

## Electronic Supplementary Information (ESI)

### Self-assembled nanoparticles based on cationic mono-/AIE tetra-nuclear Ir(III) complexes: long wavelength absorption/near-infrared emission photosensitizers for photodynamic therapy

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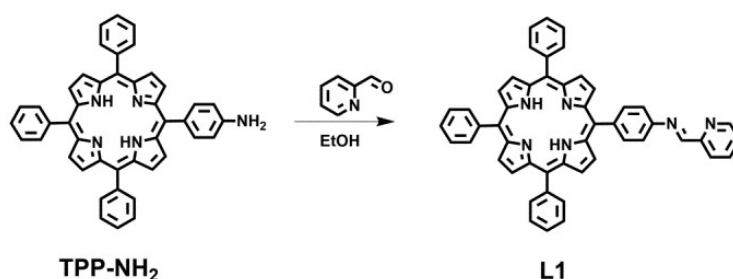
## Experimental Section

### Materials and instruments

Materials for organic synthesis, poloxamer (F127) and indocyanine green (ICG) were purchased from Energy Chemical Company. RPMI Medium 1640 was purchased from Solarbio Life Science company. Fetal bovine serum (FBS) was purchased from Sigma-Aldrich. 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) was obtained from Aladdin. 2',7'-Dichlorofluorescence diacetate (DCFH-DA) and the cell viability (live dead cell staining) assay kit were purchased from Shanghai Beyotime Biotechnology Co., Ltd.

<sup>1</sup>H NMR spectra were recorded at 25 °C on a Varian 500 MHz spectrometer. UV-vis absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. The photoluminescence spectra, excited state lifetimes ( $\tau$ ) and photoluminescence quantum yields ( $\Phi_{\text{PL}}$ ) were recorded on an Edinburgh FLS920 spectrofluorimeter under air at room temperature. Transmission electron microscopy (TEM) images of the samples were taken by a TECNAI F20 microscope. Diameter and diameter distribution of the nanoparticles were determined by a Malvern Zetasizer Nano instrument for dynamic light scattering (DLS). Confocal laser scanning microscopy (CLSM) images were taken using a ZeissLSM 700 (Zurich, Switzerland).

### Synthesis of L1

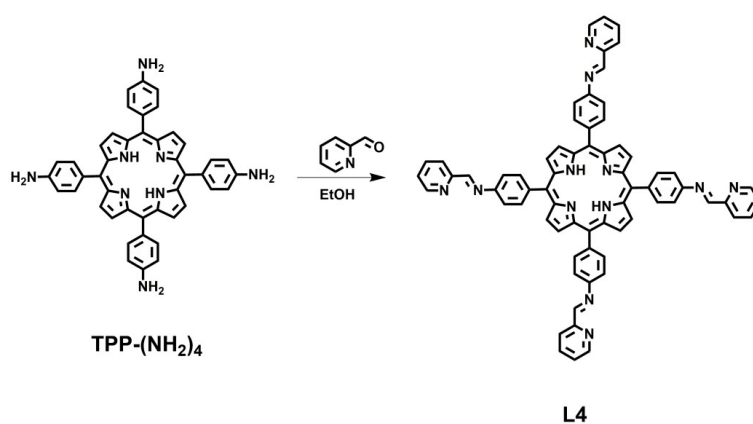


**Scheme S1.** Synthetic route to **L1**.

**TPP-NH<sub>2</sub>** (0.189 g, 0.3 mmol) and 2-pyridinecarboxaldehyde (0.039 g, 0.36 mmol) were added into ethanol (60 mL), and the mixture was stirred at 78 °C for 8 h. After

cooling to room temperature, the precipitate was filtered and recrystallized with ethanol to obtain the target compound with a yield of 83%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ,  $\delta$  [ppm]): 8.97 (s, 1H), 8.92 (d,  $J = 4.2$  Hz, 2H), 8.88-8.81 (m, 7H), 8.40 (d,  $J = 7.7$  Hz, 1H), 8.28 (d,  $J = 8.1$  Hz, 2H), 8.24-8.20 (m, 6H), 7.94-7.91 (m, 1H), 7.80-7.74 (m, 9H), 7.70 (d,  $J = 7.8$  Hz, 2H), 7.47-7.45 (m, 1H), -2.76 (s, 2H). Anal. Calcd. for  $\text{C}_{50}\text{H}_{34}\text{N}_6$ : C 83.54, H 4.77, N 11.69. Found C 83.49, H 4.52, N 11.65.

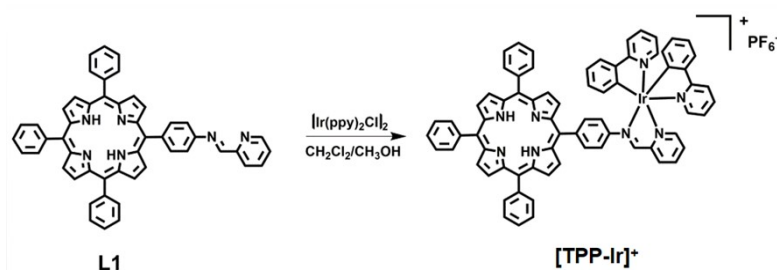
### Synthesis of L4



**Scheme S2.** Synthetic route to **L4**.

**L4** was synthesized similarly to **L1**, except that **TPP-NH<sub>2</sub>** was replaced by **TPP-(NH<sub>2</sub>)<sub>4</sub>** with a yield of 78%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ,  $\delta$  [ppm]): 8.98-8.91 (m, 6H), 8.82 (d,  $J = 4.2$  Hz, 2H), 8.41 (d,  $J = 6.0$  Hz, 2H), 8.31-8.27 (m, 4H), 7.94-7.91 (m, 2H), 7.73-7.69 (m, 4H), 7.47-7.45 (m, 2H), -2.69 (s, 1H). Anal. Calcd. for  $\text{C}_{68}\text{H}_{46}\text{N}_{12}$ : C 79.20, H 4.50, N 16.30. Found C 79.16, H 4.47, N 16.26.

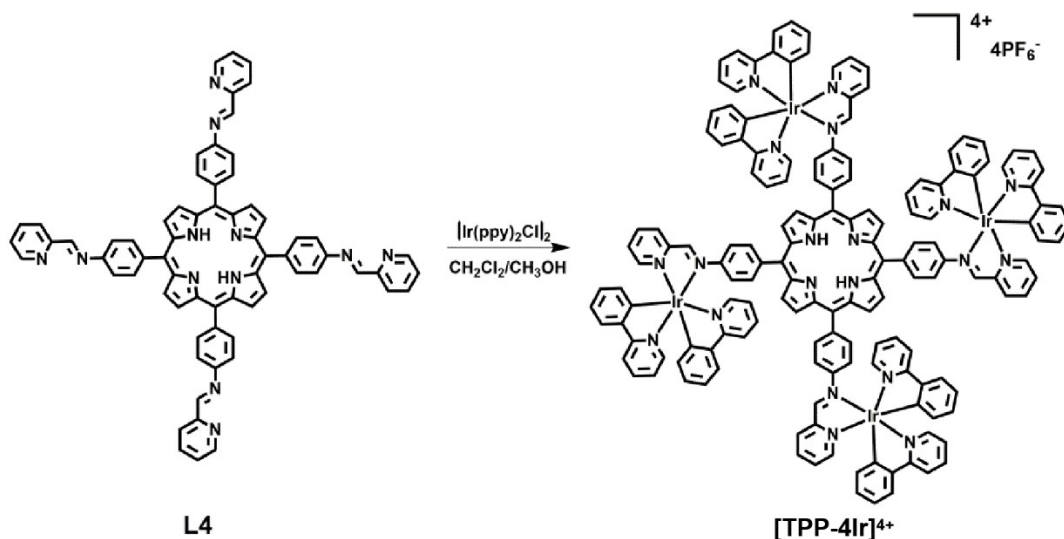
## Synthesis of [TPP-Ir]<sup>+</sup>



**Scheme S3.** Synthetic route to [TPP-Ir]<sup>+</sup>.

[Ir(ppy)<sub>2</sub>Cl]<sub>2</sub> (0.107 g, 0.1 mmol) and auxiliary ligand **L1** (0.144 g, 0.2 mmol) were dissolved in a mixture of methanol (30 mL) and dichloromethane (30 mL), and refluxed for 6 h under the protection of N<sub>2</sub>. After cooling to room temperature, excess KPF<sub>6</sub> was added to the mixture (to replace counterion Cl<sup>-</sup>). After stirring for 0.5 h, filtering to remove the excess potassium salts, and removal of the solvent from the filtrate by rotary evaporation, the crude product was obtained. Finally, the purple solid product was purified by column chromatography on silica gel (eluents dichloromethane /ethyl acetate 10/1, v/v) with a yield of 80%. <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>, δ [ppm]): 9.98 (s, 1H), 8.91-8.83 (m, 7H), 8.66 (d, J = 7.6 Hz, 1H), 8.55 (d, J = 4.4 Hz, 2H), 8.41-8.37 (m, 2H), 8.32 (d, J = 8.4 Hz, 1H), 8.25-8.21 (m, 6H), 8.08-7.97 (m, 5H), 7.88-7.82 (m, 12H), 7.81-7.80 (m, 1H), 7.44-7.41 (m, 1H), 7.37-7.34 (m, 1H), 7.17 (d, J = 8.2 Hz, 2H), 7.10-7.06 (m, 1H), 7.04-7.01 (m, 1H), 6.97-6.94 (m, 1H), 6.92-6.88 (m, 1H), 6.34 (d, J = 7.3 Hz, 1H), 6.27 (d, J = 6.0 Hz, 1H), -2.97 (s, 2H). <sup>13</sup>C {<sup>1</sup>H} NMR (151 MHz, DMSO-d<sub>6</sub>, δ [ppm]) 170.45, 167.59, 167.10, 156.02, 151.60, 150.80, 150.67, 149.97, 149.66, 147.54, 144.44, 144.33, 141.63, 141.14, 140.39, 139.58, 139.39, 134.66, 134.27, 131.79, 131.04, 130.71, 130.35, 128.64, 127.54, 127.49, 125.65, 125.20, 124.73, 124.47, 122.98, 122.70, 121.10, 120.78, 120.64, 120.12, 118.89. MS: [m/z] = 1219.3624 (calcd C<sub>72</sub>H<sub>50</sub>IrN<sub>8</sub> for M<sup>+</sup>: 1219.38). Anal. Calcd. for C<sub>72</sub>H<sub>50</sub>F<sub>6</sub>IrN<sub>8</sub>P: C 63.38, H 3.69, N 8.21. Found C 63.42, H 3.75, N 8.18.

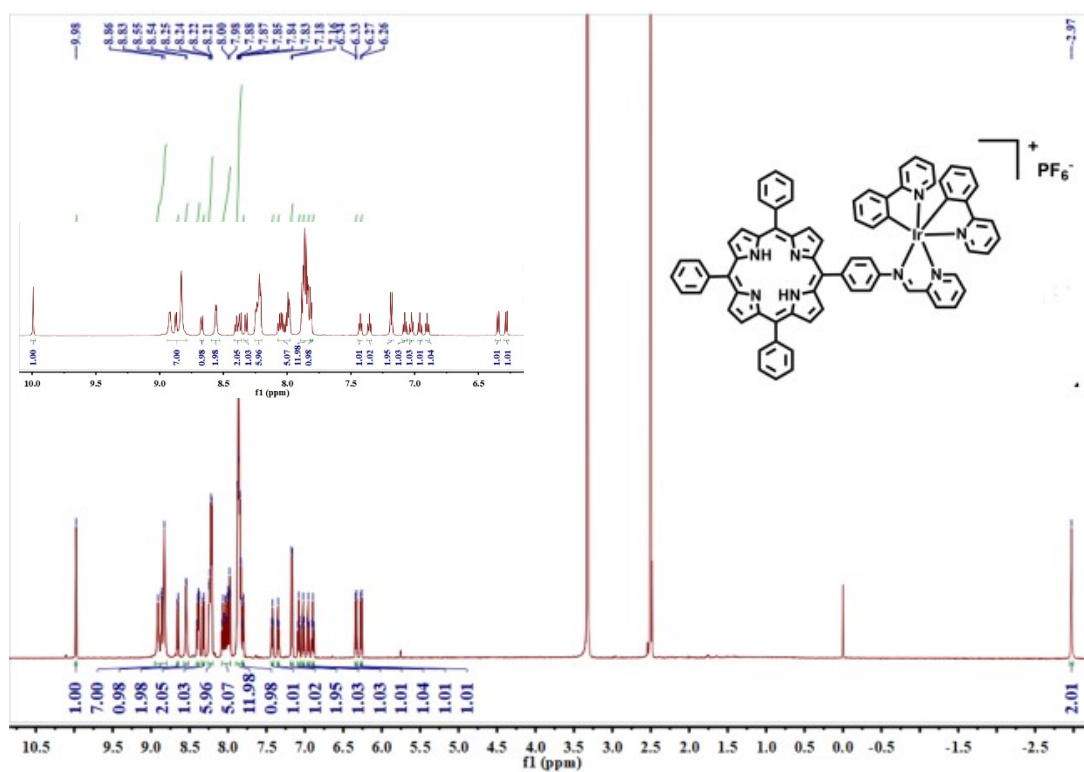
## Synthesis of [TPP-4Ir]<sup>4+</sup>



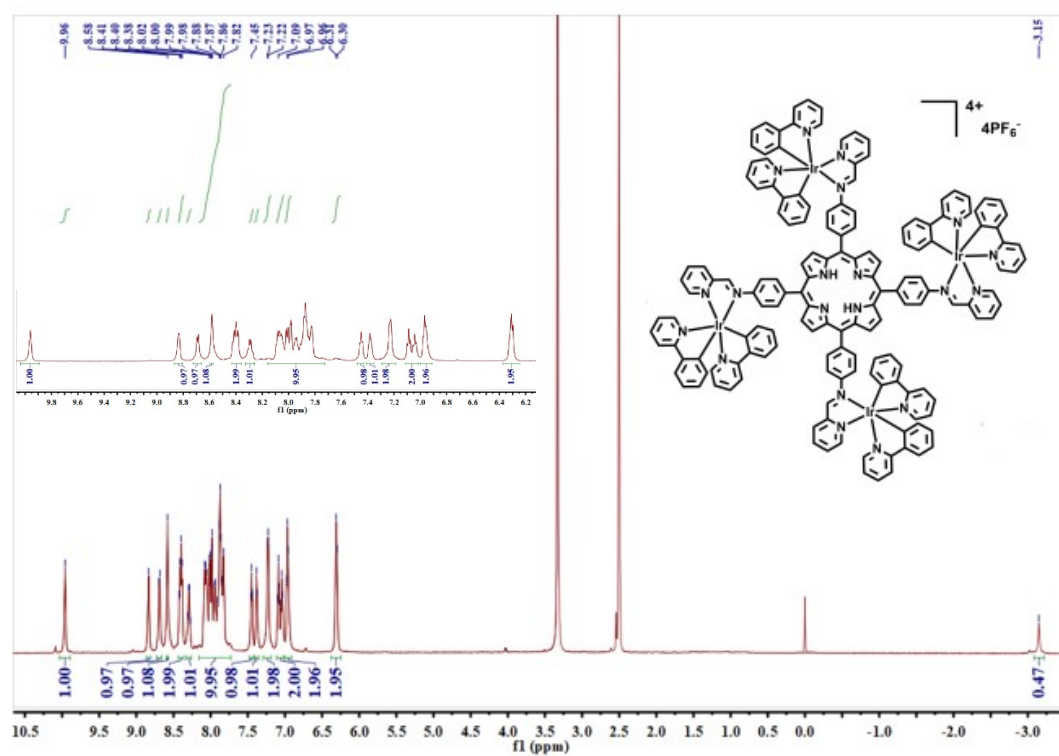
**Scheme S4.** Synthetic route of  $[\text{TPP-4Ir}]^{4+}$ .

The synthesis and purification of  $[\text{TPP-4Ir}]^{4+}$  was similar to that of  $[\text{TPP-Ir}]^+$ ,  $[\text{Ir(ppy)}_2\text{Cl}]_2$  (0.214 g, 0.2 mmol) and auxiliary ligand **L4** (0.1030 g, 0.1 mmol) were dissolved in a mixture of methanol (30 mL) and dichloromethane (30 mL), and refluxed for 8 h under the protection of  $\text{N}_2$ . After cooling to room temperature, excess  $\text{KPF}_6$  was added to the mixture (to replace counterion  $\text{Cl}^-$ ). After stirring for 0.5 h, filtering to remove the excess potassium salts, and removal of the solvent from the filtrate by rotary evaporation, the product was obtained without other purified process. The product is pure and the product yield is 99%.  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-d}_6$ ,  $\delta$  [ppm]): 10.03-9.90 (m, 1H), 8.87-8.81 (m, 1H), 8.72-8.66 (m, 1H), 8.58 (s, 1H), 8.42-8.38 (m, 2H), 8.31-8.27 (m, 1H), 8.08-7.82 (m, 10H), 7.48-7.43 (m, 1H), 7.40-7.36 (m, 1H), 7.29-7.19 (m, 2H), 7.11-7.00 (m, 2H), 6.99-6.91 (m, 2H), 6.37-6.25 (m, 2H), -3.15 (s, 0.5H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{DMSO-d}_6$ ,  $\delta$  [ppm]) 170.67, 170.64, 167.54, 167.49, 167.13, 155.97, 151.46, 151.10, 151.07, 150.72, 150.12, 150.09, 149.52, 147.86, 144.50, 144.33, 140.90, 140.45, 139.61, 139.48, 134.37, 132.01, 131.92, 131.64, 131.13, 130.78, 130.35, 125.68, 124.99, 124.74, 124.64, 123.05, 122.51, 121.15, 121.14, 120.81, 120.76, 120.14, 119.42. MS: ( $\text{M}^{4+}$ )  $[m/z] = 758.5155$  (calcd for  $\text{C}_{156}\text{H}_{110}\text{Ir}_4\text{N}_{20}$ : 3034.77). Anal. Calcd. for  $\text{C}_{156}\text{H}_{110}\text{F}_{24}\text{Ir}_4\text{N}_{20}\text{P}_4$ : C 51.85, H 3.07, N 7.75. Found C 51.79, H 3.11, N 7.81.





**Fig. S3**  $^1\text{H}$  NMR spectrum of  $[\text{TPP-Ir}]^+$  in  $\text{DMSO-d}_6$ .



**Fig. S4**  $^1\text{H}$  NMR spectrum of  $[\text{TPP-4Ir}]^{4+}$  in  $\text{DMSO-d}_6$ .

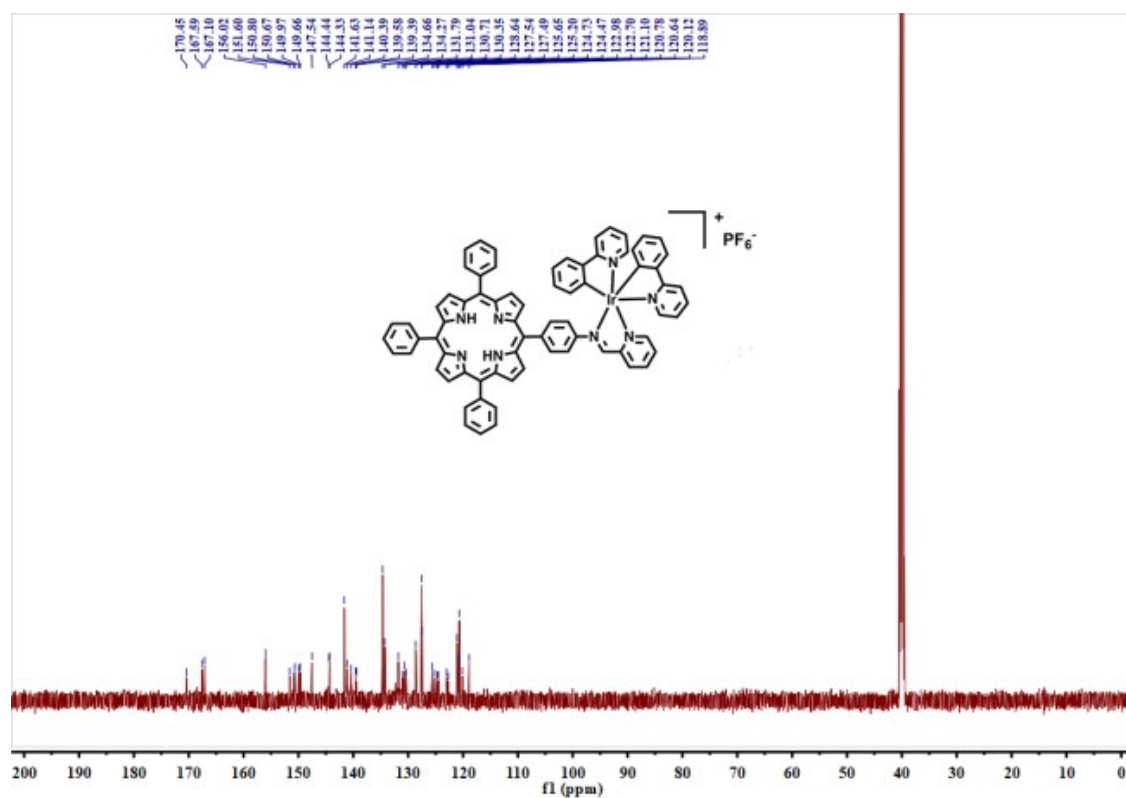


Fig. S5  $^{13}C$  NMR spectrum of  $[TPP-Ir]^+$  in  $DMSO-d_6$ .

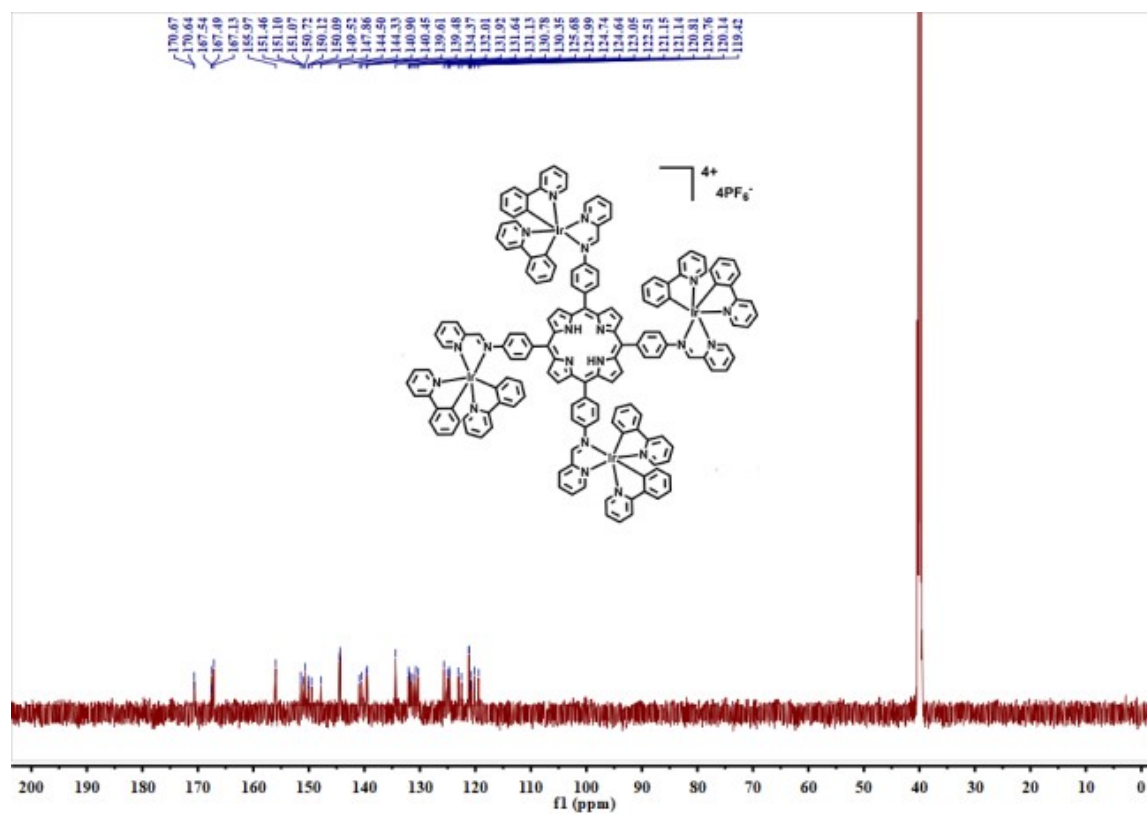
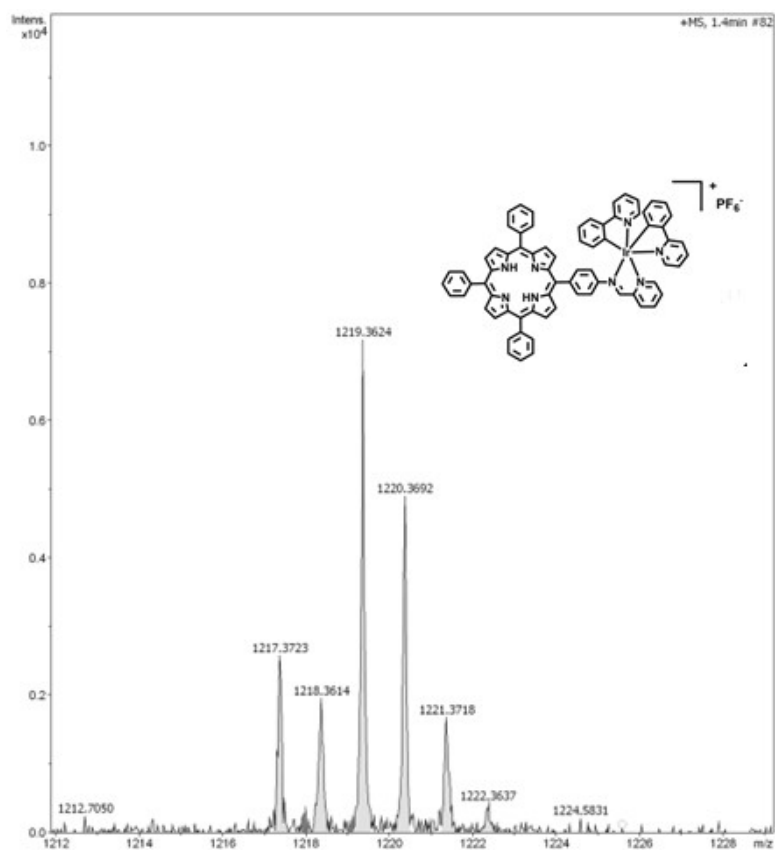
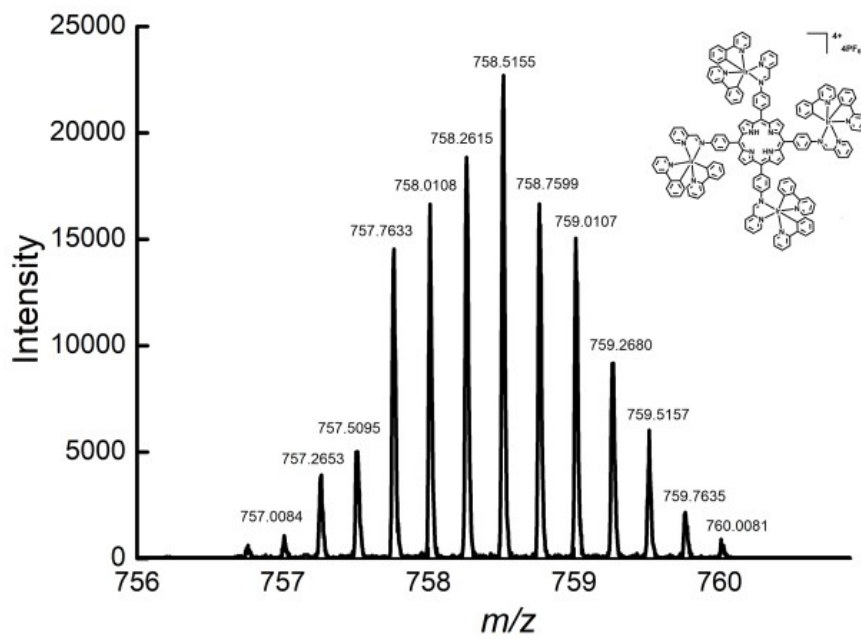


Fig.S6  $^{13}C$  NMR spectrum of  $[TPP-4Ir]^{4+}$  in  $DMSO-d_6$ .

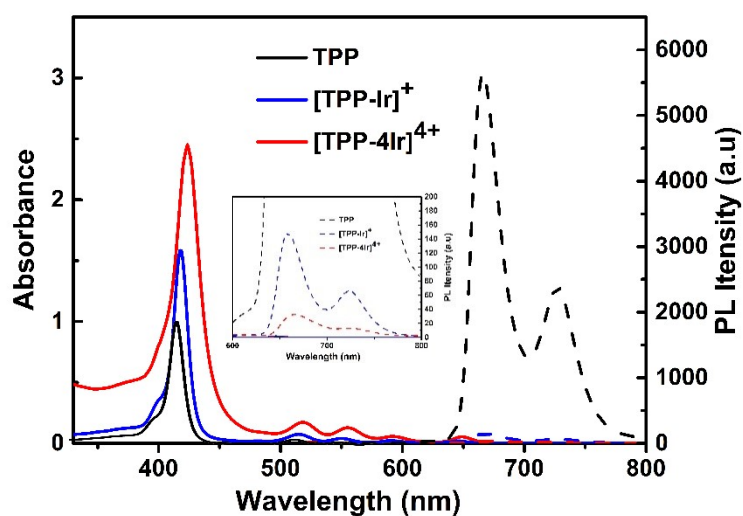




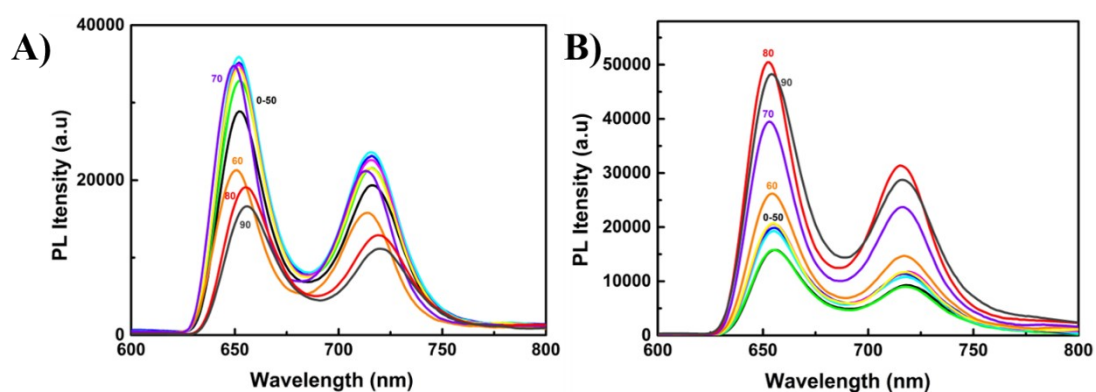
**Fig. S7** ESI mass spectrum of [TPP-Ir]<sup>+</sup>.



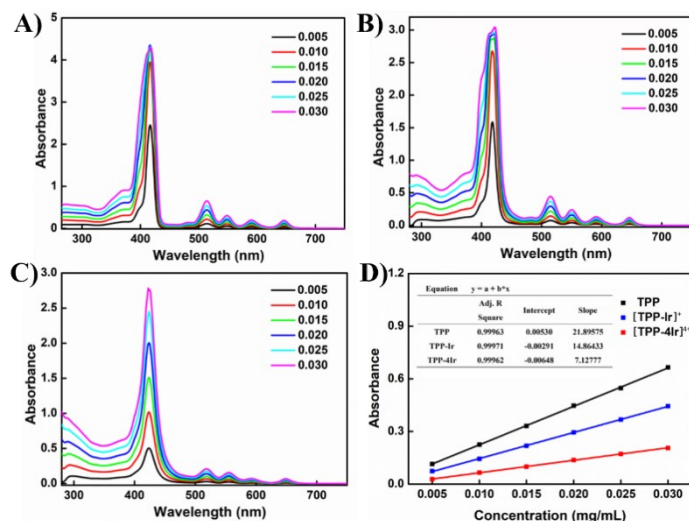
**Fig. S8** ESI mass spectrum of [TPP-4Ir]<sup>4+</sup>.



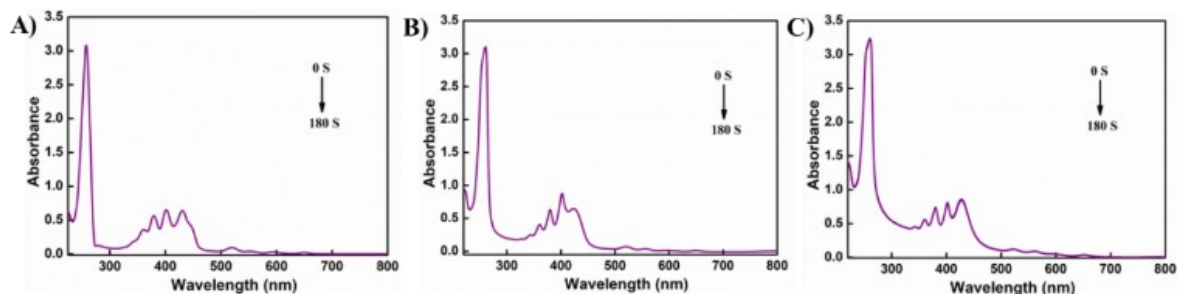
**Fig. S9** The UV-vis absorption spectra in  $\text{CH}_3\text{COCH}_3$  (solid line) and the PL spectra in  $\text{CH}_3\text{COCH}_3$  of  $[\text{TPP}]$ ,  $[\text{TPP-Ir}]^+$  and  $[\text{TPP-4Ir}]^{4+}$  ( $10^{-5}$  M) (dashed line). Inset is an expansion of PL spectra in the 600-800 nm region.



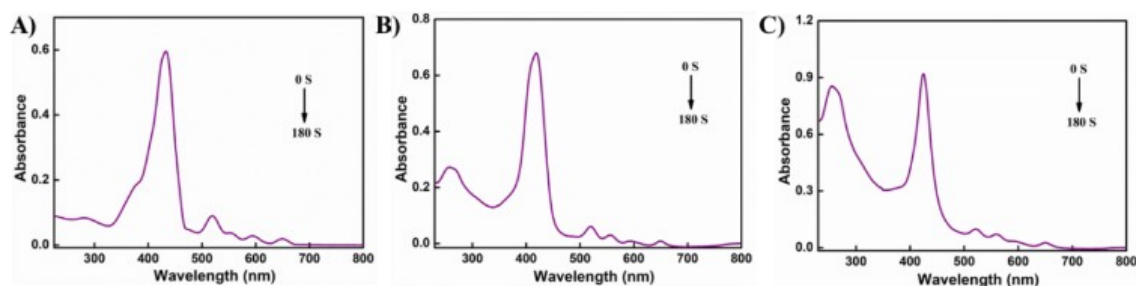
**Fig. S10** PL spectra of  $[\text{TPP-Ir}]^+$  (A) and  $[\text{TPP-4Ir}]^{4+}$  (B) in acetone- $\text{H}_2\text{O}$  mixtures (complex concentration =  $1.0 \times 10^{-5}$  M) with different water fractions (0-90% , v/v) at room temperature.



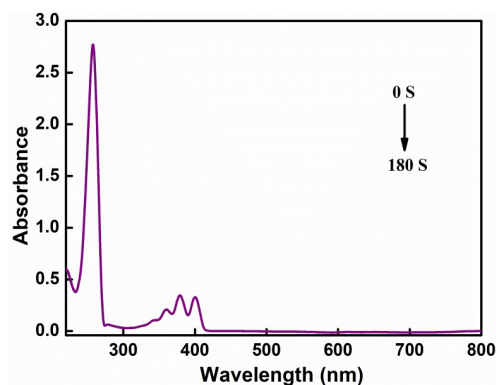
**Fig. S11** UV-vis absorption spectra of A) TPP NPs, B) [TPP-Ir]<sup>+</sup> NPs and C) [TPP-4Ir]<sup>4+</sup> NPs in DMF/H<sub>2</sub>O = 4/1 (v/v) concentration; D) Standard curves of TPP NPs, [TPP-Ir]<sup>+</sup> NPs and [TPP-4Ir]<sup>4+</sup> NPs in DMF/H<sub>2</sub>O = 4/1 (v/v).



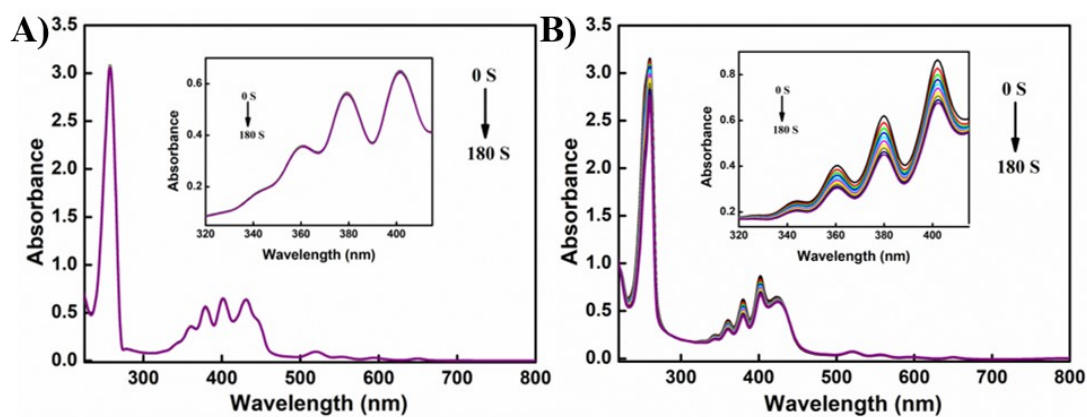
**Fig. S12** UV-visible absorption spectra of ABDA in the presence of A) TPP NPs, B) [TPP-Ir]<sup>+</sup> NPs and C) [TPP-4Ir]<sup>4+</sup> NPs ( $5 \times 10^{-6}$  M) without light irradiation.



**Fig. S13** UV-visible absorption spectra of A) **TPP NPs**, B) **[TPP-Ir]<sup>+</sup> NPs** and C) **[TPP-4Ir]<sup>4+</sup> NPs** ( $5 \times 10^{-6}$  M) upon irradiation with a white LED at  $20 \text{ mW cm}^{-2}$ .



**Fig.S14** UV-visible absorption spectra of ABDA upon irradiation with a white LED at  $20 \text{ mW cm}^{-2}$ .



**Fig.S15** UV-visible absorption spectra of ABDA in the presence of A) **TPP NPs** and B) **[TPP-Ir]<sup>+</sup> NPs** ( $5 \times 10^{-6}$  M) upon irradiation with a white LED at  $20 \text{ mW cm}^{-2}$ .

**Table S1** Photophysical data of **TPP** NPs, **[TPP-Ir]<sup>+</sup>** NPs and **[TPP-4Ir]<sup>4+</sup>** NPs

	$\lambda_{abs}$ (nm)	$\lambda_{em}$ (nm)	$\Phi_p$ (%)	$\tau_p$ (ns)	$k_r^b$ ( $\times 10^6$ s <sup>-1</sup> )	$k_{nr}^b$ ( $\times 10^8$ s <sup>-1</sup> )
<b>TPP</b> NPs <sup>[a]</sup>	251; 429; 519; 555; 594; 649	656; 717	27.1	5.47	49.45	1.33
<b>[TPP-Ir]<sup>+</sup></b> NPs <sup>[a]</sup>	257; 417; 520; 558; 594; 650	656; 720	8.1	5.72	14.21	1.61
<b>[TPP-4Ir]<sup>4+</sup></b> NPs <sup>[a]</sup>	256; 424; 521; 560; 594; 650	656; 720	3.6	5.87	6.12	1.64

<sup>[a]</sup> Measured in water,  $\lambda_{ex}$  = 365 nm, concentration is  $1.0 \times 10^{-5}$  M. Radiative transition value  $k_r$  and non-radiative transition value  $k_{nr}$  are calculated according to the following formula, which is:  $k_r = \Phi/\tau$  and  $k_{nr} = (1-\Phi)/\tau$ ,  $\Phi$  is the fluorescence quantum efficiency,  $\tau$  is the phosphorescence lifetime value.

**Table S2** Molar absorption coefficient ( $\epsilon$ ) of **TPP** NPs, **[TPP-Ir]<sup>+</sup>** NPs and **[TPP-4Ir]<sup>4+</sup>** NPs

	$\lambda_{max}^{[b]}$ (nm)	$\epsilon^{[b]}$ (M <sup>-1</sup> cm <sup>-1</sup> )
<b>TPP</b> NPs <sup>[a]</sup>	251; 429; 519; 555; 594; 649	10020; 115730; 9460; 3893; 3034; 2175
<b>[TPP-Ir]<sup>+</sup></b> NPs <sup>[a]</sup>	257; 417; 520; 558; 594; 650	54090; 138510; 13770; 7994; 4918; 4018
<b>[TPP-4Ir]<sup>4+</sup></b> NPs <sup>[a]</sup>	256; 424; 521; 560; 594; 650	163510; 184870; 20060; 15420; 9379; 6858

<sup>[a]</sup> Measured in water, concentration is  $1.0 \times 10^{-5}$  M.

<sup>[b]</sup> The maximum absorption wavelength and corresponding molar absorption coefficient of **TPP** NPs, **[TPP-Ir]<sup>+</sup>** NPs and **[TPP-4Ir]<sup>4+</sup>** NPs.