

## Supplementary Information

### Enhanced cocatalyst-free photocatalytic H<sub>2</sub> evolution by the synergistic AIE and FRET for an Ir-complex conjugated porphyrin

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### Experimental Section

#### Materials and Methods

All the starting materials were purchased from commercial sources and used without further purification. Solvents were dried by distillation based on published procedures using appropriate dehydrating agents. Molecule purification were done by column chromatography using 100-200 mesh silica gel. NMR spectra were recorded at 400 and 101 MHz ( $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR respectively) on a Bruker NMR spectrometer, and chemical shifts were obtained relative to residual solvent chloroform peaks, which is  $\delta 7.26$  ppm for  $^1\text{H}$  and  $\delta 77.0$  ppm for  $^{13}\text{C}$ . High-resolution matrix-assisted laser desorption/ionization time-of-flight and electrospray ionization mass spectrometry experiments were performed on a Bruker Autoflex MALDI-TOF mass spectrometer and AB Sciex 3200 QTRAP MS/MS system, respectively. UV-visible and photoluminescence spectra were collected on Agilent Cary 8454 UV-Vis Spectrometer and Horiba FluoroMax-4 Photoluminescence Spectrometer, respectively. Freshly prepared air equilibrated sample solutions (10  $\mu\text{M}$ ) were used for UV-vis and PL spectra at room temperature. Cyclic voltammetry experiments were conducted on an electrochemical workstation (CHI660C Instruments, China) with standard three-electrode cell. A glassy carbon working electrode, a nonaqueous  $\text{Ag}/\text{Ag}^+$  reference electrode, and a platinum wire counter electrode were used for the measurements. It was measured at room temperature in acetonitrile sample solution (200  $\mu\text{M}$ ). Tetrabutylammonium hexafluorophosphate (0.1 M) was used as supporting electrolyte. Ferrocene was added as internal reference.

### **Preparation of photocatalytic systems.**

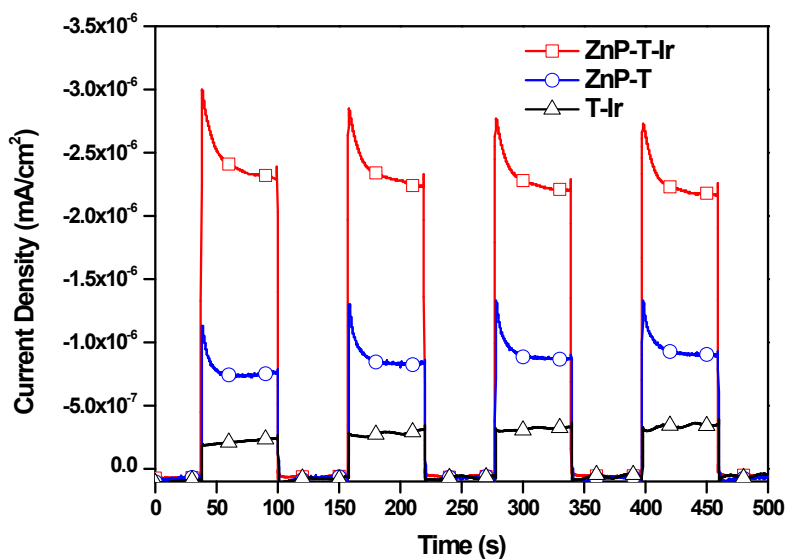
An OLED white light multichannel photochemical reaction system (PCX50B, 148.5mW/cm<sup>2</sup>) was used as the light source for photocatalytic hydrogen evolution. Reactions were performed in a quartz vial reactor (20 mL) sealed with a rubber septum,

gas-closed system, at ambient temperature and pressure. Firstly, the prepared sample was dissolved in a mixture of MeCN, water and TEOA in different ratio to obtain a  $10^{-5}$  M solution under constant stirring. Secondly, the solution was degassed with argon for 15 minutes to ensure anaerobic conditions and then it was placed in the multichannel photochemical reaction system. After 1 hour irradiation, 400  $\mu$ L gas was collected from the headspace of the reactor by a syringe and was analyzed by gas chromatography (Shimadzu, GC-2014, Japan, with ultrapure argon as a carrier gas) and a thermal conductivity detector. Finally, the total amount of photocatalytic hydrogen generation was calculated according to calibration curve. Continuous stirring was applied to the whole procedure to fulfil consistent irradiation.

### **Photoelectrochemical Measurement**

Transient photocurrent responses were collected on electrochemical workstation with a fluorine-doped tin oxide glass with sample film on conductive surface as working electrode, a nonaqueous Ag/Ag<sup>+</sup> as reference electrode, and a platinum wire as counter electrode. The working electrode was coated by dropping 5ml dichloromethane sample solution (20  $\mu$ M) on conductive surface. Aqueous Na<sub>2</sub>SO<sub>4</sub> solution (0.5 M) was prepared as supporting electrolyte. A LED monochromatic point (3 W, 420 nm) was used as the light source. The light spot effective area on working electrode was set as 28.26 mm<sup>2</sup>.

As shown in Fig. S1, the iridium motif conjugated porphyrin **ZnP-T-Ir** showed higher photocurrent response than the controlled compounds **ZnP-T** which lacks the iridium motif and **T-Ir** without porphyrin moiety **ZnP-T**. It indicates that **ZnP-T-Ir** possess efficient photogenerated hole-electron pairs separation and more electrons available at the photoexcited state for transferring to proton.



**Fig. S1** Transient photocurrent response spectra (I-t curves) of **ZnP-T-Ir**, **ZnP-T** and **T-Ir**.

## Synthesis

The pyridyl-triazole intermediates **1a** and **1b** were synthesized and characterized according to previous report.<sup>1,2</sup>

### P-T:

A mixture of **1a** (2.0 g, 8.0 mmol), benzaldehyde (2.54g, 24.0 mmol) and propionic acid (10 mL) was heated to reflux for 30 min. To this mixture, freshly distilled pyrrole (2.14 g, 32.0 mmol) in 30 mL propionic acid was added dropwise. After addition, the reaction mixture was refluxed for 3 h. After completion of the reaction, propionic acid was removed by vacuum distillation. The resulting crude product was further purified via silica gel column chromatography using chloroform/hexane (8:2, v/v) as eluent. The purified product was obtained as purple powder. Yield: 3.0% (0.18 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 8.92 (1H, s), 8.88 (7H, m), 8.71 (1H, d, *J* = 6.15 Hz), 8.42 (2H, d, *J* = 9.7 Hz), 8.37 (1H,

d,  $J = 10$  Hz), 8.23 (8H, t,  $J = 7.62$  Hz), 7.90 (1H, t,  $J = 9.7$  Hz), 7.77 (8H, d,  $J = 8.85$  Hz), 7.34 (1H, t,  $J = 7.73$  Hz), -2.77 (2H, s). MALDI-TOF:  $m/z$  calculated for  $C_{51}H_{34}N_8$ : 758.2906 found 758.1772.

#### **ZnP-T:**

A mixture of **P-T** (40 mg, 0.053 mmol), chloroform (10 mL), methanol (10 mL) and  $Zn(OAc)_2 \cdot 2H_2O$  (97mg, 0.53 mmol) was stirred at room temperature for 20 minutes. After completion of the reaction, the reaction chloroform and methanol were removed under reduced pressure. The resulting crude product was purified by silica gel column chromatography using chloroform/hexane (8:2, v/v) as eluent. The purified product was obtained as purple crystals. Yield: 85% (37mg).  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta = 8.97$  (8H, m), 8.58 (1H, d,  $J = 5$  Hz), 8.42 (2H, d,  $J = 10.65$  Hz), 8.32 (1H, d,  $J = 9.8$  Hz), 8.21 (8H, t,  $J = 9.85$  Hz), 7.88 (1H, td,  $J = 9.71, 2.2$  Hz), 7.77 (8H, d,  $J = 9.5$  Hz), 7.31 (1H, ddd,  $J = 9.51, 6.09, 1.4$  Hz).  $^{13}C$  NMR (101 MHz, DMSO):  $\delta = 149.77, 149.61, 149.41, 149.34, 149.10, 148.45, 143.25, 142.67, 137.43, 135.96, 135.31, 134.17, 131.91, 131.74, 131.69, 131.47, 127.52, 126.63, 123.44, 121.49, 120.64, 120.50, 119.94, 118.70, 118.30, 79.18$ . MALDI-TOF:  $m/z$  calculated for  $C_{51}H_{32}N_8Zn$ : 820.2041 found 820.0282.

#### **P-T-Ir:**

A mixture of **P-T** (100 mg, 0.13 mmol), chloroform (15 mL), methanol (15 mL), and 2-phenylpyridine iridium dimer (212 mg, 0.20 mmol) was degassed with nitrogen for 15 minutes. After then, the reaction mixture was stirred at reflux temperature for 24 h. After completion of the reaction, the reaction solvents were removed under reduced pressure. The resulted crude product was purified by silica gel column chromatography using

chloroform/methanol (9:1 v/v%) as eluent. The purified product was obtained as purple crystal. Yield: 91% (151 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 8.85 (6H, m), 8.77 (2H, d,  $J$  = 5.8 Hz), 8.48 (2H, d,  $J$  = 5.7 Hz), 8.34 (2H, d,  $J$  = 5.7 Hz), 8.22 (6H, dd,  $J$  = 9.23, 1.95 Hz), 8.13 (1H, td,  $J$  = 9.23, 1.7 Hz), 7.97 (3H, m), 7.77 (14H, m), 7.62 (1H, d,  $J$  = 7.2 Hz), 7.31 (1H, t,  $J$  = 8.25 Hz), 7.14 (1H, td,  $J$  = 8.6, 1.6 Hz), 7.05 (3H, m), 6.94 (2H, m), 6.40 (2H, dd,  $J$  = 17.65, 9.4 Hz), -2.81 (2H, s). MALDI-TOF:  $m/z$  calculated for  $\text{C}_{73}\text{H}_{50}\text{N}_{10}\text{Ir}$ : 1259.3849 found 1259.4120.

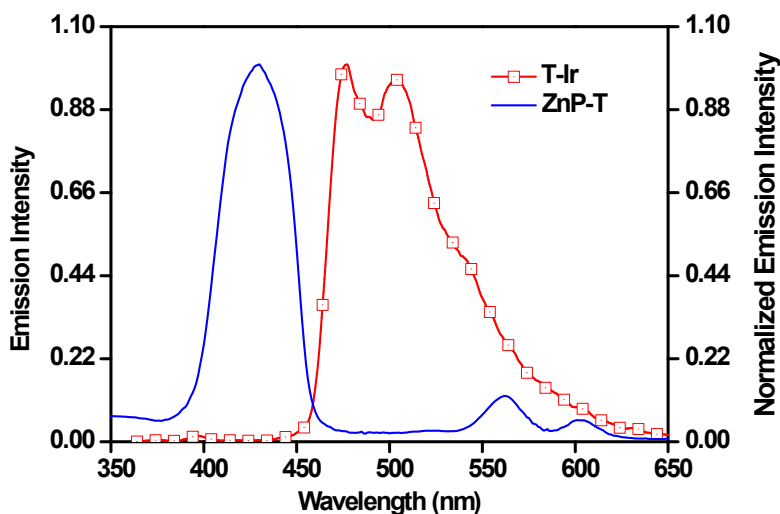
### **ZnP-T-Ir:**

A mixture of P-T-Ir (40 mg, 0.032 mmol), chloroform (10 mL), methanol (10 mL) and  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (58 mg, 0.32 mmol) was stirred at room temperature for 20 minutes. After then,  $\text{NH}_4\text{PF}_6$  (5 2mg, 0.32mmol) was added and stirred for further 15 min. After completion of the reaction, the reaction solvents were removed under reduced pressure. The resulted crude product was purified by silica gel column chromatography using chloroform. methanol (9:1, v/v%) as eluent. The purified product was obtained as green powder. Yield: 86% (36mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 8.84 (8H, m), 8.25 (4H, d,  $J$  = 27.65 Hz), 8.07 (3H, s), 7.98 (2H, d,  $J$  = 10.5 Hz), 7.88 (1H, d,  $J$  = 9.85 Hz), 7.71 (17H, m), 7.52 (1H, d,  $J$  = 4.25 Hz), 7.11 (1H, s), 7.02 (4H, m), 6.91 (3H, t,  $J$  = 7.88 Hz), 6.38 (1H, d,  $J$  = 9.5 Hz), 6.28 (1H, d,  $J$  = 8.9 Hz). MALDI-TOF:  $m/z$  calculated for  $\text{C}_{73}\text{H}_{48}\text{N}_{10}\text{IrZn}$ : 1321.2984 found 1321.3288.

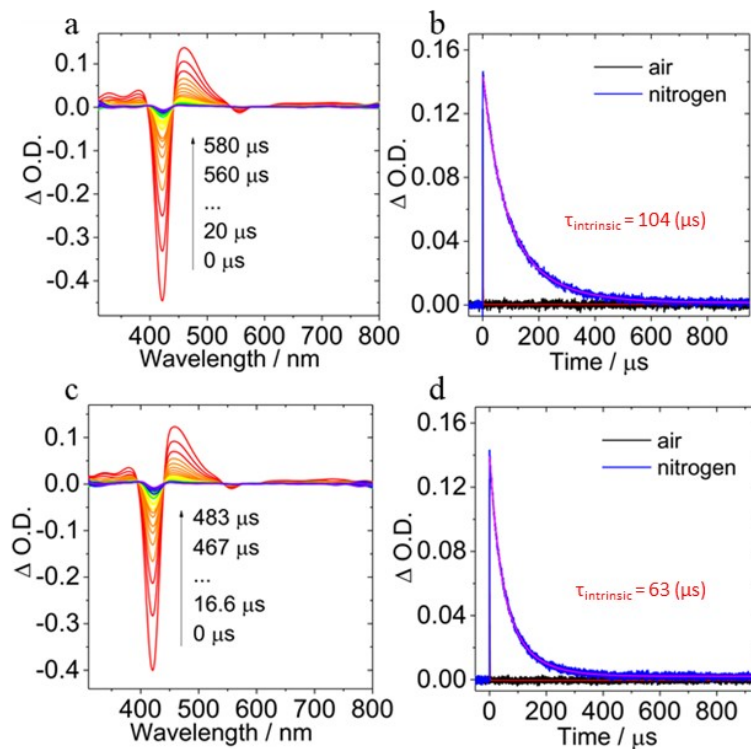
### **T-Ir:**

A mixture of **1b** (100 mg, 0.45 mmol), 2-phenylpyridine iridium dimer (483 mg, 0.45 mmol). chloroform (10 mL) and methanol (10 mL) was degassed with nitrogen for 15

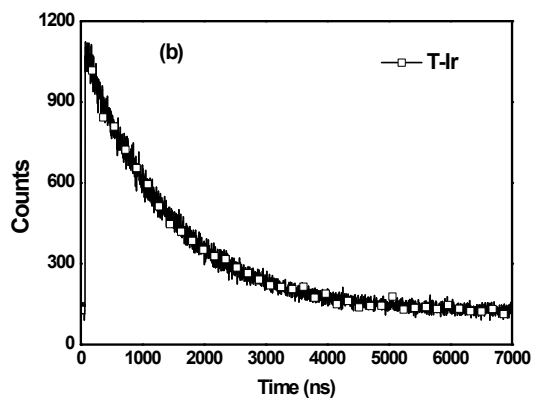
minutes. After then, the reaction mixture was stirred at reflux temperature for 24 h. Then after, it was cooled to room temperature and  $\text{NH}_4\text{PF}_6$  (733mg, 4.5mmol) was added and stirred for further 15 minutes. After completion of the reaction, the reaction solvents were removed under reduced pressure. The resulted crude product was purified by silica gel column chromatography using chloroform/methanol (9:1, v/v%) as eluent. The purified product was obtained as yellow powder. Yield 75% (0.24 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 11.57 (1H, s), 9.37 (1H, d,  $J$  = 9.95 Hz), 8.07 (3H, m), 7.92 (2H, m), 7.77 (4H, m), 7.67 (2H, dt,  $J$  = 10.15, 1.25 Hz), 7.50 (3H, m), 7.41 (1H, m), 7.24 (1H, m), 7.01 (4H, m), 6.90 (2H, m), 6.33 (2H, d,  $J$  = 9.5 Hz).  $^{13}\text{C}$  NMR (101 MHz, DMSO):  $\delta$  = 167.19, 166.46, 149.96, 149.59, 149.53, 149.04, 148.88, 148.82, 146.34, 144.05, 144.01, 140.21, 138.84, 138.74, 135.84, 131.44, 130.84, 130.20, 130.10, 129.44, 127.21, 125.61, 125.01, 124.53, 123.99, 123.78, 123.01, 122.45, 121.85, 120.85, 119.88. MALDI-TOF:  $m/z$  calculated for  $\text{C}_{35}\text{H}_{26}\text{N}_6\text{Ir}$ : 723.1848 found 723.1938.



**Fig. S2** The spectral overlap of the normalized photoluminescence spectrum of **T-Ir** excited at 350 nm with the normalized absorption spectrum of **ZnP-T**.



**Fig. S3** Nanosecond transient absorption spectra and the relative decay traces detected at 460 nm under different atmosphere of **ZnP-T-Ir** (a, b) and **ZnP-T** (c, d) in degassed MeCN ( $\lambda_{\text{ex}} = 420 \text{ nm}$ )



**Fig. S4** Photoluminescence lifetime decay spectra of **T-Ir** recorded ( $\lambda_{\text{ex}} = 340 \text{ nm}$  and lifetime monitored wavelength is 476 nm) in MeCN/H<sub>2</sub>O (1:9 v/v, 10  $\mu\text{M}$ ) at room temperature under nitrogen atmosphere.



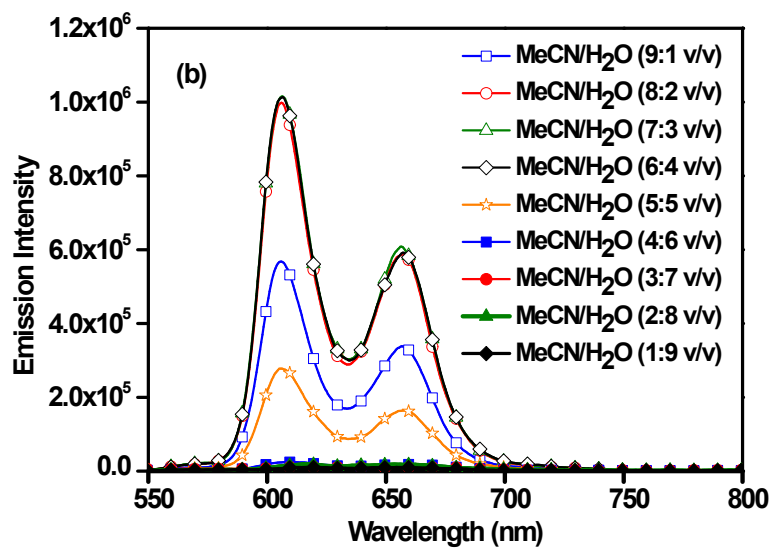


Fig. S5 Emission spectra of ZnP-T recorded in different ratio of MeCN/H<sub>2</sub>O (10  $\mu$ M).

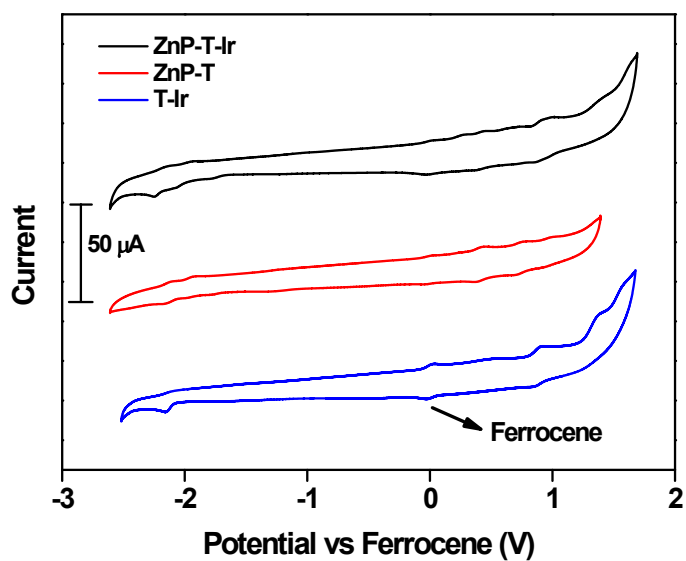
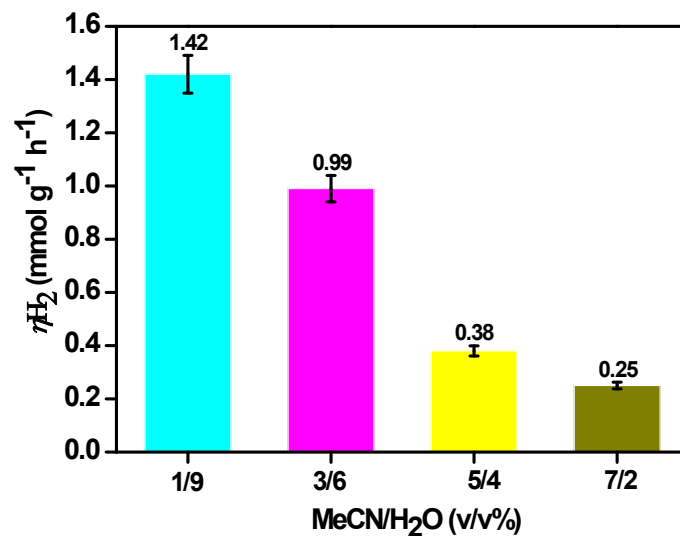
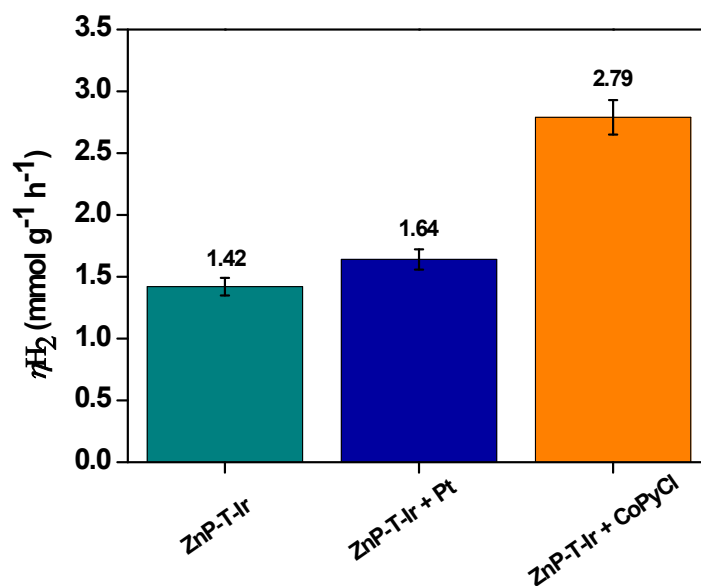


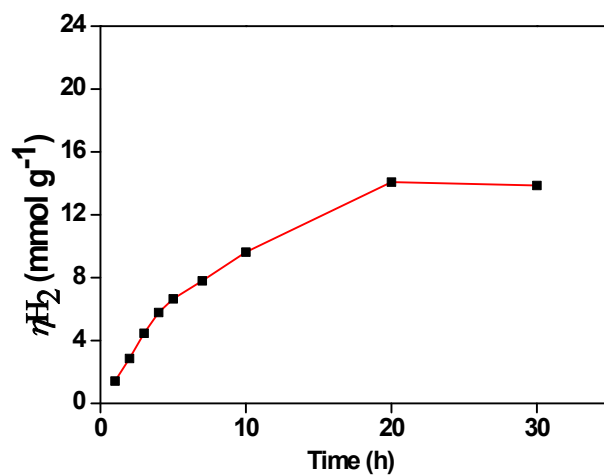
Fig. S6 Cyclic voltammograms of ZnP-T-Ir, ZnP-T and T-Ir in MeCN solution (200  $\mu$ M) at room temperature and N<sub>2</sub> atmosphere.



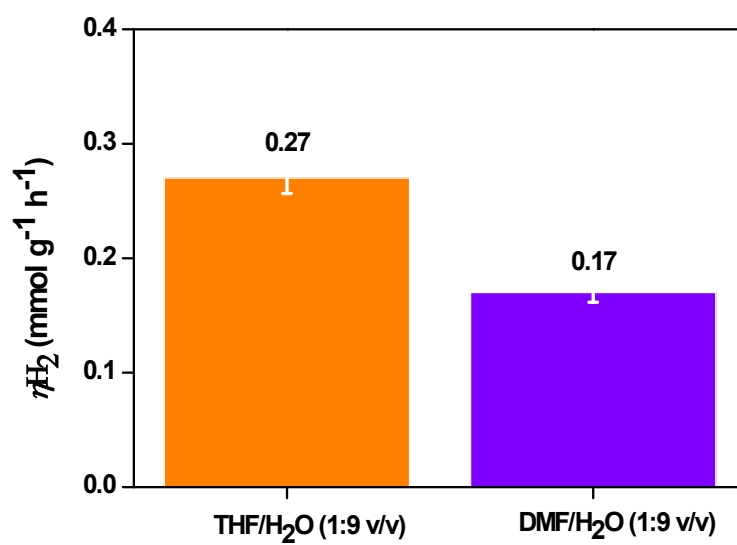
**Fig. S7**  $\eta_{\text{H}_2}$  of photocatalytic systems of **ZnP-T-Ir** recorded under irradiation for 5 h: **ZnP-T-Ir** (10  $\mu\text{M}$ ) + TEOA (0.8 M).



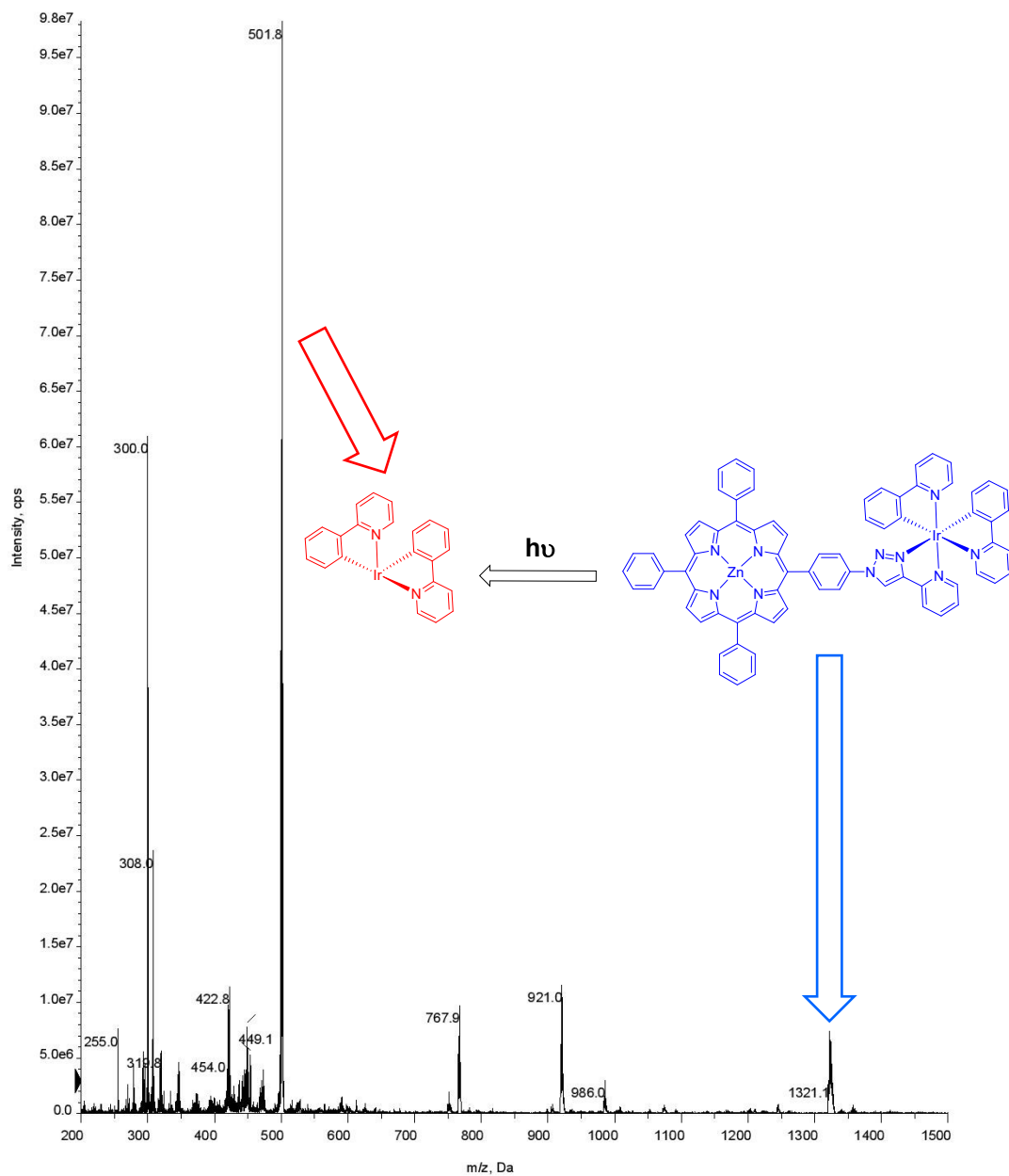
**Fig. S8**  $\eta_{\text{H}_2}$  of photocatalytic systems of **ZnP-T-Ir** recorded under irradiation for 5 h: **ZnP-T-Ir** (10  $\mu\text{M}$ ) + TEOA (0.8 M) + no cocatalyst/Pt (2 wt%)/CoPyCl (50  $\mu\text{M}$ ) + MeCN/H<sub>2</sub>O (1:9, v/v).



**Fig. S9**  $\eta_{H_2}$  of photocatalytic systems of **ZnP-T-Ir** under irradiation for 5 h: **ZnP-T-Ir** (10  $\mu\text{M}$ ) + TEOA (0.8 M).



**Fig. S10**  $\eta_{H_2}$  of photocatalytic systems of **ZnP-T-Ir** under irradiation for 5 h: **ZnP-T-Ir** (10  $\mu\text{M}$ ) + TEOA (0.8 M).



**Fig. S11** ESI-MS of **ZnP-T-Ir** in photocatalytic reaction mixture after 20 h of light irradiation.

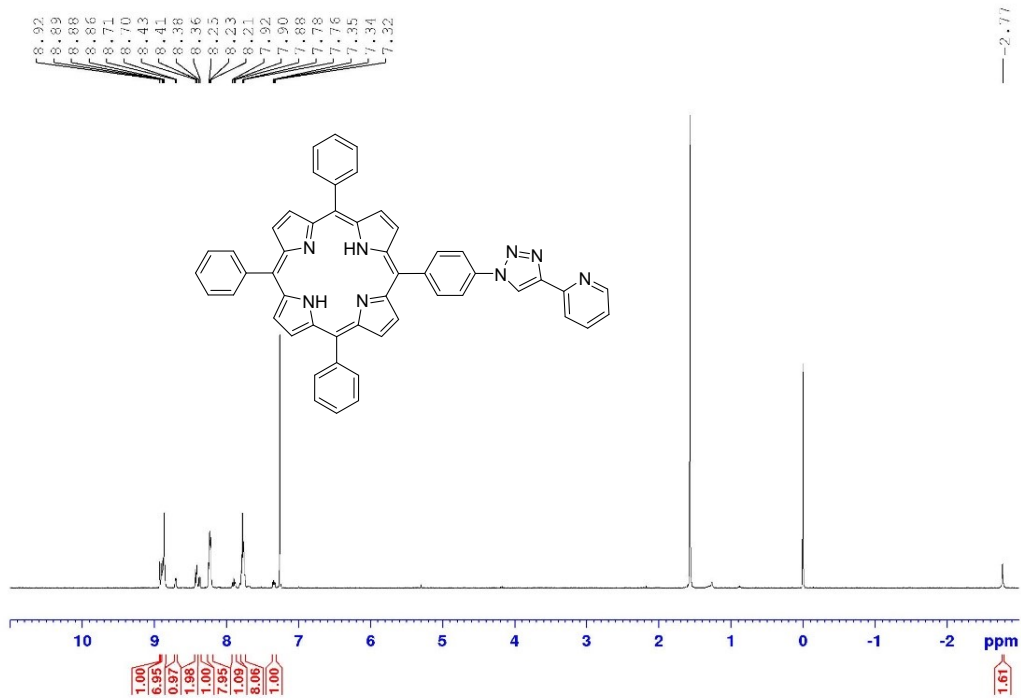


Fig. S12 <sup>1</sup>H NMR spectra of P-T recorded in CDCl<sub>3</sub>.

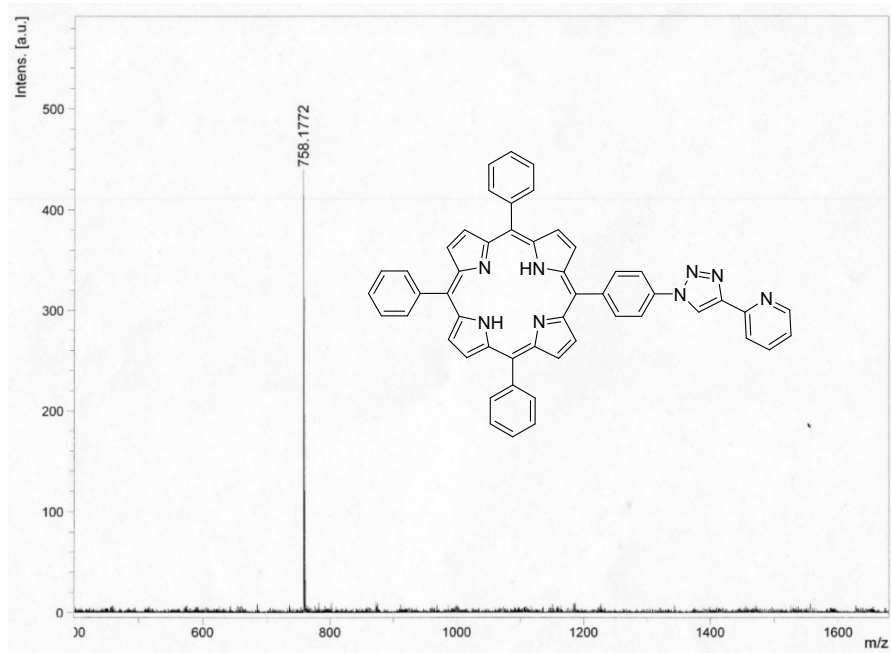


Fig. S13 MALDI-TOF mass spectra of P-T.

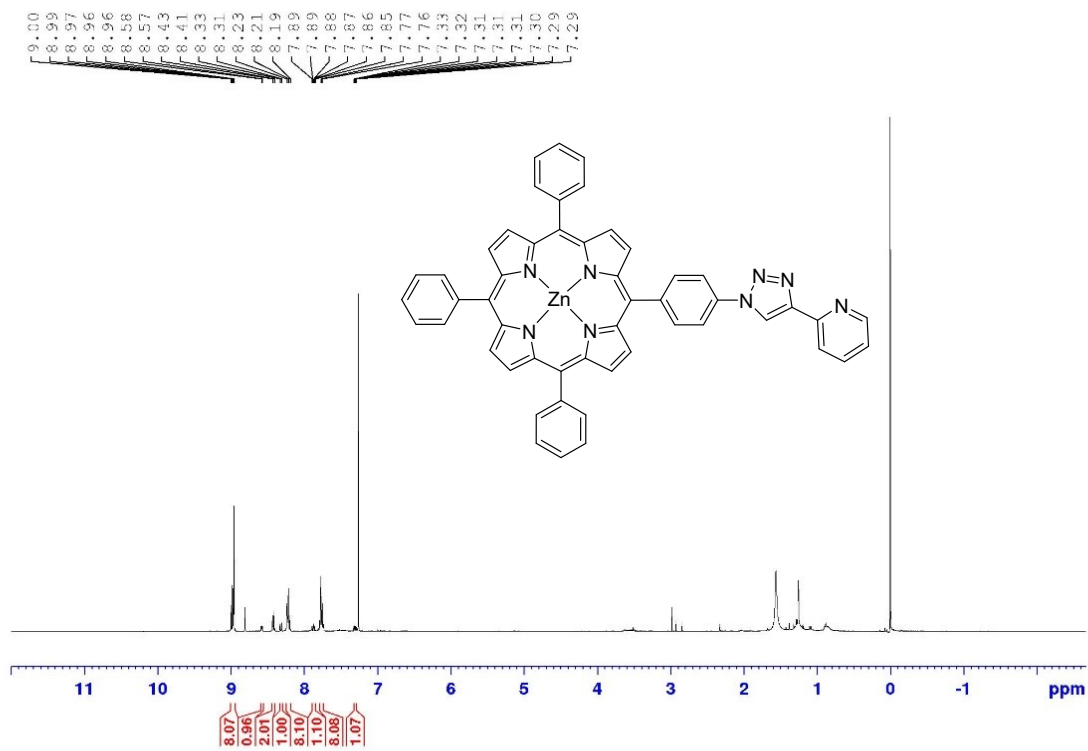


Fig. S14 <sup>1</sup>H NMR spectra of ZnP-T recorded in CDCl<sub>3</sub>.

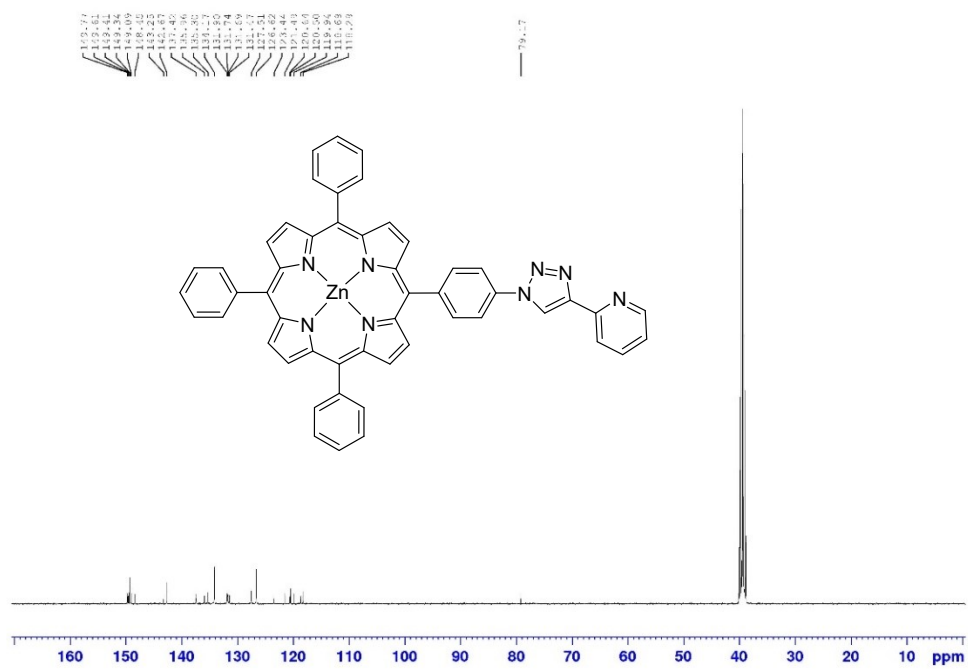


Fig. S15 <sup>13</sup>C NMR spectra of ZnP-T in DMSO-*d*<sub>6</sub>.

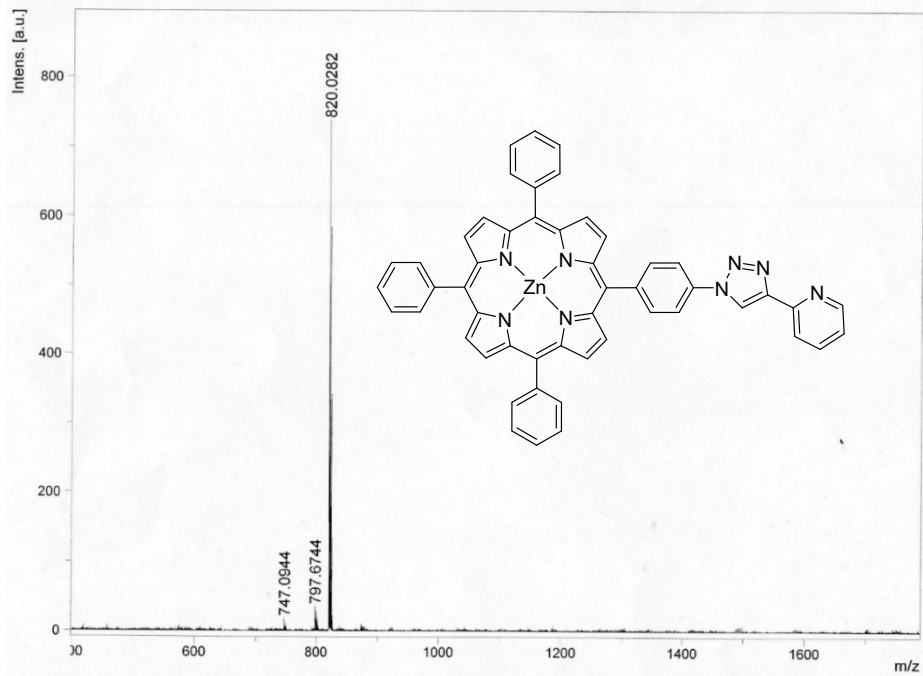


Fig. S16 MALDI-TOF mass spectra of ZnP-T.

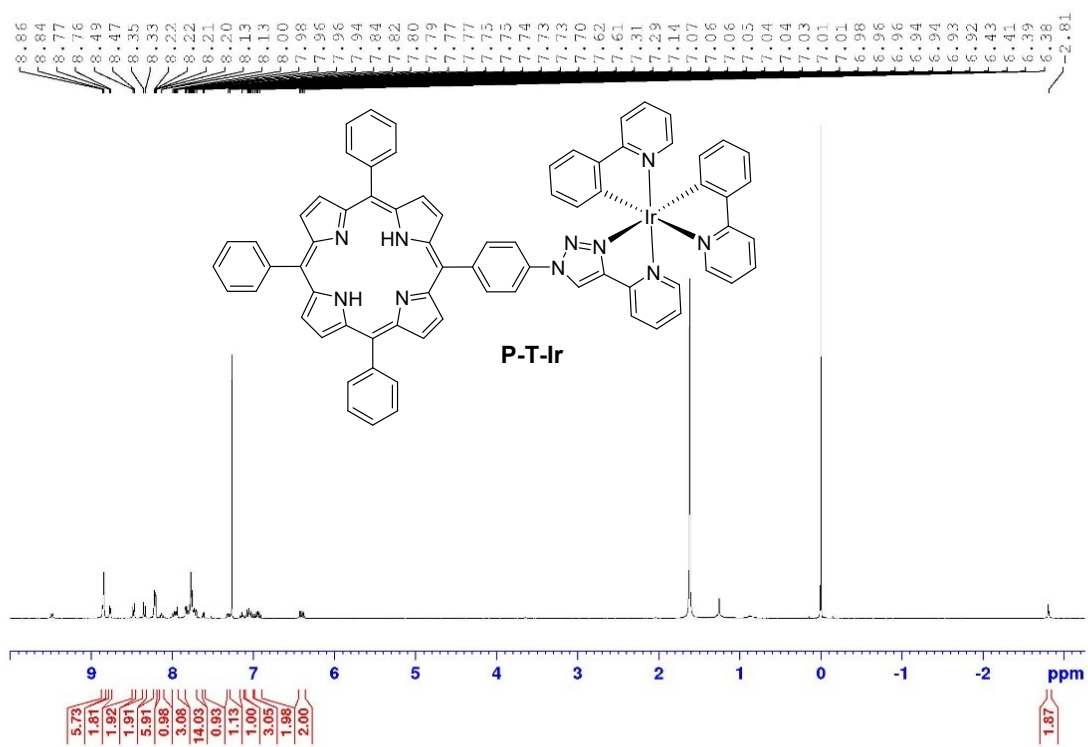
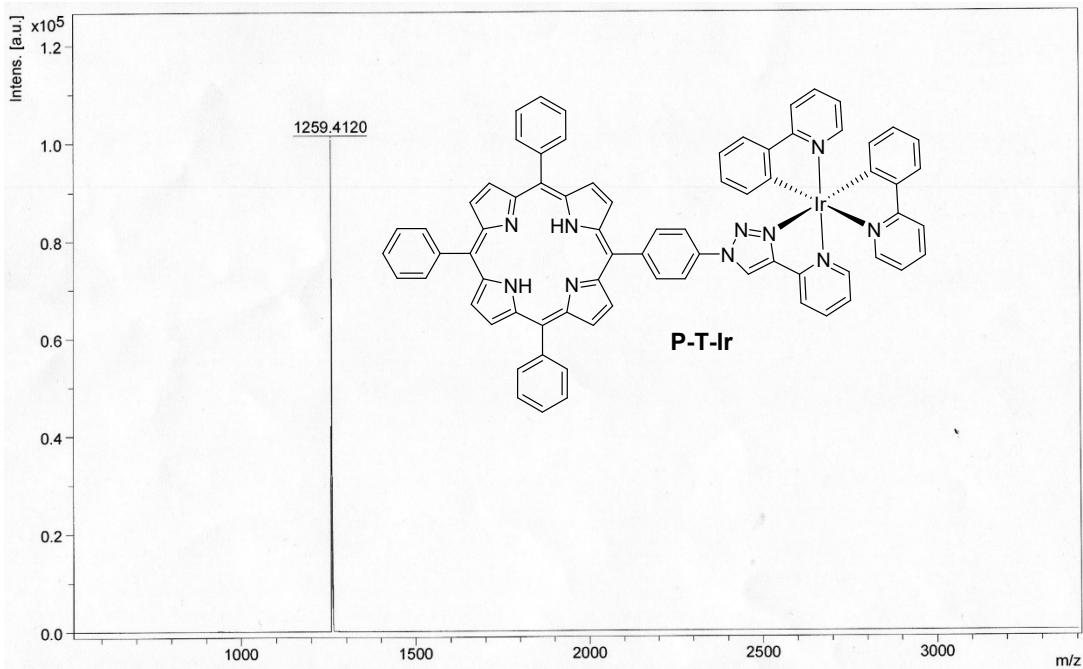
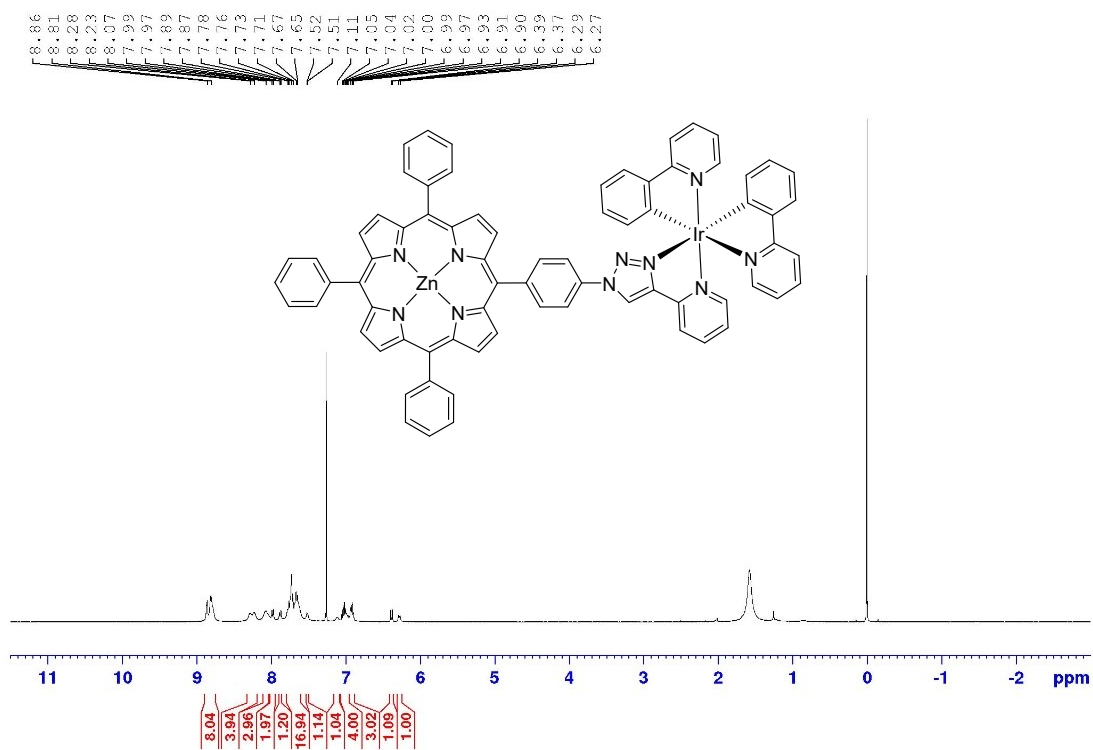


Fig. S17  $^1\text{H}$  NMR spectra of P-T-Ir in  $\text{CDCl}_3$ .

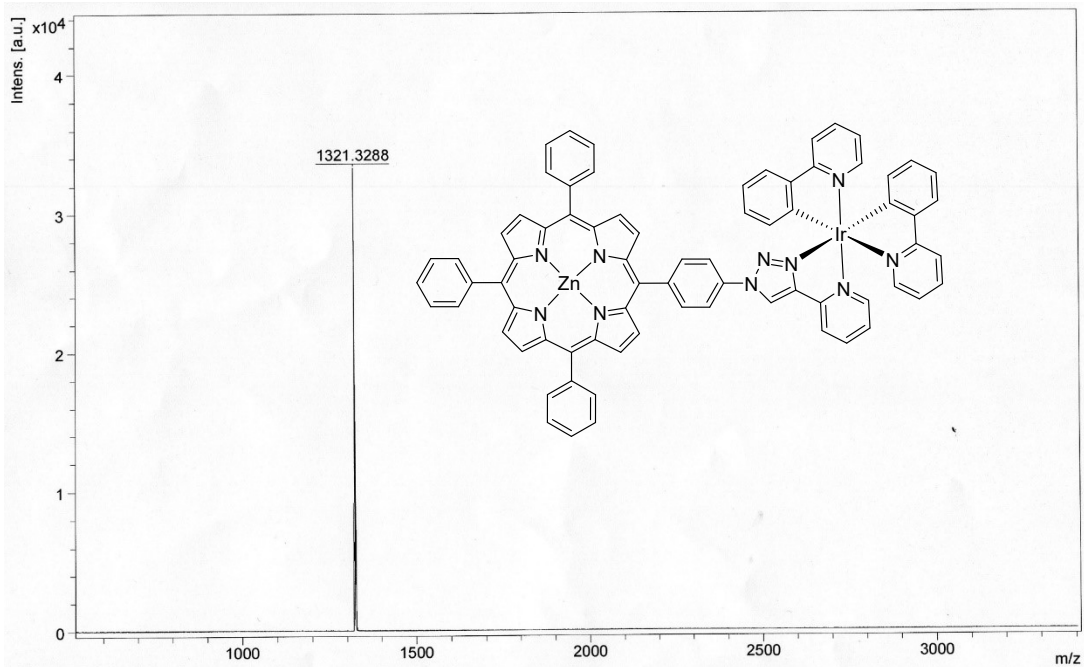


**Fig. S18** MALDI-TOF mass spectra of **P-T-Ir**.

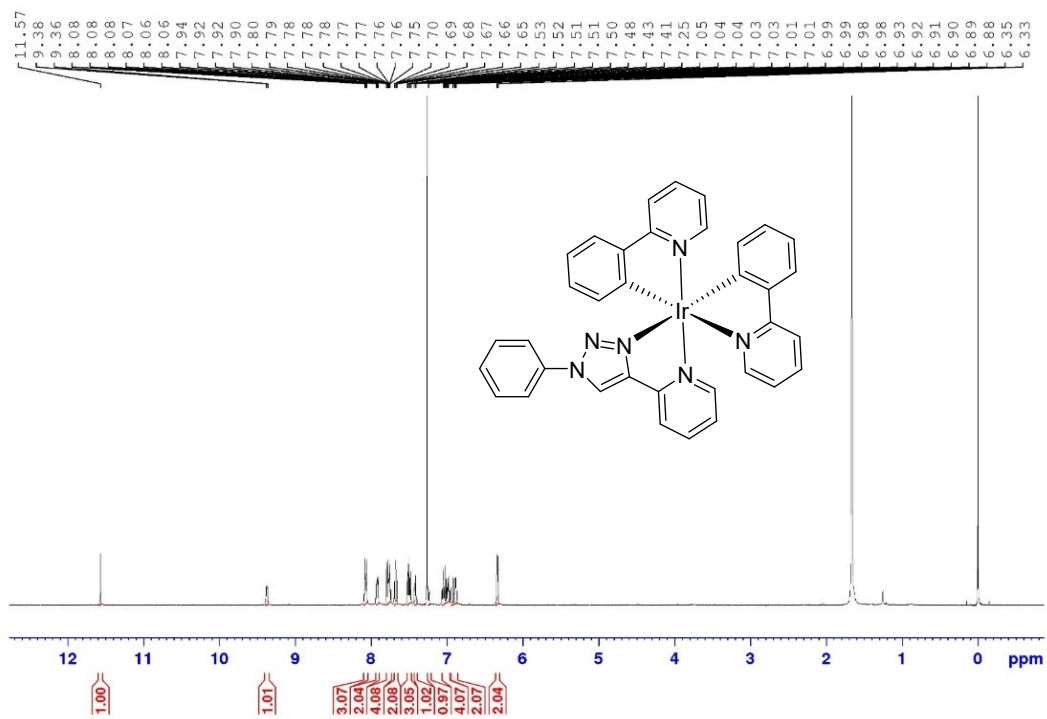


**Fig. S19**  $^1\text{H}$  NMR spectra of **ZnP-T-Ir** in  $\text{CDCl}_3$ .





**Fig. S20** MALDI-TOF mass spectra of ZnP-T-Ir.



**Fig. S21**  $^1\text{H}$  NMR spectra of T-Ir in  $\text{CDCl}_3$ .



## References

1. Á. Beltrán, I. Gata, C. Maya, J. Avó, J. C. Lima, C. A. T. Laia, R. Peloso, M. Outis and M. C. Nicasio, *Inorg. Chem.*, 2020, **59**, 10894-10906.
2. D. Zych and A. Slodek, *J. Mol. Struct.*, 2020, **1204**, 127488.