### **Electronic Supplementary Information**

For

# Highly efficient electroluminescent Pt<sup>II</sup> ppy-type complexes with monodentate ligands

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### Experimental

General information: All reactions were carried out under a nitrogen atmosphere with the use of standard Schlenk techniques. The solvents were purified by standard methods under dry nitrogen before use. All commercially available reagents were used as received unless otherwise stated. The reactions were monitored by thin-layer chromatography (TLC) with Merck pre-coated aluminum plates. Flash column chromatography and preparative TLC were carried out using silica gel.

Physical measurements: <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were measured in CDCl<sub>3</sub> with a Bruker AXS 400 MHz spectrometer with the chemical shifts quoted relative to tetramethylsilane (TMS). Fast atom bombardment (FAB) mass spectra were collected with a Finnigan MAT SSQ710 system. UV-Vis spectra were recorded with a Shimadzu UV-2250 spectrophotometer. The photoluminescent (PL) properties of the PtII complexes were measured with an Edinburgh Instruments FLS920 fluorescence spectrophotometer. The lifetimes for the excited states were measured by a single photon counting spectrometer from Edinburgh Instruments FLS920 with a 396 nm picosecond LED lamp as the excitation source. Cyclic voltammetry (CV) measurement for the sample solution was performed on the Princeton Applied Research model 2273A potentiostat with a glassy carbon working electrode, a platinum counter electrode, and a platinum-wire reference electrode at a scan rate of 100 mV s<sup>-1</sup>. The solvent was deoxygenated acetonitrile, and the supporting electrolyte was 0.1 M [*n*Bu<sub>4</sub>N][BF<sub>4</sub>]. Ferrocene (Fc) was added as an internal calibrant for the measurement, and all potentials reported were quoted with reference to the Fc-Fc<sup>+</sup> couple. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit under a nitrogen flow at a heating rate of 10 °C min<sup>-1</sup> to obtain the glass transition temperature ( $T_{o}$ ). The thermal gravimetric analysis (TGA) was conducted on NETZSCH STA 409C instrument under nitrogen with a heating rate of 20 °C min<sup>-1</sup>.



Fig. S1 Synthetic schemes of Pt-Py and Pt-Pi.

General procedures for the synthesis of ligands: Under a N<sub>2</sub> atmosphere, (4-(diphenylamino)phenyl)boronic acid (1.2 equiv), 2-bromopyridine or 2-chloropyrimidine (1 equiv) and Pd(PPh<sub>3</sub>)<sub>4</sub> (5% equiv) were heated at 110 °C for 18 h in a mixture of THF/2 M Na<sub>2</sub>CO<sub>3</sub>(v/v, 1:1, 30 ml). After cooling to room temperature and the addition of water, the mixture was extracted with dichloromethane, the organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated under reduced pressure. The residual was chromatographed using appropriate eluent to produce the title product.

**L-Py:** (Yield: 75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.66–8.64 (m, 1H), 7.88–7.85 (m, 2H), 7.73– 7.65 (m, 2H), 7.30–7.25 (m, 4H), 7.19–7.12 (m, 7H), 7.07–7.03 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 157.05, 149.56, 148.66, 147.45, 136.62, 133.09, 129.28, 127.70, 124.70, 123.19, 121.44, 119.84; FAB-MS (*m/z*): 322 [M]<sup>+</sup>.

**L-Pi:** (Yield: 82%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.73(d, J = 4.8 Hz, 2H), 8.28 (d, J = 8.8Hz, 2H), 7.30–7.25 (m, 3H), 7.16–7.05 (m, 10H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 164.157, 157.16,154.13, 134.75, 127.88, 125.58, 118.77, 34.84, 31.22; FAB-MS (*m/z*): 323 [M]<sup>+</sup>.

General procedures for the synthesis of  $Pt^{II}$  complexes: Under a N<sub>2</sub> atmosphere, each appropriate cyclometalating ligand (1.2 equiv) and K<sub>2</sub>PtCl<sub>4</sub> (1 equiv) was heated in a mixture of 2ethoxyethanol and water (3:1, v/v) for 18 h at 90 °C. After cooling to room temperature and the addition of water, the cyclometalated Pt<sup>II</sup>  $\mu$ -chloro-bridged dimer was formed as a precipitate which was collected and dried under vacuum. The dimeric Pt complex (1 equiv) and pyridine (2.5 equiv) were heated to 50 °C in chloroform for 12 h. Then the mixture was cooled to room temperature and extracted with dichloromethane. The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated under reduced pressure. The residue was chromatographed using an appropriate eluent to produce the title product.

**Pt-Py:** 75 mg (Yield: 82%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 9.63–9.54 (m, 1H), 8.83–8.72 (m, 2H), 7.77–7.73 (m, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.21 (t, *J* = 8.0 Hz, 4H), 7.11–7.00 (m, 9H), 6.80 (dd, *J* = 2.4, 8.4 Hz, 1H), 5.88–5.76 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 153.71, 151.13, 149.33, 147.17, 138.57, 137.19, 129.14, 125.72, 125.39, 124.46, 123.94, 123.39, 120.56, 117.53, 116.77; FAB-MS (*m/z*): 596 [M-Cl]<sup>+</sup>; C<sub>28</sub>H<sub>22</sub>ClN<sub>3</sub>Pt: calcd. C 53.29, H 3.51, N 6.66; found C 53.18, H 3.59, N 6.59.

**Pt-Pi:** 79 mg (Yield: 81%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 9.76–9.67 (m, 1H), 8.34–8.76 (m, 1H), 8.73–8.71 (m, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.29–7.24 (m, 6H), 7.14 (t, *J* = 7.2 Hz, 2H), 7.10–7.08 (m, 5H), 7.05 (t, *J* = 4.8 Hz, 1H), 6.84 (dd, *J* = 2.4, 8.8 Hz, 1H), 5.90–5.76(m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 158.40, 157.39, 153.66, 152.34, 146.85, 141.45, 137.37, 133.65, 129.23, 128.48, 125.91, 125.76, 123.90, 122.32, 116.36, 115.92. FAB-MS (*m/z*): 671 [M+K]<sup>+</sup>; C<sub>27</sub>H<sub>21</sub>ClN<sub>4</sub>Pt: calcd. C 51.31, H 3.35, N 8.86; found C 51.22, H 3.46, N 8.71.

OLED fabrication and measurements: The pre-cleaned ITO glass substrates were treated with

ozone for 20 min. Then, the PEDOT:PSS was deposited on the surface of ITO glass by spincoating method to form a 45 nm-thick hole injection layer. After being cured at 120 °C for 30 min in the air, the emitting layer (40 nm) was obtained by spin-coating a chloroform solution of each Pt<sup>II</sup> complex and 4,4'-*N*,*N'*-'dicarbazole-biphenyl (CBP) at various concentrations. The ITO glass was dried in a vacuum oven at 50 °C for 20 min and it was transferred to the deposition system for organic and metal deposition. TPBi (1, 3, 5-*tris*[*N*-(phenyl)-benzimidazole]-benzene) (45 nm), LiF (1 nm) and Al cathode (100 nm) were successively evaporated at a base pressure less than 10<sup>-6</sup> Torr. The EL spectra and CIE coordinates were measured with a PR650 spectra colorimeter. The *J*–*V*–*L* curves of the devices were recorded by a Keithley 2400/2000 source meter and the luminance was measured using a PR650 SpectraScan spectrometer. All the experiments and measurements were carried out under ambient conditions.

**Computational details:** Geometrical optimizations were conducted using the popular B3LYP functional theory. The basis set used for C, H and N atoms was 6-311G(d,p), while the effective core potentials with LanL2DZ basis set were employed for Pt atoms.<sup>S1</sup> The energies of the excited states of the complexes were computed by TD-DFT based on all the ground-state geometries. The various properties of these molecules, such as HOMO, LUMO and reorganization energies ( $\lambda$ ) were obtained from the computed results. All calculations were carried out by using the Gaussian 09 program.<sup>S2</sup>

**X-ray crystallography:** A single crystal of **Pt-Py** of suitable dimensions was mounted in thin glass fiber for collecting the intensity data on a Bruker SMART CCD diffractometer (Mo K $\alpha$  radiation and  $\lambda = 0.71073$  Å) in  $\Phi$  and  $\omega$  scan modes at 223 K. The structure was solved by direct methods followed by difference Fourier syntheses and then refined by full-matrix least-squares

techniques against *F*<sup>2</sup> using SHELXL-97<sup>S3</sup> program on a personal computer. The positions of hydrogen atoms were calculated and refined isotropically using a riding model. All other non-hydrogen atoms were refined isotropically. Absorption corrections were applied using SADABS.<sup>S4</sup> The crystallographic data for **Pt-Py** have been deposited at the Cambridge crystallographic Data Center with the deposition number CCDC-1503885. These data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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Table S1	Single	crystal	data	for	Pt-Py.
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Compound	Pt-Py			
CCDC No.	1503885			
formula	$C_{28}H_{22}ClN_3Pt$			
formula weight	631.03			
crystal system	monoclinic			
space group	$P2_1/c$			
<i>a</i> (Å)	10.2191(3)			
<i>b</i> (Å)	8.2286(3)			
<i>c</i> (Å)	28.0195(10)			
$\alpha$ (deg)	90			
$\beta$ (deg)	94.450(3)			
$\gamma$ (deg)	90			
$V(\text{\AA}^3)$	2349.04(15)			
Ζ	4			
$D_{\text{calcd}} \text{ (g cm}^{-3})$	1.784			
crystal size (mm <sup>3</sup> )	0.03×0.14×0.17			
F(000)	1224			
$\mu(\mathrm{mm}^{-1})$	12.378			
$\theta$ range (deg)	3.16 - 73.50			
diffrn reflns number	1000			
reflns number total	4607			
no. of parameters	298			
$R1, wR2 [I > 2.0\sigma(I)]^a$	0.0326, 0.0690			
R1, $wR2$ (all data)	0.0507, 0.0773			
GOF on $F^{2b}$	0.987			
${}^{a}\overline{R1} = \Sigma   F_{0}  -  F_{c}   / \Sigma  F_{0} . \ wR2 = \{\Sigma [w(F_{0}^{2} - Fc^{2})^{2}$	$]\Sigma [w(F_0^2)^2]^{1/2}$ . <sup>b</sup> GOF = $[(\Sigma w   F_0] -$			
$ F_c )^2/(N_{\rm obs} - N_{\rm param})]^{1/2}.$				

Table S2. Selected structural parameters of Pt-Py.

Bond Angles (°)				Bond Lengths (Å)	
C(11)-Pt(1)-N(1)	81.0(2)	C(24)-N (3)-Pt(1)	123.6(4)	Pt (1)-C(11)	1.956(5)
C(11)-Pt(1)-N(3)	95.8(2)	C(28)-N(3)-Pt(1)	118.2(4)	Pt (1)-Cl(1)	2.2006(15)
N(1)-Pt(1)-N(3)	176.12(19)	C(10)-C(11)-Pt(1)	127.5(4)	Pt (1)-N(1)	2.025(5)
C(11)-Pt(1)-Cl(1)	175.20(18)	C(6)-C(11)-Pt(1)	114.7(4)	Pt(1)-N(3)	2.032(5)
N(1)-Pt(1)-Cl(1)	96.40(14)				
N(3)-Pt(1)-Cl(1)	87.02(14)				
C(1)-N(1)- Pt (1)	124.9(4)				
C(5)-N(1)-Pt(1)	115.5(4)				

Compound	Absorption (293 K) $\lambda_{abs}$ (nm) <sup><i>a</i></sup>	Emission $\lambda_{em}$ (nm) 293 K	$\Phi_{p}{}^{b}$ Solution/film	$(ns)^{c}$	$\tau_{\rm r}$ (ns) <sup>d</sup>	$\Delta T_{5\%}/T_{\rm g}$ (°C) $^{e}$
Pt-Py	252(4.83), 311(4.56), 338(4.57),	170 510 507sh	0.02/0.51	3.62 (478 nm)	287 (540 mm)	254/125
	370(4.38), 425(4.50)	478, 540, 587	0.03/0.51	271 (540 nm)	387 (340 nm)	254/125
Pt-Pi	251(4.90), 303(4.50), 338(4.44),	101 510 500sh	0.01/0.45	5.16 (481 nm)	(40, (549,, .))	225/114
	371(4.55), 424(4.57)	481, 548, 5885	0.01/0.45	229 (548 nm)	649 (548 nm)	223/114

Table S3 Photophysical and thermal data of the Pt<sup>II</sup> complexes.

<sup>*a*</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub> at a concentration of 10<sup>-5</sup> M and log $\varepsilon$  values are shown in parentheses. <sup>*b*</sup> In degassed CH<sub>2</sub>Cl<sub>2</sub> relative to *fac*-[Ir(ppy)<sub>3</sub>] ( $\Phi_p = 0.40$ ),  $\lambda_{ex} = 360$  nm. <sup>*c*</sup> Measured in freeze-pump-thaw degassed CH<sub>2</sub>Cl<sub>2</sub> solutions at a sample concentration of *ca*. 10<sup>-5</sup> M and the excitation wavelength was set at 369 nm for all the samples at 293 K <sup>*d*</sup> Measured in PMMA film using 6 wt% doping. <sup>*e*</sup>  $\Delta T_{5\%}$  is the 5% weight-reduction temperature and  $T_g$  is the glass transition temperature.

# **Table S4** Contribution of the metal $d_{\pi}$ orbitals to the key frontier molecular orbitals together with the TD-DFT calculation results.

	Contribution	Contribution	Largest coefficient in the CI expansion of	Largest coefficient in the CI expansion of the	Oscillator strength (f) of
Compound	of metal $d_{\pi}$ orbitals <sup><i>a</i></sup>	of metal $d_{\pi}$ orbitals <sup><i>a</i></sup>	the $T_1$ state $(S_0 \rightarrow T_1)$	$S_1$ state $(S_0 \rightarrow S_1)$	the $S_0 \rightarrow S_1$
			excitation energy) <sup>b</sup>	excitation energy) <sup>b</sup>	transition
			$H \rightarrow L: 0.56661$	$H \rightarrow L: 0.66528$	
	HOMO-1: 35.44%	LUMO+1: 3.75%	64.2%	88.5%	
Pt-Py			$H \rightarrow L+1$ : -0.24885	$H-1 \rightarrow L: 0.21109$	0.1914
	HOMO: 2.12%	LUMO: 4.12%	12.4%	8.9%	
			(522 nm)	(412 nm)	
			$H \rightarrow L: 0.57653$	$H \rightarrow L: 0.66706$	
	HOMO-1: 36.19%	LUMO+1: 2.86%	66.5%	89.0%	
Pt-Pi			$H \rightarrow L+1$ : -0.25079	$H-1 \rightarrow L: 0.20040$	0.1766
	HOMO: 1.54%	LUMO: 4.49%	12.6%	8.0%	
			(528 nm)	(419 nm)	

<sup>*a*</sup> Data have been obtained by exporting DFT results with the software AOMix.

<sup>b</sup> H→L represents the HOMO to LUMO transition. CI stands for configuration interaction.

#### Table S5 Redox properties of the Pt<sup>II</sup> complexes.

Compound	$E_{\rm a}({ m V})$	$E_{\rm c}({ m V})$	$E_{ m HOMO}$ (eV) <sup>c</sup>	$E_{ m LUMO}$ (eV) <sup>d</sup>
Pt-Py	0.60 <sup><i>a</i></sup> , 0.85 <sup><i>b</i></sup>	-2.26 <sup><i>a</i></sup> , -2.53 <sup><i>a</i></sup> , -2.86 <sup><i>b</i></sup>	-5.40	-2.86
Pt-Pi	0.64 <sup><i>a</i></sup> , 0.87 <sup><i>b</i></sup>	-2.08 <sup><i>b</i></sup> , -2.43 <sup><i>b</i></sup> , -2.73 <sup><i>b</i></sup>	-5.44	-2.87

<sup>*a*</sup> Reversible. The value was set as  $E_{1/2}$ . <sup>*b*</sup> Irreversible or quasi-reversible. The value was derived from the peak potential. <sup>*c*</sup> HOMO levels were calculated according to the equation HOMO =  $-(4.8 + E_a)$ . <sup>*d*</sup> LUMO were obtained from the onset potential of the first reduction wave from the CV data.



Fig. S2 UV-vis spectra of the organic ligand L-Py and L-Pi in CH<sub>2</sub>Cl<sub>2</sub> at 293 K.



**Fig. S3** Structure for the solution-processed phosphorescent OLEDs based on **Pt-Py** and **Pt-Pi** together with molecular structures of the relevant compounds used in these devices.

Device	Phosphorescent	V <sub>turnon</sub>	Luminance L	$\eta_{\mathrm{ext}}$	$\eta_{ m L}$	$\eta_{ m p}$	$\lambda_{\max}$
	Dopant	(V)	(cd m <sup>-2</sup> )	(%)	(cd A <sup>-1</sup> )	(lm W <sup>-1</sup> )	(nm) <sup><i>d</i></sup>
A1	<b>Pt-Py</b> (6 wt%)	3.7	9314 (11.0) <sup><i>a</i></sup>	13.2 (4.0) <sup><i>a</i></sup>	47.1 (4.0)	39.2 (3.7)	540
				12.3 <sup>b</sup>	44.5	29.2	(0.43,0.56)
				11.1 <sup>c</sup>	39.7	22.2	
A2	<b>Pt-Py</b> (8 wt%)	3.1	8943 (11.3)	16.8 (3.2)	60.1 (3.2)	59.0 (3.2)	540
				14.9	52.6	36.7	(0.43,0.56)
				12.7	45.9	27.1	
A3	<b>Pt-Py</b> (10 wt%)	3.4	9870 (11.9)	12.2 (4.0)	43.6 (4.0)	35.8 (3.8)	540
				11.3	40.0	25.2	(0.43,0.56)
				10.0	35.4	18.2	
B1	<b>Pt-Pi</b> (6 wt%)	4.0	6666 (13.9)	13.0 (3.7)	47.4 (3.7)	42.5 (3.5)	540
				10.2	36.8	19.1	(0.42,0.57)
				7.3	26.6	10.5	
B2	<b>Pt-Pi</b> (8 wt%)	4.3	6801 (14.4)	14.8 (3.7)	53.8 (3.7)	45.2 (3.7)	540
				11.4	41.5	20.6	(0.42,0.57)
				8.3	29.8	11.2	
B3	<b>Pt-Pi</b> (10 wt%)	4.3	6915 (14.1)	10.9 (3.7)	39.6 (3.7)	35.6 (3.5)	540
				8.6	30.6	15.8	(0.42,0.57)
				6.6	23.5	9.1	

Table S6 Maximum EL performance for all the OLEDs based on the Pt<sup>II</sup> complexes.

<sup>*a*</sup> Maximum values of the devices. Values in parentheses are the voltages at which they were obtained. <sup>*b*</sup> Values collected at 100 cd m<sup>-2</sup>. <sup>*c*</sup> Values collected at 1000 cd m<sup>-2</sup>. <sup>*d*</sup> Values were collected at 8 V and CIE coordinates (x, y) are shown in parentheses.



**Fig. S4** Current density (*J*)-voltage (*V*)-luminance (*L*) curves of the solution-processed OLEDs based on **Pt-Py** and **Pt-Pi**.





**Fig. S5** Dependence relationship between EL efficiencies and luminance for the solution-processed OLEDs based on **Pt-Py** and **Pt-Pi**.