

# Supporting Information

## Supramolecular platinum(II) complexes with highly efficient monomer luminescence

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### 1. Materials and Instruments.

All reagents were used without further purification, or were prepared according to literature procedure. 1, 12-Dibromododecane (95%), N, N-Dimethyldodecylamine (98%) and Potassium tert-butoxide (98%) were purchased from J&K, 2-ethoxyethanol and (2, 4-difluorophenyl)boronic acid (98%) were purchased from TCI. The ultrapure water was purified by Aquapro ALH-6000-U.

#### <sup>1</sup>H NMR Experiments

<sup>1</sup>H NMR spectra were recorded on a 400 MHz Bruker spectrometer in CDCl<sub>3</sub> solutions, by using Me<sub>4</sub>Si as internal standard. Chemical shifts were reported in ppm downfield from Me<sub>4</sub>Si.

#### <sup>19</sup>F NMR Experiments

<sup>19</sup>F NMR spectra were recorded on a 500 MHz Bruker AV500 spectrometer in CDCl<sub>3</sub> solutions at room temperature (25 °C), by using CFCl<sub>3</sub> as external standard. Chemical shifts were reported in ppm downfield from CFCl<sub>3</sub>.

#### ESI-MS Experiments

ESI-MS was recorded on a Bruker APEX II Fourier transform ion cyclotron mass spectrometer resonance.

#### UV-Vis Absorption Spectra Experiments

UV-vis absorption spectra were recorded by using an Agilent Technologies Cary 60 UV-Vis spectrophotometer.

#### Emission Spectra Experiments

Luminescence measurements were made on Edinburgh FLSP920 with a 450V xenon lamp as the excitation source and optical filter.

#### Luminescent Lifetime Experiments

Lifetime data were recorded following excitation EPL375 picosecond pulsed diode laser (Edinburgh instruments), using timer-correlated single-photon counting. The excitation wavelength of the pulsed laser used for performing lifetime measurements was 374.4 nm. Lifetime were obtained by tail fitting on the data obtained using single-exponential or double-

exponential model.

### Quantum yield

Quantum yield was obtained with Quantaaurus-QY C9920-03 and detector PMA-12, using excitation wavelength at 370 nm with a 450V Xenon lamp.

### Fluorescence Microscope Experiments

Fluorescence microscope images were performed with Nikon ECLIPSE 80i. Upon excitation of these samples in water-methanol mixed medium at 330-380 nm, fluorescence microscope photos were taken. The samples in water-methanol mixed medium were prepared by taking a drop of the mixture solution on a glass slide and covered with a cover slip, and the fluorescence microscope photos were collected quickly. The samples at dry state were prepared by taking a drop of mixture solution on a glass slide and dried at room temperature.

### Scanning Electron Microscope Experiments

SEM images were obtained with a QUANTA 600F. A drop of sample was placed on a silicon slice and dried at room temperature. No conductive cover was coated before the SEM images were collected.

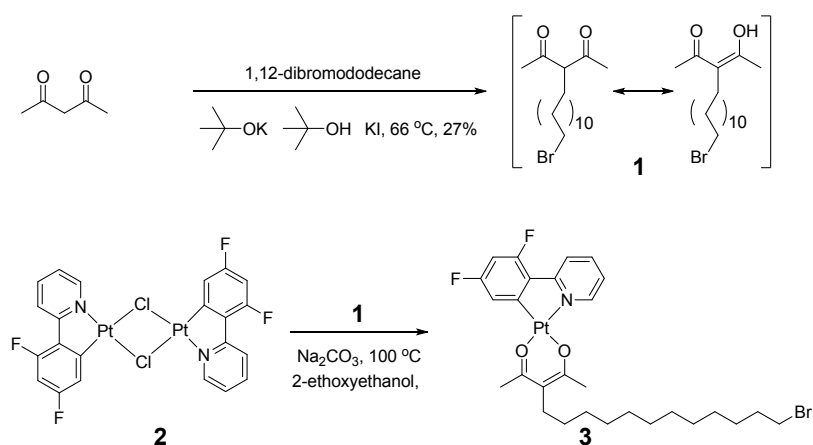
### The small angle X-ray Diffraction Experiments

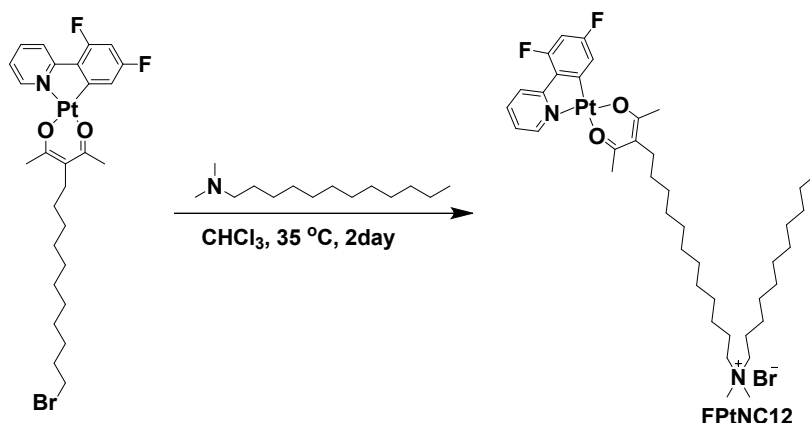
The small angle X-ray diffraction experiments were obtained with a Bruker SMART APEX II instrument.

### Atomic Force Microscope Experiments

AFM images were obtained with a 5400 PicoPlus, the type of the scanning probe is PPP-CONT-20, on contact mode. A drop of sample was placed on a silicon slice and dried at room temperature.

## 2. Synthetic route of FPtNC<sub>12</sub> complex





Scheme S1 Synthetic route of **FPtNC<sub>12</sub>** complex

**1) Synthesis of complex 1, 2 and 3.**

All of the intermediate compounds (complex 1, 2 and 3) had been successfully synthesized, and characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectra together with high-resolution electrospray ionization mass spectra by the literature methods.<sup>1,2</sup>

**2) Synthesis of FPtNC<sub>12</sub>.<sup>3</sup>**

Under a nitrogen atmosphere, complex **3** (0.307 g, 0.4 mmol, 1 eq) was dissolved in CHCl<sub>3</sub> (4 mL) followed by the addition of dodecyldimethyl ammonium bromide (1.4 g, 6.36 mmol, 15.5 eq). The reaction mixture was stirred at 35 °C for two days. After being cooled, the CHCl<sub>3</sub> was removed under reduced pressure, adding excess diethyl ether to get yellow precipitation, followed by washing the yellow precipitation with diethyl ether for several times. The compound was purified by flash chromatography (CHCl<sub>3</sub> / CH<sub>3</sub>OH, v/v, 20/1), then was recrystallized by diffusing diethyl ether to the **FPtNC<sub>12</sub> solution** in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH to get yellow solid (0.214 g, 54% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si): δ 0.88 (t, 3H, *J* = 8 Hz, CH<sub>3</sub>CH<sub>2</sub>), 1.25-1.43 (m, 36H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>), 1.69 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.14 and 2.16 (2s, 6H, CH<sub>3</sub>COCHCOCH<sub>3</sub>), 2.32 (t, *J* = 8 Hz, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>11</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>), 3.39 (s, 6H, CH<sub>2</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>), 3.47-3.53 (m, 4H, CH<sub>2</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>), 6.53-6.59 (m, 1H), 7.07-7.12 (m, 2H), 7.82 (t, *J* = 8 Hz, 1H), 7.95 (d, *J* = 8 Hz, 1H), 8.97 (d, *J* = 8 Hz, 1H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si): δ 184.62, 182.21, 164.78 (d, *J* = 7 Hz), 160.93 (d, *J* = 10 Hz), 158.34 (d, *J* = 13 Hz), 148.77, 144.62 (d, *J* = 8 Hz), 138.32, 128.13, 121.80 (d, *J* = 17 Hz), 120.88, 111.95, 98.73 (t, *J* = 26 Hz), 63.70, 50.98, 31.70, 30.82, 30.72, 29.71, 29.45, 29.40, 29.35, 29.27, 29.25, 29.27, 29.20, 29.13, 29.04, 29.02.

<sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): -106.956(d, 1F, *J* = 9.4 Hz), -112.254(d, 1F, *J* = 9.4 Hz).

HR-ESI-MS *m/z* : calcd [C<sub>42</sub>H<sub>67</sub>F<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Pt]<sup>+</sup>: 864.4817; found 864.4830.

### 3. Spectrum Analysis

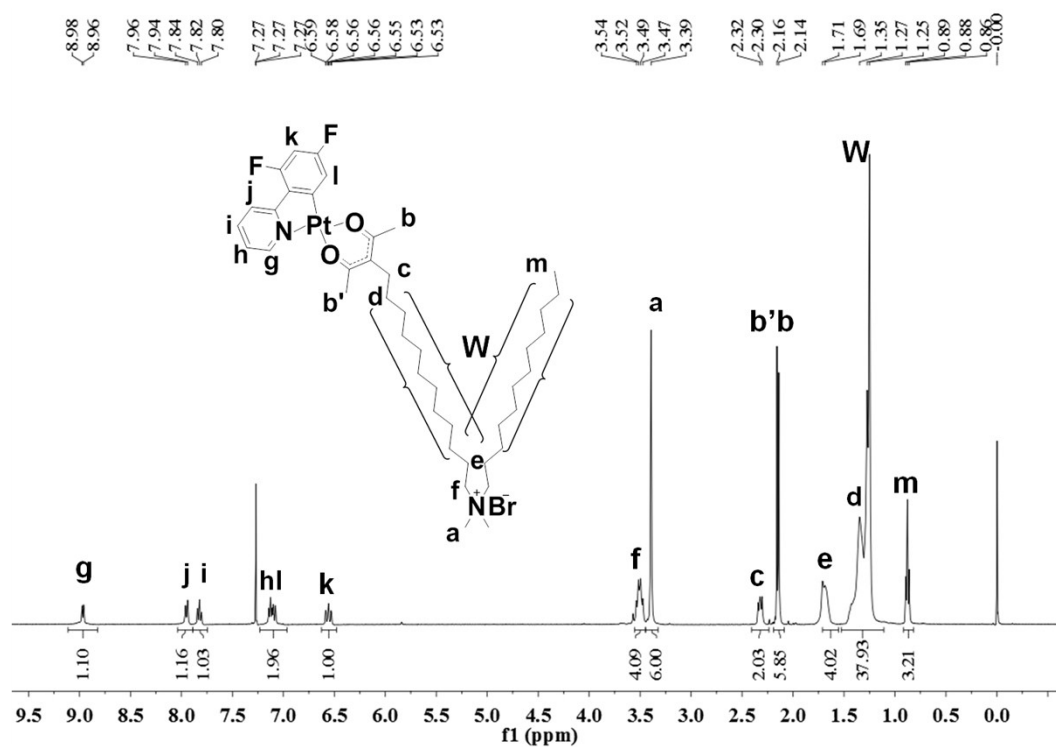


Figure S1 The <sup>1</sup>H NMR of complex FPtNC<sub>12</sub>

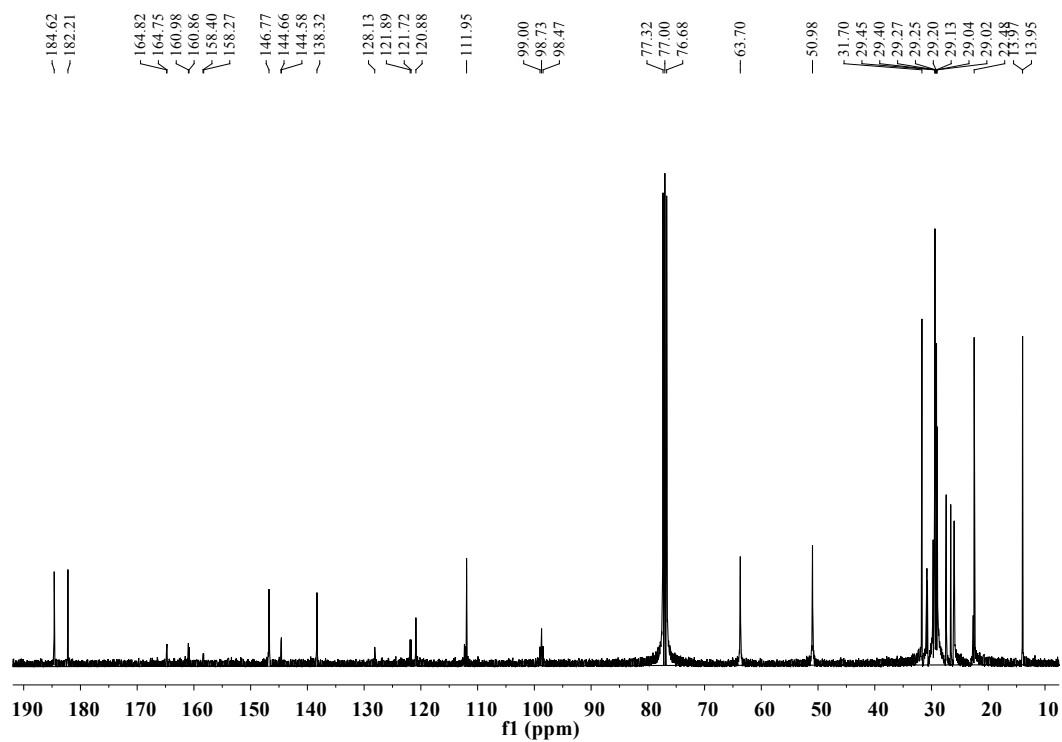


Figure S2 The <sup>13</sup>C NMR of complex FPtNC<sub>12</sub>

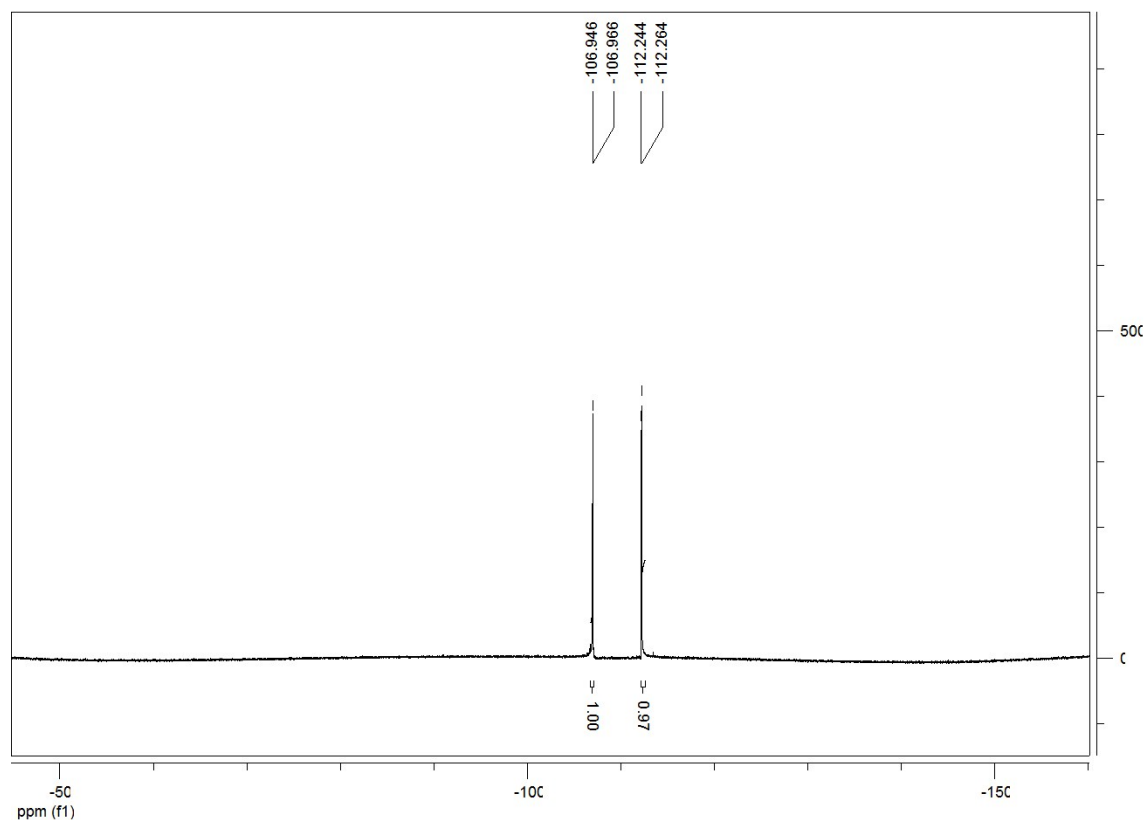


Figure S3 The  $^{19}\text{F}$  NMR of complex  $\text{FPtNC}_{12}$

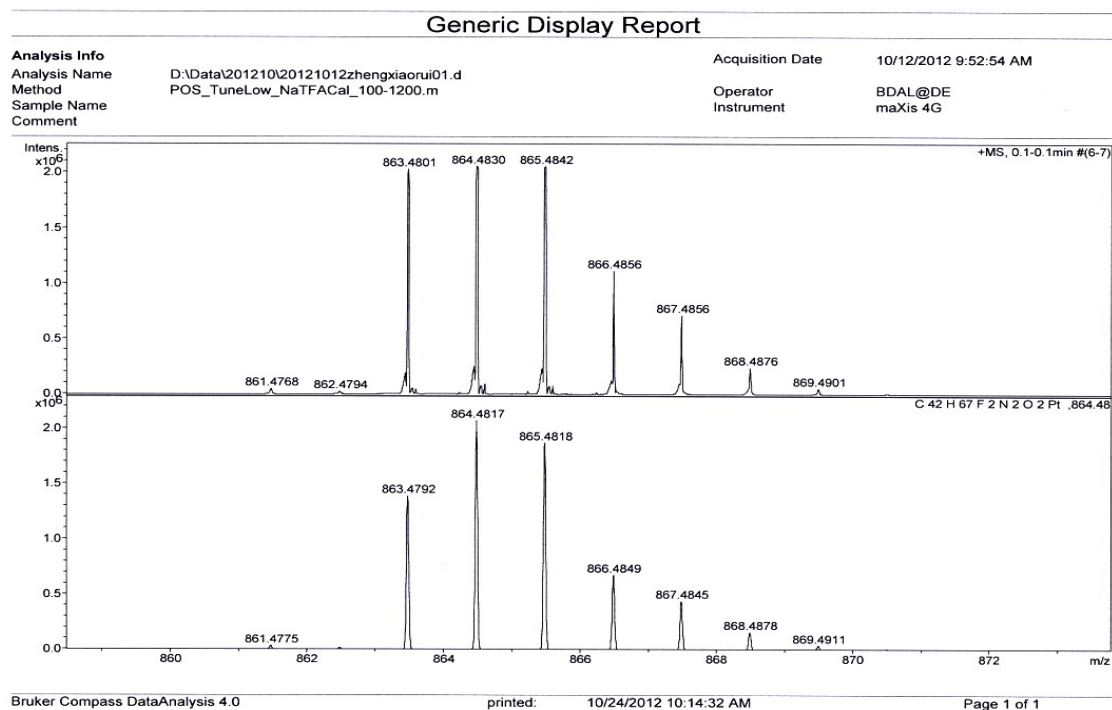


Figure S4 The HR-ESI-MS of  $\text{FPtNC}_{12}$

### 3. Self-assembly of FPtNC<sub>12</sub>

#### Solution Preparation

The concentration of **FPtNC<sub>12</sub>** solution was maintained at  $2 \times 10^{-4}$  M ( $V_{\text{water}} : V_{\text{methanol}} = 100 : 3$ ). The complex **FPtNC<sub>3</sub>** was first dissolved in methanol, and then adding deionized water into the methanol solution to give a yellow solution ( $2 \times 10^{-4}$  M,  $V_{\text{water}} : V_{\text{methanol}} = 100 : 3$ ). Assemble and some measurements were repeated to ensure the reproducibility. All the measurements are made in air-equilibrated condition.

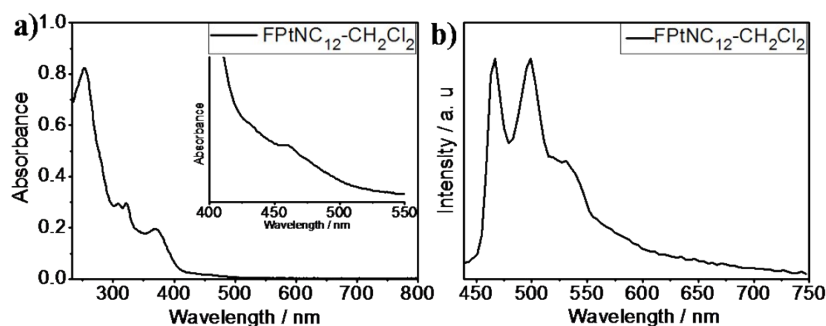


Figure S5 (a) Absorption and (b) emission spectra of **FPtNC<sub>12</sub>** in dichloromethane solution ( $2 \times 10^{-4}$  M). The triplet absorption transitions are shown in the insert.  $\lambda_{\text{exc}} = 370$  nm

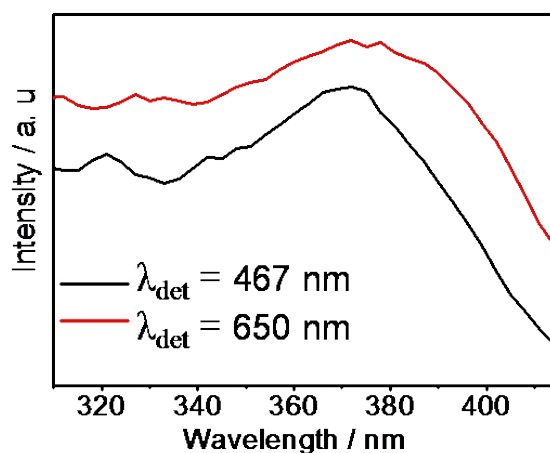


Figure S6 The excitation spectra of the **FPtNC<sub>12</sub>** solution in water and methanol ( $V_{\text{water}} : V_{\text{methanol}} = 100 : 3$ ) (red trace: emission=650 nm, black trace: emission=467 nm)

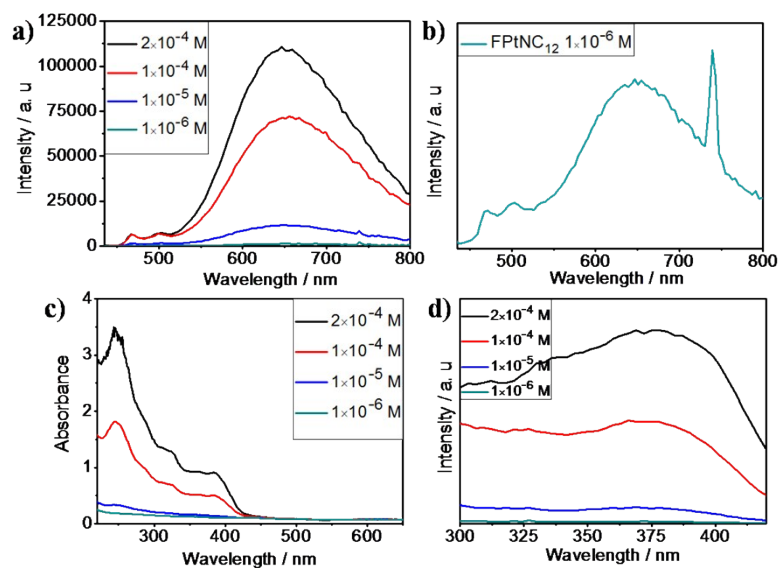


Figure S7 (a) (b) Emission, (c) Absorption and (d) Excitation spectra of the **FPtNC<sub>12</sub>** solution at the concentration range from  $1 \times 10^{-6}$  M to  $2 \times 10^{-4}$  M ( $\lambda_{\text{exc}} = 370$  nm, emission=650 nm, the sharp peak observed at 740 nm corresponds to the second order transmission of the monochromator.)

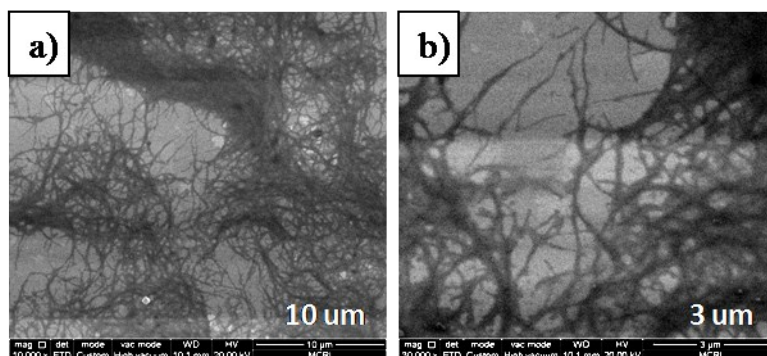


Figure. S8 (a,b) SEM images of the yellow solution of **FPtNC<sub>12</sub>** on the silicon substrate after the mixed solvent evaporated.

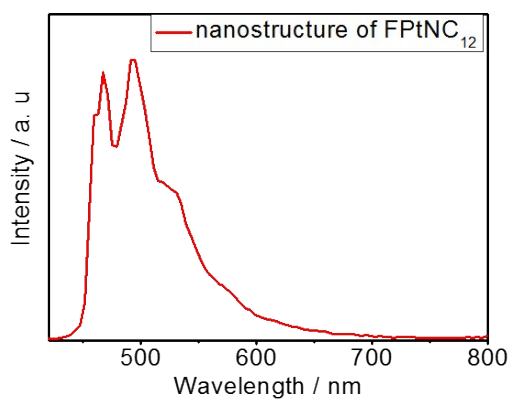


Figure S9 (c) emission spectra of the microcrystal from a drop of the suspension of **FPtNC<sub>12</sub>** after the solvent evaporated on a quartz substrate. ( $\lambda_{\text{exc}} = 370$  nm).

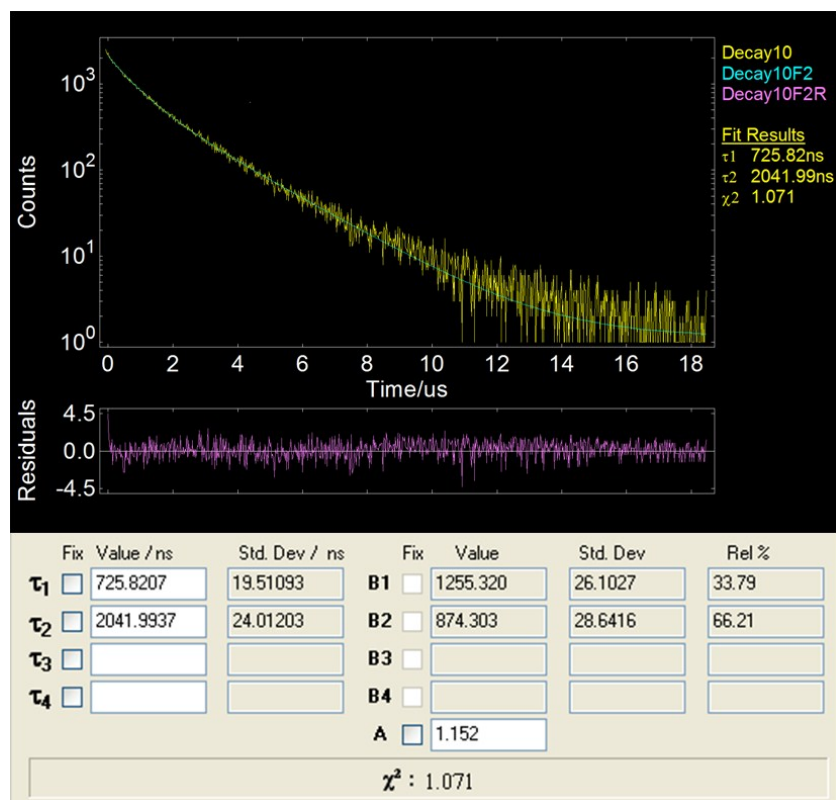


Figure S10 Room temperature transient PL decays of microcrystal of **FPtNC<sub>12</sub>** on microsecond time scale after excitation using light at 374.4 nm. ( $T_{ave} = (A_1 \cdot T_1^2 + A_2 \cdot T_2^2) / (A_1 \cdot T_1 + A_2 \cdot T_2)$ ,  $A_1 = 1255.320$ ,  $T_1 = 725.8207$ ,  $A_2 = 874.303$ ,  $T_2 = 2041.9937$ )

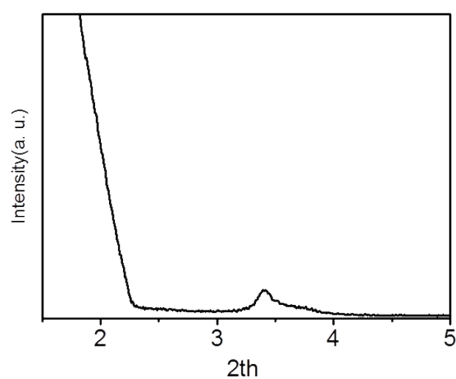


Figure S11 The small angle X-ray diffraction (XRD) pattern of the microcrystal from the suspension of **FPtNC<sub>12</sub>** after the solvent evaporated.



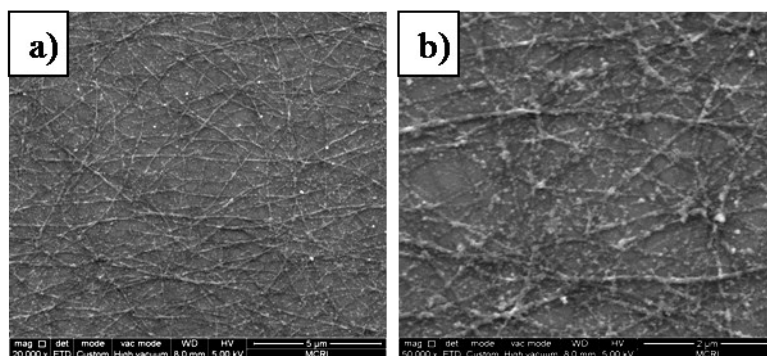


Figure S12 (a, b) SEM images of the dried state of the **FPtNC<sub>3</sub>** solution ( $2 \times 10^{-4}$  M,  $V_{\text{water}}$  :  $V_{\text{methanol}} = 100 : 3$ ) on the silicon substrate.

#### References:

- 1 (a) J. Brooks, Y. Babayan, S. Lamansky, P. I. Djurovich, I. Tsyba, R. Bau and M. E. Thompson, *Inorg. Chem.*, **2002**, *41*, 3055. (b) P. T. Furuta, L. Deng, S. Gatton, M. E. Thompson, and J. M. J. Fréchet, *J. Am. Chem. Soc.* **2004**, *126*, 15288-15389;
- 2 X. Zheng, H. Wang, Y. Li, *RSC Adv.*, **2016**, *6*, 88174-88178;
- 3 W. Park, D. Yu, K. Na, K. E. Jelfs, B. Slater, Y. Sakamoto, R. Ryoo, *Chem. Mater.* **2011**, *23*, 5131-5137