The Effect of a Heavy Atom on the Radiative Pathways of an Emitter with Dual Conformation, Thermally-Activated Delayed Fluorescence and

Room Temperature Phosphorescence

(Supporting Information)

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Materials



Scheme S1. The synthetic route to PSeZTRZ.



10H-phenoselenazine (PSeZ)

The synthetic method of PSeZ is described in a previous paper ¹. Crystals for X-ray analysis were grown by slow evaporation from acetone / hexane (1/3 v/v) solvent mixture.



10-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-10*H*-phenoselenazine (PSeZTRZ). 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (1.00)g, 2.58 mmol), 10Hphenoselenazine (0.76 g, 3.09 mmol), sodium tert-butoxide (0.62 g, 6.44 mmol), tri-tertbutylphosphine (0.26 g, 1.29 mmol) and palladium acetate (0.06 g, 0.26 mmol) were dissolved in toluene (50 ml). The solution was refluxed for 8 h under nitrogen atmosphere and cooled down to room temperature. The reaction mixture was dissolved in dichloromethane and washed with distilled water three times and then the organic layer was dried over magnesium sulfate. The solution was condensed using a rotary evaporator and purified by column chromatography on silica gel using dichloromethane:hexane (1:1 v/v) as the eluent. Then the collected product was recrystallized from ethyl acetate and finally purified by thermal gradient sublimation. As a result, 0.88 g of PSeZTRZ was obtained as a yellow powder. Yield : 0.88 g, 62%. T_g : 95.0 °C, Tm : 312.1°C. MS(FAB+) : Calc for 554.1010 m/z; Found 554.1014 m/z, ¹H NMR (700 MHz, CD_2Cl_2) : δ 8.74 (d, J = 7.7 Hz, 4H), 8.61 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 7.7 Hz, 2H), 7.61-7.62 (m, 2H), 7.54-7.58 (m, 6H), 7.41 (t, J = 7.0 Hz, 2H), 7.24 (t, J = 6.5 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H). ¹³C NMR (125 MHz, CD_2Cl_2): δ 170.7, 149.6, 141.5, 136.3, 132.4, 131.0, 130.3, 128.7, 127.7, 127.4, 126.3, 122.4, 114.8. Anal. Calc. for $C_{33}H_{22}N_4$ Se: C, 71.61; H, 4.01; N, 10.12. Found: C, 71.58; H, 4.14; N, 10.07. m.p. = 309-311 °C. Crystals for X-ray analysis were grown by slow evaporation from chloroform / hexane (1/3 v/v) solvent mixture.



10-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-10*H***-phenothiazine (PTZ-TRZ).** PTZ-TRZ was prepared according to the literature procedure² to afford a white crystalline solid (0.88 g, 62%). ¹H NMR (700 MHz, CD_2Cl_2) δ 8.86 (d, *J* = 8.7 Hz, 2H), 8.80 – 8.78 (m, 4H), 7.65 (dd, *J* = 10.2, *J* = 4.2 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 4H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.25 (dd, *J* = 7.7, *J* = 1.4 Hz, 2H), 7.12 – 7.10 (m, 2H), 7.03 (td, *J* = 7.6, *J* = 1.2 Hz, 2H), 6.84 (dd, *J* = 8.1, *J* = 1.0 Hz, 2H). ¹³C NMR (125 MHz, CD_2Cl_2): δ 170.9, 146.9, 142.8, 136.2, 132.9, 132.5, 130.9, 128.7, 128.6, 127.5, 127.1, 126.1, 124.3, 124.1, 120.7.



Scheme S2. The synthetic route to PSeZBPTRZ.



2,4-diphenyl-6-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine (TrzBE). 2-(4-Bromophenyl)-4,6-diphenyl-1,3,5-triazine (3.00 mmol), g, 7.73 bis(pinacolato)diboron (2.36 g, 9.27 mmol), potassium acetate (2.28 g, 23.18 mmol) and [1,1']bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.19 g, 0.23 mmol) were dissolved in 50 ml of 1,4-dioxane. The solution was refluxed for 8 h under nitrogen atmosphere and then cooled down to room temperature. The reaction mixture was dissolved in dichloromethane and washed with distilled water three times and then the organic layer was dryed over magnesium sulfate. The solution was condensed using rotary evaporator and purified by column chromatography on silica gel using dichloromethane:hexane (1:1) as a eluent. As a result, 2.70 g of TrzBE was obtained as a white powder. Yield : 2.70 g, 80%. MS(ACPI+) : Calc for 435.21 m/z; found 436.20 m/z. ¹H NMR (500 MHz, CDCl₃) : δ 1.37 (s, 12H), 7.57~7.62 (m, 6H), 8.01 (d, 2H, J=8.00 Hz), 8.75~8.79 (m, 6H).



10-(4-Bromophenyl)-10*H***-phenoselenazine (BrPhPSeZ).** The synthetic procedures of BrPhPSeZ are the same as PSeZTrz. 1-Bromo-4-iodobenzene was used instead of Trz. As a result, 2.58 g of BrPhPSeZ was obtained as a white powder. Yield : 2.58 g, 53%. MS(ACPI+) : Calc for 402.92 m/z; Found 402.10 m/z. ¹H NMR (500 MHz, CDCl₃) : δ 6.87 (d, 2H, J=9.50 Hz), 7.01 (t, 2H, J=8.00 Hz), 7.07 (d, 2H, J=9.00), 7.12 (t, 2H, J=8.50 Hz), 7.39 (d, 2H, 9.00 Hz), 7.50 (d, 2H, J=9.00 Hz).



10-Phenyl(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-10H-phenothiazine

(PSeZBTRZ). TrzBE (0.40 g, 0.92 mmol), BrPhPSeZ (0.37 g, 0.92 mmol) were dissolved in tetrahydrofuran (30 ml) and then potassium carbonate (0.32 g, 2.30 mmol) dissolved distilled water (10 ml) was poured into the above solution. After nitrogrn bubbling of 30 min, tetrakis(triphenylphosphine)palladium(0) (0.03 g, 0.03 mmol) was added. The above reaction mixture was refluxed for 8 h under nitrogen atmosphere and then cooled down to room temperature. The reaction mixture was dissolved in dichloromethane and washed with distilled water three times and then the organic layer was dryed over magnesium sulfate. The solution was condensed using rotary evaporator and purified by column chromatography on silica gel using dichloromethane:hexane (1:1) as a eluent. As a result, 0.48 g of PSeZBPTrz was obtained as a yellow powder. MS(ACPI+): Cal for 630.13 m/z; Found 631.30 m/z. ¹H NMR (600 MHz, CD₂Cl₂) δ 8.86 (d, *J* = 8.6 Hz, 2H), 8.83 – 8.79 (m, 4H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.67 – 7.63 (m, 2H), 7.63 – 7.59 (m, 4H), 7.46 (dd, *J* = 7.7, *J* = 1.2 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H). ¹³C NMR (150 MHz, CD₂Cl₂) δ 171.56, 144.37, 136.23, 135.71, 134.81, 132.51, 129.40, 128.88, 128.62, 128.43, 127.44, 126.81, 124.78, 123.19.

S1. NMR

1. ¹H and ¹³C NMR spectra of PseZ recorded in acetone-d₆.







3. ^1H and ^{13}C NMR spectra of PSeZTRZ recorded in $\text{CD}_2\text{Cl}_2.$



4. ¹H and ¹³C NMR spectra of PTZ-TRZ recorded in CD_2Cl_2 .



5. ^1H and ^{13}C NMR spectra of PSZBTRZ recorded in $\text{CD}_2\text{Cl}_2.$



S2. X-ray crystallography

X-ray diffraction experiments (Table S2.1) were carried out on a Bruker 3-circle D8 Venture diffractometer with a PHOTON 100 CMOS area detector, using Mo- K_{α} radiation from IµS microsources with focussing mirrors. Crystals were cooled to 120 K using a Cryostream (Oxford Cryosystems) open-flow N₂ gas cryostat. The structures were solved by direct methods using SHELXT program,³ and refined by full-matrix least squares using SHELXL 2018/3⁴ software on OLEX2⁵ platform.

The PSeZ crystal showed a 2-component (0.6:0.4) non-merohedral twinning by 180° rotation around the reciprocal axis z^* ; the data were deconvoluted using CELL_NOW 2008/4 program, integrated with two orientation matrices using SAINT 8.38A (Bruker AXS, 2017) and scaled using TWINABS 2012/1 program (Bruker AXS, 2008-2012). The crystals, grown by sublimation, present a new polymorph of PSeZ, distinct from the previously reported⁶ orthorhombic phase (space group $P2_12_12_1$) crystallised from CS₂.

The available literature on the crystal structure of PTZ is outdated and controversial. A monoclinic lattice (space group $P2_1$) was reported⁷ in 1968 with some geometrical parameters (e.g. the folding angle of 26.7°) but atomic coordinates were not published, even though the reported R=4.6% was low by the standards of the time. In 1976, McDowell described⁸ an orthorhombic form of PTZ (space group Pnma). Shortly afterwards, van der Waal & Feil⁹ suggested that *Pnma* symmetry was spurious and caused by polysynthetic twinning, the true space group being $P2_1/c$. They also reported to observe an order-disorder phase transition at 224.6 K (from heat capacity measurements) and to have determined the crystal structures at 300 and 120 K, for which they published atomic vibration parameters, but (strangely) no atomic coordinates. Later¹⁰ the phase transition in PTZ was established by Raman spectroscopy, DSC and polarized-light microscopy to occur at 251.0±0.5 K, subsequently corrected to 248.8 K and found to depend on the specimen quality.¹¹ The Raman spectra of the high- and low-temperature phases obey the selection rules required for the orthorhombic and monoclinic structures, respectively (note that van der Waal & Feil believed the structure to be monoclinic at *both* temperatures).¹¹ Although this transition (also observed at high pressure¹²) has been studied extensively in connection with ferroelasticity of the low-temperature phase, to the present day the only crystal structure for which the atomic coordinates are in the public domain is the McDowell's orthorhombic one.

To clarify this issue, we carried out a variable-temperature study of PTZ crystals prepared by sublimation. At room temperature and at 250 K, we found essentially the same structure as reported by McDowell (see Table S1, Figures S2.1 and S2.3), the molecule lying astride a mirror plane and folded along the N...S vector, with the dihedral angle (ω) between the arene ring planes of 21.5°. We did not observe the "marked diffuse streaking parallel to c*" reported by van der Waal & Feil (from Weissenberg photographs) – indeed, no significant diffuse scattering of any kind away from Bragg peaks, although atomic displacement parameters are rather large. Intensity statistics gives no indication of twinning. The phase transition occurred below 250 K; at 240 K the lattice was monoclinic (Table S1) with twinning by a 180° rotation about the direct axis x. On further cooling, the diffraction pattern remained substantially unaltered to 120 K, at which temperature a full structure determination was carried out on the data deconvoluted and scaled as above. The crystal was a 2-component twin with the twin fractions of 0.787(2):0.213(2) and the twin law

 $\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ -0.607 & 0 & -1 \end{pmatrix}$

which resulted in 97% of reflections overlapping. The space group $(P2_1/n)$ and the lattice parameters are in agreement with those reported by van der Waal & Feil (in the $P2_1/c$ setting), see Table S1. The asymmetric unit comprises one molecule, folded with ω =20.2°.

The crystal packing is shown in Figure S2.3. The monoclinic forms of PTZ and PSeZ are isomorphous and closely resemble the orthorhombic PTZ, while the orthorhombic PSeZ and its isomorphous analogue PTeZ¹³ show an entirely different packing pattern, notwithstanding very similar unit cell parameters. The latter two structures show much stronger folding of the molecule (Table S2.3). It is remarkable that the orthorhombic PSeZ is *denser* at room temperature than the monoclinic form even at 120 K – especially as centrosymmetric polymorphs are *usually* denser than chiral ones (Wallach's rule¹⁴). This may indicate that the more bent molecular conformation is energetically more favourable.

Full crystallographic data (including structure factors) is available as SI and have been deposited with Cambridge Structural Database.

1. X-ray molecular structures of PSeZTrz (a) and PSeZ (b), PTZ at 293 K (c) and 120 K (d). Thermal ellipsoids are drawn at the 50% probability level, primed atoms are symmetrically related via a mirror plane.



2. Crystal packing of PseZTrz.



3. Crystal packing of PTZ, PSeZ and PTeZ (H atoms are omitted for clarity).



PTZ, high-temperature phase (orthorhombic)



PSeZ, monoclinic



PTeZ (orthorhombic)

Table S2.1. Crystal data and experimental parameters. Neither the crystal structure nor the gas-phase structure (from electron diffraction) of PXZ being available, its sterically unencumbered derivatives can be used for comparison, viz. 3-(tricyanovinyl)-phenoxazine (ω =5.2°)¹⁵ and 10-ethylphenoxazine (ω =8.5° and 12.2° in two independent molecules).¹⁶

Compound	PSeZ	PSeZTrz	PTZ	PTZ	PTZ	PTZ	
CCDC	1873559	1873560	1902674	1902672		1902673	
Formula	C ₁₂ H ₉ NSe	$C_{33}H_{22}N_4Se$	$C_{12}H_9NS$	$C_{12}H_9NS$	$C_{12}H_9NS$	$C_{12}H_9NS$	
Formula Weight	246.16	553.50	199.26	199.26	199.26	199.26	
<i>Т/</i> К	120	120	293	250	240	120	
Crystal System	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic	monoclinic	
Space Group	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	$P2_1/c$ (no. 14)	Pnma	Pnma	P2 ₁ /n (?)	$P2_1/n$	
a/Å	5.9066(4)	13.4469(9)	7.9000(8)	7.8739(8)	5.868(2)	5.8254(11)	
b/Å	7.9984(5)	19.0511(11)	20.937(2)	20.921(2) 7.870(2)		7.7897(14)	
c/Å	20.6824(12)	9.6130(6)	5.8824(6)	5.8718(6) 20.888(9)		20.803(4)	
β/°	93.912(2)	96.035(2)	90	90	92.441(13)	94.929(5)	
V/Å ³	974.83(11)	2449.0(3)	973.0(2)	967.3(2)	963.9(8)	940.5(3)	
Ζ	4	4	4	4	4	4	
$D_{calc.}$ / g cm ⁻³	1.677	1.501	1.360	1.368	1.373	1.407	
μ/mm^{-1}	3.81	1.57	0.29	0.29	0.29	0.30	
$\Theta_{\max}/^{\circ}$	30	30	25	25		30	
Measured Reflections	2291	49411	12391	9837		8188	
Independent Reflections	1905	7152	877	876		2268	
with $l > 2\sigma(l)$	1778	5530	622	654		1902	
R _{int}	0.050	0.059	0.0841	0.0488		0.0633	
Parameters/restraints	131/108	343 /0	71/0	71 / 0		132 /0	
Largest Peak	0.66, -0.54	0.47, -0.47	0.16, -0.18	0.21, -0.25		0.45, -0.36	
Goodness of fit	1.035	1.026	1.066	1.076		1.096	
R_1 , wR_2 (all data)	0.057, 0.070	0.061, 0.081	0.069, 0.126	0.063, 0.115		0.074, 0.138	
$R_{1}, wR_{2} \left[I > 2\sigma(I) \right]$	0.033, 0.065	0.037, 0.074	0.044, 0.112	0.044, 0.105		0.058, 0.132	

	crystallisation	Temp.	Space gr.	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	<i>β</i> , °	<i>V</i> , Å ³	ω, °	Ref.
PTZ	acetone/EtOH	Room	<i>P</i> 2 ₁	7.82(3)	5.93(1)	10.70(8)	74.01	477.0	26.7	7
	МеОН	Room	Pnma	7.916(10)	20.974(10)	5.894(10)	90	978.6	21.5	8
	?	300	P2 ₁ /c	5.882(2)	7.918(2)	21.755(4)	74.33(2)	975.6	?	9
	?	120	P2 ₁ /c	5.808(1)	7.783(3)	22.009(3)	69.87(2)	934.1	?	9
			P_{2_1}/n^*	5.808(1)	7.783(3)	20.740(3)	94.89(2)	934.1	?	
	Sublimation	293	Pnma	7.9000(8)	20.937(2)	5.8824(6)	90	973.0(2)	21.5	†
	Sublimation	250	Pnma	7.8739(8)	20.921(2)	5.8718(6)	90	967.3(2)	21.5	†
	Sublimation	120	P_{2_1}/n	5.8254(11)	7.7897(14)	20.803(4)	94.929(5)	940.5(3)	20.2	†
PSeZ	CS ₂	room	$P2_12_12_1$	5.927(7)	7.829(5)	20.909(4)	90	970.2(7)	30.4	6
	sublimation	120	P_{2_1}/n	5.9066(4)	7.9984(5)	20.682(1)	93.912(2)	974.8(1)	23.4	†
PTeZ	DCM	296	$P_{2_1}^2 2_1^2 2_1$	6.023(2)	8.007(3)	20.877(9)	90	1006.8(7)	29	13

Table S2.2. Polymorphs of PTZ, PSeZ and PteZ.

* Standard setting of the above, for comparison;

† this work

S3. The optimized structures along with profiles, frontier orbitals and corresponding HOMO/LUMO values of PXZ, PTZ, PSeZ, obtained at the rBMK/6.31G(d) (GS) level of theory.



S4. (a) Theoretically calculated UV/Vis spectra along with the oscillator strengths of the electronic transitions and (b) energy diagram of the equatorial and axial conformers of PSeZTRZ.



S5. Natural transition orbitals (NTO) corresponding to the first three singlet transitions in the absorption of the equatorial and axial conformers of PSeZTRZ (TD-DFT rBMK/6-31G(d)).



S6. Natural transition orbitals (NTO) corresponding to the first three triplet transitions in the absorption of the equatorial and axial conformers of PSeZTRZ (TD-DFT rBMK/6-31G(d)).



S7. Normalised absorption of PSeZTRZ in methylcyclohexane (MCH), toluene and dichloromethane (DCM). Inset shows that the low energy band (between 300 and 450 nm) undergoes a positive solvatochromatic shift with polarity.



S8. Normalised PL intensity of 1,3,5-triphenyl-2,4,6-triazine (blue dotted line) and phenoselenazine (red dashed line) in a DCM solution. Excitation 260 nm.



S9. Photophysics of PTZ-TRZ

1. Decay profile of PTZ-TRZ in a 1% wt:wt matrix of zeonex at room temperature (RT). From early ns to late ms, the regions are identified by I. -2.7 – 12.3 ns; II. 12.3 – 100 ns; III. 0.1 – 10 μ s; IV. 10 – 1000 μ s; V. 1 – 10 ms; VI. 10 – 100 ms. A TD below 0 ns means we are considering phenomena that are happening before the maximum of the excitation laser.



2. Normalised emission of PTZ-TRZ at different time delays (TD) and RT. At a TD = 100 ns, the gaussian-like emission is assigned as a relaxed charge transfer (¹CT) singlet state, with an onset energy of 2.63 \pm 0.02 eV. At a TD = 100 ms, a structured emission, blueshifted from the CT is visible and is assigned as room temperature phosphorescence (RTP) with an onset energy of 2.79 \pm 0.02 eV and an energy gap of -160 meV.



3. Polarity-dependant photoluminescence (PL) spectra of PTZ-TRZ in methylcyclohexane (MCH) and Toluene under a 355 nm excitation. Similarly to PSeZTRZ, the emission profile shows two bands, a high energy CT_{Ax} that strongly overlaps with the emission band of PTZ (S9.1) and a low energy band CT_{Eq} . While the Ax emission possesses a large local character, the Eq emission shows strong solvatochromism.



4. Prompt fluorescence (PF) and phosphorescence (PH) spectra of phenothiazine (PTZ) donor. Excitation at 266 nm.



S10. a) Normalised intensity of the axial (Ax) and equatorial (Eq) conformers of PSeZTRZ taken at different time delays. The overlapped grey area indicates that there is a contribution from Eq even at the earliest times of the emission. b) Photoluminescence (PL) intensity between 12 and 70 ns after excitation. At 12 ns, two different species can be clearly distinguished, proving that the Eq conformer is emitting independently to the Ax.



S11. Area normalised emission of PSeZTRZ in different stages of its time-resolved decay curves at 320 K. From early ns to late ms, the distinct regions are identified by I. 1.5 - 100 ns; II. 100 - 1.000 ns; III. $1 - 10 \mu$ s; IV. $10 - 500 \mu$ s; V. 0.5 - 32 ms; VI. 32 - 100 ms.



S12. The normalised phosphorescence (PH) emission of 1,3,5-triphenyl-2,4,6-triazine (blue dotted line) and phenoselenazine (red dashed line) in a zeonex matrix collected with a time delay of 0.09 s and integrated over 9 ms.



S13. Energy levels (onset) of PSeZTRZ taken from the decay profiles at 80 K. a) Fluorescence spectra of the charge transfer (CT) conformers and b) Phosphorescence (PH) spectra of different units. Onsets with an error of \pm 0.02 eV.



S14. Emission dependence of PSeZTRZ on the laser fluence at room temperature between 35 and 550 ns, assigned as the delayed fluorescence (DF) region.



S15. Increasing the bridge between donor and acceptor: photophysics of PSeZBTRZ.

In an effort to further twist the donor and the acceptor, a phenyl ring was inserted between them and the directly comparable photophysical characterisation performed. Spectral data on phenoselenazine – benzene – triazine (PSeZBTRZ) are shown here. With the extended bridge, only one emitting species at high energies appears, with similar emission to that of PSeZTRZ Ax conformer. In the solid-state, no DF from PSeZBTRZ is seen and the phosphorescence has the same relative energy to that of PSeZTRZ's conjugated acceptor unit. Therefore, contrarily to what intended, adding a phenyl bridge planarized the entire system in the excited state, which results in the lower CT strength (seen by the smaller redshift with polarity) and increases the total conjugation. This structural change has an effect on conformation, increases the S-T energy gap and prevents TADF.



a) Normalised absorption spectrum overlapped with each individual unit, showing similar absorption to PSeZTRZ with more contribution from the donor. b) Normalised absorption spectrum in solvents with increased polarity. Inset shows the solvatochromic effect in the normalised CT band. c) Normalised photoluminescence (PL) spectra in solvents with increasing polarity: methylcyclohexane, toluene and dichloromethane. d) energy levels – prompt fluorescence consistent with the PL and phosphorescence – of PSeZBTRZ in a zeonex matrix.



S16. Cyclic Voltammetry of PSeZTRZ.

Cyclic voltammetry was used to examine the electrochemical stability and to determine the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies for PSeZTRZ. Reversible oxidation as well as quasi-reversible reduction can be observed in the CV scans, as expected for a molecule comprising strong D and A units. The values of HOMO and LUMO were calculated using the approximations HOMO = -5.1 + (-Eonsetox) and LUMO = -5.1 + (-Eonsetox) and were found to be -5.43 eV and -2.26 eV, giving an energy gap of 3.17 eV.



Experimental details: A cell comprised of a platinum electrode with a 1 mm diameter working area as a working electrode, an Ag/AgCl electrode as a reference electrode and a platinum coil as an auxiliary electrode. Cyclic voltammetry (CV) measurements were conducted in a solution of 1 mM concentration of PSeZTRZ and using 0.1 M of Bu₄NBF₄ as an electrolyte, 99% (Sigma Aldrich). Scans were made at room temperature with a potential rate of 50 mV/s and were calibrated against a ferrocene/ferrocenium redox couple. With a relatively wide HOMO-LUMO gap of the emitter, two solvents were used: tetrahydrofuran (THF) for reduction down to -3.5 V and dichloromethane (DCM) for oxidations up to +2.0 V.

LUMO²

(eV)

-2.26

S17. a) Normalised photoluminescence (PL) spectra of PSeZTRZ doped films in mCBP at different concentrations: black 10 %, red 30 % and green 50 %. b) Area normalised emission of PSeZTRZ in a mCBP layer at different ratios (10, 30 and 50%).



S18. Photoluminescence quantum yield (PLQY) measurements on PSeZTRZ doped films in a mCBP at different concentrations: a) 10 %, b) 30 % and c) 50 %. PLQYs were measured in air and in a nitrogen (N_2) environment to assess the contributions from both singlet and triplet states.



S19. Energy diagram of the device structure used in this study: ITO (120 nm)/ PEDOT:PSS (60 nm)/ TAPC (20 nm)/ mCP (10 nm)/ mCBP:PSeZTRZ (25 nm, x wt%)/ TSPO1 (5 nm)/ TPBi (40 nm)/ LiF (1.5 nm)/ Al (200 nm).



S20. Device performance of PSeZTRZ in different concentrations (10, 30 and 50% wt.%). Luminous efficacy (a) and current efficiency (b) of devices with 10, 30 and 50% concentrations in mCBP.



S21. Performance of a device with PTZ-TRZ in a similar device structure to the one used for PSeZTRZ: ITO (120 nm)/ PEDOT:PSS (60 nm)/ TAPC (20 nm)/ mCP (10 nm)/ mCBP:PTZ-TRZ (25 nm, x wt%)/ TSPO1 (5 nm)/ TPBi (40 nm)/ LiF (1.5 nm)/ Al (200 nm). a) Current-density dependence with voltage; b) external quantum efficiency (η_{ext}) dependence with brightness. The inset shows the electroluminescence (EL) spectra.



S16. Thermal characterisation of PSeZTRZ and PSeZBTRZ

S22. TGA analysis under N_2 with ramping temperature at 10 °C min-1 for compounds **PSeZTRZ** and **PSeZBTRZ** with reported 5% wt. loss values.



Thermal stability of the derivatives was probed by thermal gravimetric analysis (TGA). The TGA curves along with the decomposition temperatures (T_d) at the 5% wt. loss points are presented in **Figure S22**. The T_d value of **PSeZBTRZ** is by 76°C higher than that of **PSeZTRZ** due to the incorporation of an additional phenyl ring prolonging the conjugation system and greatly improving the thermal stability.

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