Supporting information
Simultaneous enhancement of thermally activated delayed fluorescence and photoluminescence quantum yield via homoconjugation
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1. Experimental Section

General

All reactants and reagents were purchased from commercial suppliers and used without further purification unless otherwise stated. Column chromatography was carried out using silica gel 60, 40–60 μm mesh (Fluorochem) and Aluminium oxide 90 active neutral 0.063–0.200 mm (70–230 mesh ASTM, Merck). Analytical thin-layer chromatography was performed on precoated aluminum silica gel 60 F254 plates (Merck) and Macherey-Nagel ALUGRAM Alox N/UV254 Aluminum Sheets (Fisher), which were approximately 2 cm x 6 cm in size and visualized using ultraviolet light (254/365 nm).

NMR spectra were recorded on Jeol ECS 400 MHz and Jeol ECZ 500 MHz spectrometers. Chemical shifts are reported in ppm downfield of tetramethylsilane (TMS) using TMS or the residual solvent as an internal reference. NMR spectra were processed using MestReNova. Multiplicities are reported as singlet (s), doublet (d), triplet (t), and multiplet (m). Melting points were determined in open-ended capillaries using a Stuart Scientific SMP10 melting point apparatus at a ramping rate of 1 °C/min. They are recorded to the nearest 1 °C and are uncorrected. IR spectra were collected on a Thermo Scientific Nicolet FTIR spectrometer.

Electrochemistry

Cyclic voltammetry was recorded using a Princeton Applied Research VersaSTAT 3. A glassy carbon disk, Pt wire, and Ag/Ag⁺ (AgNO₃ in acetonitrile) were used as the working, counter, and reference electrodes, respectively. Measurements were corrected to the ferrocene/ferrocenium redox couple as an internal standard. 1,2-Dichlorobenzene was used as the solvent with an analyte molarity of ca. 10⁻⁵ M in the presence of 10⁻¹ M (n-Bu₄N)(PF₆) as a supporting electrolyte. Solutions were degassed with Ar and experiments run under a blanket of Ar.

Photophysics

UV−vis absorbance spectra were measured using a UV-1800 UV−vis spectrophotometer (Shimadzu) and UVProbe version 2.33 software. Photoluminescence (PL) spectra of solutions were recorded using a QePro compact spectrometer (Ocean Optics), FluoroMax-3 fluorescence spectrometer (Jobin Yvon) or a SPEX Fluoromax luminescence spectrometer (Jobin Yvon). Solid-state emission spectra and photoluminescence quantum yield (PLQY) were obtained using an integrating sphere (LabSphere) coupled with a 365 nm LED light source and QePro (Ocean Optics) detector. Photoluminescence decays in film and solution were recorded using nanosecond gated luminescence and lifetime measurements (from 400 ps to 1 s) using the third harmonic of a high-energy pulsed Nd:YAG laser emitting at 355 nm (EKSPLA) as an excitation source. The emitted light was focused onto a spectrograph and detected with a sensitive gated ICCD camera (Stanford Computer Optics) with sub-nanosecond resolution. Time-resolved measurements were performed by exponentially increasing gate and integration times. Further details are available in reference 1. Low temperature experiments were conducted using a liquid nitrogen cryostat VNF-100 (sample in flowing vapour, Janis Research) under nitrogen atmosphere, while measurements at room temperature were recorded under vacuum in the same cryostat. Solutions were degassed using five freeze-pump-thaw cycles. Thin films were deposited from toluene solutions through drop cast or spin coat and dried under vacuum at room temperature.

OLED devices

OLEDs were fabricated by spin-coating / evaporation hybrid method. The hole injection layer (PEDOT AL4083), hole transport / electron blocking layer (PVKH) and emitting layer
(PVK:PBD + emitter) were spin-coated, whereas the electron transport layer (TPBi) and cathode (LiF/Al) were evaporated. Devices of 4 × 2 mm pixel size were fabricated. 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene, (TPBi, LUMTEC); poly(N-vinylcarbazole), M = 1.1 × 10^6 Da (PVKH, Sigma Aldrich); poly(N-vinylcarbazole), M = 90000 Da (PVK, Acros Organics); 5-(4-tert-butylphenyl)-1,3,4-oxadiazole, (PBD, Sigma Aldrich); LiF (99.995%, Sigma Aldrich); and Aluminium pellets (99.9995%, Lesker) were purchased from the companies indicated in parentheses. OLED devices were fabricated using pre-cleaned with ozone plasma indium-tin-oxide (ITO) coated glass substrates with a sheet resistance of 20 Ω cm^−2 and ITO thickness of 100 nm. PEDOT AL4083 was spun-coated and annealed onto a hotplate at 120 °C for 15 min to give a 30 nm film. PVKH layer was spun from chloroform:chlorobenzene (95:5 v/v) (3 mg mL^−1) to give a 10 nm layer. Emitting layer was spun from toluene (10 mg mL^−1). The dopant was dissolved in the solution of blend host in order to obtain final 5 wt % concentration in the emitting layer. All solutions were filtrated directly before application using a PVDF (organic solvents) and PES (PEDOT AL4083) syringe filter with 0.45 μm pore size. All other electron transport and cathode layers were thermally evaporated using Kurt J. Lesker Spectros II deposition system at 10^{-6} mbar base pressure. All organic materials and aluminium were deposited at a rate of 1 Å s^−1. The LiF layer was deposited at a rate of 0.1–0.2 Å s^−1. Characterisation of OLED devices was conducted in a 10-inch integrating sphere (Labsphere) connected to a Source Measure Unit and coupled with a spectrometer USB4000 (Ocean Optics). Further details are available in reference 2.
2. Synthetic Methods

Scheme S2.1 Synthesis of 1 and 2.

Compound 1:

2,3-Bis(4-(10H-phenoxazin-10-yl)phenyl)quinoxaline:

A two-neck flask fitted with a condenser was placed under a N₂ atmosphere. 1,2-Benzenediamine (7 mg, 0.052 mmol) and diketone 3 (30 mg, 0.052 mmol, 1.0 eq.) were added to the flask followed by glacial AcOH (5 mL). The mixture was thoroughly degassed by bubbling with N₂ for 30 min and then heated to reflux overnight. Water (25 mL) was added and the mixture was extracted with EtOAc (3 × 25 mL). The combined organic extracts were washed with satd. NaHCO₃ (aq.) (100 mL), dried over MgSO₄, filtered and the solvent removed under reduced pressure. The residue was recrystallised from an EtOH/CHCl₃ mixture. 1 was isolated via filtration as a yellow crystalline solid (25 mg, 71%). m.p. 270-273°C

₁H NMR (400 MHz, Chloroform-d, ppm) δ = 8.28 (dd, J = 6.4, 3.4 Hz, 2H), 7.88 (dd, J = 6.4, 3.4 Hz, 2H), 7.79 (d, J = 8.2 Hz, 4H), 7.39 (d, J = 8.2 Hz, 4H), 6.74 - 6.56 (m, 8H), 6.51 (t, J = 7.8 Hz, 4H), 5.95 (d, J = 7.6 Hz, 4H). Characterisation in agreement with literature.³
Compound 2:

2,3,9,10,18,19-Hexakis(4-(10H-phenoxazin-10-yl)phenyl)-6,13-dihydro-6,13-[6,7]-epiquinoxalinobenzo[1,2-γ;4,5-γ']diquinoxaline:

A two-neck flask fitted with a condenser was placed under a N₂ atmosphere. Hexaamine hexachloride 4 (32 mg, 0.058 mmol) and diketone 3 (100 mg, 0.17 mmol, 3.0 eq.) were added to the flask followed by AcOH (30 mL). The mixture was thoroughly degassed by bubbling with N₂ for 30 min and then heated to reflux overnight. Water (25 mL) was added and the mixture was extracted with CH₂Cl₂ (3 × 25 mL). The combined organic extracts were washed with satd. NaHCO₃ (aq.), dried over MgSO₄, filtered and the solvent removed under reduced pressure. The residue was purified by column chromatography on neutral alumina (20% CH₂Cl₂/hexane). After evaporation of the column solvent under reduced pressure, the resulting solid was sonicated in MeOH and then isolated via filtration to obtain 2 as a yellow crystalline solid (52 mg, 46%). m.p. > 300 °C

¹H NMR (400 MHz, Chloroform-d, ppm) δ = 8.43 (s, 6H), 7.76 (d, J = 8.2 Hz, 12H), 7.38 (d, J = 8.2 Hz, 12H), 6.73 – 6.57 (m, 24H), 6.51 (t, J = 7.6 Hz, 12H), 6.28 (s, 2H), 5.94 (d, J = 7.6 Hz, 12H).

¹³C NMR (101 MHz, Chloroform-d, ppm) δ = 152.8, 144.4, 144.1, 140.8, 140.1, 138.9, 134.0, 132.7, 131.1, 124.4, 123.5, 121.8, 115.7, 113.3, 53.4.

HRMS (ESI): m/z 1953.6318 [M⁺]. Calcd. for C₁₃₄H₈₀N₁₂O₆+: 1953.6352.
Compound 3:

1,2-Bis(4-(10H-phenoxazin-10-yl)phenyl)ethane-1,2-dione:

10-(4-Bromophenyl)-10H-phenoxazine (300 mg, 0.89 mmol) was dissolved in dry THF (4 mL) and cooled to −78 °C. n-BuLi (0.34 mL, 0.85 mmol, 2.5M in hexanes) was added dropwise and the reaction stirred for 1 hr at −78 °C. Diphenylparabanic acid (97 mg, 0.40 mmol) in dry THF (4 mL) was added dropwise to the mixture. The reaction was stirred for 6 hr while maintaining the temperature at −78 °C. Without warming to room temperature, the mixture was poured directly into saturated aqueous NH₄Cl and then allowed to warm to ambient temperature. The mixture was transferred to a separating funnel and extracted with EtOAc (3 x 15 mL) and the combined organic portions washed with brine (75 mL), dried over MgSO₄, filtered and the solvent removed under reduced pressure. The resulting solid was washed with chloroform and any solids removed by filtration. The filtrate was purified by column chromatography on SiO₂ (30% CH₂Cl₂/hexane) followed by recrystallisation from EtOH to obtain 3 as a dark red crystalline solid (30 mg, 13%). m.p. 186-188 °C

¹H NMR (400 MHz, Chloroform-d, ppm) δ = 8.30 – 8.22 (m, 4H), 7.61 – 7.54 (m, 4H), 6.78 – 6.69 (m, 8H), 6.68 – 6.61 (m, 4H), 6.05 (dd, J = 7.9, 1.3 Hz, 4H).

¹³C NMR (101 MHz, Chloroform-d, ppm) δ = 192.7, 146.0, 144.4, 133.4, 132.9, 132.3, 131.3, 123.5, 122.5, 116.1, 113.9.

IR (v_max/cm⁻¹) 3061, 1678, 1591, 1486, 1463, 1330, 1271, 1203, 1014, 871, 728

HRMS (ESI): m/z 572.1724 [M⁺]. Calcd. for C₃₈H₂₄N₂O₄⁺: 572.1736.

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Elemental Composition Report

Tolerance = 1000.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: OFF

Monoisotopic Mass, Odd and Even Electron Ions

4 formulas calculated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:
C: 0.38 H: 14.24 N: 0.2 O: 0.4

GCD-Dcalc GCD-Dcalc 4 (0.104 Cm (28))

Minimum: 5.0

Maximum: 1000.0

Mass Calc. Mass mDa PPM DBE Formula
572.1724 572.1736 -1.2 -2.1 28.0 C₃₈H₂₄N₂O₄
3. NMR spectra

Figure S3.1. Compound 1 $^1$H NMR spectrum.
Figure S3.2. Compound 2 $^1$H NMR spectrum.
Figure S33. Compound 2 13C spectrum.
Figure S3.4. Compound 3 $^1$H NMR spectrum.
Figure S3.5. Compound 3 $^{13}$C NMR spectrum.
4. **X-ray crystallography**

1A·CDCl$_3$ (needles) and 1B·CDCl$_3$ (blocks) were grown from the same deuterochloroform solution, and the diffraction data were collected at the ALS synchrotron, beam line 12.2.1 due to small crystal size. The data for 1B·CDCl$_3$ showed evidence of twinning via a ca. 2-3° rotation between domains and the approximately de-twinned data gave the best overall result. Diffraction data for 2·7CHCl$_3$ were collected on a sealed tube micro-source diffractometer. Full data collection and refinement details are provided in Tables S4.1-4.3, while Figures S4.1-4.7 show molecular and packing plots. In both 1A·CDCl$_3$ and 1B·CDCl$_3$ the deuterochloroform makes a weak Cl$_3$C–D···N interaction and the molecular conformations are also quite similar. However, the packing motifs between the two polymorphs are different. For 1A·CDCl$_3$ there are a number of π···π stacking interactions, some of them slipped or not fully perpendicular. The most significant, in terms of having parallel rings, is an intramolecular interaction between ring N(1)/C(1)/C(6)/O(1)/C(7)/C(12) and ring C(20) > C(25). Here the shortest contacts are as short as ca. 3.27 Å between O(1) and C(20'). Unlike 1A·CDCl$_3$, there are some weak Cl(3)···O(2) interactions at 3.169 Å in 1B·CDCl$_3$. While there are some edge-to-face interactions between aromatic rings, the is no close π···π stacking, the closest being at ca. 3.9 Å. The molecules form into thick bands/layers in the a/b plane. For 2·7CHCl$_3$ there was some evidence of partial de-solvation, so the total number of solvent molecules of crystallisation should be taken as approximate. One of the four chloroform molecules was refined at half weight. The molecule lies on a symmetry element, so half is unique.
Table S4.1 Experimental details for the monoclinic polymorph 1A·CDCl₃.

| Crystal data |        |
|--------------|--------|
| Chemical formula | C₄₄H₂₈N₄O₂·CDCl₃ |
| M (g/mol) | 765.08 |
| Crystal system, space group | Monoclinic, P2₁/c |
| Temperature (K) | 100 |
| a, b, c (Å) | 10.6447 (4), 30.3665 (11), 11.1066 (4) |
| β (°) | 98.961 (1) |
| V (Å³) | 3546.3 (2) |
| Z | 4 |
| Radiation type | Synchrotron, λ = 0.7288 Å |
| μ (mm⁻¹) | 0.32 |
| Crystal size (mm³) | 0.30 x 0.05 x 0.02 |

| Data collection |        |
|----------------|--------|
| Diffractometer | Bruker D8 with PHOTON 100 detector, silicon 111 monochromator. |
| Absorption correction | Multi-scan SADABS v2016/2, Sheldrick, G.M., (2016) |
| Tmin, Tmax | 0.702, 0.746 |
| No. of measured, independent and observed [F > 2σ(F)] reflections | 257132, 10853, 10213 |
| Rint | 0.037 |
| (sin θ/λ)max (Å⁻¹) | 0.715 |

| Refinement |        |
|-------------|--------|
| R[F > 2σ(F)], wR(F), S | 0.046, 0.124, 1.11 |
| No. of reflections | 10853 |
| No. of parameters | 603 |
| No. of restraints | 3 |
| H-atom treatment | All H-atom parameters refined |
| Δu(max), Δu(min) (e Å⁻³) | 0.93, -0.67 |

Computer programs: Bruker APEX2, Bruker SAINT v8.38a, SHELXT 2014/5 (Sheldrick, 2014), SHELX2018/3 (Sheldrick, 2018), Bruker SHELXTL.
### Table S4.2 Experimental details for the triclinic polymorph 1B·CDCl₃.

| Crystal data                                      |       |
|--------------------------------------------------|-------|
| Chemical formula                                  | C₉₄H₇₈N₄O₂·CDCl₃ |
| **M**                                            | 765.08 |
| Crystal system, space group                       | Triclinic, P’ 1 |
| Temperature (K)                                   | 100   |
| **a, b, c (Å)**                                   | 10.6041 (7), 11.1981 (7), 15.4055 (10) |
| **α, β, γ (°)**                                   | 78.882 (3), 82.039 (3), 80.742 (3) |
| **V (Å³)**                                        | 1760.7 (2) |
| **Z**                                            | 2     |
| Radiation type                                    | Synchrotron, λ = 0.7288 Å |
| **µ (mm⁻¹)**                                      | 0.33  |
| Crystal size (mm³)                                | 0.12 × 0.10 × 0.07 |

| Data collection                                   |       |
|--------------------------------------------------|-------|
| Diffractometer                                    | Bruker D8 with PHOTON 100 detector, silicon 111 monochromator. |
| Absorption correction                             | Multi-scan TWINABS v2012/1, Sheldrick, G.M., (2012) |
| **T_{min}, T_{max}**                              | 0.962, 0.978 |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 57756, 10733, 9162 |
| **R_{int}**                                       | 0.046 |
| (sin θ/λ)_{max} (Å⁻¹)                             | 0.716 |

| Refinement                                        |       |
|--------------------------------------------------|-------|
| **R(F² > 2σ(F²)), wR(F²), S**                     | 0.043, 0.125, 1.11 |
| No. of reflections                                | 10733 |
| No. of parameters                                 | 487   |
| H-atom treatment                                  | H-atom parameters constrained |
| Δψ_{max}, Δσ_{min} (e Å⁻³)                         | 0.64, -0.62 |

Computer programs: Bruker APEX 2, Bruker SAINT v8.38a, SHELXT 2014/5 (Sheldrick, 2014), SHELXL2018/3 (Sheldrick, 2018), Bruker SHELXTL.
Table S4.3 Experimental details for 2·7CHCl₃.

| Crystal data |  |
|--------------|---|
| Chemical formula | C₁₃₄H₈₀N₁₂O₆·7(CHCl₃) |
| M | 2789.67 |
| Crystal system, space group | Orthorhombic, Fdd2 |
| Temperature (K) | 180 |
| a, b, c (Å) | 55.721 (3), 20.5478 (10), 22.9320 (11) |
| V (Å³) | 26256 (2) |
| Z | 8 |
| Radiation type | Cu Kα |
| μ (mm⁻¹) | 4.50 |
| Crystal size (mm³) | 0.18 × 0.18 × 0.12 |

| Data collection |  |
|----------------|---|
| Diffractometer | Bruker D8-QUEST PHOTON-III |
| Absorption correction | Multi-scan SADABS (Bruker, 2014) |
| Tmin, Tmax | 0.579, 0.753 |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 142603, 12043, 11300 |
| Rint | 0.071 |
| (sin θ/λ)max (Å⁻¹) | 0.603 |

| Refinement |  |
|-------------|---|
| R[F > 2σ(F²)], wR(F²), S | 0.074, 0.206, 1.04 |
| No. of reflections | 12043 |
| No. of parameters | 829 |
| No. of restraints | 172 |
| H-atom treatment | H-atom parameters constrained |
| w = 1/[σ²(F²)² + (0.1408P)² + 101.4564P] where P = (F² + 2Fc²)/3 |
| Δρmax, Δρmin (e Å⁻³) | 0.71, -0.62 |
| Absolute structure | Flack x determined using 5083 quotients [((I+)-(I-))/((I+)+(I-))] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259). |
| Absolute structure parameter | 0.026 (14) |

Computer programs: APEX3 (Bruker, 2016), SAINT (Bruker, 2016), SHELXT 2018/2 (Sheldrick, 2018), SHELXL2018/3 (Sheldrick, 2018), Mercury (Macrae et al., 2008) & SHELXTL, SHELXL.
Figure S4.1. X-ray structure of the monoclinic polymorph 1A·CDCl₃.

Twist angles between planes:
3 rings N(1) > C(12) vs C(13) > C(18) = 64.81(3)°
C(13) > C(18) vs 2 rings C(19) > C(26) = 63.04(3)°
2 rings C(19) > C(26) vs C(27) > C(32) = 40.63(5)°
C(27) > C(32) vs 3 rings N(4) > C(44) = 79.18(4)°
3 rings N(4) > C(44) vs 3 rings N(1) > C(12) = 34.76(2)°
C(13) > C(18) vs C(27) > C(32) = 65.50(4)°
Figure S4.2. Packing plot of the monoclinic polymorph 1A·CDCl₃ viewed parallel to a.

Figure S4.3. Packing plot of the monoclinic polymorph 1A·CDCl₃ viewed parallel to c.
Figure S4.4. X-ray structure of the triclinic polymorph 1B·CDCl₃.

Twist angles between planes:

- 3 rings N(1) > C(12) vs C(13) > C(18) = 65.90(3)°
- C(13) > C(18) vs 2 rings C(19) > C(26) = 63.72(3)°
- 2 rings C(19) > C(26) vs C(27) > C(32) = 43.19(4)°
- C(27) > C(32) vs 3 rings N(4) > C(44) = 71.74(3)°
- 3 rings N(4) > C(44) vs 3 rings N(1) > C(12) = 22.41(2)°
- C(13) > C(18) vs C(27) > C(32) = 65.90(3)°
Figure S4.5. Packing plot of the triclinic polymorph 1B·CDCl₃ viewed parallel to a.

Figure S4.6. Packing plot of the triclinic polymorph 1B·CDCl₃ viewed parallel to b.
Figure S4.7. Alternative plot of 2·7CHCl₃ showing the location of chloroform molecules and the C–H···π interaction with aromatic rings. Non-chloroform H atoms have been omitted for clarity.
5. **Electrochemistry**

Table S5.1 Electrochemical data.

|       | $E^{ox}$ a,b (V) | $E^{red1}$ (V) | $E^{red2}$ (V) | $E^{red3}$ (V) | HOMOc (eV) | LUMOc (eV) |
|-------|------------------|----------------|----------------|----------------|------------|------------|
| Mono  | +0.40/+0.21      | -2.21/-2.06    | -              | -              | -5.35      | -3.07      |
| Trip  | +0.38/+0.13(sp)c | -2.08/-2.01    | -2.20/-2.12    | -2.28/-2.19    | -5.33      | -3.12      |

a Recorded by cyclic voltammetry (ca. 10^{-4} M in 1,2-dichlorobenzene) using a glassy carbon working electrode, Pt wire counter electrode and Ag/Ag(NO$_3$)$_2$+ reference electrode with (nBu)$_4$NPF$_6$ as supporting electrolyte (0.1 M) at a scan rate of 100 mV s$^{-1}$. The data were referenced to the FcH/FcH$^+$ redox couple, which has a HOMO of −5.10 eV. b The peaks are quoted as anodic/cathodic for oxidation and cathodic/anodic for reduction. c HOMO and LUMO levels calculated from the onset of the first oxidation and reduction waves respectively and are referenced the HOMO of ferrocene at −5.10 eV. sp = stripping peak.

Cyclic voltammetry reveals a single oxidation wave and a single reduction wave for 1. Both of which are essentially reversible. The current response for the oxidation wave is twice that of the reduction but no narrowing of the peak separation occurs. This indicates that both phenoxazine moieties are oxidised simultaneously to radical cations with no significant electronic coupling between the two donors. The reduction occurs over the quinoxaline acceptor to form a radical anion.

The voltammetry of 2 is much more complex. Similarly to 1 and in line with previous observations, as the voltage increases beyond the oxidation potential a multi-electron oxidation occurs. Upon reversal of polarity the reverse wave is cathodically shifted and displays an even larger peak current response which tails off sharply. This cathodic stripping peak indicates that upon oxidation the molecule undergoes electrodeposition onto the electrode surface via the phenoxazine rings of either two or three fins of the triptycene. While this could be eliminated by introducing substituents to the reactive 3- and 7- positions of the phenoxazine rings, it indicates that such scaffolds have the potential for surface functionalisation of electrodes.

The reduction wave for 2 presents itself as three closely overlapping single electron reductions, one for each fin. This is further experimental proof of homoconjugation in the LUMO manifold as without any significant electronic communication between the fins one single, well-defined reduction would be expected.

The oxidation potential for both molecules is similar and the onset of oxidation identical showing that the position of the HOMO has not changed between the single fin and the iptycene. The first reduction potential is marginally higher for iptycene 2 so the LUMO is slightly more accessible. This indicates that 2 has a narrower band gap which is replicated by the redshift in the onset of absorbance and through DFT analysis.
6. Density Functional Theory

Geometries were optimised using PBE0/def2svp with Gaussian 09.6

Electron-hole analysis

Natural transition orbitals for states calculated in the ground state geometry with TD-PBE0/def2svp are shown in figures S6.1–6.32. Hole densities are in blue and particle densities in green. The results from electron-hole analysis used to determine excited state character are shown in Table S6.1

Hole-electron analysis was conducted using Multiwfn.7-9. In electron-hole analysis the Sr index is a measure to characterize the overlapping extent of holes and electrons by integration of the geometric mean of their charge densities over all space, which approaches zero as CT character increases. The D index is the total magnitude of CT length as measured by the distance between the centres of mass of electrons and holes, hence D typically increases with CT character. The t index represents the difference between the D index and the average spatial extension degree of hole and electron distribution in the CT direction, characterizing the separation degree of holes and electrons in the CT direction. Negative t indices imply that the holes and electrons are not substantially separated due to CT.

It is important to consider all parameters when assigning state character. For example, a CT state spread symmetrically across all the three iptycene fins of 2 (e.g., the T3 state – Figure S6.8) will demonstrate a small D index as the hole and electron centroids are each technically over the centre of the molecule. However, hole and electron overlap is still low, and so the state can be assigned as CT based on the Sr index being close to zero. During analysis, we also noticed that when spread across multiple fins of 2, negative t indices could be observed even for states of clear CT character based on Sr and D indices e.g. S1 and T1.

The S1 state of 2 is assigned as CT in nature due to the low Sr index and high D index. Both the hole and electron are primarily localised over fin A. A marginally negative t index is observed for S1, although not as negative as for states of clear LE character such as T13 (Figure S6.30). The slightly negative t index of S1 is expected to be related to the molecular symmetry of 2, which complicates assignment of a clear CT direction.

The electron-hole analysis for T1 is near-identical to that of S1, meaning both states are the same in configuration (CT) with the same spatial distribution.

The difference in the localisation of the CT state T8 compared to S1 is indicated by electron-hole analysis - T8 has a significantly larger D index than S1, and a more positive t index.
Table S6.1. Computational results for SOCME calculations and electron-hole analysis.

| Compound | State | $\Delta E_{S_1-T_n}$ / eV$^a$ | SOCME$_{S_1-T_n}$ / cm$^{-1}$ $^b$ | $S_r$ index/ a.u.$^c$ | D index/ Å$^d$ | t index/ Å$^e$ | Assignment$^c$ |
|----------|-------|-------------------------------|-----------------------------------|----------------|----------------|---------------|----------------|
| S1       |       | -                             | -                                 | 0.08           | 6.8            | 5.0           | CT            |
| 1        | $T_1$ | 0.01                          | 0.05                              | 0.08           | 6.8            | 4.9           | CT            |
|          | $T_3$ | -0.19                         | 0.23                              | 0.72           | 0.6            | -2.0          | LE            |
| S1       |       | -                             | -                                 | 0.12           | 4.3            | -1.1          | CT            |
|          | $T_1$ | 0.03                          | 0.05                              | 0.12           | 4.6            | -0.6          | CT            |
|          | $T_7$ | -0.17                         | 0.29                              | 0.09           | 7.0            | 1.7           | CT            |
| 2        | $T_8$ | -0.17                         | 0.90                              | 0.11           | 5.7            | 0.0           | CT            |
|          | $T_{13}$ | -0.32                       | 0.11                             | 0.59           | 0.5            | -3.4          | LE            |
|          | $T_{14}$ | -0.32                       | 0.08                             | 0.58           | 0.4            | -3.7          | LE            |
|          | $T_{15}$ | -0.35                       | 0.12                             | 0.65           | 0.1            | -4.6          | LE            |

$^a$Calculated energy gap between $S_1$ and $T_n$; $^b$Calculated spin-orbit coupling matrix element between $S_1$ and $T_n$; $^c$CT = charge transfer, LE = locally excited.

Commented [PPH1]: Shouldn't this be called "spin-orbit coupling matrix element (SOCME)?" I use term SOCME after Tom Penfold and others, but perhaps simply spin-orbit coupling is sort of clear enough?
**Compound 1**

$T_1$

Figure S6.1. Overlaid HONTO and LUNTO for $T_1$.

Sm index (integral of Sm function): 0.01797 a.u.

Sr index (integral of Sr function): **0.08210 a.u. = CT state**

Centroid of hole in X/Y/Z: -0.018595 -2.199800 0.001119 Å

Centroid of electron in X/Y/Z: 0.002782 4.630975 -0.000767 Å

$D_z$: 0.021  $D_y$: 6.831  $D_x$: 0.002  D index: **6.831 Å = CT state**

$\Gamma$ index: 4.943 Å

Excitation energy of this state: 2.292 eV
Figure S6.2. Overlaid HONTO and LUNTO for T₂.

Sm index (integral of Sm function): 0.01722 a.u.
Sr index (integral of Sr function): 0.07873 a.u. = CT state
Centroid of hole in X/Y/Z: 0.013482 -2.204666 -0.000892 Å
Centroid of electron in X/Y/Z: 0.002769 4.625544 -0.000764 Å
D₀: 0.911 D₀: 6.830 D₀: 0.000 D index: 6.830 Å = CT state
τ index: 4.944 Å
Excitation energy of this state: 2.296 eV
**Figure S6.3.** Overlaid HONTO and LUNTO for $S_1$

- Sm index (integral of Sm function): 0.01791 a.u.
- Sr index (integral of Sr function): 0.08190 a.u. = CT state
- Centroid of hole in X/Y/Z: -0.018768 -2.199774 0.001130 Å
- Centroid of electron in X/Y/Z: 0.002802 4.639737 -0.000771 Å
- $D_h$: 0.022 $D_z$: 6.840 $D_t$: 0.002 $D$ index: 6.840 Å = CT state
- L index: 4.955 Å
- Excitation energy of this state: 2.300 eV
Figure S6.4. Overlaid HONTO and LUNTO for $S_2$.

Sm index (integral of Sm function): 0.01723 a.u.

Sr index (integral of Sr function): 0.07884 a.u. = CT state

Centroid of hole in X/Y/Z: 0.013708 -2.204701 -0.000906 Å

Centroid of electron in X/Y/Z: 0.002796 4.637011 -0.000769 Å

$D_x$: 0.011 $D_y$: 6.842 $D_z$: 0.000  D index: 6.842 Å = CT state

t index: 4.959 Å

Excitation energy of this state: 2.303 eV
Figure S6.5. Overlaid HONTO and LUNTO for T₃.

Transition dipole moment in X/Y/Z: -0.003249 -0.002337 0.142537 a.u.
Sm index (integral of Sm function): 0.49505 a.u.
Sr index (integral of Sr function): 0.71856 a.u. = LE state
Centroid of hole in X/Y/Z: -0.002244 4.978975 0.000849 Å
Centroid of electron in X/Y/Z: 0.002234 4.390585 -0.000646 Å

Dₓ: 0.004 Dᵧ: 0.588 Dz: 0.001 D index: 0.588 Å = LE state

t index: -1.954 Å
Excitation energy of this state: 2.493 eV
Figure S6.6. Overlaid HONTO and LUNTO for T₁

Sm index (integral of Sm function): 0.02491 a.u.

Sr index (integral of Sr function): **0.11870 a.u.** = CT state

Centroid of hole in X/Y/Z: -3.612638 -5.517071 0.003541 Å

Centroid of electron in X/Y/Z: -1.168159 -1.587959 -0.005204 Å

D₀: 2.444 Dₓ: **3.929** Dᵧ: **0.009** D index: **4.627 Å** = CT state
t index: -0.635 Å

Excitation energy of this state: **2.194 eV**
Figure S6.7. Overlaid HONTO and LUNTO for $T_2$.

Sm index (integral of Sm function): 0.02466 a.u.
Sr index (integral of Sr function): 0.11662 a.u. = CT state
Centroid of hole in X/Y/Z: 3.192713 4.891586 0.030674 Å
Centroid of electron in X/Y/Z: 1.080336 1.423999 -0.006728 Å
$D_x$: 2.112 $D_y$: 3.468 $D_z$: 0.037 D index: 4.061 Å = CT state
t index: -1.057 Å
Excitation energy of this state: 2.194 eV
Figure S6.8. Overlaid HONTO and LUNTO for $T_3$.

Sm index (integral of Sm function): 0.02470 a.u.
Sr index (integral of Sr function): 0.11861 a.u. = CT state
Centroid of hole in X/Y/Z: 0.249664 0.185004 0.018569 Å
Centroid of electron in X/Y/Z: 0.097605 0.108792 -0.006053 Å

$D_x$: 0.152 $D_y$: 0.076 $D_z$: 0.025 D index: 0.172 Å = CT state (small due to symmetry)

t index: -5.870 Å
Excitation energy of this state: 2.195 eV
Figure S6.9. Overlaid HONTO and LUNTO for $S_1$

$S_1$ index (integral of $S_m$ function): 0.02560 a.u.
$S_r$ index (integral of $S_r$ function): 0.12199 a.u. = CT state
Centroid of hole in X/Y/Z: -3.292293 -5.145993 0.004706 Å
Centroid of electron in X/Y/Z: -1.061822 -1.445942 -0.005265 Å

$D_x$: 2.230  $D_y$: 3.700  $D_z$: 0.010  D index: 4.320 Å = CT state
r index: -1.070 Å
Excitation energy of this state: 2.218 eV
S₂

Figure S6.10. Overlaid HONTO and LUNTO for S₂.

Sm index (integral of Sm function): 0.02526 a.u.
Sr index (integral of Sr function): 0.11948 a.u. = CT state
Centroid of hole in X/Y/Z: 3.181854 4.900438 0.030657 Å
Centroid of electron in X/Y/Z: 1.051525 1.386288 -0.006683 Å
D_x: 2.130   D_y: 3.514   D_z: 0.037   D index: 4.110 Å = CT state
t index: -1.013 Å
Excitation energy of this state: 2.218 eV
Figure S6.11. Overlaid HONTO and LUNTO for T₄.

Sm index (integral of Sm function): 0.02130 a.u.

Sr index (integral of Sr function): 0.10509 a.u. = CT state
Centroid of hole in X/Y/Z: -4.250599 -5.208709 -0.007709 Å
Centroid of electron in X/Y/Z: -1.246657 -1.691663 -0.005135 Å
Dₛ: 3.004 Dᵢ: 3.517 Dᵣ: 0.003 D index: 4.625 Å = CT state
l index: -0.615 Å
Excitation energy of this state: 2.223 eV
Figure S6.12. Overlaid HONTO and LUNTO for $T_5$.

Sm index (integral of Sm function): 0.02119 a.u.
Sr index (integral of Sr function): 0.10332 a.u. = CT state
Centroid of hole in X/Y/Z: 3.582035 4.610399 0.002459 Å
Centroid of electron in X/Y/Z: 1.084457 1.429547 -0.006732 Å

$D_x$: 2.498 $D_y$: 3.181 $D_z$: 0.009 D index: 4.044 Å = CT state
$t$ index: -1.218 Å

Excitation energy of this state: 2.223 eV
Figure S6.13. Overlaid HONTO and LUNTO for T₆.

Sm index (integral of Sm function): 0.02132 a.u.

Sr index (integral of Sr function): **0.10461 a.u. = CT state**

Centroid of hole in X/Y/Z: -0.071166 -0.412190 -0.002612 Å

Centroid of electron in X/Y/Z: 0.124547 0.145206 -0.006065 Å

Dₓ: 0.196  Dᵧ: 0.557  Dᵦ: 0.003  D index: 0.591 Å = CT state (small due to symmetry)

t index: -5.452 Å

Excitation energy of this state: 2.224 eV
Figure S6.14. Overlaid HONTO and LUNTO for $S_3$.

Sm index (integral of Sm function): 0.02536 a.u.
Sr index (integral of Sr function): 0.12191 a.u. = CT state

Centroid of hole in X/Y/Z: 0.065425 0.009600 0.017932 Å
Centroid of electron in X/Y/Z: 0.039405 0.030226 -0.005999 Å
$D_x$: 0.026  $D_y$: 0.021  $D_z$: 0.024  $D$ index: 0.041 Å = CT state (small due to symmetry)

$t$ index: -5.209 Å

Excitation energy of this state: 2.225 eV
Figure S6.15. Overlaid HONTO and LUNTO for $S_4$.

Sm index (integral of Sm function): 0.02201 a.u.

Sr index (integral of Sr function): 0.10832 a.u. = CT state

Centroid of hole in X/Y/Z: -6.143287 -7.936123 -0.010269 Å

Centroid of electron in X/Y/Z: -1.711425 -2.317432 -0.004840 Å

$D_x$: 4.432 $D_y$: 5.619 $D_z$: 0.065 $D$ index: 7.156 Å = CT state

$t$ index: 3.235 Å

Excitation energy of this state: 2.244 eV
Figure S6.16. Overlaid HONTO and LUNTO for \( S_5 \).

Sm index (integral of Sm function): 0.02217 a.u.

Sr index (integral of Sr function): 0.10810 a.u. = CT state

Centroid of hole in X/Y/Z: 3.585129 4.608671 0.002461 Å

Centroid of electron in X/Y/Z: 1.050644 1.384846 -0.006687 Å

\( D_x: 2.534 \) \( D_y: 3.224 \) \( D_z: 0.009 \) D index: 4.101 Å = CT state

\( t \) index: -1.169 Å

Excitation energy of this state: 2.244 eV
Figure S6.17. Overlaid HONTO and LUNTO for S₆.

Sm index (integral of Sm function): 0.02245 a.u.
Sr index (integral of Sr function): 0.10994 a.u. = CT state
Centroid of hole in X/Y/Z: 2.602688 3.374401 0.000943 Å
Centroid of electron in X/Y/Z: 0.706331 0.924736 -0.006439 Å
Dₓ: 1.896 Dᵧ: 2.320 Dz: 0.007 D index: 2.996 Å = CT state
t index: -2.682 Å
Excitation energy of this state: 2.244 eV
Figure S6.18. Overlaid HONTO and LUNTO for T7.

Sm index (integral of Sm function): 0.02009 a.u.

Sr index (integral of Sr function): 0.09367 a.u. = CT state

Centroid of hole in X/Y/Z: 3.138583 4.936183 0.030583 Å

Centroid of electron in X/Y/Z: -0.653708 -0.906086 -0.005545 Å

Dh: 3.792 Dh: 5.842 Dh: 0.036 D index: 6.965 Å = CT state

t index: 1.688 Å

Excitation energy of this state: 2.383 eV
Figure S6.19. Overlaid HONTO and LUNTO for $T_8$.

Sm index (integral of Sm function): 0.02367 a.u.

Sr index (integral of Sr function): 0.11326 a.u. = CT state
Centroid of hole in X/Y/Z: -2.381561 -4.117229 0.007989 Å
Centroid of electron in X/Y/Z: 0.545773 0.714738 -0.006196 Å
$D_h$: 2.927 $D_v$: 4.832 $D_e$: 0.014 $D$ index: 5.650 Å = CT state
$t$ index: 0.004 Å
Excitation energy of this state: 2.383 eV
Figure S6.20. Overlaid HONTO and LUNTO for S7.

Sm index (integral of Sm function): 0.02009 a.u.

Sr index (integral of Sr function): 0.09367 a.u. = CT state
Centroid of hole in X/Y/Z: 3.138818 4.936284 0.030585 Å
Centroid of electron in X/Y/Z: -0.655489 -0.908493 -0.005544 Å
Dx: 3.794 Dy: 5.845 Dz: 0.036 D index: 6.968 Å = CT state
l index: 1.691 Å

Excitation energy of this state: 2.383 eV
Figure S6.21. Overlaid HONTO and LUNTO for $S_8$.

Sm index (integral of Sm function): 0.02416 a.u.
Sr index (integral of Sr function): 0.11543 a.u. = CT state
Centroid of hole in X/Y/Z: -2.060481 -3.719732 0.009179 Å
Centroid of electron in X/Y/Z: 0.488122 0.636835 -0.006165 Å
$D_x$: 2.549 $D_y$: 4.357 $D_z$: 0.015 D index: 5.047 Å = CT state
$t$ index: -0.675 Å
Excitation energy of this state: 2.383 eV
Figure S6.22. Overlaid HONTO and LUNTO for T₉.

Sm index (integral of Sm function): 0.02532 a.u.

Sr index (integral of Sr function): 0.12199 a.u. = CT state

Centroid of hole in X/Y/Z: -0.437840 -0.469819 0.016189 Å

Centroid of electron in X/Y/Z: 0.147465 0.176516 -0.005980 Å

Dₓ: 0.585  Dᵧ: 0.646  Dz: 0.022  D index: 0.872 Å = CT state (small due to symmetry)

t index: -5.183 Å

Excitation energy of this state: 2.384 eV
Figure S6.23. Overlaid HONTO and LUNTO for $S_9$.

Sm index (integral of Sm function): 0.02520 a.u.

Sr index (integral of Sr function): 0.12139 a.u. = CT state

Centroid of hole in X/Y/Z: -0.619185 -0.642524 0.015566 Å

Centroid of electron in X/Y/Z: 0.204954 0.254200 -0.006011 Å

$D_z: 0.824 \ D_y: 0.897 \ D_x: 0.022 \ D$ index: 1.218 Å = CT state (small due to symmetry)

t index: -4.831 Å

Excitation energy of this state: 2.384 eV
Figure S6.24. Overlaid HONTO and LUNTO for T_{10}.

Sm index (integral of Sm function): 0.01733 a.u.
Sr index (integral of Sr function): **0.08232 a.u. = CT state**

Centroid of hole in X/Y/Z: 3.594375 4.604988 0.002480 Å
Centroid of electron in X/Y/Z: -0.660556 -0.915339 -0.005541 Å

**D_x**: 4.255  **D_y**: 5.520  **D_z**: 0.008  **D index**: **6.970 Å = CT state**

t index: 1.622 Å

Excitation energy of this state: **2.410 eV**
Figure S6.25, Overlaid HONTO and LUNTO for S₁₀.

Sm index (integral of Sm function): 0.01717 a.u.

Sr index (integral of Sr function): **0.08150** a.u. = CT state

Centroid of hole in X/Y/Z: 3.587187 4.609040 0.002477 Å
Centroid of electron in X/Y/Z: -0.668027 -0.925435 -0.005537 Å

Dₓ: 4.255  Dᵧ: 5.534  Dₜ: 0.008  D index: **6.981** Å = CT state

t index: 1.635 Å

Excitation energy of this state: **2.410** eV
Figure S6.26. Overlaid HONTO and LUNTO for T₁₁.

Sm index (integral of Sm function): 0.02030 a.u.
Sr index (integral of Sr function): 0.09900 a.u. = CT state
Centroid of hole in X/Y/Z: 2.502977 3.724325 0.001087 Å
Centroid of electron in X/Y/Z: -0.402923 -0.567207 -0.005681 Å
Dₓ: 2.906 Dᵧ: 4.292 Dₜ: 0.067 D index: 5.163 Å = CT state
l index: -0.439 Å
Excitation energy of this state: 2.410 eV
Figure S6.27. Overlaid HONTO and LUNTO for S_{11}.

Sm index (integral of Sm function): 0.01997 a.u.
Sr index (integral of Sr function): 0.09701 a.u. = CT state
Centroid of hole in X/Y/Z: 2.623446 3.861379 0.001215 Å
Centroid of electron in X/Y/Z: -0.535572 -0.746452 -0.005609 Å
D_x: 3.159 D_y: 4.608 D_z: 0.007 D index: 5.587 Å = CT state
l index: 0.007 Å
Excitation energy of this state: 2.410 eV
Figure S6.28. Overlaid HONTO and LUNTO for $T_{12}$.

Sm index (integral of Sm function): 0.01404 a.u.

Sr index (integral of Sr function): 0.07006 a.u. = CT state

Centroid of hole in X/Y/Z: -5.249123 -7.439308 -0.009407 Å

Centroid of electron in X/Y/Z: 1.072040 1.425867 -0.006481 Å

$D_x$: 6.321 $D_y$: 8.865 $D_z$: 0.003 D index: 10.886 Å = CT state

f index: 6.469 Å

Excitation energy of this state: 2.410 eV
Figure S6.29. Overlaid HONTO and LUNTO for $S_{\text{12}}$.

Sm index (integral of Sm function): 0.00960 a.u.

Sr index (integral of Sr function): 0.04829 a.u. = CT state

Centroid of hole in X/Y/Z: -6.191527 -8.567761 -0.010582 Å

Centroid of electron in X/Y/Z: 1.240238 1.653148 -0.006573 Å

$D_x$: 7.432 $D_y$: 10.221 $D_z$: 0.004 $D$ index: 12.637 Å = CT state

Excitation energy of this state: 2.410 eV
Figure S6.30. Overlaid HONTO and LUNTO for T_{13}.

Sm index (integral of Sm function): 0.40151 a.u.
Sr index (integral of Sr function): 0.58534 a.u. = LE state
Centroid of hole in X/Y/Z: -1.037610 -1.374274 0.001246 Å
Centroid of electron in X/Y/Z: -1.428693 -1.707979 -0.005203 Å
D_x: 0.391 D_y: 0.334 D_z: 0.006 D index: 0.514 Å = LE state
Excitation energy of this state: 2.534 eV
Figure S6.31. Overlaid HONTO and LUNTO for T_{14}.

Sm index (integral of Sm function): 0.39896 a.u.
Sr index (integral of Sr function): 0.58480 a.u. = LE state
Centroid of hole in X/Y/Z: 1.085387 1.495412 -0.002686 Å
Centroid of electron in X/Y/Z: 1.440357 1.682246 -0.006740 Å
D_x: 0.355 D_y: 0.187 D_z: 0.004 D index: 0.401 Å = LE state
t index: -3.720 Å
Excitation energy of this state: 2.534 eV
Figure S6.32. Overlaid HONTO and LUNTO for T₁₅.

Sm index (integral of Sm function): 0.43951 a.u.
Sr index (integral of Sr function): 0.64513 a.u. = LE state
Centroid of hole in X/Y/Z: -0.018423 -0.058960 0.001566 Å
Centroid of electron in X/Y/Z: 0.023742 0.007746 -0.005811 Å
Dₓ: 0.042 Dᵧ: 0.067 Dz: 0.007 D index: 0.079 Å = LE state
t index: -4.586 Å
Excitation energy of this state: 2.566 eV
Figure S6.33. Selected molecular orbital plots for 1 with calculated orbital energies.
Figure S6.34. Selected molecular orbital plots for 2 with calculated orbital energies.
7. Photophysical Calculations

Calculation of kinetic parameters of luminescent decay of TADF emitters

While there exist models to describe kinetics of TADF emitters the typical assumptions used require high (>0.9) triplet formation yield. Given a relatively modest contribution of TADF to overall emission in 1 and 2 it can be reasonably assumed that triplet formation yield is much lower than 0.9 and cannot be approximated with unity. The aim of the reasoning below is to establish a model with the minimal possible number of assumptions. Yet such assumptions should be reasonable in the context of the particular emitter.

In case of 1 and 2 the triplet formation yield, \( \phi_{\text{ISC}} < 1 \). On the other side, both luminophores present strong fluorescent properties and invariance of prompt fluorescence lifetime with temperature. This suggests the non-radiative decay rate of the \( S_1 \) state might be relatively low and thus can be neglected.

We know that:

\[
\phi_{\text{PL}} = \phi_{\text{PF}} + \phi_{\text{DF}}
\]

(1)

One can then establish a ratio between \( \phi_{\text{PF}} \) and \( \phi_{\text{DF}} \) from the luminescence decay and then calculate the partial luminescence yields of each decay component.

Assuming the only non-radiative process affecting singlet decay to be intersystem crossing, the \( \phi_{\text{ISC}} \) can be estimated as follows:

\[
\phi_{\text{ISC}} = 1 - \phi_{\text{PF}}
\]

(2)

Now, using the known relation below it is possible to give an estimate of \( \phi_{\text{VISC}} \):

\[
\frac{\phi_{\text{PF}} + \phi_{\text{DF}}}{\phi_{\text{PF}}} = \frac{1}{1 - \phi_{\text{ISC}}\phi_{\text{VISC}}}
\]

(3)

The value of \( \phi_{\text{VISC}} \) can then be used to calculate \( k_{\text{VISC}} \) as all other parameters are known.

\[
k_{\text{VISC}} = \frac{\phi_{\text{VISC}} \cdot \phi_{\text{PF}} + \phi_{\text{DF}}}{\phi_{\text{PF}}} \cdot \frac{1}{\tau_{\text{DF}}}
\]

(3)
8. Steady State Photophysics and Additional Absorption Spectra in Solution

Solvatochromism

Figure S8.1. Emission spectra recorded in different polarity solvents to highlight positive solvatochromism (Methylene chloride, THF, Toluene: $\lambda_{exc} = 415$ nm) for a) compound 1 and b) compound 2.

Figure S8.2. Extinction coefficient spectra recorded for 1 and 2 in toluene solution expanded to show only the ICT band. The intensity of the spectrum for 1 is multiplied by a factor of three to illustrate that the maximum extinction coefficient of the ICT band for 2 is greater than three times that of 1.
9. Photophysics in Zeonex matrix

Photoluminescent behaviour of 1 and 2 in Zeonex matrix is generally not very complex and is reminiscent of the properties in toluene solution. However, in this case the emission spectrum is significantly blue shifted due to lesser stabilisation of the ICT by the aliphatic Zeonex matrix (Figure S9.1). Interestingly, the TADF photoluminescence spectrum is not identical with the prompt fluorescence, but nevertheless they are very similar. We believe that Zeonex restricts vibrations of luminophores leading to formation of a distribution of ICT energy, as opposed to toluene, where all molecules have identical energy of the ICT state. As a result of this distribution prompt and delayed fluorescence no longer follow monoexponential decay laws so that each of the exponential regions can be approximated with two or more monoexponential terms. Further to that, molecules with slightly lower CT energy (i.e. CT is more stabilised) show a shorter TADF decay than those with higher CT energy. This leads to an apparent blue shift of emission spectrum with increasing time delay in the TADF decay region (Figure S9.3). On the other side, in the prompt fluorescence region the luminescence spectrum appears to red shift at larger delay after excitation (Figure S9.4). This behaviour can be explained by a smaller transition oscillator strength of the stabilised CT states leading to their smaller singlet radiative rate. This description is in a good agreement with behaviour of 1 and 2 in Zeonex matrix.

Zeonex provides poor solubilisation of dispersed molecules 2 leading to aggregation at 1 wt % load (Figure S9.6). This leads to an emergence of another emissive species which show distinctive luminescent behaviour (Figure S9.7 and Figure S9.8). As we aim to study the intrinsic properties of 1 and 2 we choose to use conditions at which both present characteristics typical of individual molecules, thus 2 is studied at reduced load, 0.01% wt. The results obtained from 0.01 wt % films with 2 are used for comparison with the 1 wt % loaded films with 1. Importantly, both 1 and 2 demonstrate TADF at room temperature confirmed by laser fluence experiment (Figure S9.9). It is worth to point out as a side note that another evidence for the intramolecular mechanism of delayed fluorescence in 2, i.e. TADF, is the invariance of the decay characteristics of the monomolecular emission with concentration (Figure S9.6).

The aggregate emission identified in 2 1 wt % Zeonex films shows an interesting behaviour which deserves an extended discussion (Figure S9.6 and Figure S9.7). At 295 K the decay of the aggregated species appears to involve a single exponential component visible at ~100ns – 1 μs delay which can be attributed to prompt fluorescence. At 80 K apart from the prompt fluorescence component appearing in the same delay of ~100ns – 1 μs as at 295 K, there exists another, longer lived exponential component at ~10 μs – 1 ms delay. Given the conditions of the experiment this decay component might be attributed to phosphorescence emerging from the aggregate. However, given a great degree of similarity between time resolved spectra at the two distinct decay regions it is more likely the longer-lived component is related with delayed fluorescence of the aggregate. The apparent lack of this delayed fluorescence component at 295 K may be related to non-radiative triplet decay on one side. On the other side, the emission appears to be generally weaker than the monomolecular delayed fluorescence of 2, therefore it may not be clearly visible in the decay nor time-resolved spectra. As a final note, we believe the longer-lived decay component of aggregate photoluminescence to be most likely related with triplet-triplet annihilation due to facilitated triplet-triplet interactions in the aggregated state.
Figure S9.1. Steady-state photoluminescence spectra of 1 and 2 in Zeonex matrix. Note the different weight concentration of emitters: 1 wt % for 1 and 0.01 wt % for 2.

Figure S9.2. Time-resolved photoluminescence spectra of (left) 1 in a 1 wt % doped Zeonex film and (right) 2 in a 0.01 wt % doped Zeonex film. PF = prompt fluorescence, DF = delayed fluorescence, PH = phosphorescence.
Figure S9.3. Time-resolved photoluminescence spectra of 1 (left) and 2 (right) in Zeonex matrix. Note the different weight concentration of emitters: 1 wt % for 1 and 0.01 wt % for 2.

Figure S9.4. Time-resolved prompt fluorescence spectra of 1 (left) and 2 (right) in Zeonex matrix. Note the different weight concentration of emitters: 1 wt % for 1 and 0.01 wt % for 2.
Figure S9.5. Photoluminescence decay of 1 in Zeonex matrix at 1 wt % emitter load at two temperatures shown in figure legend. Note the ~1 μs–10 ms region at 295 K is attributed to TADF, while the ~1–100 ms region at 80 K to phosphorescence.

Figure S9.6. Photoluminescence decay of 2 in Zeonex matrix at 0.01-1 wt % emitter load at two temperatures shown in figure legend. Note the regions indicated as aggregate occur only at higher emitter load, while the traces at the lowest load represent exclusively unimolecular emission. The ~100 ns–10 ms region at 295 K is attributed to TADF, while the ~1–100 ms region at 80 K to phosphorescence (both for unimolecular emission of molecule 2).
Figure S9.7. Time-resolved photoluminescence spectra of 2 in Zeonex matrix at 1 wt % emitter load and temperatures indicated in the figure legend. Emission spectra characteristic of aggregate and unimolecular emission of 2 are identified.

Figure S9.8. Area normalised time resolved photoluminescence spectra for the first 600 ns after excitation of 2 in Zeonex matrix at 1 wt % emitter load. Note the clear iso-emissive point.
Figure S9.9. Dependence of delayed fluorescence intensity of 1 and 2 on the excitation dose in a time-resolved experiment. Note the different weight concentration of emitters: 1 wt % for 1 and 0.01 wt % for 2.
10. Time-resolved Photophysics in Solution

![Graph showing time-resolved photoluminescence spectra of 1 in toluene solution (c = 10^{-5} M) showing the prompt and delayed fluorescence spectra.]

**Figure S10.1.** Time-resolved photoluminescence spectra of 1 in toluene solution (c = 10^{-5} M) showing the prompt and delayed fluorescence spectra.
Photophysics in OLED host

Luminescent behaviour of 1 and 2 in PVK:PBD matrix is more complex than in toluene and somewhat more similar to Zeonex films. Similarly to other studied media, 1 and 2 show TADF also in the PVK:PBD matrix used as host in solution processed OLEDs 1 and 2 (Figure S11.4 and Figure S11.6). In contrary to films cast in Zeonex matrix the films obtained with PVK:PBD matrix show a much more significant distinction between early prompt fluorescence and delayed fluorescence (Figure S11.2. Time-resolved photoluminescence spectra of 1 in PVK:PBD matrix at 5 wt % emitter load in the prompt fluorescence region. Note the thicker black line indicates delayed fluorescence spectrum at 2 μs (left) and 1 μs (right) delay., Figure S11.3 and Figure S11.5). Most importantly, delayed fluorescence is red shifted in respect to prompt fluorescence at any time delay with the difference being larger in 1 than in 2. We believe this behaviour indicates that in the distribution of excited states only the ones with the most stabilised ICT produce any TADF at all, while others emit only through prompt fluorescence. This description would seem to indicate that triplet states produced through intersystem crossing in molecules with high ICT energy might be lost, increasing non-radiative losses. However, we believe these triplet states will most likely be scavenged by those molecules able to form low energy ICT through triplet hopping. In other words, molecules with low ICT energy will show behaviour reminiscent of triplet traps – despite the triplet energy being identical to other luminophores in the blend they show accelerated triplet decay via. TADF.

While there is observed a distribution in energy of the $S_1$ ICT state the same does not apply to the $T_1$. At 80 K prompt fluorescence behaves in a similar fashion as it does at 295 K with the distribution of $S_1$ energy reflected by the time-resolved spectra (Figure S11.3 and Figure S11.5). Phosphorescence of 1 and 2 can be identified as a long-lived emission appearing in the 10-100 ms region of the decay. For both compounds the phosphorescence spectrum does not undergo any shifts or changes with time delay. This important observation indicates there is no distribution in $T_1$ energy in both molecules and all emit phosphorescence from a state with identical energy. Such behaviour of $S_1$ and $T_1$ states suggests the effect on excited state energy is not related to strong ground state interactions, such as aggregation. Similar behaviour in solid film has been observed earlier,\textsuperscript{11,12}
Figure S11.1. Steady-state photoluminescence spectra of 1 and 2 in PVK:PBS matrix at 5 wt % emitter load.

Figure S11.2. Time-resolved photoluminescence spectra of 1 in PVK:PBD matrix at 5 wt % emitter load in the prompt fluorescence region. Note the thicker black line indicates delayed fluorescence spectrum at 2 μs (left) and 1 μs (right) delay.
Figure S11.3. Time-resolved photoluminescence spectra of 1 in PVK:PBD matrix at 5 wt % emitter load and temperatures indicated in the figure legend. Note prompt fluorescence, TADF and phosphorescence spectra are indicated with arrows.

Figure S11.4. Photoluminescence decay of 1 in PVK:PBD matrix at 5 wt %. emitter load at two temperatures shown in figure legend (left). Note the ~1 μs–1 ms region at 295 K is attributed to TADF, while the ~10–100 ms region at 80 K to phosphorescence. Dependence of delayed fluorescence intensity of 1 in the same matrix on the excitation dose in a time-resolved experiment (right).
Figure S11.5. Time-resolved photoluminescence spectra of 2 in PVK:PBD matrix at 5 wt % emitter load and temperatures indicated in the figure legend. Note prompt fluorescence, TADF and phosphorescence spectra are indicated with arrows.

Figure S11.6. Photoluminescence decay of 2 in PVK:PBD matrix at 5 wt % emitter load at two temperatures shown in figure legend (left). Note the ~1 μs–1 ms region at 295 K is attributed to TADF, while the ~100 ms region at 80 K to phosphorescence. Dependence of delayed fluorescence intensity of 2 in the same matrix on the excitation dose in a time-resolved experiment (right).
12. OLED devices

The device structure comprises a hole injection layer (PEDOT:PSS Al4083), hole transport / electron blocking layer (poly(N-vinylcarbazole), PVKH, $M_w = 1.1 \times 10^6$ Da), emitting layer (poly(N-vinylcarbazole), PVK, $M_w = 90000$ Da, and 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole, PBD blend + 1/2], electron transport layer (1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene, TPBi), electron injection layer LiF and Al as cathode: ITO | Al4083 (30 nm) | PVKH (10 nm) | PVK:PBD (60:40 w/w) co 5% (30 nm) | TPBi (50 nm) | LiF (0.8 nm) | Al (100 nm).

Table S12.1 Characteristics of OLED devices.

|                 | Dev 1 | Dev 2 |
|-----------------|-------|-------|
| Emitter        |       |       |
| $V_{on}/V$      | 6     | 5.5   |
| $L_{max}/cdm^2$ | 8900  | 14800 |
| $\lambda_{max}/nm$ | 546   | 557   |
| CIE 1931 (x; y) | (0.39; 0.56) | (0.43; 0.54) |
| FWHM / nm      | 98    | 95    |
| $CE_{max}/cdA$ | 33.4  | 38.6  |
| EQE_{max}/%    | 9.7   | 11.9  |

$^a$ turn-on voltage at 10 cd m$^{-2}$; $^b$ maximum luminance; $^c$ electroluminescence spectrum maxima; $^d$ colour coordinates of electroluminescence spectrum as defined in International Commission on Illumination color space CIE 1931; $^e$ full width at half maximum; $^f$ maximum current efficiency; $^g$ maximum external quantum efficiency.
Figure S12.1. Current efficiency – current density characteristics of OLED devices Dev 1 and Dev 2.
13. References

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