Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Homoleptic platinum(II) complexes with pyridyltriazole ligands:

Excimer-forming phosphorescent emitters for solution-processed OLEDs

Melissa T. Walden,[a] *Piotr Pander,*[b] *Dmitry Yufit,*[a] *Fernando B. Dias**[b]

*and J. A. Gareth Williams**[a]

[a] Department of Chemistry and [b] Department of Physics, Durham University, Durham, DH1 3LE, UK.

*E-mails: j.a.g.williams@durham.ac.uk f.m.b.dias@durham.ac.uk

1. Crystallography

Table S1 Crystal data and structure refinement parameters

Identification code	HL^1	PtL^1_2	PtL^2_2
Empirical formula	$C_{17}H_{18}N_4$	$C_{34}H_{34}N_8Pt$	$C_{54}H_{58}N_8Pt$
Formula weight	278.35	753.81	1014.17
Temperature/K	120.0	120.0	120.0
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	P-1
a/Å	5.9123(6)	11.6673(5)	6.5952(3)
b/Å	13.2287(13)	5.5870(3)	10.7367(5)
c/Å	18.6718(19)	21.8713(10)	16.1585(8)
α/°	90	90	88.6300(17)
β/°	98.757(4)	101.0279(15)	83.5014(17)
γ/°	90	90	85.8827(17)
Volume/$Å^3$	1443.3(3)	1399.36(12)	1133.76(9)
Z	4	2	1
$\rho_{calc}g/cm^3$	1.281	1.789	1.485
μ/mm^{-1}	0.079	5.055	3.141
F(000)	592.0	752.0	516.0
Reflections collected	27498	21893	22013
Independent refl., R_{int}	3480, 0.0696	4081, 0.0489	5458, 0.0470
Data/restraints/parameters	3480/0/262	4081/0/199	5458/15/292
Goodness-of-fit on F^2	1.031	1.161	1.067
Final R_1 indexes [I≥2σ (I)]	0.0467	0.0377	0.0343
Final wR_2 indexes [all data]	0.1057	0.0847	0.0729

2. Photophysics in solution

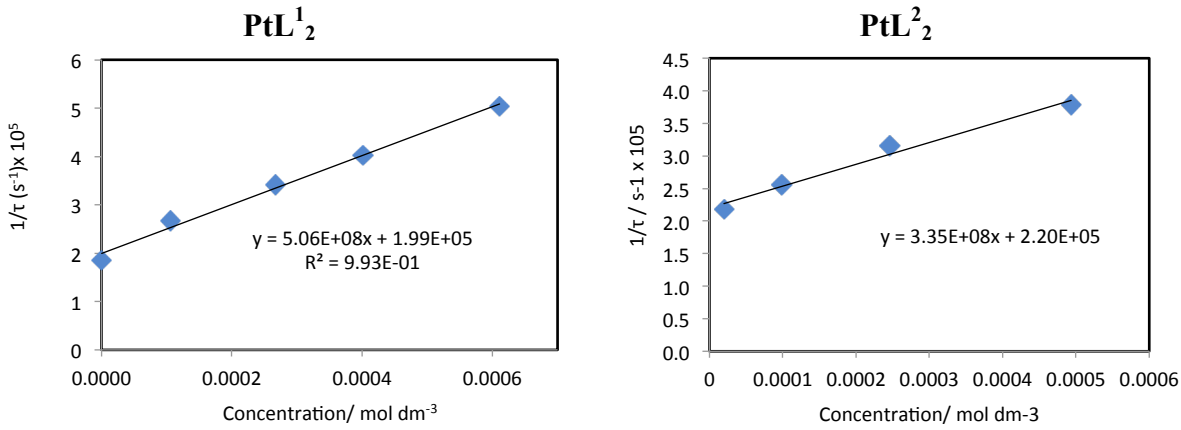

Figure S1 *Pots of 1/τ versus concentration for complexes PtL$^1_2$ and PtL$^2_2$.*

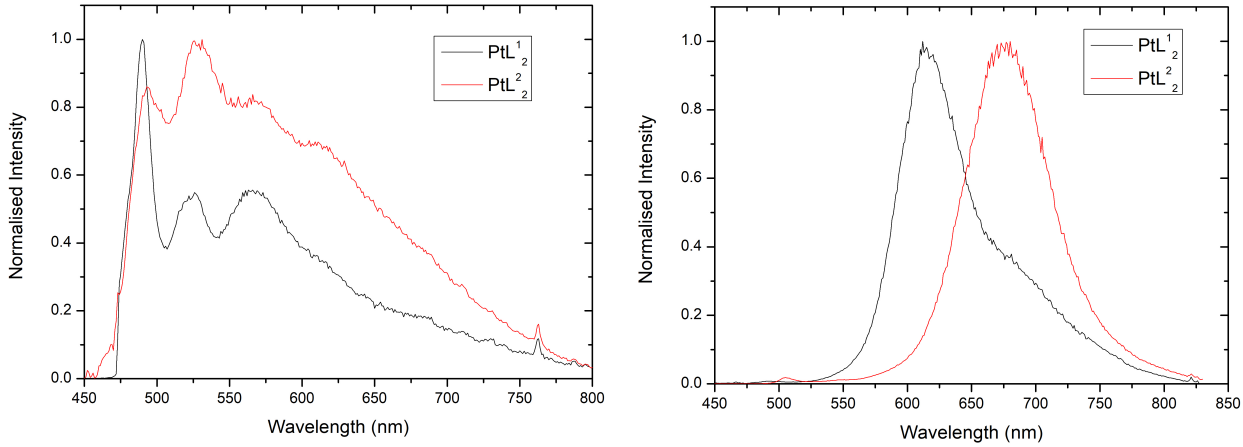

Figure S2 *Photoluminescence spectra of PtL$^1_2$ and PtL$^2_2$ at 77 K.*
Left: at low concentration, showing the unimolecular emission. Right: at high concentration showing the bimolecular emission.

3. Photophysics in solid state

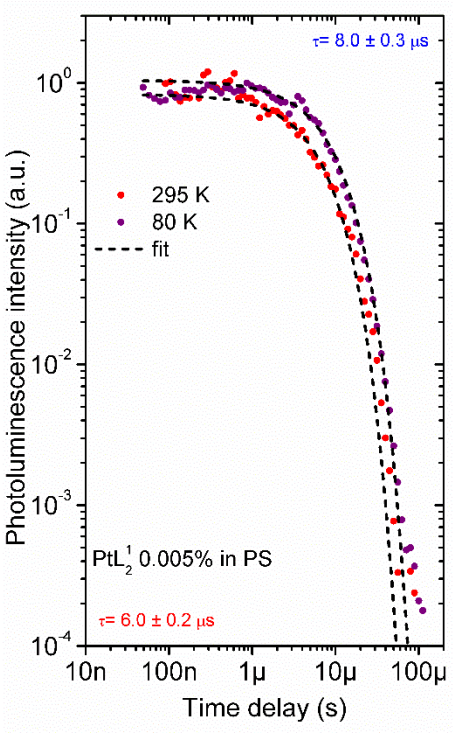

Figure S3 *Photoluminescence decay of PtL$^1_2$ 0.005% (w/w) doped in polystyrene (PS).*

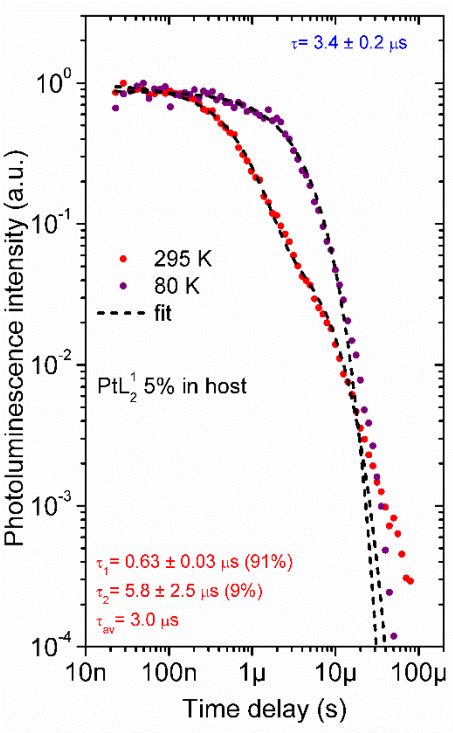

Figure S4 *Photoluminescence decay of PtL$^1_2$ 5% (w/w) doped in OLED host (mCP:OXD7 80:20).*

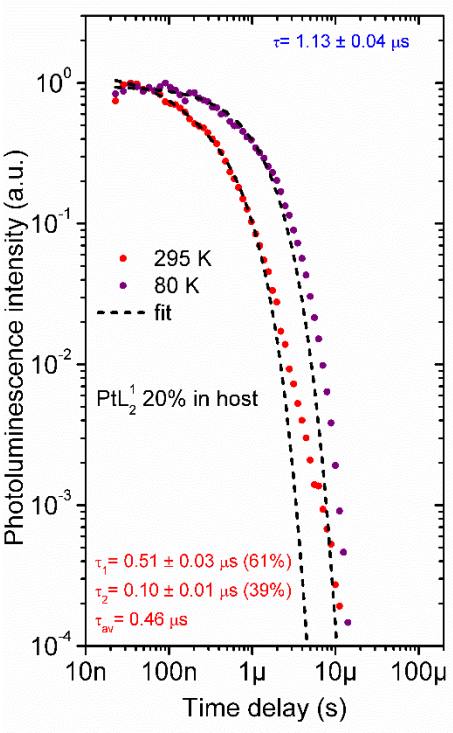

Figure S5 *Photoluminescence decay of PtL^1_2 20% (w/w) doped in OLED host (mCP:OXD7 80:20).*

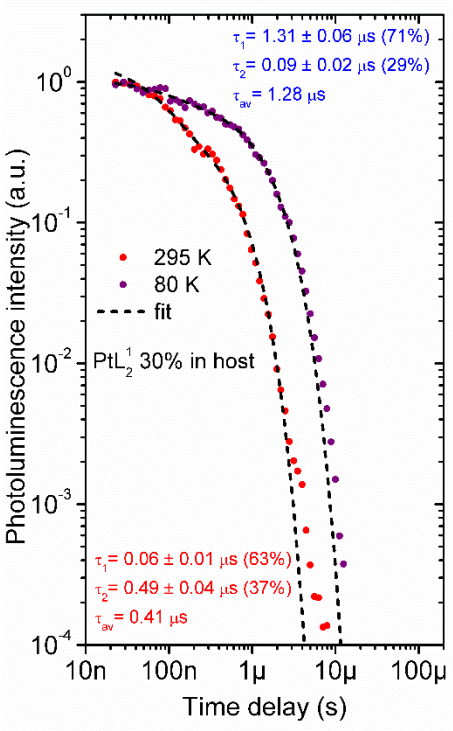

Figure S6 *Photoluminescence decay of PtL^1_2 30% (w/w) doped in OLED host (mCP:OXD7 80:20).*

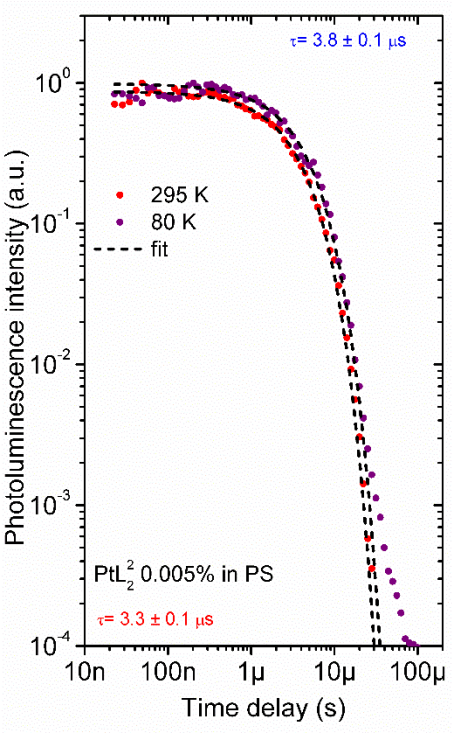

Figure S7 *Photoluminescence decay of PtL^2_2 0.005% (w/w) doped in polystyrene (PS).*

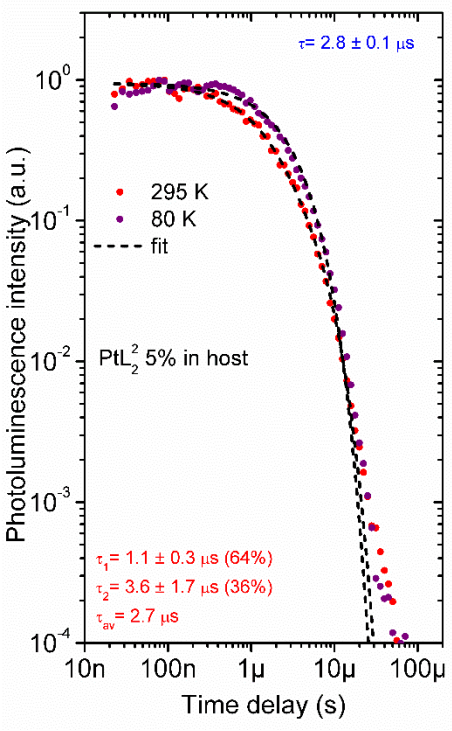

Figure S8 *Photoluminescence decay of PtL^2_2 5% (w/w) doped in OLED host (mCP:OXD7 80:20).*

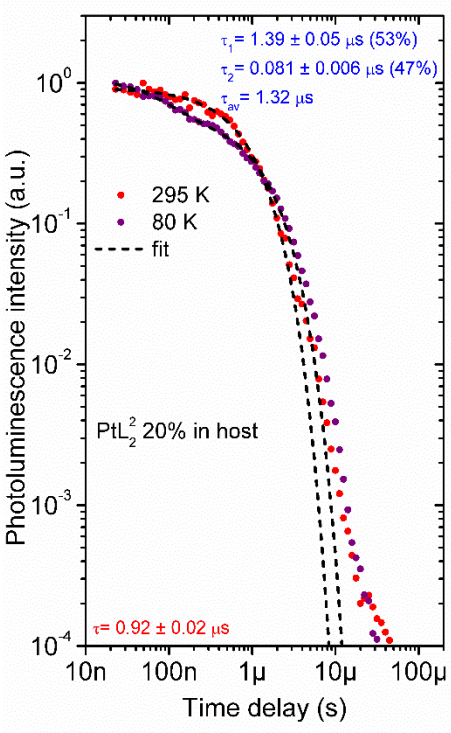

Figure S9 *Photoluminescence decay of PtL^2_2 20% (w/w) doped in OLED host (mCP:OXD7 80:20).*

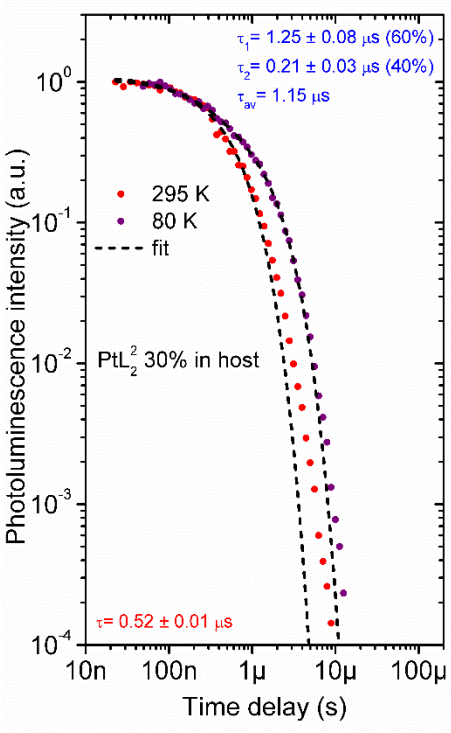

Figure S10 *Photoluminescence decay of PtL^2_2 30% (w/w) doped in OLED host (mCP:OXD7 80:20).*

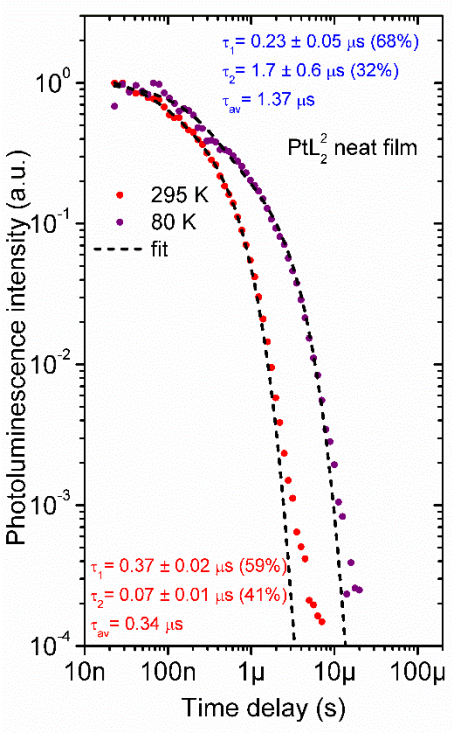

Figure S11 *Photoluminescence decay of PtL^2_2 neat film.*

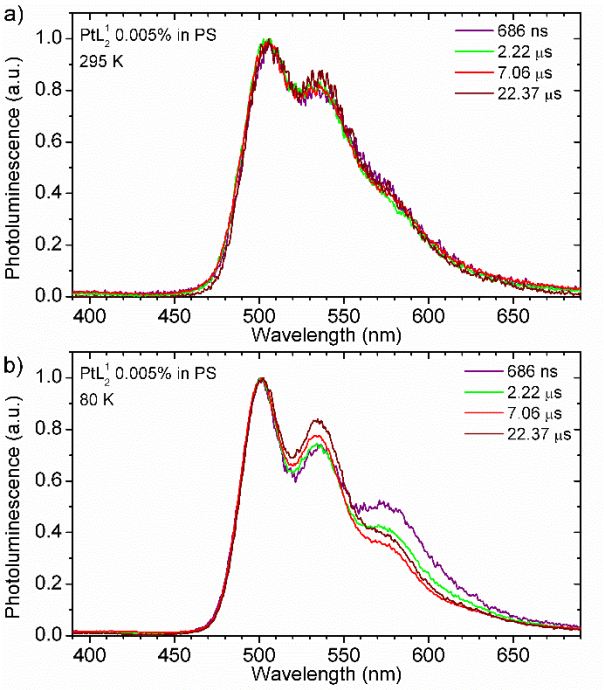

Figure S12 *Time-resolved photoluminescence spectra of PtL^1_2 0.005% doped PS film.*

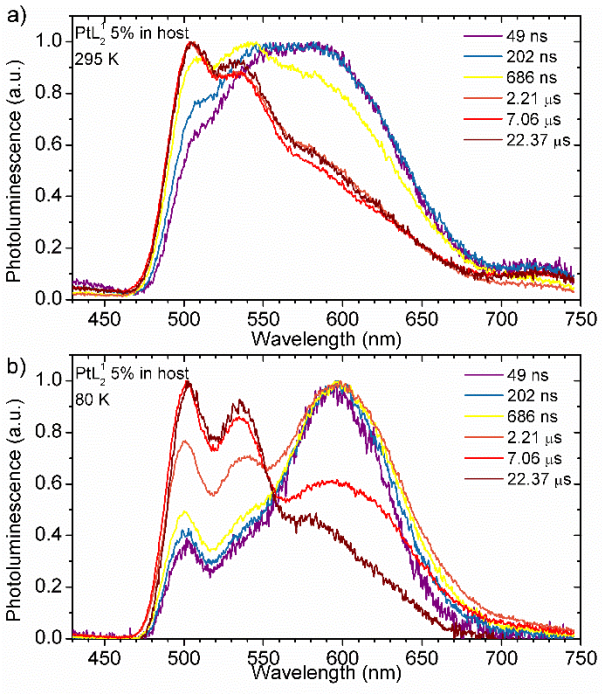

Figure S13 *Time-resolved photoluminescence spectra of PtL$^1_2$ 5% (w/w) doped in OLED host (mCP:OXD7 80:20).*

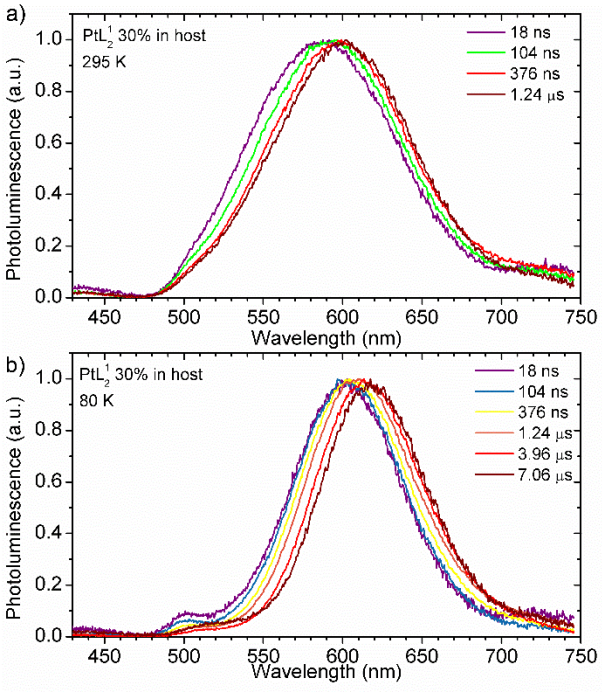

Figure S14 *Time-resolved photoluminescence spectra of PtL$^1_2$ 30% (w/w) doped in OLED host (mCP:OXD7 80:20).*

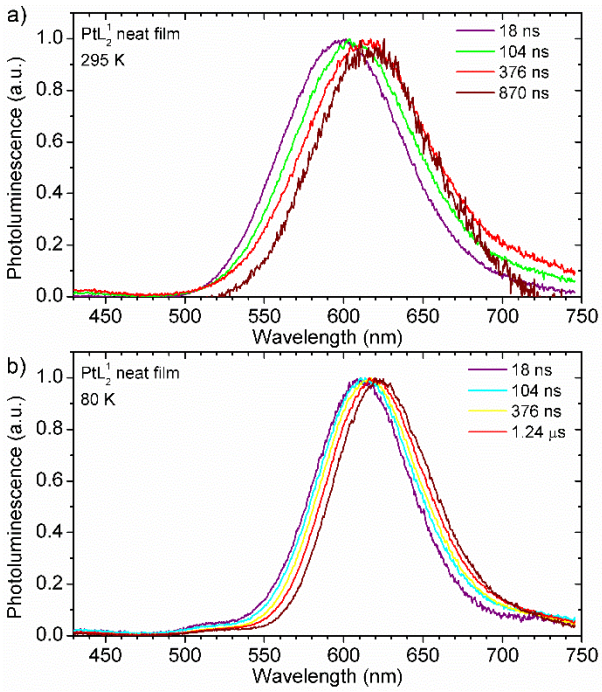

Figure S15 *Time-resolved photoluminescence spectra of PtL$^1_2$ neat film.*

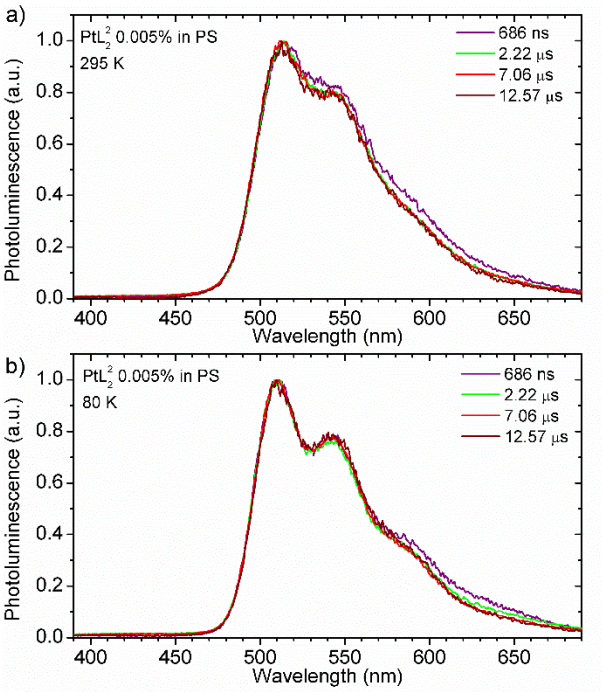

Figure S16 *Time-resolved photoluminescence spectra of PtL$^2_2$ 0.005% doped PS film.*

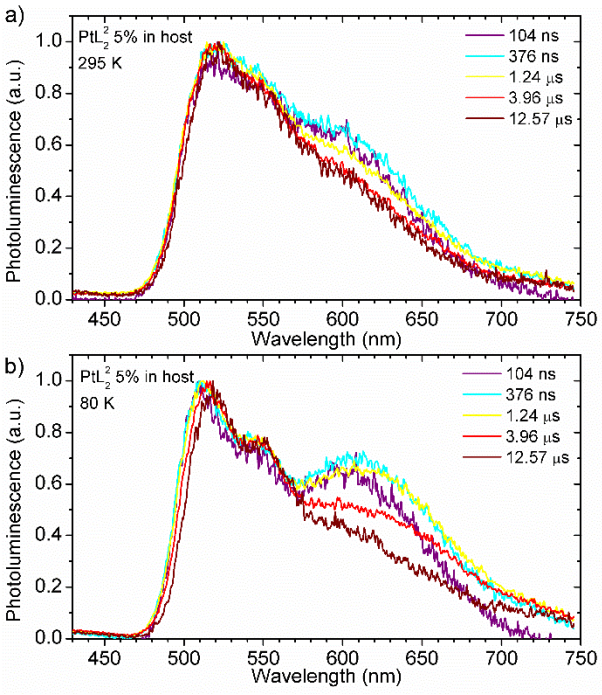

Figure S17 *Time-resolved photoluminescence spectra of PtL^2_2 5% (w/w) doped in OLED host (mCP:OXD7 80:20).*

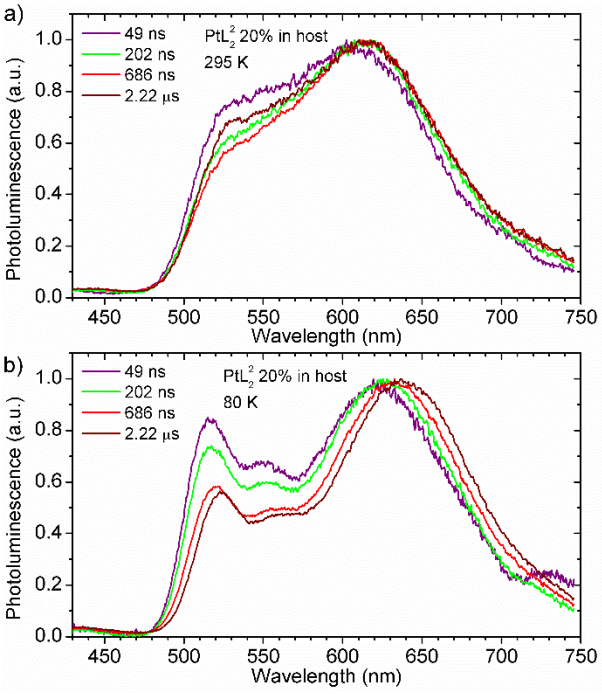

Figure S18 *Time-resolved photoluminescence spectra of PtL^2_2 20% (w/w) doped in OLED host (mCP:OXD7 80:20).*

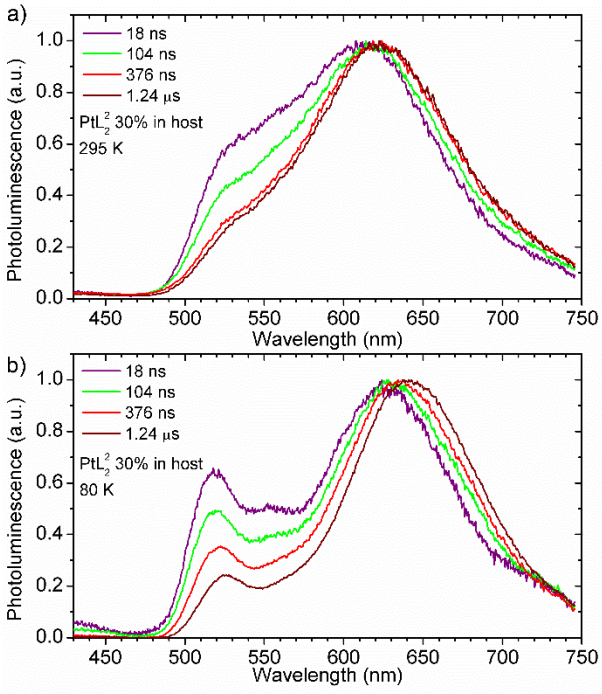

Figure S19 *Time-resolved photoluminescence spectra of PtL^2_2 30% (w/w) doped in OLED host (mCP:OXD7 80:20).*

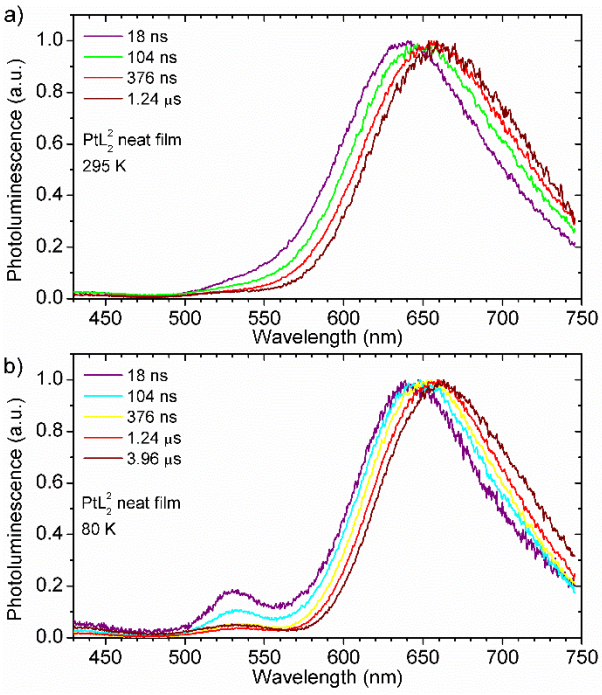

Figure S20 *Time-resolved photoluminescence spectra of PtL^2_2 neat film.*

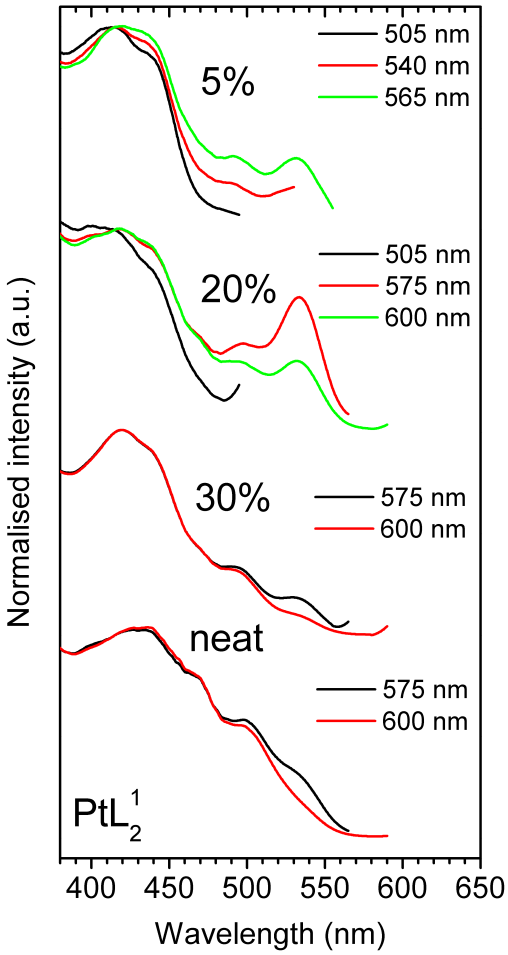

Figure S21 *Excitation spectra of thin films of PtL^1_2. The % represents the weight concentration of the emitter in mCP:OXD7 (80:20) host. The wavelength at which the emission was registered is given in the figure legend.*

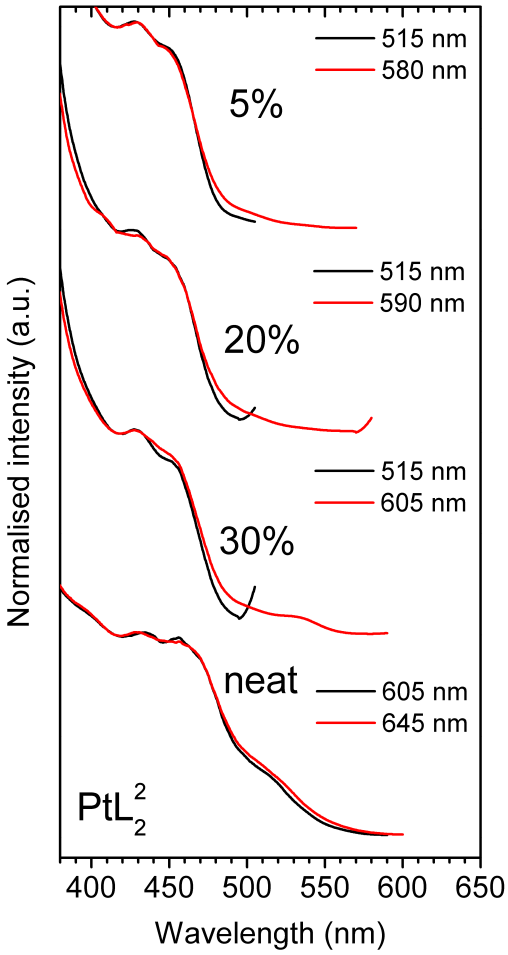

Figure S22 *Excitation spectra of thin films of PtL^2_2. The % represents the weight concentration of the emitter in mCP:OXD7 (80:20) host. The wavelength at which the emission was registered is given in the figure legend.*

4. OLED devices

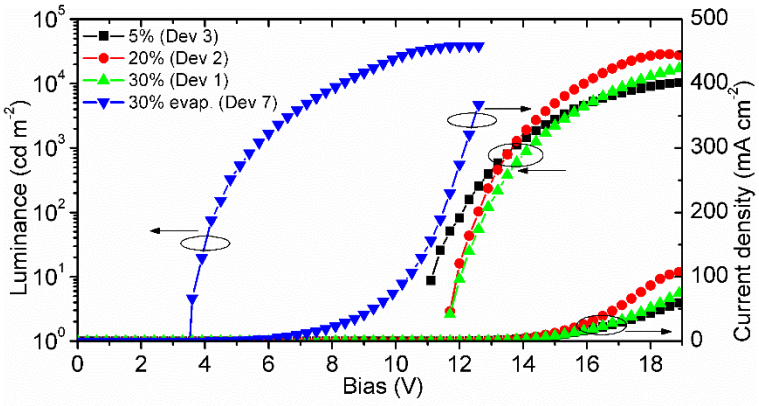

Figure S23 *Luminance-voltage and current density-voltage characteristics of devices 1-3 and 7.*

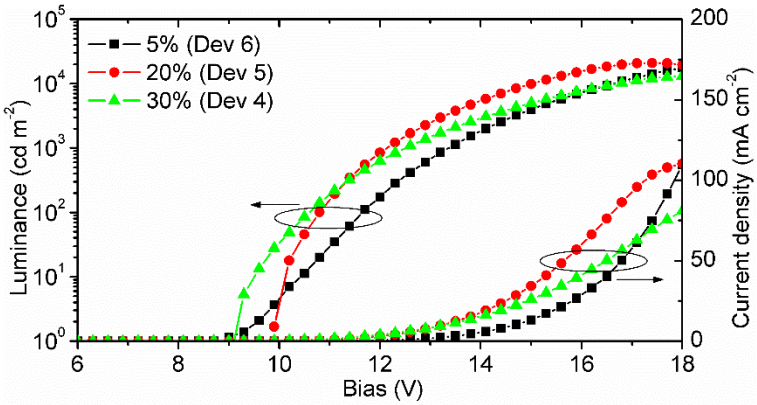

Figure S24 *Luminance-voltage and current density-voltage characteristics of devices 4-6.*

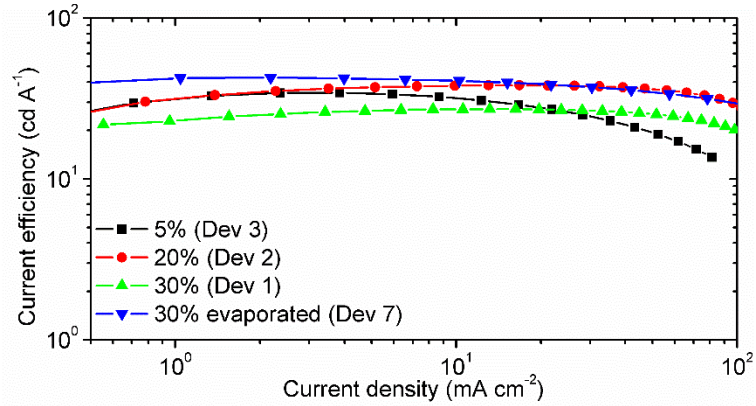

Figure S25 *Current efficiency-current density characteristics of devices 1-3 and 7.*

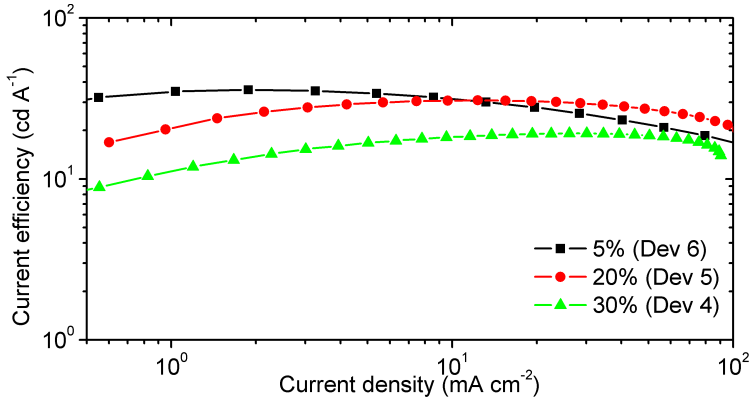

Figure S26 *Current efficiency-current density characteristics of devices 4-6.*

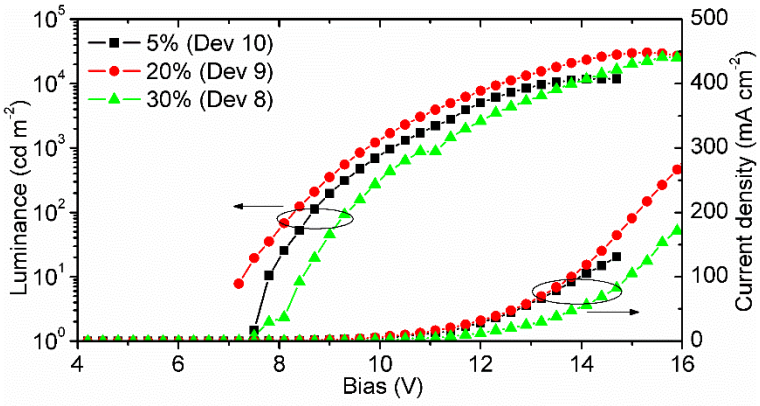

Figure S27 *Luminance-voltage and current density-voltage characteristics of devices 8-10.*

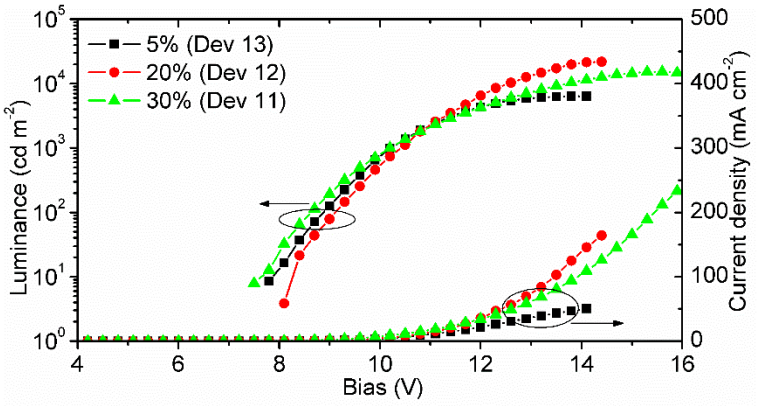

Figure S28 *Luminance-voltage and current density-voltage characteristics of devices 11-13.*

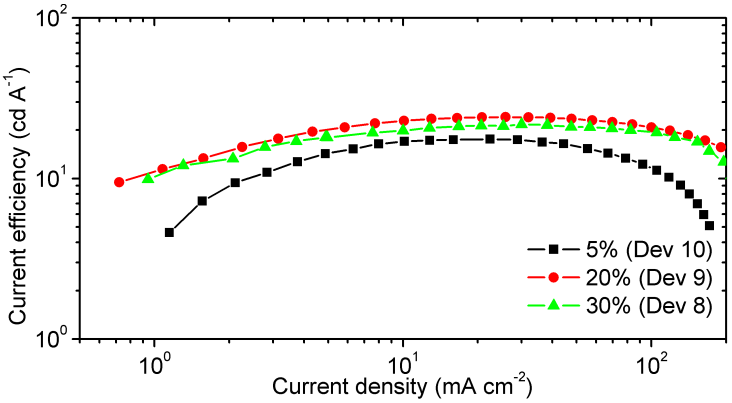

Figure S29 *Current efficiency-current density characteristics of devices 8-10.*

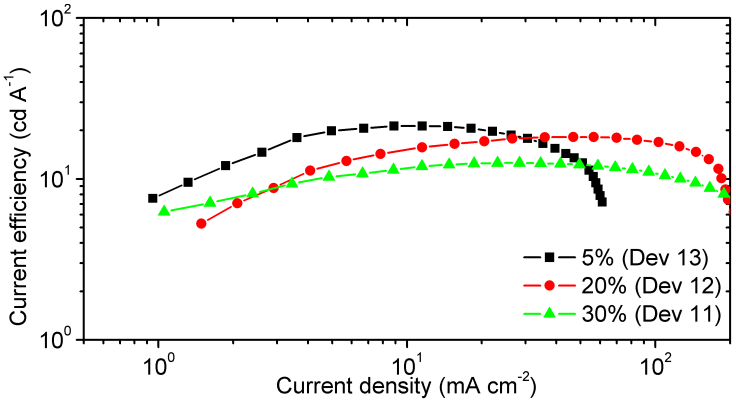

Figure S30 *Current efficiency-current density characteristics of devices 11-13.*

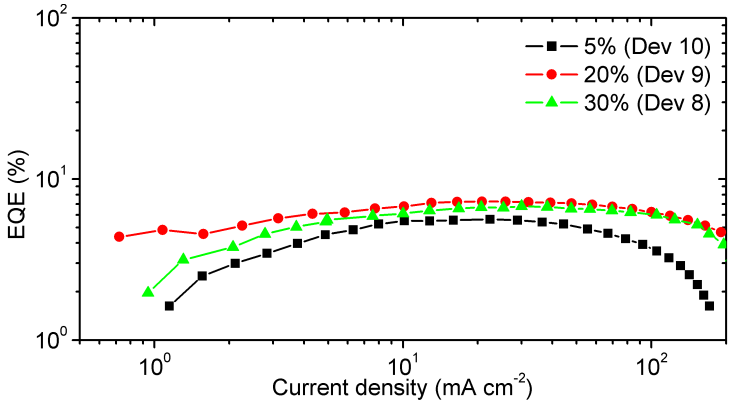

Figure S31 *External quantum efficiency (EQE)-current density characteristics of devices 8-10.*

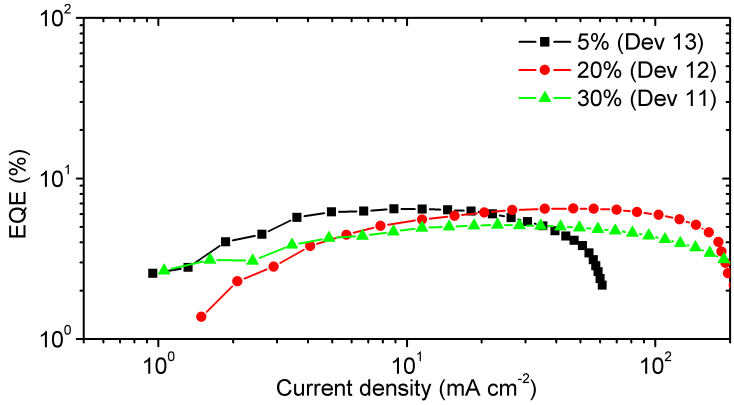

Figure S32 *External quantum efficiency (EQE)-current density characteristics of devices 11-13.*

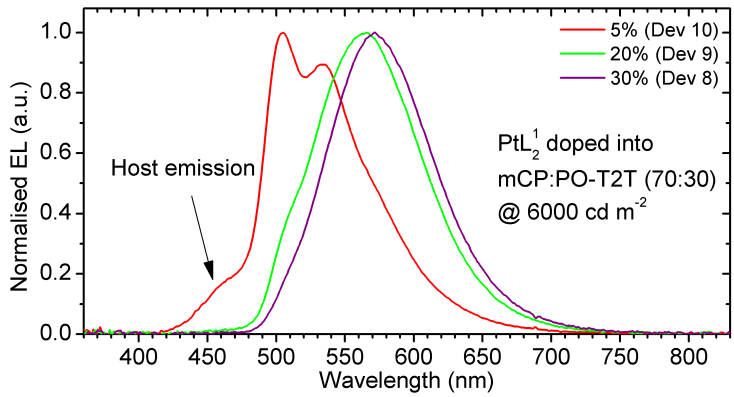

Figure S33 *Electroluminescence spectra of devices 8-10.*

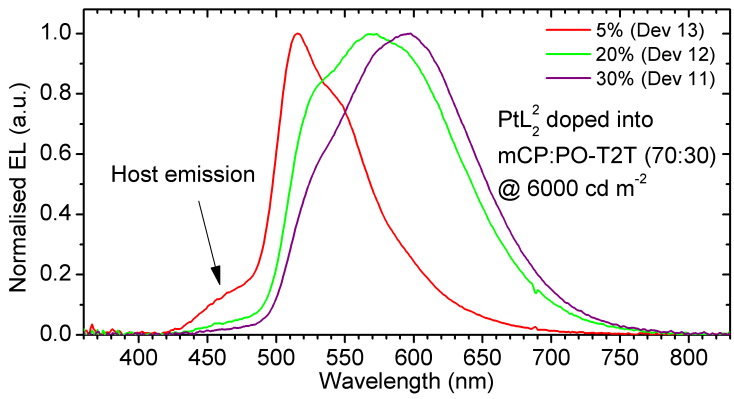

Figure S34 *Electroluminescence spectra of devices 11-13.*

Table S2 *Summary of OLED device characteristics.*

Device	**Dopant**	**Dopant conc. %**	**Φ_{PL} in film**	**V_{ON} @ 10 cd m^{-2} / V**	**EQE, %: max / at 1 mA cm^{-2} / at 10 mA m^{-2}**	**CE, cd A^{-1}: max / at 1 mA cm^{-2} / at 10 mA m^{-2}**	**L_{max}, cd m^{-2}**	**CIE (x,y) at L_{max}**
Dev 1	PtL^1_2	30	0.55 ±0.06	12.0	9.6 / 7.6 / 9.7	27.2 / 22.5 / 26.5	19800	0.50, 0.49
Dev 2	PtL^1_2	20	0.61 ±0.06	11.9	12.5 / 10.1 / 12.3	38.2 / 30.9 / 37.9	28700	0.47, 0.51
Dev 3	PtL^1_2	5	0.63 ±0.06	11.1	10.4 / 9.2 / 9.7	34.3 / 30.9 / 32.4	26100	0.41, 0.55
Dev 4	PtL^2_2	30	0.58 ±0.06	9.5	8.8 / 5.2 / 8.3	19.2 / 11.2 / 18.1	13400	0.52, 0.47
Dev 5	PtL^2_2	20	0.57 ±0.06	10.1	11.4 / 6.2 / 11.4	30.8 / 20.3 / 30.3	21000	0.47, 0.51
Dev 6	PtL^2_2	5	0.85 ±0.09	10.4	10.9 / 10.4 / 9.7	35.8 / 34.1 / 30.3	26900	0.35, 0.58
Dev 7*	PtL^1_2	30*	-	3.8	15.0 / 15.0 / 14.5	42.7 / 41.8 / 40.3	38800	0.45, 0.51
Dev 8	PtL^1_2	30	-	8.4	6.8 / 2.1 / 6.1	21.4 / 10.4 / 20.2	25900	0.45, 0.53
Dev 9	PtL^1_2	20	-	7.3	7.3 / 4.7 / 6.9	24.1 / 11.2 / 22.8	30300	0.42, 0.55
Dev 10	PtL^1_2	5	-	7.8	5.6 / - / 5.5	17.6 / - / 17.0	12000	0.29, 0.54
Dev 11	PtL^2_2	30	-	7.7	5.1 / 2.6 / 4.8	12.6 / 6.1 / 11.8	15300	0.49, 0.49
Dev 12	PtL^2_2	20	-	8.3	6.5 / - / 5.4	18.2 / - / 15.0	21800	0.45, 0.52
Dev 13	PtL^2_2	5	-	7.9	6.5 / 2.6 / 6.3	21.4 / 7.7 / 21.4	8300	0.30, 0.57

***** This device was prepared by vacuum thermal evaporation. The 30% concentration relates to the 30% evaporation rate contribution of dopant during co-evaporation of the emissive layer.

Device structures were as follows (overpage):

Dev 1-6: ITO | HIL 1.3N (45 nm) | mCP:OXD7 (80:20) co x% dopant (60±5 nm) | TPBi (50 nm) | LiF (0.8 nm) | Al (100 nm)

Dev 7: ITO | NPB (35 nm) | TSBPA (10 nm) | mCP (5 nm) | mCP co 30% Triaz 1 (20 nm) | TPBi (50 nm) | LiF (0.8 nm) | Al (100 nm)

Dev 8-13: ITO | HIL 1.3N (45 nm) | mCP:PO-T2T (70:30) co x% dopant (70±5 nm) | PO-T2T (50 nm) | LiF (0.8 nm) | Al (100 nm)

DFT calculations

The calculations were carried out using the Gaussian 09 suite of programs[¶] to predict energy-minimized structures of the singlet ground states. The LANL2DZ basis set was used for all atoms, and the B3LYP functional was selected. Harmonic vibrational wavenumber calculations were performed to confirm that the structures obtained correspond to minima on the potential energy surface. Time-dependent calcualtions were carried out on the optimised structures to probe the orbital parentage of the lowest-energy spin-allowed transitions.

Table S3 *TD-DFT B3LYP/LANL2DZ excitation energies for the five lowest-lying singlet states of* PtL^1_2 *with their corresponding oscillator strengths, transitions and contributions.*

Excited state	Energy (eV)	Wavelength (nm)	Oscillator strength	Transition	Contribution
S1	2.53	489.18	0.030	HOMO → LUMO HOMO–1 → LUMO	0.697 0.101
S2	2.89	429.39	0.000	HOMO–1 → LUMO	0.704
S3	3.09	400.83	0.000	HOMO → LUMO+1	0.695
S4	3.45	359.38	0.128	HOMO–1 → LUMO+1	0.697
S5	3.97	346.89	0.051	HOMO → LUMO+2	0.688

[¶] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Montgomery, {Jr.}, J. A., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, 2009, Gaussian 09.

Table S4 *TD-DFT B3LYP/LANL2DZ excitation energies for the five lowest-lying singlet states of PtL^2_2 with their corresponding oscillator strengths, transitions and contributions.*

Excited state	Energy (eV)	Wavelength (nm)	Oscillator strength	Transition	Contribution
S1	2.49	498.81	0.0453	HOMO → LUMO	0.699
S2	2.86	434.19	0.000	HOMO–1 → LUMO HOMO → LUMO+1	0.695 0.115
S3	2.95	419.68	0.000	HOMO → LUMO+1	0.690
S4	3.32	372.94	0.098	HOMO–1 → LUMO+1	0.701
S5	3.48	355.36	0.374	HOMO–2 → LUMO	0.554

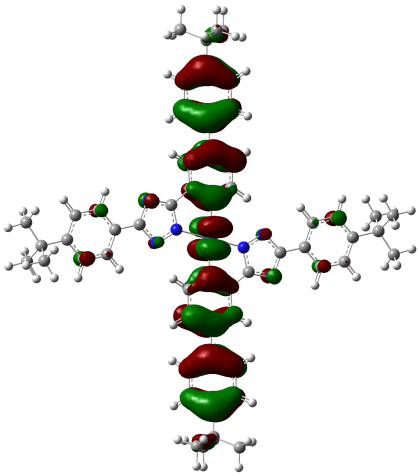

Figure S35 *The HOMO–2 orbital of PtL^2_2, which features in the $S_0 \rightarrow S_5$ transition (principal contribution is HOMO–2→LUMO).*