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Supporting Information

Deep-red to NIR Solution-Processed OLEDs of Donor-Decorated Quinoxaline-based TADF Aggregates

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General information

General Synthetic Procedures.

All commercially available chemicals and reagent-grade solvents were used as received. Airsensitive reactions were performed under a nitrogen atmosphere using Schlenk techniques. Flash column chromatography was carried out using silica gel (Silia-P, Silicycle, 60 Å, 40-63 µm). Analytical thin-layer-chromatography (TLC) was performed with silica plates with aluminium backings (250 µm with F-254 indicator). TLC visualization was accomplished using a 254/365 nm UV lamp. HPLC analysis was conducted on a Shimadzu LC-40 HPLC system. HPLC traces were performed using a Shim-pack GIST 3µm C18 reverse phase analytical column. ¹H and ¹³C NMR spectra were recorded on a Bruker Advance spectrometer (400 MHz, 500 MHz for ¹H and 126 MHz for ¹³C). The following abbreviations have been used for multiplicity assignments: "s" for singlet, "d" for doublet, "dd" for doublet of doublets, "td" for triplet of doublets and "m" for multiplet. Deuterated chloroform (CDCl₃) or THF (THF- d_8) was used as the solvent of record. ¹H and ¹³C NMR spectra were referenced to the solvent peak. Melting points were measured using open-ended capillaries on an electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed at the University of Edinburgh. HRMS was performed on a maXis impact with positive ion polarity at the University of Leeds.

DFT Calculations

All ground-state optimizations have been carried out at the Density Functional Theory (DFT) level with Gaussian16¹ using the PBE0 functional² and the 6-31G(d,p) basis set.³ Excited-state calculations have been performed at Time-Dependent DFT (TD-DFT) within the Tamm-Dancoff approximation (TDA)⁴ using the same functional and basis set as for ground state geometry optimization. Spin-orbit coupling matrix elements (ξ) were calculated based on the optimized singlet excited state geometry. Molecular orbitals were visualized using GaussView 6.0.⁵ Calculations were automated using an in-house designed software package, *Silico*, which uses a number of 3rd party libraries and programs, including extraction and processing of results: cclib,⁶ generations of 3D images⁷: VMD & Tachyon.⁸

Powder X-ray diffraction (PXRD)

PXRD patterns were recorded on STOE STADIP diffractometer using Mo $K_{\alpha 1}$ radiation at room temperature from 0.5-41.7 (2 θ) in capillary Debye-Scherrer mode.

TGA/DSC measurements

TGA and DSC were conducted on a Netzsch STA449C with a heating rate of 10 °C/min under a nitrogen atmosphere. The samples were heated from 35 to 700 °C and the thermal decomposition (T_d) was determined at a threshold of 5% weight loss.

Electrochemistry

Cyclic Voltammetry (CV) and Differential pulse voltammetry (DPV) analysis were performed on an Electrochemical Analyzer potentiostat model 620E from CH Instruments. Samples were prepared in dichloromethane (DCM) solution, which were degassed by sparging with DCMsaturated nitrogen gas for 5 minutes prior to measurements. All measurements were performed using 0.1M tetra-*n*-butylammonium hexafluorophosphate, [*n*Bu₄N]PF₆, as an electrolyte, in DCM at scan rate of 100 mV s⁻¹. A Ag/Ag⁺ electrode was used as the reference electrode, a platinum disk electrode was used as the working electrode, and a platinum wire was used as the counter electrode. The redox potentials are reported relative to a saturated calomel electrode (SCE) with a ferrocene/ferrocenium/ (F_c/F_c^+) redox couple as the internal standard (0.46 V vs SCE).⁹ The HOMO and LUMO energies were determined using $E_{HOMO/LUMO} = -(E^{ox}/E^{red} + 4.8)eV$,¹⁰ where E^{ox} is anodic peak potential and E^{red} is cathodic peak potential determined from the DPV relative to F_c/F_c^+ .

Photophysical measurements

Absorption spectra were recorded at RT using a Shimadzu UV-2600 double beam spectrophotometer. The steady-state emission, phosphorescence and time-resolved emission spectra or PL decays were recorded at 300, 200, and 77 K using an Edinburgh Instruments FS5 spectrofluorometer. An Edinburgh Instruments FS5 spectrofluorometer equipped with a 150 W ozone free Xenon lamp was used to collect steady-state emission and a 5 W pulsed Xenon flashlamp was used to collect phosphorescence and an EPL UV picosecond pulsed diode laser (EPL-375, $\lambda_{exc} = 375$ nm) was used to collect time-resolved decays. An Edinburgh instruments FLS-980 equipped with a picosecond laser (PicoQuant, LDH-D-C-375) driven by a laser driver (PDL 800-D) with the sample being excited at 379 nm was used to measure the time-resolved measurements of the neat film of **4PXZ-TPPQ**.

Photophysical measurement in solution

Optically diluted solutions of concentrations on the order of 10^{-5} or 10^{-6} M were prepared in spectroscopic or HPLC grade solvents for absorption and emission analysis. Molar absorptivity values were determined in toluene from at least four solutions, followed by linear regression analysis, having concentration 2.40×10^{-5} M, 1.37×10^{-5} M, 9.60×10^{-6} M and 7.38×10^{-6} M with corresponding absorbances of 1.65, 0.959, 0.665 and 0.507, respectively, at an absorption wavelength of 314 nm for **TPPQ**, at 2.54×10^{-5} M, 1.45×10^{-5} M, 1.02×10^{-5} M and 7.82×10^{-6} M with corresponding absorbances of 1.76, 1.02, 0.73 and 0.56, respectively, at an absorption wavelength of 314 nm for **4DMAC-TPPQ**, and at 1.34×10^{-5} M, 1.01×10^{-5} M, 8.06×10^{-6} M and 6.71×10^{-6} M with corresponding absorbances of 1.18, 0.86, 0.70 and 0.586, respectively, at an absorption wavelength of 314 nm for **4DMAC-TPPQ**.

The aggregation-induced emission (AIE) studies of all emitters were done in THF/H₂O mixtures with increasing water fraction (f_w) from 0%, 20%, 40%, 60%, 80% to 95% in THF solution. The concentration of emitters was maintained 5×10⁻⁵ M for each solution. Before each PL measurement, the freshly prepared solutions of specific THF/H₂O ratio were shaken for 10 s to produce a uniform solution.

The steady-state PL spectra and time-resolved PL decays of emitters under nitrogen atmosphere were measured in toluene solutions, which were degassed via three freeze-pump-thaw cycles using an in-house adapted fluorescence cuvette whereas aerated solutions were prepared by bubbling with compressed air for 5 minutes prior to emission and life-time analysis. PL decays were measured using time-correlated single photon counting (TCSPC) mode and data was fitted with respect to instrument response function (IRF).

An open 150 mL EPR Dewar was used for the singlet-triplet splitting energy (ΔE_{ST}) measurements of solution samples. The ΔE_{ST} , was determined by recording the steady-state fluorescence and the phosphorescence spectra of 2-MeTHF or methylcyclohexane solutions of emitter at 77 K. The phosphorescence spectra were measured after 1 ms excitation ($\lambda_{exc} = 315$ nm) of the Xenon flashlamp operating at 100 Hz with an exposure time of 9 ms. The singlet (S₁) and triplet (T₁) energies are then determined from the corresponding onsets of steady-state and phosphorescence spectra at 77 K and ΔE_{ST} calculated by using equation $\Delta E_{ST} = S_1 - T_1$.

Photoluminescence quantum yields (PLQY) in solution

Photoluminescence quantum yields for degassed and aerated solutions were determined using the optically dilute method¹¹ in which four sample solutions with absorbance of 0.092, 0.069, 0.046 and 0.023 at 420 nm were used for **4DMAC-TPPQ**, 0.106, 0.079, 0.053 and 0.026 at

420 nm were used for **4PXZ-TPPQ** and 0.101, 0.076, 0.050 and 0.025 at 410 nm were used for **TPPQ**. For **4DMAC-TPPQ** and **4PXZ-TPPQ**, their emission intensities were compared with those of a reference, $[Ru(bpy)_3]Cl_2$, whose quantum yield (Φ_r) in H₂O was determined to be 2.8%,^{12, 13} and for **TPPQ**, their emission intensities were compared with those of a reference, coumarin 153, whose quantum yield (Φ_r) in ethanol was determined to be 38%^{13, 14} using the absolute method. The quantum yield of the sample, Φ_{PL} , can be determined by the equation $\Phi_{PL} = \Phi_r(A_r/A_s)(I_s/I_r)(n_s/n_r)^2$, where A stands for the absorbance at the excitation wavelength, I is the integrated area under the corrected emission curve and n is the refractive index of the solvent with the subscripts "s" and "r" representing sample and reference respectively.¹³

Photophysical measurement in the solid state

Samples for PL decay measurements were prepared by spin-coating a thin film from chloroform (Sigma Aldrich, HPLC grade) at 1500 RPM in ambient environment on sapphire substrates and were annealed at 55 °C for 1 min. Neat films of **4PXZ-TPPQ** were prepared by drop-casting and were annealed at 70 °C for 1 min.

Steady-state emission and time-resolved PL decay of thin film samples

Steady-state PL spectra and time-resolved PL decays were recorded at 300, 200, and 77 K using an Edinburgh Instruments FS5 fluorimeter in an oxygen-free atmosphere. Oxygen-free samples were obtained by placing the sample inside a cold finger cryostat (Oxford Instruments) under vacuum. All the samples for the steady-state measurements were excited at 340 nm using a Xenon lamp, while the samples for the time-resolved measurements were excited at 375 nm using a pico-second laser (PicoQuant, LDH-D-C-375) driven by a laser driver (PDL 800-D). PL decays were measured using time-correlated single photon counting (TCSPC) mode and multi-channel scaling (MCS). For quantify the long-delayed lifetime, the samples were excited at 340 nm by using a 5 W pulsed Xenon flashlamp under vacuum.

Photoluminescence quantum yields (PLQY) in solid thin film

A Hamamatsu C9920-02 integrating sphere was employed for PLQY measurements for spincoated thin film samples.¹⁵ A xenon lamp coupled to a monochromator enabled selective excitation, chosen here to be 305 or 340 nm, for thin films. The output was then fed into the integrating sphere via a fibre, exciting the sample. PL spectra were collected with a multimode fibre and detected with a back-thinned CCD under a nitrogen or oxygen atmosphere as required.

ΔE_{ST} measurements

The film for ΔE_{ST} measurement was prepared by spin-coating of 5, 10, 50 and 100 wt% emitter in a chloroform solution of 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP) host, on cleaned sapphire substrates. All samples were loaded inside a cold finger cryostat (Oxford Instruments) and samples were placed under vacuum. The S₁, T₁, and ΔE_{ST} energies of films were determined using the same methodology as for measurements in the glass at 77 K (*vide-supra*) after excitation the sample at 340 nm.

Experimental

Synthetic procedures and analytical data

Compounds DMAC-a-DK and PXZ-a-DK were synthesised according to literature.¹⁶

2,3,7,8-tetraphenylpyrazino[2,3-g]quinoxaline (TPPQ)



The compound **TPPQ** was synthesized according to the literature synthetic procedure.¹⁷ 1,2,4,5-tetraaminobenzene tetrahydrochloride (0.250 g, 0.88 mmol, 1.0 equiv.), benzil (0.389 g, 1.85 mmol) and 2-iodoxybenzoic acid (45 wt%, 0.011

g, 0.018 mmol, 0.02 equiv.) were dissolved in glacial acetic acid (10 mL). The resulting solution was heated at 110 °C to reflux for 24 h and then cooled. Upon addition of deionized water (60 mL), the product precipitated as a yellow solid, which was isolated by filtration, washed with H₂O (2 × 50 mL) then EtOH (4 × 50 mL). The product was recrystallized from hot dichloromethane (DCM) and acetonitrile (MeCN) in a ratio of 2:5. A second recrystallization from a DCM and hexane (2:5) mixture by slow evaporation yielded a greenish-yellow colour needle-like crystals of suitable quality for SC XRD. **Yield**: 0.340 g 79%. **R**_{*f*}: 0.09 (DCM: hexane = 7: 3). **Mp**: 296-300 °C. ¹**H NMR (400 MHz, CDCl₃) \delta (ppm) 9.03 (s, 2H), 7.66 – 7.59 (m, 8H), 7.47 – 7.34 (m, 12H). ¹³C NMR (126 MHz, CDCl₃) \delta (ppm): 155.27, 140.39, 138.75, 129.98, 129.45, 128.82, 128.37. HR ESI-MS:** [M + H]⁻: calcd for [C₃₄H₂₂N₄ + H]⁺: 487.1923 found: 487.1902 **Elemental analysis:** Calcd for TPPQ C₃₄H₂₂N₄: C, 83.93; H, 4.56; N, 11.51 Found: C, 83.45; H, 4.13; N, 11.24. The data match those reported in the literature.¹⁷ HPLC (65% Tetrahydrofuran and 35% Water): 99.95% pure, retention time 6.473 min.



Figure S1.¹H NMR spectrum of TPPQ in CDCl₃.



Figure S2. ¹³C NMR spectrum of TPPQ in CDCl₃.





HPLC Trace Report01Jul2024

<Sample Information>

Sample Name Sample ID	: TPPQ.3 :		
Method Filename	: 65% THF 35% water 0.4 mlmin 20	mins.lcm	
Batch Filename	: TPPQ.lcb		
Vial #	: 1-2	Sample Type	: Unknown
Injection Volume	: 10 uL	1 71	
Date Acquired	: 27/06/2024 17:07:46	Acauired by	: System Administrator
Date Processed	: 27/06/2024 17:27:49	Processed by	: System Administrator



Figure S4. HPLC of TPPQ with 65% THF and 35% water.

Elemental Analysis Sample Results

Name	Abhishek
Organisation Name	University of St Andrews
Purchase order number	P00016109

Standard – Acetanilide			
Element Expected % Found			
Carbon	71.10 (+/- 0.23)	70.87	
Hydrogen	6.71 (+/- 0.07)	6.65	
Nitrogen	10.34 (+/- 0.09)	10.25	

Analysis – TPPQ			
Element	Expected %	Found (1)	Found (2)
Carbon	83.93	83.48	83.43
Hydrogen	4.56	4.18	4.09
Nitrogen	11.51	11.25	11.23

Date completed	07.10.2024
Signature	O. McCullough
Comments	

Figure **S5**. Elemental analysis of **TPPQ**.

2,3,7,8-tetrakis(4-(9,9-dimethylacridin-10(9H)-yl)phenyl)pyrazino[2,3-g]quinoxaline (4DMAC-TPPQ)



The compound **4DMAC-TPPQ** was synthesized according to an analogous procedure to that used for the synthesis of **TPPQ**. 1,2,4,5-Tetraaminobenzene tetrahydrochloride (0.11 g, 0.387 mmol, 1.0 equiv.), **DMAC-α-DK** (0.508 g, 0.813 mmol) and 2-iodoxybenzoic acid (45 wt%,

0.005 g, 0.008 mmol, 0.02 equiv.) were dissolved in glacial acetic acid (20 mL). The orange solid powder of 4DMAC-TPPQ was extracted by adding 100 mL of deionized water (100 mL) which was isolated similarly like TPPQ (vide supra). Additionally, the obtained orange powder was washed with acetonitrile and diethyl ether and dried under vacuum. The crude product was purified by column chromatography on silica gel (DCM: hexane = 7: 3) to afford compound 4DMAC-TPPQ as a dark-orange solid. R_f : 0.57 (DCM: hexane = 7:3). The product was recrystallized from hot dichloromethane (DCM) and acetonitrile (MeCN) in a ratio of 2:5. A second recrystallization from a DCM and Hexane (2:5) mixture by slow evaporation yielded orange colour needle-like crystals of suitable quality for SC XRD. Yield: 0.350 g, 69%. Mp: 454- 462 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.24 (s, 2H), 7.98 (dd, J = 8.3, 3.0 Hz, 8H), 7.47 (td, J = 5.2, 2.6 Hz, 16H), 6.93 – 6.84 (m, 16H), 6.38 (d, J = 7.9 Hz, 8H), 1.70 (s, 24H). ¹³C NMR (126 MHz, CDCl₃) δ (ppm): 155.01, 142.76, 140.68, 140.62, 138.31, 132.61, 131.42, 130.39, 129.38, 126.56, 125.16, 120.94, 114.11, 36.07, 30.88. HR ESI-MS: [M + H]⁻ : calcd for $[C_{94}H_{74}N_8 + H]^+$: 1316.6148, found: 1316.6141. Elemental analysis: Calcd for **4DMAC-TPPQ** C₉₄H₇₄N₈: C, 85.81; H, 5.67; N, 8.52 Found: C, 85.68; H, 5.00; N, 7.76. HPLC (75% Tetrahydrofuran and 25% Water): 97.17% pure, retention time 6.204 min.





Figure S7. ¹³C NMR spectrum of 4DMAC-TPPQ in CDCl₃.



Figure **S8**. HRMS spectrum of **4DMAC-TPPQ**. The peak at 1316.6141 corresponds to $[C_{94}H_{74}N_8 + H]^+$.

HPLC Trace Report01Jul2024

<Sample Information>

Sample Name Sample ID Method Filename Batch Filename	: 4-dmac-tppq : : 75% THF 25% water 0.5 mlmin 20 m	nins.lcm	
Vial #	: 1-3 : 10 ul	Sample Type	: Unknown
Date Acquired Date Processed	: 01/07/2024 14:46:39 : 01/07/2024 15:06:40	Acquired by Processed by	: System Administrator : System Administrator

<Chromatogram>



<Peak Table>

Detect	or A 280nm					
Peak#	Ret. Time	Area	Height	Area%	Area/Height	Width at 5% Height
1	4.721	66045	3389	1.410	19.486	0.426
2	6.204	4551877	163385	97.166	27.860	0.880
3	7.510	66738	3059	1.425	21.819	0.463
Total		4684660	169833	100.000		

Figure **S9**. HPLC of **4DMAC-TPPQ** with 75% THF and 25% water.

Elemental Analysis Sample Results

Name	Abhishek
Organisation Name	University of St Andrews
Purchase order number	P00016109

Standard – Acetanilide			
Element	Expected %	Found	
Carbon	71.10 (+/- 0.23)	70.87	
Hydrogen	6.71 (+/- 0.07)	6.65	
Nitrogen	10.34 (+/- 0.09)	10.25	

Analysis – 4DMAC-TPPQ			
Element	Expected %	Found (1)	Found (2)
Carbon	85.81	86.04	85.33
Hydrogen	5.67	4.85	5.15
Nitrogen	8.52	7.75	7.77

Date completed	07.10.2024
Signature	O. McCullough
Comments	

Figure S10. Elemental data of 4DMAC-TPPQ.

2,3,7,8-tetrakis(4-(10H-phenoxazin-10-yl)phenyl)pyrazino[2,3-g]quinoxaline (4PXZ-TPPQ)



The compound **4PXZ-TPPQ** was synthesized according by an analogous procedure to that used for the synthesis of **TPPQ** and **4DMAC-TPPQ**. 1,2,4,5-Tetraaminobenzene tetrahydrochloride (0.09 g, 0.32 mmol, 1.0 equiv.), **PXZ-α-DK** (0.36 g, 0.63 mmol, 2 equiv.) and 2-iodoxybenzoic acid (45 wt%, 0.004 g, 0.006 mmol, 0.02 equiv.) were

dissolved in glacial acetic acid (18 mL). The product was purified by column chromatography with 70% DCM/Hexane to afford compound **4PXZ-TPPQ** as deep-red solid. X-ray quality crystals were grown from a CDCl₃ and TFH (1:1) mixture by slow evaporation, yielding a dark red plate-like crystal. **Yield**: 0.250 g 65%, dark-red powder. **R**_{*f*}: 0.53 (DCM:hexane = 3:7 on silica gel). **Mp**: 469- 475 °C. ¹**H NMR (500 MHz, CDCl₃) δ (ppm)**: 9.18 (s, 2H), 7.91 (d, J = 8.1 Hz, 8H), 7.46 (d, J = 8.3 Hz, 8H), 6.75 – 6.50 (m, 24H), 6.00 (d, J = 8.0 Hz, 8H) ¹³**C NMR (126 MHz, THF-***d***₈) δ (ppm)**: 154.72, 144.02, 140.61, 139.18, 134.06, 132.91, 130.54, 128.64, 123.32, 121.33, 115.22, 113.18. **HR ESI-MS:** [**M** + **H**]⁻: calcd for [C₈₂H₅₀N₈O₄ + H]⁺: 1211.4033, found: 1211.4021. **Elemental analysis:** Calcd for C₈₂H₅₀N₈O₄ C, 81.31; H, 4.16; N, 9.25 Found: C, 80.56; H, 3.41; N, 9.03. HPLC (73% Tetrahydrofuran and 27% Water): 99.33% pure, retention time 7.672 min.





Figure S11. ¹H NMR spectrum of 4PXZ-TPPQ in CDCl₃.



Figure S12. ¹³C NMR spectrum of **4PXZ-TPPQ** in THF-*d*₈.



Figure S13. HRMS spectrum of 4PXZ-TPPQ. The peak at 1211.4021 corresponds to $[C_{82}H_{50}N_8O_4 + H]^+$.

HPLC Trace Report03Jul2024

<Sample Information>

Sample Name Sample ID Method Filename	: 4pxz-tppq-t4 : : 73% THF 27% water 0.4 mlmin 20 n	nins.lcm	
Vial #	: pxz-1LC-tak2.icb : 1-6	Sample Type	: Unknown
Injection Volume Date Acquired Date Processed	: 15 uL : 03/07/2024 15:30:45 : 03/07/2024 15:50:47	Acquired by Processed by	: System Administrator : System Administrator





Deleci						
Peak#	Ret. Time	Area	Height	Area%	Area/Height	Width at 5% Height
1	6.892	3133	1457	0.045	2.150	
2	7.672	6854810	159934	99.333	42.860	1.294
3	9.111	42862	1476	0.621	29.035	0.162
Total		6900805	162868	100.000		

Figure S14. HPLC of 4PXZ-TPPQ with 73% THF and 27% water.

Elemental Analysis Sample Results

Name	Abhishek Gupta
Organisation Name	University of St Andrews
Purchase order	P00007447

Standard – Acetanilide				
Element	Expected %	Found		
Carbon	71.10 (+/- 0.23)	71.06		
Hydrogen	6.71 (+/- 0.07)	6.64		
Nitrogen	10.34 (+/- 0.09)	10.27		

Analysis – 4PXZ-TPPQ						
Element	Expected %	Found (1)	Found (2)			
Carbon	81.31	80.21	80.92			
Hydrogen	4.16	3.40	3.42			
Nitrogen	9.25	9.03	9.03			

Date completed	14.06.2024
Signature	O. McCullough
Comments	

Figure S15. Elemental data of 4PXZ-TPPQ.



Figure S16. TGA/DSC results of a) **TPPQ**, b) **4DMAC-TPPQ** and c) **4PXZ-TPPQ**. The measurement was performed with continuous N_2 and at a temperature ramp rate of 10 °C/min from room temperature to 700 °C.

X-Ray structural analysis

X-ray diffraction data for TPPO, 4PXZ-TPPO and 4DMAC-TPPO were collected at 173 K using a Rigaku MM-007HF High Brilliance RA generator/confocal optics with XtaLAB P100 or P200 diffractometer [Cu K α radiation ($\lambda = 1.54187$ Å)]. Intensity data were collected using either CrystalClear¹⁸ (using both ω and φ steps) and processed (including correction for Lorentz, polarization and absorption) using CrysAlisPro.¹⁹ Structures were solved by dual-space methods (SHELXT²⁰) and refined by full-matrix least-squares against F² (SHELXL-2018/3²¹). Non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were refined using a riding model. The structure of **TPPQ** is a DCM solvate form of the previously reported structure.²² It shows a very similar molecular conformation to that in the previous structure, with dihedral angles between phenyl rings and the meanplane of the PQ moiety showing good agreement with those previously reported (28.24, 59.04°). The molecular packing does differ significantly, however, with **TPPQ** showing a herringbone arrangement (Figure S17a), rather than the previously encountered parallel sheet structure. The structure of 4DMAC-TPPQ contained disordered dichloromethane solvent. The disordered atoms were modelled over two sites with some bond distance and thermal similarity restraints applied. The structure of **4PXZ-TPPO** showed high proportions of void space (1458 $Å^3$) and the SOUEEZE²³ routine implemented in PLATON²⁴ was used to remove the contribution to the diffraction pattern of the unordered electron density in the void spaces. One of the phenyl-PXZ groups showed disorder which was modelled over two sites with bond distance and thermal similarity restraints applied. In addition, another PXZ showed approximately 10% substitution of hydrogen by chlorine on one of its phenyls, ortho to the nitrogen. This presumably occurred during its crystallisation from a CDCl₃/THF mixture. The chlorine was modelled with bond distance and to thermal similarity restraints. All calculations except SQUEEZE were performed using the Olex2²⁵ interface. Selected crystallographic data are presented in Table S1, and packing plots of the structures shown in Figure S17. CCDC 2406567-2406569 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

	TPPQ	4DMAC-TPPQ	4PXZ-TPPQ
Empirical formula	C ₃₆ H ₂₆ Cl ₄ N ₄	$C_{98}H_{82}Cl_8N_8$	$C_{82}H_{49.91}Cl_{0.09}N_8O_4$
Formula mass	656.41	1655.31	1214.48
Colour, habit	Yellow needle	Orange plate	Red plate
Crystal size (mm ³)	0.25×0.02×0.01	0.24×0.21×0.03	0.29×0.07×0.01
Temperature (K)	173	173	100
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_{1}/c$	$P2_{1}/n$	$P2_{1}/n$
a (Å)	12.9390(17)	17.9994(2)	13.82288(19)
b (Å)	5.9335(5)	9.45216(10)	16.2734(3)
c (Å)	20.706(3)	26.0069(3)	31.2646(8)
β (°)	102.627(12)	105.6276(13)	93.6059(18)
Volume (Å ³)	1551.2(3)	4261.07(9)	7018.9(2)
Ζ	2	2	4
$\rho_{calc} (g \text{ cm}^{-3})$	1.405	1.290	1.149
μ (mm ⁻¹)	3.727	2.824	0.603
F(000)	676	1724	2526
Reflections collected	14931	43986	70675
Independent reflections (R_{int})	2826 (0.1470)	7758 (0.0241)	14021 (0.0942)
Parameters, restraints	199, 0	556, 101	1011, 670
Goodness-of-fit on F ²	1.065	1.083	1.061
$R_1 \left[I > 2\sigma(I) \right]$	0.0883	0.0609	0.0859
R_1 (all data)	0.1169	0.0637	0.1392
$wR_2 [I > 2\sigma(I)]$	0.2508	0.1791	0.2585
wR_2 (all data)	0.2746	0.1824	0.2988
Largest diff. peak/hole / e Å ⁻³	0.778, -0.541	0.669, -0.752	0.794, -0.217

Table S1. Selected crystallographic data for TPPQ, 4DMAC-TPPQ and 4PXZ-TPPQ.



Figure S17. Views down the *a*-axis of the packing of the structures of a) **TPPQ**, b) **4DMAC-TPPQ** and c) **4PXZ-TPPQ** showing the herringbone, brickwork, and undulating-layered arrangements. Minor components of disorder are omitted.

DFT calculations



Figure **S18.** Optimized molecular structure of (a) **TPPQ**, (b) **4DMAC-TPPQ**, and (c) **4PXZ-TPPQ** by DFT with twisted angle between electron deficient (acceptor) and electron rich (donor) moiety.



Figure S19. TDA-DFT simulation and experimental UV-Vis absorption spectrum in the gas phase of (a) TPPQ, (b) 4DMAC-TPPQ and (c) 4PXZ-TPPQ.

Compound	State	Energy / eV	f	Transitions (probability)
TPPQ	S_1	3.11	0.8083	$HOMO \rightarrow LUMO (0.90)$
	S_2	3.11	0.0071	HOMO-1 \rightarrow LUMO (0.49)
	T1	2.07	-	$\frac{\text{HOMO-4} \rightarrow \text{LUMO (0.44)}}{\text{HOMO-1} \rightarrow \text{LUMO (0.91)}}$
	T ₂	2.52	-	HOMO \rightarrow LUMO (0.92)
	T3	2.77	-	HOMO-3→ LUMO (0.80) HOMO-4 → LUMO+2 (0.11)
	T4	2.82	-	$HOMO-4 \rightarrow LUMO (0.80)$ $HOMO-3 \rightarrow LUMO+2 (0.12)$
4DMAC-TPPQ	S 1	2.02	0.0270	$\frac{110100 \text{ J} + 120100 \text{ HOMO} + 2(0.12)}{10000 \text{ HOMO} + 2(0.12)}$
	S_2	2.03	0.0000	$HOMO-1 \rightarrow LUMO (0.99)$
	T ₁	2.01	-	HOMO \rightarrow LUMO (0.98)
	T ₂	2.02	-	HOMO-1 \rightarrow LUMO (0.99)
	T ₃	2.08		HOMO-1 → LUMO (0.52) HOMO-7 → LUMO (0.25)
4PXZ-TPPQ	S_1	1.59	0.0906	$\frac{10000 + 10000}{1000} \text{HOMO} \rightarrow \text{LUMO} (0.99)$
	S_2	1.61	0.0000	HOMO-1 \rightarrow LUMO (0.99)
	T_1	1.57	-	HOMO \rightarrow LUMO (0.98)
	T ₂	1.58	-	HOMO-1 \rightarrow LUMO (0.99)
	T3	1.64	-	HOMO-2 \rightarrow LUMO (0.98)
	T 4	1.65	-	HOMO-3 \rightarrow LUMO (0.99)
	T5	2.10	-	HOMO-8 \rightarrow LUMO (0.86)

Table S2. Optimized excited state energies and transition probabilities for TPPQ and 4DMAC-TPPQ and 4PXZ-TPPQ.

Table **S3**. Singlet energy, oscillator strength, composition and density plots of dominant molecular orbital transitions of **TPPQ** (isovalue = 0.02).

Excited State	Energy/eV	Oscillator Strength	Dominant orbital transition	Corresponding occupied orbital	Corresponding unoccupied orbital
S ₁	3.11	0.8083	$HOMO \rightarrow LUMO (0.90)$		
S ₂	3.11	0.0071	HOMO-1 \rightarrow LUMO (0.49)	I STORES	Post
			HOMO-4 \rightarrow LUMO (0.44)		
S ₃	3.21	0.0000	HOMO-3 \rightarrow LUMO (0.92)		- Content
S ₄	3.40	0.0052	HOMO-4 \rightarrow LUMO (0.49)	10000 C	- Content
			HOMO-1 \rightarrow LUMO (0.44)	ALCONT.	

S ₅	3.65	0.0000	HOMO-2 → LUMO (0.96)		
S ₆	3.86	0.0015	HOMO-5 → LUMO (0.96)		
S ₇	3.89	0.0000	HOMO-6 \rightarrow LUMO (0.97)	an a start a s	
S_8	4.00	0.0000	HOMO-7 \rightarrow LUMO (0.97)		
S9	4.10	0.0126	HOMO-8 \rightarrow LUMO (0.95)		
S ₁₀	4.12	0.8912	$HOMO-1 \rightarrow LUMO+1$ (0.63)	RACESSA	Sarah .
			$HOMO-11 \rightarrow LUMO (0.20)$		

Table **S4**. Singlet energy, oscillator strength, composition and density plots of dominant molecular orbital transitions of **4DMAC-TPPQ** (isovalue = 0.02).

Excited State	Energy/eV	Oscillator Strength	Dominant orbital transition	Corresponding occupied orbital	Corresponding unoccupied orbital
S ₁	2.02	0.0270	HOMO \rightarrow LUMO (0.99)		
S ₂	2.03	0.0000	HOMO-1 → LUMO (0.99)		1000¢*
S ₃	2.12	0.0104	HOMO-2 → LUMO (0.99)		See
S ₄	2.12	0.0000	HOMO-3 → LUMO (0.99)		1000¢
S ₅	3.11	0.0268	HOMO \rightarrow LUMO+1 (0.85)		Ş.
S ₆	3.11	0.0000	HOMO-1 \rightarrow LUMO+1 (0.86)		() me
S ₇	3.15	0.1283	HOMO-20 \rightarrow LUMO (0.48)		1000¢
			HOMO-6 \rightarrow LUMO (0.33)		10000
S ₈	3.16	1.0029	HOMO-7 \rightarrow LUMO (0.43)		Jose

	HOMO-6 \rightarrow LUMO (0.36)	estime.	10000
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Table **S5**. Singlet energy, oscillator strength, composition and density plots of dominant molecular orbital transitions of **4PXZ-TPPQ** (isovalue = 0.02).

Excited State	Energy/eV	Oscillator Strength	Dominant orbital transition	Corresponding occupied orbital	Corresponding unoccupied orbital
S ₁	1.59	0.0906	HOMO \rightarrow LUMO (0.99)	No. of Street,	
S ₂	1.61	0.0000	HOMO-1 → LUMO (0.99)	No.	
S ₃	1.66	0.0099	HOMO-2 → LUMO (0.99)	No.	
S ₄	1.66	0.0000	HOMO-3 → LUMO (0.99)	W. Con	
S ₅	2.63	0.0401	HOMO \rightarrow LUMO+1 (0.88)	No.	
S ₆	2.64	0.0000	HOMO-1 \rightarrow LUMO+1 (0.88)	No. of Contraction	
S ₇	2.70	0.1664	HOMO-2 → LUMO+1 (0.86)	No.	
S ₈	2.72	0.0000	HOMO-3 → LUMO+1 (0.87)	No.	
S ₉	3.01	0.2838	HOMO-4 \rightarrow LUMO (0.53)		
			$HOMO-1 \rightarrow LUMO+2 (0.32)$	William Barris	

Table S6. Triplet energy, spin-orbit coupling between S_1 and corresponding triplet energy (T_x) composition from T_1 geometry, and density plots of dominant molecular orbital transitions of **TPPQ**, **4DMAC-TPPQ** and **4PXZ-TPPQ** (isovalue = 0.02).

Excited State	Excited State Energy/eV $S_1 H_{SO} T_x/cm^{-1}$ Dominant orbital		Corresponding	Corresponding				
			transition	occupied orbital	unoccupied orbital			
			TPPQ					
T ₁	2.07	3.99	$\begin{array}{c} \text{HOMO-1} \rightarrow \text{LUMO} \\ (0.91) \end{array}$	ALCOCKE				
T ₂	2.52	1.36	$\begin{array}{c} \text{HOMO} \rightarrow \text{LUMO} \\ (0.92) \end{array}$					
T ₃	2.77	0.00	$\begin{array}{c} \text{HOMO-3} \rightarrow \text{LUMO} \\ (0.80) \end{array}$					
			HOMO-4 → LUMO+2 (0.11)					
T ₄	2.82	8.22	$\begin{array}{c} \text{HOMO-4} \rightarrow \text{LUMO} \\ (0.80) \end{array}$					
			HOMO-3 → LUMO+2 (0.12)					
4DMAC-TPPQ								
T ₁	2.01	0.01	$\begin{array}{c} \text{HOMO} \rightarrow \text{LUMO} \\ (0.98) \end{array}$		Ş.			
T ₂	2.02	0.02	$\begin{array}{c} \text{HOMO-1} \rightarrow \text{LUMO} \\ (0.99) \end{array}$		Č.			
T ₃	2.08	0.03	$\begin{array}{c} \text{HOMO-2} \rightarrow \text{LUMO} \\ (0.52) \end{array}$		Šanč			
			$\begin{array}{c} \text{HOMO-7} \rightarrow \text{LUMO} \\ (0.25) \end{array}$	A COMPANY	5000¢			
			$\begin{array}{c} \text{HOMO-6} \rightarrow \text{LUMO} \\ (0.17) \end{array}$	Steres.	Ş əm Ş			
			4PXZ-TPPQ					
T ₁	1.57	0.02	$\begin{array}{c} \text{HOMO} \rightarrow \text{LUMO} \\ (0.98) \end{array}$	No. of the second secon				
T ₂	1.58	0.00	$\begin{array}{c} \text{HOMO-1} \rightarrow \text{LUMO} \\ (0.99) \end{array}$	No.				

T ₃	1.64	0.06	HOMO-2 → LUMO (0.98)	N. ANA	
T ₄	1.65	0.00	HOMO-3 → LUMO (0.99)	ALC IN COLUMN	
T ₅	2.10	0.29	$\begin{array}{c} \text{HOMO-8} \rightarrow \text{LUMO} \\ (0.86) \end{array}$		

Table **S7**. DFT predicted HOMO (blue), LUMO (red), S_1 and T_1 energies, calculated at the optimized ground-state geometries of **TPPQ**, **4DMAC-TPPQ** and **4PXZ-TPPQ** (isovalue = 0.02).







Figure S20. TDA-DFT simulation of TPPQ-monomer and TPPQ-dimer in the gas phase.

Photophysical studies



Figure **S21**. Photoluminescence measurement of **TPPQ** before and after exposure of UV light in (a) tetrahydrofuran (THF), (b) dioxane, (c) diethyl ether (Et₂O) (d) dichloromethane (DCM), $\lambda_{exc} = 315$ nm.



Figure S22. Photoluminescence measurement of TPPQ in 2-MeTHF at RT and at 77 K after exposure of UV light for 4 minutes $\lambda_{exc} = 315$ nm.



Figure S23. ¹H NMR spectrum of TPPQ before and after UV exposure in THF-d₈.



Figure S24. Photoluminescence measurement of (a) 4DMAC-TPPQ and (b) 4PXZ-TPPQ before and after exposure of UV light in THF, $\lambda_{exc} = 315$ nm.

Emitters	λ _{PL} / nm	$\tau_{\rm p}{}^{\rm c}$ / ns	$\tau_d / \mu s$	Φ _{PL} ^e / %	$E_{\rm S1}/E_{\rm T1}^{\rm f}/{\rm eV}$	$\Delta E_{\rm S1T1}$ g/ eV
			Toluene	a		
TPPQ	456	6.9/6.4	-	2.1 (1.9)	2.82/1.85	0.97
4DMAC-TPP	Q 650	20.1/11.2	-	13.7 (7.3)	2.26/1.85	0.41
4PXZ-TPPQ	762	2.0/1.8	-	0.8 (0.6)	2.08/1.84	0.24
		10 wt	% doped in	n PMMA ^b		
TPPQ	466	2.1	-	4.7 (4.4)	-	-
4DMAC-TPP	Q 635	27.1	390.9^{d}	14.3 (13.0)	-	-
PXZ-TPPO	681	13.6	342.5^{d}	3.0 (2.0)	-	

Table S8. Photophysical measurements of 4DMAC-TPPQ and 4PXZ-TPPQ in toluene and PMMA.

^{*a*} At 298 K, values quoted are in degassed solutions, which were prepared by three freeze-pump-thaw cycles; ^{*b*} Thin films were prepared by spin-coating 10 wt% doped samples in PMMA. Steady-state and time-resolved emission spectra were recorded at 298 K under an O₂-free atmosphere ($\lambda_{exc} = 315$ nm for steady-state and $\lambda_{exc} = 375$ nm for time-resolved emission); ^{*c*} prompt lifetime was measured by TCSPC ($\lambda_{exc} = 375$ nm), reported lifetime values are average lifetime ($\tau_{avg} = \Sigma A_i \tau_i^2 / \Sigma A_i \tau_i$, where A_i is the pre-exponential for lifetime τ_i); ^{*d*} delayed emission was measured by MCS, using microsecond flash lamp as an excitation source, $\lambda_{exc} = 315$ nm; ^{*e*} photoluminescence quantum yields (Φ_{PL}) of emitters in toluene were measure under degassed and aerated conditions; however, Φ_{PL} in PMMA films were determined using an integrating sphere ($\lambda_{exc} = 305$ nm or 340 nm) under N₂ atmosphere at 298 K. The values in parentheses are in the presence of O₂. ^{*f*} E_{S1} and E_{T1} were obtained from the onset of the steady-state emission and phosphorescence spectra (time window: 1–9 ms), respectively of **4DMAC-TPPQ** and **4PXZ-TPPQ** in 2-MeTHF at 77 K, however, the E_{S1} and E_{T1} of **TPPQ** were measured in methylcyclohexane (MCH) at 77 K, $\lambda_{exc} = 315$ nm. ^{*g*} $\Delta E_{ST} = E_{S1} - E_{T1}$.

Table S9. Photophysical properties of TPPQ in CBP host.

Doping ^a / wt%	λ _{PL} ^b / nm	Φ _{PL} ^c / %
	TPPQ in C	CBP
5	546	10.4
10	548	8.8
20	556	6.3
30	558	5.8

^{*a*} Spin-coated film and annealed at 55 °C for 1 minute; ^{*b*} PL measured under vacuum, $\lambda_{exc} = 340$ nm for all doped films ^{*c*} photoluminescence quantum yield (Φ_{PL}) of thin films were determined using an integrating sphere ($\lambda_{exc} = 305$ nm or 340 nm) under a N₂ atmosphere at 298 K.



Figure S25. (a) Normalized absorbance and PL spectra ($\lambda_{exc} = 315 \text{ nm}$) of **TPPQ** in toluene. (b) Normalized absorbance and PL spectra ($\lambda_{exc} = 315 \text{ nm}$) of **4DMAC-TPPQ** in toluene. (c) Normalized absorbance and PL spectra ($\lambda_{exc} = 420 \text{ nm}$) of **4PXZ-TPPQ** in toluene.



Figure **S26**. (a) Emission spectra ($\lambda_{exc} = 410 \text{ nm}$) and (b) time-resolved PL decay ($\lambda_{exc} = 375 \text{ nm}$ and $\lambda_{em} = 456 \text{ nm}$) of **TPPQ** in toluene solution with optical density 0.05 under aerated and degassed conditions. (c) Emission spectra ($\lambda_{exc} = 315 \text{ nm}$) and (d) time-resolved PL decay ($\lambda_{exc} = 375 \text{ nm}$ and $\lambda_{em} = 650 \text{ nm}$) of **4DMAC-TPPQ** in toluene solution with optical density 0.07 under aerated and degassed conditions. (e) Emission spectra ($\lambda_{exc} = 315 \text{ nm}$) and (f) time-resolved PL decay ($\lambda_{exc} = 375 \text{ nm}$ and $\lambda_{em} = 762 \text{ nm}$) of **4PXZ-TPPQ** in toluene solution with optical density 0.10 under aerated and degassed conditions.



Figure S27. a) The steady-state PL (SS) of **TPPQ** at room temperature (RT) and SSPL and phosphorescence spectra (time range 1-9 ms) at 77 K of **TPPQ** in methylcylohexane (MCH); b) SSPL and phosphorescence spectra (time range 1-9 ms) of **4DMAC-TPPQ** at 77 K in 2_MeTHF; and c) SSPL and phosphorescence spectra (time range 1-9 ms) of **4PXZ-TPPQ** at 77 K in 2-MeTHF ($\lambda_{exc} = 315$ nm).



Figure S28. Relative PL intensity (I/I_0) with respect to water fraction (f_w) in THF; where, I_0 is the PL intensity corresponds to $f_w = 0$ and I correspond to PL intensity on the addition of water in THF solution of a) **TPPQ**, b) **4DMAC-TPPQ** and c) **4PXZ-TPPQ**.



Figure **S29**. a) Powder sample isolated from THF/water mixture and calculated / simulated powder X-ray diffraction pattern of a) **TPPQ**, b) **4DMAC-TPPQ**, and c) **4PXZ-TPPQ**.



Figure S30. The PL spectra of isolated solid samples of TPPQ, 4DMAC-TPPQ and 4PXZ-TPPQ obtained from a THF/water mixture ($f_w = 80\%$) at RT, ($\lambda_{exc} = 405$ nm).



Figure S31. a) The absorbance of 10 wt% TPPQ, 4DMAC-TPPQ and 4PXZ-TPPQ doped in PMMA; b) PL spectra of 10 wt% TPPQ, 4DMAC-TPPQ and 4PXZ-TPPQ doped in PMMA at 300K, ($\lambda_{exc} = 315$ nm).



Figure S32. The prompt lifetime by TCSPC of 10 wt% PMMA doped films of (a) TPPQ; (b) 4DMAC-TPPQ; and (c) 4PXZ-TPPQ. $\lambda_{exc} = 375$ nm.



Figure S33. Temperature-dependent PL decays by multichannel scaling (MCS) of 10 wt% PMMA doped films of (a) **4DMAC-TPPQ**; and (b) **4PXZ-TPPQ**. Films was excited by microsecond flash lamp with $\lambda_{exc} = 315$ nm. IRF is the instrument response function.



Figure S34. PL spectra of (a) TPPQ, (b) 4DMAC-TPPQ and (c) 4PXZ-TPPQ in CBP at various doping concentrations and in neat film ($\lambda_{exc} = 340$ nm for all films save for $\lambda_{exc} = 465$ nm for 4PXZ-TPPQ neat film).



Figure S35. The Φ_{PL} of 4DMAC-TPPQ and 4PXZ-TPPQ with respect to emission wavelength and doping concentration ($\lambda_{exc} = 340$ nm).



Figure **S36**. (a) Time-resolved PL decay under 500 ns time window (λ_{exc} = 375 nm); (b) Time-resolved PL decay under 4 ms time window at 300 K (λ_{exc} = 340 nm) of 10 wt% **TPPQ** doped in CBP.



Figure S37. Time-resolved PL decay under 500 ns time window at 300 K (λ_{exc} = 375 nm) of 10 wt% 4DMAC-TPPQ doped in CBP.



Figure S38. a) PL spectra at 300 K, 200 K and 77 K; b). Time-resolved PL decay under 500 ns time window at 300, K (λ_{exc} = 375nm); c) Temperature-dependent time-resolved PL decay (λ_{exc} = 340 nm) and d) Steady-state fluorescence at 77 K and phosphorescence spectra in time range the 1–9 ms time at 77 K (λ_{exc} = 340 nm) of neat 4DMAC-TPPQ.



Figure S39. Time-resolved PL decay under 200 ns time-window at 300 K of 5 wt% 4PXZ-TPPQ doped in CBP (λ_{exc} = 375 nm).



Figure **S40**. a) PL spectra at 300, 200 and 77 K (λ_{exc} = 465 nm; b). Time-resolved PL decay at 300 K (λ_{exc} = 379 nm); c) Temperature-dependent time-resolved PL decay (λ_{exc} = 379 nm); d). Steady-state fluorescence at 77 K of neat film and phosphorescence spectra in time range the 1–9 ms time at 77 K (λ_{exc} = 465 nm) of neat **4PXZ-TPPQ**.

10 wt% 4D	MAC-TPPQ dop	ed in CBP	5 wt% 4PXZ-TPPQ doped in CBP					
	Temperature / K		Temperature / K					
300 K	300 K 200 K 77 K			300 K 200 K 77 K				
T_1^{300} / eV	T_1^{200} / eV	T_1^{77} / eV	T_1^{300} / eV	T_1^{200} / eV	T_1^{77} / eV			
(λ_{Ph}^{300}) / nm	$(\lambda_{Ph}^{\overline{2}00})$ / nm	$(\lambda_{Ph}^{\overline{77}})$ / nm	$(\lambda_{Ph}^{\overline{3}00})$ / nm	$(\lambda_{Ph}^{\overline{2}00})$ / nm	$(\lambda_{Ph}^{\overline{77}})$ / nm			
2.15 (656)	2.06 (695)	1.94 (763)	2.10 (684)	2.02 (708)	1.92 (760)			

Table S10. Triplet energy of 4DMAC-TPPQ and 4PXZ-TPPQ in CBP at 300, 200 and 77 K.

OLED fabrication and characterization

In this work, we fabricated mostly solution processed OLEDs (SP-OLEDs) and one set of devices of 5 wt% **4PXZ-TPPQ** doped in 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP) by vacuum deposition (VD-OLEDs) in a bottom-emitting architecture on indium-doped tin oxide (ITO, resistivity: 15 Ω sq^-1) substrates. For SP-OLEDs, ITO with dimension of 12 mm \times 12 mm × 1.1 mm and for V-OLEDs a pre-patterned glass substrate coated with ITO were used. Both types of ITO substrates were washed sequentially by ultrasonication in acetone, and isopropanol for 20 min and then exposed to oxygen plasma for 3 min to remove all the dust and organics on the ITO surface and to increase the work function of ITO anode for better hole injection from the anode to organic layer. For SP-OLEDs, the hole injection layer poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS; Clevios™ P VP AI 4083 from Ossila; conductivity: 0.0002 - 0.002 S/cm) were spin coated onto the ITO surface under 4000 rpm for 1 min, and baked at 130 °C for 15 min to remove the residual water, then transferred all substrates inside a nitrogen-filled glovebox. The 5 mg/mL toluene solution of poly(9,9dioctylfluorene-alt-N-(4-sec-butylphenyl)-diphenylamine) (F8-TFB) from Ossila was spincoated with spin speed 4000 rpm on PEDOT:PSS layer and annealed at 180-190 °C for 2 h under a N2 atmosphere to obtain 20-25 nm thickness of F8-TFB layer as an electron blocking layer (EBL). After cooling down the substrates at room temperature, the CHCl₃ solution of both emitters (X = 5 to 50 wt% emitters in CBP or neat emitter for non-doped device) were spin-coated under 3000 rpm and then annealed at 55 °C for 1 minute in the nitrogen-filled glovebox to obtain 20-25 nm thickness of EML layer. For VP-OLED, the organic layer sequence and the metal cathode were deposited onto the pre-cleaned ITO substrates which has a sheet resistance of around 30 Ω /sq. Organic layers were deposited at a rate of 0.3-0.6 Å/s, which was controlled in situ using quartz crystal monitors. Doping of the emission layers was achieved through co-evaporation of the emitter and host materials. In both OLEDs, the electron transporting layer (2,2',2"-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole), TmPyPB, 70 nm) and the electron injecting layer (lithium fluoride, LiF 1 nm) were successively thermally evaporated in a vacuum chamber under $< 1 \times 10^{-6}$ mbar. The aluminium cathode (100 nm) was deposited at a rate of 0.5 Å/s (to obtain 10 nm thickness initially) followed the final evaporation rate of 3 Å/s (to obtain 90 nm thickness) through the shadow mask defining the top electrode. The spatial overlap of the anode and cathode electrodes determined the active area of the OLED which was estimated to be 4 mm² for SP-OLEDs and 2 mm² for V-OLEDs. After the evaporation, the OLEDs were taken out from the evaporator and encapsulated inside the

glovebox. Then, the devices were taken out from the glovebox for current–voltage–luminance characteristics. The luminance-current-voltage characteristics were measured in an ambient environment using a Keithley 2400 source meter combined with a homemade photodiode connected to a Keithley 2000 multimeter for the voltage reading. The external quantum efficiency was calculated assuming Lambertian emission distribution. The electroluminescence spectra were recorded by an Andor DV420-BV CCD spectrometer.



Figure **S41**. Device structure and energy level diagram of materials employed in the a) solution process devices (SP-OLEDs) and b) vacuum deposited device (V-OLEDs); (c) Molecular structure of materials used in the devices.



Figure **S42**. Current density and luminance versus voltage characteristics for the SP-OLEDs of a) 10, 50 wt% doped in CBP and non-doped **4DMAC-TPPQ**; b) 5, 50 wt% doped in CBP and non-doped **4PXZ-TPPQ** and 5 wt% **4PXZ-TPPQ** doped in CBP based vapour deposition (V) OLEDs.

S.No.	Compound	Medium	λ _{PL} / nm	Φ_{PL}	τ_d / μs	$\Delta E_{\rm ST}$	λ _{EL} / nm	EQE_m	Ref.
1	NC CN NN N TPA-QCN	15 wt% TPBi	649	~70	285.0	0.23	644	14.5	R1 ²⁶
2	6,7-DCQx-Ac	1 wt% polystyrene	~570	91	9.0	0.13	578	21.1	R2 ²⁷
3	NC	1 wt% polystyrene	~590	72	3.1	0.11	602	16.4	R2 ²⁷
4	^{NC} CN NN ^{(Bu (Bu ^{(Bu} (Bu 6.7-DCOx-Ca}	1 wt% polystyrene	~540	93	409.0	0.19	541	21.5	R2 ²⁷
5	^{NC-CN} ^{NN} ^{Bu} ^{Bu} ^{Bu} ^{Bu} ^{Bu} ^{Bu}	1 wt% polystyrene	~575	96	176.0	0.17	569	20.1	R2 ²⁷
6 (a)	PCNQ-TPA	50wt% CBP	691	90	14.0	-	660	30.3	R3 ²⁸
6 (b)		Non-doped	754	31	13.0	0.04	700	4.6	R3 ²⁸
7	5,8-DCQx-DICz	1 wt% polystyrene	651	40	1.6	0.028	578	12.5	R4 ²⁹

Table S11. Properties of quinoxaline based red TADF emitters.

0	NC CN								
8	6,7-DCQx-DICz	1 wt% polystyrene	603	73	2.5	0.064	603	23.9	R4 ²⁹
9	TFM-QP	5 wt% CBP	N/A	61	5.0	0.04	584	10.7	R5 ³⁰
10		5 wt% CBP	N/A	62	1.6	0.03	584	9.7	R5 ³⁰
11	PXZ-POM	5 wt% DCzDPy	588	70	5.4	0.03	592	20.4	R7 ³¹
12	DPXZ-PQM	5 wt% DCzDPy	586	88	3.8	0.02	590	26	R7 ³¹
13	PXZ-TTPZ	5 wt% PMMA	547	54	10.0	0.09	536	13.9	R8 ³²
14	PTZ-TTPZ	5 wt% PMMA	563	16	9.1	0.07	542	7.6	R8 ³²
15	DMAC-TTPZ	5 wt% PMMA	540	36	20.5	0.15	456	6.5	R8 ³²



	~~~~	5 wt% CBP SP-OLED	682	10.2	303.9	0.15	686	1.7	This work
4PXZ-TPPQ		50 wt% CBP SP-OLED	713	3.5	164.0	0.10	735	0.3	This work
		Non-doped SP-OLED	770	1.5	2.1	0.04	780	0.04	This work
	4PXZ-TPPQ	5 wt% CBP VD-OLED	-	-	-	-	681	3.2	This work



Figure S43. EQE_{max} of reported quinoxaline-based D-A TADF OLEDs as a function of  $\lambda_{EL}$ . Reported quinoxaline-based D-A TADF emitters shown in Table S11.

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