoxaline (PQ) acceptor with a particularly deep LUMO at -2.74 eV. The compounds **4DMAC-TPPQ** and **4PXZ-TPPQ** emit at 650 and 762 nm in toluene, which are significantly red-shifted in comparison to the donor-free parent compound **TPPQ** (λ<sub>PL</sub> = 456 nm). AIE behavior was observed in THF:water mixtures of all compounds. While **TPPQ** is fluorescent, both **4DMAC-TPPQ** and **4PXZ-TPPQ** exhibit TADF as both doped films in CBP and as neat films. The 10 wt% doped film of **4DMAC-TPPQ** in CBP emits at 635 nm and the ΔE<sub>ST</sub> is 0.29 eV, while the neat film emits at 654 nm yet has the same ΔE<sub>ST</sub>. On the other hand, the 5 wt% doped film of **4PXZ-TPPQ** in CBP emits at 682 nm and the ΔE<sub>ST</sub> is 0.15 eV, while the neat film emits at 770 nm and the ΔE<sub>ST</sub> is much smaller at 0.04 eV. The undoped solution-processed OLEDs (SP-OLEDs) with **4DMAC-TPPQ** and **4PXZ-TPPQ** are particularly remarkable, emitting at 685 and 780 nm and exhibiting EQE<sub>max</sub> of 0.3 and 0.04%, respectively.

## Data availability

The research data supporting this publication can be accessed at <https://doi.org/10.17630/63338f36-6958-437d-acb2-447a2ff03f96>.

## Conflicts of interest

There are no conflicts to declare.

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