

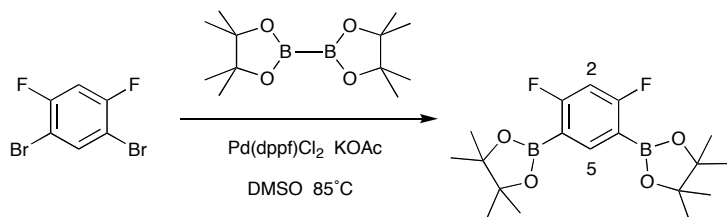
Blue-shifting the monomer and excimer phosphorescence of tridentate cyclometallated platinum(II) complexes for optimal white-light OLEDs

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Electronic Supporting Information

1. Synthesis procedures and characterisation of new compounds

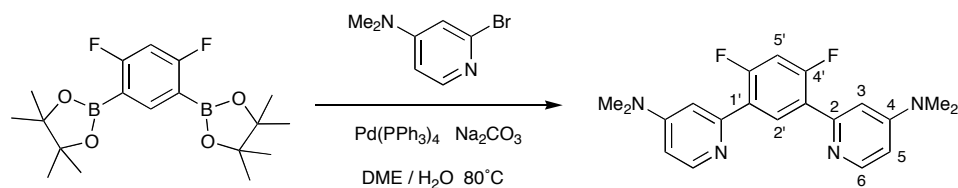
1,3-Difluoro-4,6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene



Anhydrous DMSO (5 mL) was transferred under nitrogen to a Schlenk tube containing 1,3-dibromo-4,6-difluorobenzene (300 mg, 1.1 mmol), bispinacolatodiboron (620 mg, 2.4 mmol), Pd(dppf)Cl₂ (54 mg, 0.07 mmol) and KOAc (545 mg, 5.6 mmol). The mixture was heated at 85°C under a nitrogen atmosphere for 18 h. On cooling to room temperature, a mixture of EtOAc and water (25 mL of each) was added, and the organic phase was separated. This solution was washed with water (2 × 30 mL) and brine (2 × 50 mL), dried with MgSO₄, and the solvent removed under reduced pressure. The crude product was purified by column chromatography (silica, hexane/EtOAc 100:0 → 80:20). The product was obtained as a white crystalline solid (330 mg, 0.96 mmol, 86%) R_f = 0.75 (silica, hexane/EtOAc 50:50). ¹H NMR (500 MHz, CDCl₃) δ_H = 1.33 (24H, s, CH₃), 6.71 (1H, t, J = 9.9, H²), 8.11 (1H, t, J = 7.7, H⁵). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ_C = 25.0 (s, CH₃), 84.2 (s, OCM₂), 103.6 (t, J = 28.0, C²), 146.1 (t, J = 10.3, C⁵), 170.4 (dd, J = 258.8 and 13.8, C¹), 207.5 (m, C⁴). ¹⁹F NMR (376 MHz, CDCl₃) δ_F = -94.6 (2F, t, J = 8.4). HRMS (ASAP): *m/z* 366.2076 [62%, ¹¹B, M], calcd for [C₁₈H₂₆¹¹B₂F₂O₄], 366.19853.

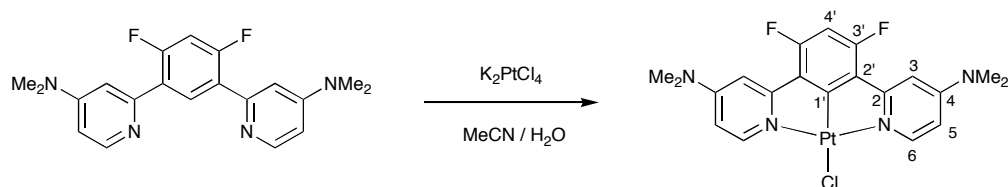
continued

HL³⁰: 1,3-di(4-dimethylamino-2-pyridyl)-4,6-difluorobenzene



A mixture of 1,3-difluoro-4,6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (100 mg, 0.27 mmol), 2-bromo-4-dimethylamino-pyridine (121 mg, 0.6 mmol), Na₂CO₃ (1M in 3 mL water), dimethoxyethane (3 mL) and water (3 mL) was degassed by three freeze-pump-thaw cycles and placed under nitrogen. Under a fast flow of nitrogen, Pd(PPh₃)₄ (32 mg, 0.03 mmol) was added, and the mixture then heated at 80°C under nitrogen for 48 h. Upon cooling to room temperature, water (30 mL) was added, and the product extracted into dichloromethane (3 × 25 mL). The resulting solution was dried over MgSO₄, filtered, and the solvent removed under reduced pressure. The product was purified by column chromatography (alumina, hexane/EtOAc, 100:0 → 0:100, then DCM/MeOH 100:0 → 90:10) and was obtained as a white oily solid (50 mg, 0.14 mmol, 51%), R_f = 0.43 (alumina, 100% EtOAc). ¹H NMR (700 MHz, CDCl₃) δ_H = 3.04 (12H, s, CH₃), 6.45 (2H, dd, J = 6.1 and 2.6, H⁵), 6.90 (2H, d, J = 2.1, H³), 6.94 (1H, t, J = 10.6, H^{5'}), 8.29 (2H, d, J = 5.9, H⁶), 8.35 (1H, t, J = 8.9, H^{2'}). ¹³C {¹H} NMR (176 MHz, CDCl₃) δ_C = 39.2 (s, CH₃), 104.8 (t, J = 27.0, C⁵), 105.7 (s, C⁵), 107.4 (t, J = 3.6, C³), 125.5 (dd, J = 11.4, 4.8, C^{1'}), 133.9 (t, J = 4.5, C^{2'}), 149.7 (s, C⁶), 153.1 (s, C²), 154.9 (s, C⁴), 160.2 (dd, J = 254.1 and 12.4, C^{4'}). ¹⁹F NMR (376 MHz, CDCl₃) δ_F = -112.8 (2F, br m). HRMS (ES⁺): *m/z* 377.15462 [22%, M+Na⁺], 355.17257 [100, M+H⁺]; calcd for [C₂₀H₂₁F₂N₄], 355.17288, calcd for [C₂₀H₂₀F₂N₄²³Na], 377.15482.

PtL³⁰Cl



A solution of K₂PtCl₄ (47 mg, 0.11 mmol) in water (1 mL) was de-aerated via three freeze-pump-thaw cycles and transferred via cannula to a similarly de-aerated solution of HL³⁰ (40 mg, 0.11 mmol) in CH₃CN (3 mL). The mixture was heated at 120°C under a nitrogen atmosphere for 72 h. On cooling, the pale green precipitate was collected by centrifugation and washed

successively with water, ethanol, ether and acetone (3×10 mL of each), to give the analytically pure product PtL^{30}Cl (44 mg, 0.075 mmol, 67%). ^1H NMR (400 MHz, CDCl_3) 3.13 (12H, s, CH_3), 6.38 (2H, dd, $J = 6.9$ and 2.9 , H^5), 6.63 (1H, t, $J = 11.6$, H^4), 7.08 (2H, d, $J = 2.7$, H^3), 8.77 (2H, d, $J = 6.8$, $^3J(^{195}\text{Pt}) = 37$, H^6). ^{19}F NMR (376 MHz, CDCl_3) $\delta_{\text{F}} = -111.5$ (2F, d, $J = 11.3$, $^4J(^{195}\text{Pt}) = 59$). MS (MALDI): m/z 584.1 [M], 1129.1 [2M–Cl]. HRMS (MALDI): 547.1200 [100%, M–Cl]. HRMS (ASAP): m/z 547.1215 [80%, M–Cl]; calcd for $[\text{C}_{20}\text{H}_{19}^{35}\text{F}_2\text{N}_4^{195}\text{Pt}]$, 547.1205. Anal. $\text{C}_{20}\text{H}_{19}\text{ClF}_2\text{N}_4\text{Pt}$ (583.91): calcd. C, 41.14; H, 3.28; N, 9.60 %. Found C, 40.12; H, 2.81; N, 8.05 %.



Fig. S1 Frontier orbital plots of PtL^1Cl from TD-DFT calculations. The calculations confirm that the lowest-energy S_1 and T_1 states do have predominantly HOMO–LUMO character, 92% and 75%, respectively [D. L. Rochester, S. Develay, S. Zális and J. A. G. Williams, *Dalton Trans.*, 2009, 1728].

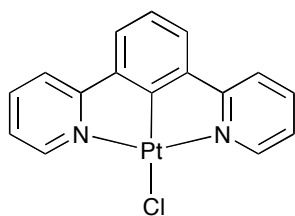
Photophysical measurements in solution

UV-vis absorption spectra were recorded with a Biotek Instruments XS spectrometer using quartz cuvettes of 1 cm path length. Steady-state emission spectra were measured using a JobinYvon FluoroMax 2 spectrometer. The spectra shown are corrected for the wavelength dependence of the detector, and the quoted emission maxima refer to the values after correction. Luminescence quantum yields were determined using $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ in degassed aqueous solution as the standard, for which $\Phi_{\text{lum}} = 0.042$ [J. Van Houten and R. J. Watts, *J. Am. Chem. Soc.*, 1976, **98**, 4853]. Estimated uncertainty in Φ_{lum} is $\pm 20\%$ or better. The luminescence lifetimes of the complexes were measured by time-correlated single-photon counting (TCSPC), following excitation at 374 nm with an EPL-375 pulsed-diode laser. The emitted light was detected at 90° using a Peltier-cooled R928 PMT after passage through a monochromator. The estimated uncertainty in the quoted lifetimes is $\pm 10\%$ or better.

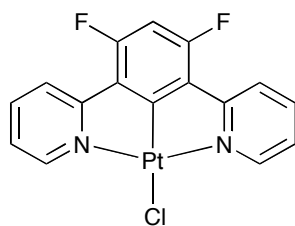
Table S1 Photophysical data for the new complex PtL³⁰Cl, together with data for PtL¹Cl and PtL²²Cl for comparison^(a)

Complex	Absorbance λ_{\max} / nm (ϵ / M ⁻¹ cm ⁻¹)	Emission monomer λ_{\max} / nm	Emission excimer λ_{\max} / nm	Φ_{lum} (^b)	τ_0 / ns ^(c) degassed [aerated]	k_{sq} / 10 ⁹ M ⁻¹ s ⁻¹ (^c)	k_r / 10 ⁴ s ⁻¹ (^d)	Σk_{nr} / 10 ⁴ s ⁻¹ (^d)	Emission at 77 K ^(e)	
									λ_{\max} / nm	τ / ns
PtL ¹ Cl	332 (6510), 380 (8690), 401 (7010), 454 (270), 485 (240)	491, 524, 562	696	0.60	7200 [500]	5.3	8.3	5.6	486, 516, 548 sh	6400
PtL ²² Cl ^(f)	320 (6690), 334 (9180), 360 (7340), 374 (8500), 437 (140), 467 (140)	472, 502, 536	677	0.85	7900 [670]	6.0	11	1.9	467, 478, 496, 526	5800
PtL ³⁰ Cl	319 (6580), 352 sh (9310), 370 (13910), 443 (160)	453, 482, 517 sh	596	0.60	4700 [130]	2.1	13	8.5	449, 478, 516, 539 sh	3900

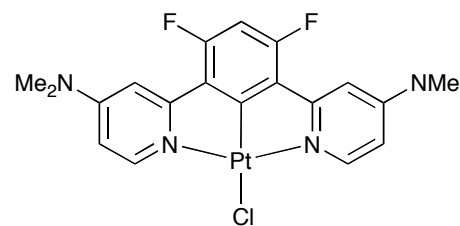
(a) In CH₂Cl₂ at 298 ± 3 K, except where indicated otherwise. (b) Luminescence quantum yield measured using [Ru(bpy)₃]Cl₂ in degassed water as the standard, $\Phi = 0.042$ [J. Van Houten and R. J. Watts, *J. Am. Chem. Soc.*, 1976, **98**, 4853]. (c) τ_0 and k_{sq} are the lifetime at infinite dilution and the bimolecular rate constant for self-quenching, obtained from the intercept and gradient, respectively, of a plot of the measured lifetime τ against concentration. (d) k_r and Σk_{nr} are the rate constants of radiative and non-radiative decay, respectively, estimated from the luminescence lifetimes and quantum yields, assuming that the emitting state is formed with unitary efficiency upon excitation into the lowest-energy spin-allowed band. (e) In diethyl ether / isopentane / ethanol (2:2:1 v/v). (f) M. Cocchi, J. Kalinowski, V. Fattori, J. A. G. Williams and L. Murphy, *Appl. Phys. Lett.*, 2009, **94**, 073309; L. Murphy, PhD. Thesis, Durham University, 2010.



PtL¹Cl



PtL²²Cl



PtL³⁰Cl

Details of OLED structures and fabrication

OLEDs were fabricated by growing a sequence of thin layers on clean glass substrates pre-coated with a 150 nm-thick layer of indium tin oxide (ITO) with a sheet resistance of 20 Ω per square. A 60 nm-thick (TPD:PC) blend hole-transporting layer was deposited on top of ITO by spin coating from a 10mg/ml dichloromethane solution at room temperature. All remaining organic layers were deposited in succession by thermal evaporation under vacuum of $\sim 10^{-6}$ hPa, followed by high vacuum ($\sim 10^{-6}$ hPa) thermal-evaporation of the cathode layer consisting of 0.5 nm-thick LiF and by a 100 nm-thick Al cap. The EML was evaporated by flash-deposition of the three materials: PtL³⁰Cl, TCTA and TCP, from one thermal source to form a 30 nm-thick blend film. All measurements were carried out at room temperature under argon atmosphere and were reproduced for many runs, excluding any irreversible chemical and morphological changes in the devices. Compound abbreviations: TPD = N,N'-bis(3-tolyl)-1,1'-biphenyl-4,4'-diamine; PC biphenol-A-polycarbonate; TCTA = 4,4',4''-tris-(N-carbazolyl)-triphenylamine; TCP = 1,3,5-tris(N-carbazolyl)benzene; TAZ = 3-phenyl-4-(1'-naphthyl)-5-phenyl-1,2,4-triazole.

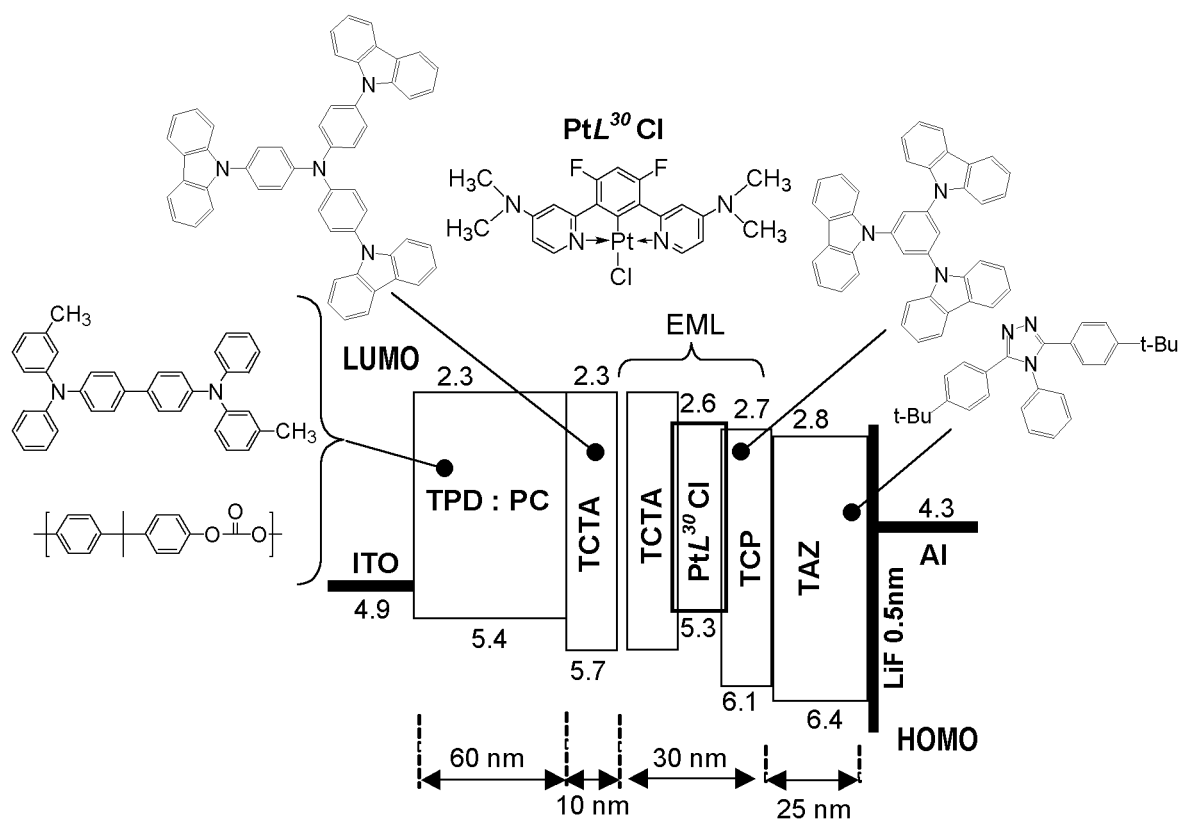


Fig. S2 OLED architecture, molecular structures and electronic energy levels of the materials used. The energy values are derived from the redox potential measured by cyclic voltammetry (HOMO) and from the spectroscopic energy gap (LUMO).

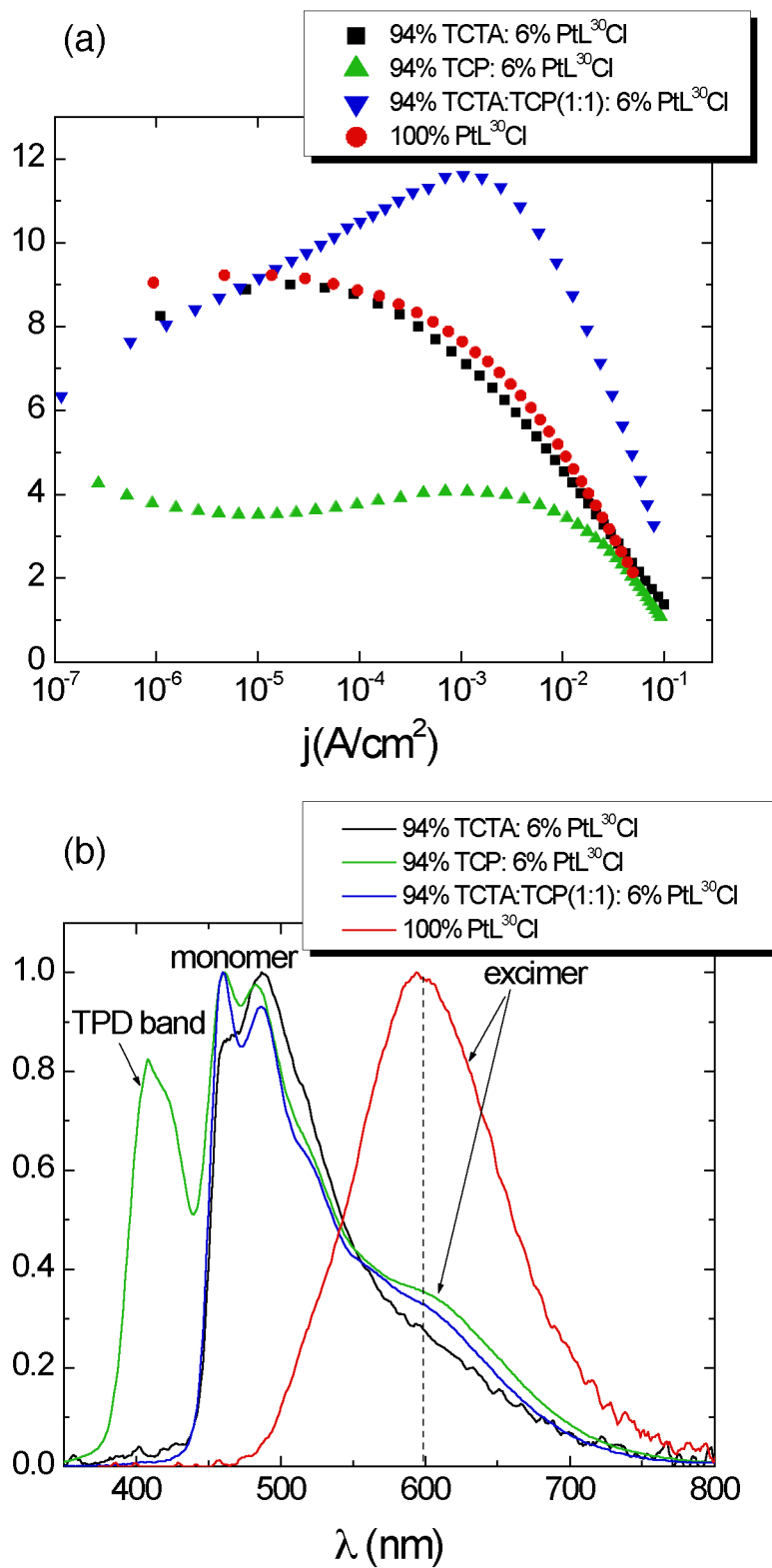


Fig. S3 (a) EL quantum efficiency (QE) vs current density (j) and (b) EL spectra of the devices with different EML compositions as reported in the legend. The curves for a neat PtL³⁰Cl film as the EML are also reported for comparison.

Table S2 Performance data for the OLEDs prepared.^(a) Each device is listed by concentration (*x*) of PtL³⁰Cl in the emitting layer. All data are for a brightness value of ~ 500 cd/mq.

PtL ³⁰ Cl complex <i>x</i> (wt %)	Bias (V)	<i>j</i> (mA/cm ²)	QE (%ph/e)	LE (cd/A)	CIE (<i>x</i> , <i>y</i>)	CCT (°K)	CRI
3	9	6.0	3.9	6.9	0.20; 0.30	—	—
6	9.3	2.5	11.3	23.5	0.26; 0.34	—	—
12	12.9	3.6	7.1	14.3	0.32; 0.37	5826	84
20	10.5	3.6	3.7	7.4	0.36; 0.37	4470	87
25	11.1	8.9	2.7	5.5	0.37; 0.39	3806	88
100	7.8	3.9	6.4	14	0.52; 0.47	—	—

(a) OLED configuration: ITO / 75 wt% TPD: 25 wt% PC (50nm) / TCTA (10nm) / *x* % PtL³⁰Cl : 100-*x* % [TCTA: TCP] [1:1] (30 nm) / TAZ (30 nm) / LiF / Al (see Fig. S1 for scheme). Driving voltage bias (V); current density (*j*); external quantum efficiency (QE); luminous efficiency (LE); CIE coordinates; correlated color temperature (CCT); color rendering index (CRI).