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Supporting information

Enhancement of Thermally Activated Delayed Fluorescence Properties by Substitution of Ancillary Halogen in Multiple Resonance-Like Diplatinum(II) Complex

Piotr Pander, Andrey V. Zaytsev, Amit Sil, J. A. Gareth Williams, Valery N. Kozhevnikov and Fernando B. Dias

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1. General

Theory

To assist the interpretation of the experimental results, we have performed density functional theory (DFT) and time-dependent density functional theory (TDDFT) simulations with Tamm-Dancoff approximation (TDA) on the di- and mononuclear complexes using ORCA 4.2.1 quantum chemistry software^[1-3]. All molecular orbital (MO) iso surfaces were visualised using Gabedit 2.5.0.^[4]

Geometry optimisations were performed at the B3LYP^[5,6]/def2-TZVP^[7] level of theory with RIJCOSX^[12,13] approximation to accelerate calculations and def2/J^[10] auxiliary basis set. Atompairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ)^[13,14] was included in the calculation. Single point energy calculations were performed using ZORA-corrected variants of the def2-TZVP basis set. Ground state geometries were verified to be true energy minima by a frequency calculation. All optimisations were performed with tight SCF and geometry convergence criteria.

A triple-zeta def2-TZVP basis set with the def2/J^[8] auxiliary basis set were used for all atoms for an accurate assessment of the ground state geometry S_0 of the mono- and the di-Pt(II) complexes. Excited state energy of TDDFT states was calculated using the resulting S_0 geometry. In this case relativistically corrected triple-zeta basis sets with the zeroth-order regular approximation (ZORA)^[9,10] were used: ZORA-def2-TZVP^[7] with the SARC/J^[11] auxiliary basis for all atoms except Pt where a segmented all-electron relativistically contracted (SARC) SARC-ZORA-TZVP^[11] basis set was used. Authors also used the "old-ZORA-TZVP" basis set for iodine (I) atoms. Spin-orbit coupling (SOC) calculations were performed as implemented in the ORCA software. SOC matrix elements (SOCME) and SOC-corrected excitations (SOC-TDDFT states) were computed at the same level of theory as the TDDFT states. In order to accelerate the calculations RIJCOSX^[12,13] approximation was used in all cases and the RI-SOMF(1X) setting was used to accelerate SOC calculations. All computations were performed using a dense grid (Grid6, GridX6).

Dipole moments in the ground (S_0) and triplet excited state (T_1) have been obtained from the geometries optimised at the BP86^[8]/def2-SVP^[7] level of theory, using def2-SVP/C^[9] and def2/J^[10] auxiliary basis sets, RI approximation, dense grid (Grid6) and the D3BJ correction.

We have performed all calculations of excited state energies using ground state geometries obtained at the B3LYP/def2-TZVP level of theory, as described above. The calculation of ΔE_{ST} using SOC states (Table S4.1) was based on the energy difference between these states (Γ_1 and Γ_4 for example) at the S₀ geometry. Geometry optimisation of the T₁ state at the B3LYP/def2-TZVP level of theory was not possible for dinuclear complexes 1 and 3. This is because of the highly resource-demanding nature of this task. Similarly, optimisation of the excited state geometry of specific SOC states would require relativistic corrections to be included, which is practical only for small systems due to the large computational cost.

Calculation of singlet and triplet radiative rates using simulated parameters

Relationship between transition oscillator strength and radiative rate is described by^[14]:

$$k_r = \frac{n^2 \nu^2 f}{1.5}$$

Where k_r – radiative rate of a given transition, s⁻¹; n – refractive index of the medium; ν – energy of the state represented as a wavenumber, cm⁻¹; f – transition oscillator strength.

Obtaining k_r of a singlet state is therefore straightforward. In order to obtain radiative phosphorescence rate we consider the thermal equilibrium between the three triplet substates as set out earlier by Mori and others^[15]:

$$k_r^{av} = \frac{k_r^1 + k_r^2 e^{-\frac{\Delta E_{1,2}}{k_b T}} + k_r^3 e^{-\frac{\Delta E_{1,3}}{k_b T}}}{1 + e^{-\frac{\Delta E_{1,2}}{k_b T}} + e^{-\frac{\Delta E_{1,3}}{k_b T}}}$$

Where: k_r^{av} – average radiative rate, s⁻¹; k_r^1 , k_r^2 , k_r^3 – radiative rates of the SOC-TDDFT states 1-3, s⁻¹; k_b – Boltzmann constant, 8.617×10⁻⁵ eV K⁻¹; $\Delta E_{1,2}$ – energy difference between SOC-TDDFT states 1 and 2, eV; $\Delta E_{1,3}$ – energy difference between SOC-TDDFT states 1 and 3, eV; T – temperature, K. In the calculation of the average triplet radiative rate we consider the thermal equilibrium at 295 K for

comparison with experimental radiative rates obtained at room temperature.

Electrochemistry

Cyclic voltammetry was conducted in a three-electrode, one-compartment cell. All measurements were performed using 0.1 M Bu₄NBF₄ (99%, Sigma Aldrich, dried) solution in dichloromethane (ExtraDry AcroSeal®, Acros Organics). All solutions were purged with nitrogen prior to measurement and the measurement was conducted in a nitrogen atmosphere. Electrodes used in the experiment were: working (Pt disc d = 1 mm), counter (Pt wire), reference (Ag/AgCl calibrated against ferrocene). All cyclic voltammetry measurements were performed at room temperature with a scan rate of 50 mV s^{-1} .

The ionization potential (IP) and electron affinity (EA) are obtained from onset redox potentials; these figures correspond to HOMO and LUMO values, respectively. The ionization potential is calculated from onset oxidation potential IP = E_{ox}^{CV} + 5.1 and the electron affinity is calculated from onset reduction potential EA = E_{red}^{CV} + 5.1.^{[16],[17],[18],[19]} An uncertainty of ±0.02 V is assumed for the electrochemical onset potentials.

Photophysics

Absorption spectra of 10^{-5} M solutions were recorded with UV-3600 double beam spectrophotometer (Shimadzu). Photoluminescence (PL) spectra of solutions and films were recorded using a QePro compact spectrometer (Ocean Optics) or FluoroLog fluorescence spectrometer (Jobin Yvon). Photoluminescence decays in film 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). The emitted light was focused onto a spectrograph and detected with a sensitive gated iCCD camera (Stanford Computer Optics) having sub-nanosecond resolution. Timeresolved measurements were performed by exponentially increasing gate and integration times. Further details are available in reference^[20]. Time-resolved decays in solution were recorded with a Horiba DeltaFlex TCSPC system using a 330 nm SpectraLED light source. Temperature-dependent 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 in polystyrene and pristine layers were deposited from chloroform solutions. The films were fabricated through spin-coating and dried under vacuum at room temperature. Solid state emission spectra and photoluminescence quantum yield were obtained using an integrating sphere (Labsphere) coupled with a 365 nm LED light source and QePro (Ocean Optics) detector.

Deconvolution of dual emission spectra to determine TADF-to-phosphorescence ratios

We are able to deconvolute the photoluminescence spectrum of **3** in toluene using the assumption that the two luminescent bands: TADF and phosphorescence do not change their shape with temperature, but temperature affects their proportion in the spectrum. We select two arbitrarily chosen spectra recorded at different temperatures and subtract one from another in order to obtain TADF spectrum as a product. We then subtract hence obtained TADF spectrum from a chosen experimental spectrum to obtain the phosphorescence spectrum. In the two subtractions we re-scale one spectrum in respect to the other in order to cancel out the contributions of the band that is not intended to appear in the product. Once obtained, TADF and phosphorescence spectra are used to fit every experimental spectrum and we can demonstrate that each spectrum can be presented as a sum of TADF and phosphorescence bands (Figure S5.4). This confirms the initial assumptions of the TADF and phosphorescence spectrum not changing shape with temperature was correct.

Once a photoluminescence spectrum at given temperature is fitted with the sum of TADF and phosphorescence the ratio between the bands can be obtained from the area under each of the individual components.

Determination of photoluminescence quantum yields in solution

Photoluminescence quantum yields were obtained using a gradient method in which we study relation (gradient) between total photoluminescence intensity and absorbance at the excitation wavelength (same for both standard and analyte) in a range of concentrations for both analyte and standard – see equation below. We only consider data points with a constant gradient, so that the relation between photoluminescence intensity and absorbance is linear – indication of the photoluminescence yield being independent of concentration in this region. The eligible concentration range was ~1-5 × 10⁻⁶ M in case of complexes **2** and **3** while absorbance of standards was kept at below 0.05 for Rhodamine 6G and 0.05 for Coumarine 153 at the respective excitation wavelengths.

$$\Phi_{x} = \Phi_{standard} \left(\frac{grad_{x}}{grad_{standard}} \right) \left(\frac{\eta_{x}^{2}}{\eta_{standard}} \right)$$

Where: Φ_x , $\Phi_{standard}$ – photoluminescence quantum yield of analyte and standard, respectively; g^{rad}_x , $g^{rad}_{standard}$ - gradient (slope) of the linear relation between photoluminescence intensity and solution absorbance at the excitation wavelength, for analyte and standard, respectively; η_x , $\eta_{standard}$ - refractive index of solvent used for analyte and standard, respectively.

OLED devices

OLEDs were fabricated by spin-coating / evaporation hybrid method. The hole injection layer (PEDOT AL4083), hole transport layer PVKH, and emitting layer (mCP:PO-T2T + dopant, mCP:PBD + dopant or pristine) were spin-coated, whereas the electron transport layer (PO-T2T or TmPyPB) and cathode (LiF/Al) were evaporated. Devices of $4 \times 2mm$ pixel size were fabricated. 2,4,6-Tris[3-(diphenylphosphinyl)phenyl]-1,3,5-triazine (PO-T2T, LUMTEC), 1,3-bis(carbazol-9-yl)benzene (mCP, sublimed, LUMTEC), 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD, Sigma Aldrich), poly(*N*-vinylcarbazole) (PVKH, Sigma Aldrich, M = 10⁶ Da), 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB, Lumtec), 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 on 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) solution while emitting layer was spun from the same mixture of solvents or from toluene. The dopant was dissolved in the solution of blend host in order to obtain final 5-33% 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 Keithley 2400 and coupled with a spectrometer USB4000 (Ocean Optics). Further details are available in reference ^[21].

2. Synthesis



A suspension containing 1 (86 mg, 0.07 mmol), NaI (210 mg, 1.40 mmol) and acetone (25 mL) was heated under reflux under Ar atmosphere for 24 h. Acetone was removed under reduced pressure, and the residue was suspended in DCM (20 mL). The insolubilities were filtered and washed with DCM. DCM was evaporated from the filtrate and the remaining solid was re-dissolved in DCM (5 mL), filtered through a microfilter (PTFE, 0.45 μ m) and the desired compound was isolated as a dark-purple solid (93 mg, 94 %) by evaporating DCM under reduced pressure.

¹H NMR (400 MHz, CD_2Cl_2) δ 10.50 (s, 1H), 9.31 (d, J = 6.2 Hz, 2H), 8.25 (s, 1H), 7.66 (s, 2H), 7.01 (dd, J = 6.3, 2.2 Hz, 2H), 4.15 (t, J = 6.6 Hz, 4H), 1.81 – 1.74 (m, 4H), 1.52 – 1.44 (m, 4H), 1.43 – 1.36 (m, 8H), 1.31 (s, 18H), 0.95 (app t, 6H).

¹⁹F NMR (376 MHz, CDCl₃) δ -118.9 (d, J = 15 Hz), -119.7 (d, J = 15 Hz).

Elemental (CHN) analysis: calc. for C₄₆H₅₂I₂F₄N₄O₂Pt₂, %: C, 39.10; H 3.71; N, 3.97. Found, %: C, 39.11; H, 3.64; N, 3.88.



2 (58 mg, 81.7 μ mol) was dissolved in acetone (10 mL), NaI (122 mg, 817 μ mol) was added and reaction mixture was heated to reflux under argon atmosphere for 2 h. The solvent was evaporated under reduced pressure and the residue was suspended in DCM. The precipitate was filtered through a plug of silica and the top running band was collected and the solvent was evaporated. The residue was suspended in pet.ether, filtered off and air-dried to give 4 (39 mg, 60%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 9.67 (d, *J* = 6.3 Hz, 2H), 7.89 (d, *J* = 2.2 Hz, 2H), 7.19 (dd, *J* = 6.3 and 2.2 Hz, 2H), 4.10 (t, *J* = 6.6 Hz, 2H), 1.82 (app quint, 2H), 1.54 – 1.48 (m, 2H), 1.39 – 1.35 (m, 22H), 0.93 (t, *J* = 7.0 Hz, 3H).

¹⁹F NMR (376 MHz, CDCl₃) δ -126.7.

Elemental (CHN) analysis: calc. for $C_{30}H_{37}IF_2N_2OPt$, %: C, 44.95; H, 4.65; N, 3.49. Found, %: C,44.51; H, 4.65; N 3.49.



Figure S2.1. ¹H NMR spectrum of complex 4 in CDCl₃.



Figure S2.2. ¹⁹F NMR spectrum of complex 4 in CDCl₃.



Figure S2.3. ¹³C NMR spectrum of complex 4 in CDCl₃.



Figure S2.4. ¹³C (DEPT135) NMR spectrum of complex 4 in CDCl₃.



Figure S2.5. ¹H NMR spectrum of complex 3 in CDCl₃.



OC₆H₁₃

 OC_6H_{13}

-108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122 -123 -124 -125 -126 -127 -128 -129 -130 -131 -132 -133 -134 -135 -13 f1 (ppm)

Figure S2.6. ¹⁹F NMR spectrum of complex 3 in CDCl₃.



Figure S2.7. ¹³C NMR spectrum of complex 3 in CDCl₃.



Figure S2.8. ¹³C (DEPT135) NMR spectrum of complex 3 in CDCl₃.

3. X-ray crystallography

Equipment and refinement methods for X-ray crystallography were as described in our previous paper on the dichloro parent complex; see ref.^[22] X-ray diffraction analysis was attempted on several different crystals of complex **3**, obtained from separate crystallisations. Unfortunately, it was not possible to refine the structure to a level satisfactory for detailed consideration of bond lengths and angles, but the analysis does provide confirmation of the identity of the complex (**Figure S3.1** with corresponding crystal data given in **Table S3.1**). There are two complexes and two DCM molecules with fixed half occupancy in the independent part of the unit cell. Another DCM molecule could not be properly modelled and has been treated using the MASK procedure in Olex2.^[23] The hexyl tails are strongly disordered. Crystallographic data for the structure have been deposited at CCDC, as supplementary publication CCDC-2121802. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif



Figure S3.1. Molecular structure of the dinuclear complex 3 determined by X-ray diffraction.

Identification code	20srv198
Empirical formula	$C_{46.5}H_{53}ClF_4I_2N_4O_2Pt_2$
Formula weight	1455.36
Temperature/K	120.0
Crystal system	triclinic
Space group	P-1
a/Å	17.3665(10)
b/Å	17.6434(11)
c/Å	17.7883(10)
α/°	79.742(2)
β/°	81.140(2)
γ/°	81.931(2)
Volume/Å ³	5263.4(5)
Ζ	4
$\rho_{calc}g/cm^3$	1.837
µ/mm ⁻¹	6.585
F(000)	2764.0
Crystal size/mm ³	$0.49 \times 0.05 \times 0.02$
Radiation	Μο Κα (λ = 0.71073)
2Θ range for data collection/°	4.33 to 53
Index ranges	$-21 \le h \le 21, -22 \le k \le 22, -22 \le l \le 22$
Reflections collected	102341
Independent reflections	$21790 [R_{int} = 0.0768, R_{sigma} = 0.0671]$
Data/restraints/parameters	21790/135/1099
Goodness-of-fit on F ²	1.028
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0568, wR_2 = 0.1464$
Final R indexes [all data]	$R_1 = 0.0891, wR_2 = 0.1642$
Largest diff. peak/hole / e Å ⁻³	2.19/-1.81

 Table S3.1. Crystal data and structure refinement for complex 3.

4. Theory



Figure S4.1. Energy of molecular orbitals in complexes 1-4. H-HOMO, L-LUMO. The lines connecting orbitals of 1 and 3 (or 2 and 4) indicate the same type of the orbital, for example: HOMOs of 2 and 4 are connected with a line and so are LUMOs, etc. The line serves as an eye-guide for the reader to easily identify the orbital.



Figure S4.2. Energy of selected molecular orbitals of complexes **1-4**. H-HOMO, L-LUMO. Orbitals of the same topology are connected with thin dotted lines.

		1	3	2	4
	S ₁ / eV ^a	2.246	1.718	2.945	2.654
	T ₁ / eV ^b	1.942	1.679	2.545	2.404
TDDFT	$\Delta E_{ST} / eV^{c}$	0.304	0.039	0.400	0.250
	f (S ₁) ^d	0.19	$6.0 imes 10^{-5}$	8.4×10^{-3}	0.024
	k _r ^{S-1} / s ^e	2.4 × 10 ⁻⁸ (24 ns)	1.3 × 10 ⁻⁴ (130 μs)	3.2 × 10 ⁻⁷ (320 ns)	1.4 × 10 ⁻⁷ (140 ns)
	G ₁ (triplet) / eV ^f	1.893	1.458	2.559	2.298
	G _n (singlet) / eV ^g	2.149 (G ₇)	1.530 (G ₄)	2.872 (G ₇)	$2.449 (G_4)$
	$\Delta E_{ST} / eV^{h}$	0.256	0.072	0.313	0.151
SOC- TDDFT	f (G _n) (singlet) ⁱ	0.15	0.018	1.3×10^{-3}	2.2×10^{-3}
	k _r ^{S-1} / s ^j	3.4 × 10 ⁻⁸ (34 ns)	5.6 × 10 ⁻⁷ (560 ns)	2.2 × 10 ⁻⁶ (2.2 μs)	1.8 × 10 ⁻⁶ (1.8 μs)
	k _r ^{T -1} / s ^k	7.6 × 10 ⁻⁴ (0.76 ms)	5.7 × 10 ⁻⁵ (57 μs)	7.1 × 10 ⁻⁶ (7.1 μs)	8 × 10 ⁻⁶ (8 μs)
	$\Delta E(G_3-G_1), (ZFS) / cm^{-11}$	9	94	58	43

Table S4.1. Summary of calculated properties of organometallic complexes 1-4 at 295 K.

^a lowest singlet TDDFT state energy; ^b lowest triplet TDDFT state energy; ^c energy difference between lowest TDDFT singlet and triplet states; ^d oscillator strength of lowest TDDFT singlet state; ^e reciprocal lowest excited TDDFT singlet state decay rate; ^f lowest triplet SOC-TDDFT state energy; ^g energy of lowest SOC-TDDFT state attributed to have dominant singlet character; ^h energy difference between SOC-TDDFT states attributed as lowest singlet and triplet; ⁱ oscillator strength of the lowest singlet SOC-TDDFT state; ^j reciprocal lowest excited SOC-TDDFT singlet state decay rate; ^k reciprocal average triplet state lifetime at 295 K calculated using methods reported earlier^[14,15]; ¹ energy difference between the first and third lowest SOC-TDDFT triplet states also referred to as zero-field splitting (ZFS).

Table S4.2. Summar	y of relevant TDE	OFT excited state	s in complex 1.
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Excited state	Energy / eV	f	Transition*	Character
S ₁	2.246	0.19	HOMO→LUMO (98%)	$d_{xz(Pt1 Pt2)} + p_{z(Cl1 Cl2)} + \pi_{ph} \rightarrow \pi_{pyrim}^{*}$
S_2	2.369	0.018	HOMO-1→LUMO (96%)	$d_{xz(Pt1 Pt2)} + p_{z(C11 C12)} + \pi_{ph} \rightarrow \pi_{pyrim}^{*}$
S ₃	2.438	6.5 × 10 ⁻⁵	HOMO-2→LUMO (98%)	$d_{xy(Pt1 Pt2)} + p_{y(C11 C12)} + \pi_{ph} \rightarrow \pi_{pyrim}^{*}$
T ₁	1.942	0	HOMO→LUMO (96%)	$d_{xz(Pt1 Pt2)} + p_{z(C11 C12)} + \pi_{ph} \rightarrow \pi_{pyrim}^{*}$
T ₂	2.094	0	HOMO-1→LUMO (95%)	$d_{xz(Pt1 Pt2)} + p_{z(C11 C12)} + \pi_{ph} \rightarrow \pi_{pyrim}^{*}$
T ₃	2.398	0	HOMO-2→LUMO (96%)	$d_{xy(Pt1 Pt2)} + p_{y(C11 C12)} + \pi_{ph} \rightarrow \pi_{pyrim}^{*}$

* Transitions with contribution < 10% are not shown.

Excited state	Energy / eV	f	Transition*	Character
S ₁	2.945	8.4×10^{-3}	HOMO→LUMO (98%)	$d_{xz(Pt)} + p_{z(Cl)} + \pi_L \rightarrow \pi_L^*$
S ₂	2.986	0.098	HOMO-1→LUMO+1 (97%)	$d_{xy(Pt)} + p_{y(Cl)} + \pi_L \rightarrow \pi_L^*$
T ₁	2.545	0	HOMO→LUMO (85%)	$d_{xz(Pt)} + p_{z(Cl)} + \pi_L \rightarrow \pi_L^*$
T ₂	2.677	0	HOMO-1→LUMO+1 (90%)	$d_{xy(Pt)} + p_{y(Cl)} + \pi_L \rightarrow \pi_L^*$

 Table S4.3.
 Summary of relevant TDDFT excited states in 2.

* Transitions with contribution < 10% are not shown.

Excited state	Energy / eV	f	Transition*	Character			
S ₁	1.718	6.0 × 10 ⁻⁵	HOMO→LUMO (99%)	$d_{xy(Pt1 Pt2)} + p_{y(I1 I2)} \rightarrow \pi_{pyrim}^{*}$			
S ₂	1.882	0.087	HOMO-1→LUMO (99%)	$d_{xz(Pt1 Pt2)} + p_{z(11 I2)} \rightarrow \pi_{pyrim}^{*}$			
S ₃	1.939	0.034	HOMO-2→LUMO (98%)	$d_{xz(Pt1 Pt2)} + p_{z(I1 I2)} \rightarrow \pi_{pyrim}^{*}$			
T ₁	1.679	0	HOMO-1→LUMO (96%)	$d_{xz(Pt1 Pt2)} + p_{z(I1 I2)} \rightarrow \pi_{pyrim}^{*}$			
T ₂	1.689	0	HOMO→LUMO (90%)	$d_{xy(Pt1 Pt2)} + p_{y(I1 I2)} \rightarrow \pi_{pyrim}^{*}$			
T ₃	1.716	0	HOMO-2→LUMO (90%)	$d_{xz(Pt1 Pt2)} + p_{z(11 12)} \rightarrow \pi_{pyrim}^{*}$			
* Transiti	* Transitions with contribution < 10% are not shown.						

 Table S4.4.
 Summary of relevant TDDFT excited states in 3.

Table S4.5.	Summarv	of relevant	TDDFT	excited	states	in 4 .
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Excited state	Energy / eV	f	Transition*	Character
\mathbf{S}_1	2.654	0.24	HOMO→LUMO (99%)	$d_{xz(Pt)} + p_{z(I)} + \pi_L \rightarrow \pi_L^*$
S ₂	2.728	8.2 × 10 ⁻⁴	HOMO-1→LUMO (97%)	$d_{xy(Pt)} + p_{y(I)} \rightarrow \pi_L^*$
T ₁	2.404	0	HOMO→LUMO (91%)	$d_{xz(Pt)} + p_{z(I)} + \pi_L \rightarrow {\pi_L}^*$
T ₂	2.570	0	HOMO-1→LUMO+1 (89%)	$d_{xy(Pt)} + p_{y(I)} \rightarrow \pi_L^*$

* Transitions with contribution < 10% are not shown.

Complex	State	Energy / eV	f	Contribution of zero-order states*
	G ₁	1.8931	1.8 × 10-5	$T_1^{M_s=0}$ (49.8%), $T_1^{M_s=1}$ (19.4%), $T_1^{M_s=-1}$ (19.4%)
	G ₂	1.8937	2.2×10^{-6}	$T_1^{M_s=0}$ (37.9%), $T_1^{M_s=1}$ (25.4%), $T_1^{M_s=-1}$ (25.4%)
1	G 3	1.8942	5.2 × 10 ⁻⁶	$T_1^{M_s=1}$ (43.7%), $T_1^{M_s=-1}$ (43.7%)
	G ₇	2.1488	0.15	$ \begin{array}{c} S_1 (70.3\%), T_3^{M_S = 1} (8.4\%), T_3^{M_S = -1} (8.4\%), \\ T_4^{M_S = 0} (6.4\%) \end{array} $
	G ₁	2.5590	3.6×10^{-5}	$T_1^{M_s=1}$ (43.2%), $T_1^{M_s=-1}$ (43.2%), $T_6^{M_s=0}$ (7.4%)
	G ₂	2.5591	1.2×10^{-3}	$T_1^{Ms=0}$ (86.2%)
2	G 3	2.5662	1.6×10^{-4}	$T_1^{M_s=1}$ (43.9%), $T_1^{M_s=-1}$ (43.9%)
	G ₇	2.8719	1.3 × 10 ⁻³	$ \begin{array}{l} S_1 (70.3\%), T_6^{M_8 = 1} (6.3\%), T_6^{M_8 = -1} (6.3\%), \\ T_5^{M_8 = 1} (5.5\%), T_5^{M_8 = -1} (5.5\%) \end{array} $
	G ₁	1.4582	2.1 × 10 ⁻⁵	$T_2^{M_s=0}$ (41.6%), $T_1^{M_s=1}$ (24.4%), $T_1^{M_s=-1}$ (24.4%)
3	G ₂	1.4619	5.1 × 10 ⁻⁴	$T_1^{M_s=0}$ (49.3%), $T_2^{M_s=1}$ (21.6%), $T_2^{M_s=-1}$ (21.6%)
	G 3	1.4699	1.6×10^{-5}	S_1 (44.6%), $T_1^{M_s=1}$ (25.1%), $T_1^{M_s=-1}$ (25.1%)
	G 4	1.5298	0.018	S_2 (25.2%), $T_2^{M_s = 1}$ (28.4%), $T_2^{M_s = -1}$ (28.4%)
	G ₁	2.2980	1.4×10^{-3}	$T_1^{M_s=0}$ (72.1%), $T_3^{M_s=1}$ (11.1%), $T_3^{M_s=-1}$ (11.1%)
4	G 2	2.2996	7.9×10^{-5}	$T_1^{M_s = 1}$ (36.4%), $T_1^{M_s = -1}$ (36.4%), $T_3^{M_s = 0}$ (22.7%)
	G 3	2.3032	1.0×10^{-5}	$T_1^{M_s = 1}$ (36.7%), $T_1^{M_s = -1}$ (36.7%), S_2 (20.0%)
	G ₄	2.4493	2.2×10^{-3}	S_1 (50.5%), $T_3^{M_s = 1}$ (20.4%), $T_3^{M_s = -1}$ (20.4%)

 Table S4.6 Composition of relevant SOC states in complexes 1-4.

* States with contributions < 5% are not shown.

Table S4.7. SOC matrix for the lowest TDDFT excited states in 1 (values in cm⁻¹).

Excited state	S ₁	S ₂	S ₃
T ₁	11	102	880
T ₂	470	25	48
T ₃	869	279	116

Excited state	S_1	S_2	S ₃
T ₁	3	67	6
T ₂	16	2	540
T ₃	938	54	427

Table S4.8. SOC matrix for the lowest TDDFT excited states in 2 (values in cm⁻¹).

Table S4.9. SOC matrix for the lowest TDDFT excited states in 3	(values	in cm ⁻¹).
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Excited state	S_1	S ₂	S_3
T ₁	2276	289	459
T ₂	226	2231	734
T ₃	169	375	118

Table S4.10. SOC matrix for the lowest TDDFT excited states in 4 (values in in cm⁻¹).

Excited state	S ₁	S ₂	S ₃
T ₁	16	242	773
T ₂	4	92	2344
T ₃	2106	10	1

 Table S4.11. Calculated dipole moments of complexes 3 and 4 at the BP86/def2-SVP level of theory.

Complex	S ₀	T ₁
3	7.94	3.12
4	5.56	3.81

5. Photophysics

a) Solution state



Figure S5.1. Photoluminescence spectra of complex 3 in CH_2Cl_2 at concentrations indicated in figure legend.



Figure S5.2. Photoluminescence spectra of complex 4 in CH_2Cl_2 at concentrations indicated in figure legend.



Figure S5.3. Photoluminescence decay of complex 4 at 5×10^{-5} M concentration in degassed CH₂Cl₂. The dark gray line (515 nm) represents exciton, "monomer" decay, while the red line (660 nm) represents excimer decay. Exciton decay is fitted with monoexponential expression 1, while excimer with biexponential expression 2. The respective lifetime values for exciton and excimer decay are: $\tau_M = 1.7 \ \mu s$ and $\tau_E = 1.5 \ \mu s$, respectively.

$$I(t) = A \cdot exp\left(-\frac{t}{\tau_M}\right)$$
(1)
$$I(t) = A\left[exp\left(-\frac{t-t_0}{\tau_M}\right) - exp\left(-\frac{t-t_0}{\tau_E}\right)\right]$$
(2)

The equations 1 and 2 are used for fitting of monoexponential exciton ("monomer") decay (1) and biexponential excimer decay (2), where: I(t) – luminescence intensity, a.u.; A – pre-exponential factor, a.u.; t – time, s; t₀ – correction for decay not starting from t = 0, s; τ_M – exciton ("monomer") decay constant at given conditions, s; τ_E – excimer decay constant, s.



Figure S5.4. Deconvolution of photoluminescence spectrum of **3** in toluene, examples. Spec – experimental spectrum at given temperature; Fluo – fluorescence spectrum; Phos – phosphorescence spectrum; Sum – sum Fluo + Phos.



Figure S5.5. Photoluminescence decay traces of complex 3 at temperatures from 160 to 300K in 10^{-5} M toluene solution. Detection at 630 nm.



Figure S5.6. Photoluminescence decay lifetime of **3** at temperatures from 160 to 300K in 10⁻⁵ M toluene solution. Detection at 700 nm.



Figure S5.7. Photoluminescence decay lifetime of **3** at temperatures from 160 to 300K in 10⁻⁵ M toluene solution. Detection at 650 nm.



Figure S5.8. Photoluminescence spectra of complex **4** at temperatures from 294 to 363K in 10⁻⁵ M chlorobenzene solution.

b) Solid film (polymer matrix)



Figure S5.9. Photoluminescence decay traces of complex 3 at temperatures from 80 to 300K in 0.1% w/w doped polystyrene film.



Figure S5.10. Time-resolved photoluminescence spectra of complex 3 in 0.1% w/w doped polystyrene film at delay and temperature indicated in figure legend.



Figure S5.11. Area normalised (area = 1000) photoluminescence spectra of complex 3 in 0.1% w/w doped polystyrene film at temperatures indicated in figure legend.



Figure S5.12. Normalised photoluminescence spectra of complex 3 in 0.1% w/w doped polystyrene film at temperatures from 80 to 120 K.



Figure S5.13. Normalised photoluminescence spectra of complex 4 in 0.1% w/w doped polystyrene film at temperatures from 80 to 300 K.



Figure S5.14. Photoluminescence decay lifetime of complex **4** in 0.1% w/w doped polystyrene film at temperatures from 80 to 300 K.



Figure S5.15. Photoluminescence spectra of complex 3 dispersed in polystyrene at the various concentrations shown in the figure legend, 100% denotes neat film.



Figure S5.16. Photoluminescence decay traces of excimer band (850 nm) of complex **3** doped in polystyrene or in pristine film. Decay lifetimes: $\tau_1 = 24$ ns (69%), $\tau_1 = 86$ ns (31%), $\tau_{av} = 62$ ns [10%]; $\tau_1 = 23$ ns (23%), $\tau_1 = 76$ ns (77%), $\tau_{av} = 58$ ns [neat]; Note the extremely short lifetime (~60 ns), more typical of fluorescent than phosphorescent emitters, is rather a manifestation of a large k_{nr} than large k_r .

6. Electrochemistry



Figure S6.1 Cyclic voltammograms (CV) of 3 (top) and 4 (bottom) at $c = 10^{-3}$ M in 0.1 M Bu₄NBF₄/ CH₂Cl₂ solution.

Electrochemical behaviour of complexes **3** and **4** is generally identical to that of the related complexes **1** and **2**.^[22] Mononuclear complexes **2** and **4** show both irreversible oxidation and reduction processes. Dinuclear complexes **1** and **3** demonstrate first reduction to be reversible, $E_{\frac{1}{2}} = -1.29$ V in **3**, very close to the value reported in **1**, $E_{\frac{1}{2}} = -1.33$ V. The second reduction process is irreversible. Oxidation is irreversible in both cases. First (E_{red1}) and second (E_{red2}) reduction onset potentials are virtually identical considering typical \pm 0.05 V errors in this technique. This is in agreement with calculations as the replacement of the ancillary chloride with iodide does not appear to significantly alter the distribution or energy of the LUMO. On the other side, oxidation potentials of the Pt-I analogues **3** and **4** are significantly lower by around 0.3 V than those of the Pt-Cl analogues **1** and **2**, again in line with the changes in the calculated distributions and energies of HOMOs.

Complex	E _{ox} , V	E _{red1} , V	E _{red2} , V
1	0.50	-1.26	-2.12
2	0.54	-2.19	-
3	0.18	-1.21	-2.05
4	0.23	-2.21	-

Table S6.1. Electrochemical onset redox potentials of complexes 1-4 recorded in 0.1 M Bu₄NBF₄/ CH_2Cl_2 solution at c = 10⁻³ M. Values for complexes 1 and 2 were adapted from an earlier work.^[22]

7. OLED devices

Device	Architecture
Dev 1	ITO Al4083 (30 nm) PVKH (10) mCP:PO-T2T (70:30) co. 3 (5 %) (30 nm) PO- T2T (50 nm) LiF (0.8 nm) Al (100 nm)
Dev 2	ITO Al4083 (30 nm) PVKH (10) mCP:PBD (60:40) co. 3 (5 %) (30 nm) TmPyPB (50 nm) LiF (0.8 nm) Al (100 nm)
Dev 3	ITO Al4083 (30 nm) mCP:PO-T2T (80:20) co. 3 (33 %) (65 nm) PO-T2T (50 nm) LiF (0.8 nm) Al (100 nm)

 Table S7.1. OLED device architecture for devices 1-3 presented in the main article.



Figure S7.1. Current density-voltage (J-V) characteristics of devices 1-3.

In addition to the OLED devices presented in the main text, we have also produced a device comprising neat layer of **3** as the emissive layer. Similarly to the case of complex **1**, the radiosity of the device was too low in order to obtain reliable estimate of external quantum efficiency. The electroluminescence spectrum of this OLED is presented in the figure below. Note the $\lambda_{el} = 824$ nm which is at longer wavelength than that reported in complex **1** ($\lambda_{el} = 805$ nm). The shoulder at 600-700 nm is attributed to residual monomer electroluminescence.



Figure S7.2 Electroluminescence spectrum of device ITO | PEDOT:PSS Al4083 (30 nm) | 3 (\approx 60 nm) | PO-T2T (50 nm) | LiF (0.8 nm) | Al (100 nm). Note $\lambda_{el} = 824$ nm.

8. References

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