## Electronic Supplementary Information

## First Member of an Appealing Class of Cyclometalated 1,3-Di-(2-Pyridyl)Benzene Platinum(II) Complexes for Solution-Processable OLEDs

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## NMR spectra

NMR spectra of [Pt(5-mesityl-1,3-di-(2-pyridyl)benzene)(1-phenyl-1H-tetrazole-5-thiolate)], [Pt(5-mesityl-dpyb)(SCN<sub>4</sub>Ph)].







 $^{13}\mbox{C-NMR}$  and HSQC spectra in  $\mbox{CD}_2\mbox{Cl}_2$ 

## Photoluminescence properties in solution and in the solid state

Electronic absorption spectra were recorded at room temperature in  $CH_2Cl_2$  solution, using a Shimadzu UV3600 spectrophotometer and quartz cuvettes with 1 cm optical path length.



**Figure S1**. Absorption spectra vs concentration of the complex in  $CH_2Cl_2$ . Inset: Normalized absorption spectra of complex at a concentration of  $1 \cdot 10^{-6}$  and  $2 \cdot 10^{-4}$  M.



Figure S2. Absorption spectra vs concentration of the complex at 520 nm.



Figure S3. Absorption spectra vs concentration of the complex at 388 nm.

Absolute photoluminescence quantum yield,  $\Phi$ , was measured using a C11347 Quantaurus Hamamatsu Photonics K.K spectrometer, equipped with a 150 W Xenon lamp, an integrating sphere and a multichannel detector.  $\Phi$  was calculated through Equation:

$$\Phi = \frac{PN(em)}{PN(abs)} = \frac{\int \frac{\lambda}{hc} \left[ I_{em}^{sample}(\lambda) - I_{em}^{reference}(\lambda) \right] d\lambda}{\int \frac{\lambda}{hc} \left[ I_{exc}^{reference}(\lambda) - I_{exc}^{sample}(\lambda) \right] d\lambda}$$

where PN(em) is the number of emitted photons, PN(abs) the number of absorbed photons,  $\lambda$  the wavelength, h the Planck's constant, c the speed of light,  $I^{sample}_{em}$  and  $I^{reference}_{em}$  the photoluminescence intensities of the sample solution and reference in DCM,  $I^{sample}_{exc}$  and  $I^{reference}_{exc}$  the excitation light intensities of the sample solution and reference in DCM. The error made was estimated at around 5%. Before performing absolute photoluminescence quantum yield measurements, the solution was dearerated by three freeze-pump-thaw cycles using a turbomolecular pump in order to remove dissolved oxygen.

Steady state and time-resolved fluorescence data were obtained using a FLS980 spectrofluorimeter (Edinburg Instrument Ltd). Emission spectra were recorded exciting at 389 and 489 nm, corrected for background intensity and quantum efficiency of the photomultiplier tube. Excitation spectra were carried out at maximum of the emission spectrum of the monomer and aggregate at 498 and 650 nm, respectively, corrected for the intensity fluctuation of a 450 W Xenon arc lamp.

Time-resolved fluorescence measurements were performed through the time-correlated single photon counting technique with an Edinburgh Picosecond Pulsed Diode Laser-374: emitted wavelength 373 nm, temporal pulse width (FWHM) 857 ps. Time-resolved fluorescence curves were reconvoluted using a multi-exponential impulse response function:

$$I(\lambda,t) = \sum_{i=1}^{n} \alpha_i(\lambda) \exp\left(\frac{-t}{\tau_i}\right)$$

where n is the number of exponentials,  $\alpha_i$  ( $\lambda$ ) is the amplitude at wavelength  $\lambda$  and  $\tau_i$  is the lifetime of the component i. The quality of the fit was evaluated through the reduced  $\chi^2$  values.

Quantum efficiency measurements	were carried out at room	n temperature in $CH_2Cl_2$ solution.
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Concentration (M)	∲ <sub>lum</sub> before freeze- pump-thaw	∲ <sub>lum</sub> after freeze- pump-thaw	Lifetime $\lambda_{ex}$ 374 nm $\rightarrow \lambda_{em}$ 498 nm.	K <sub>r</sub> (s <sup>-1</sup> )	K <sub>nr</sub> (s <sup>-1</sup> )
1.0 x10 <sup>-6</sup>	0.05	0.90	7.39 μs (100%)	1.23· 10 <sup>5</sup>	1.38· 10 <sup>4</sup>
1.0x10 <sup>-5</sup>	0.05	0.39	$\tau_1 = 0.79 \ \mu s$ (8.97%) $\tau_2 = 6.94 \ \mu s$ (91.03%)		
5.0x10 <sup>-5</sup>	0.04	0.20	$\tau_1 = 0.75 \ \mu s$ (39.52%) $\tau_2 = 4.68 \ \mu s$ (60.48%)		
2.0x10 <sup>-4</sup>	0.03	0.12	$\tau_1 = 0.73 \ \mu s$ (72.11%) $\tau_2 = 2.43 \ \mu s$ (27.89%)		

Table S1



Figure S4. QY vs monomer concentration.

Luminescence measurements at room temperature were performed on complex solutions in  $CH_2Cl_2$  after three freeze-pump-thaw. The emission spectra were collected changing the concentration of the monomer at two different excitation wavelengths at 389 nm and 489 nm respectively (Figures S5, S6 and S7). The normalization of the spectra was carried out at the  $\lambda$  of 550 nm. This  $\lambda$  was chosen in an intermediate spectral region between the emission of the aggregate and its absorption. The coincidence of the spectra, independent of the concentration

of the monomer, over a wavelength region around 550 nm verifies that the latter has been suitable chosen.



**Figure S5**. Normalized emission spectra of the complex  $(1 \cdot 10^{-6} \text{ M})$  at two excitation wavelengths (389 and 489 nm).



Figure S6. Emission spectra vs concentration of the complex. Excitation at 389 nm.



Figure S7. Emission spectra vs concentration of the complex. Excitation at 489 nm.

Excited state decay measurements of Pt complex solutions at different concentration were performed exciting at 374 nm at the emission wavelength of 498 nm (Figures S8-S12):



Figure S8







Figure S10







Figure S12

Excited state decay measurements of Pt complex solutions at different concentration were performed exciting at 374 nm at the emission wavelength of 713 nm (Figures S13-S14).



Figure S13



Figure S14

Steady state measurements at room temperature of Pt complex as solid powder:





Excited state decay measurements at room temperature of Pt complex as solid powder:



**Figure S16.**  $\lambda_{ex} = 374 \text{ nm} \rightarrow \lambda_{em} = 703 \text{ nm}$ 

Steady state measurements at low temperature (77K) of Pt complex as solid powder:





Excited state decay measurements at low temperature (77K) of Pt complex as solid powder:



**Figure S18.**  $\lambda_{ex} = 374 \text{ nm} \rightarrow \lambda_{em} = 713 \text{ nm}$