Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

Self-assembly of Pt(II)-tetrakis(pentafluorophenyl)porphyrin via F···F interaction for efficient cocatalyst-free photocatalytic hydrogen evolution

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Materials and methods

All the chemicals used in this work were purchased from commercial sources and used as received. Solvents were dried by distillation over suitable dehydrating agents according to the standard procedures. Purification of the compounds was performed by column chromatography with 100-200 mesh silica. ^{1}H and ^{13}C NMR spectra were recorded on an NMR spectrometer operating at 400.00 and 100.00 MHz, respectively. The chemical shifts were calibrated from the residual peaks observed for the deuterated chloroform ($CDCl_3$) at δ 7.26 and 77.0 ppm for ^1H and ^{13}C, respectively. High-resolution matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained with a Bruker Autoflex MALDI-TOF mass spectrometer. The optical absorption and emission spectra of the porphyrins were measured for the freshly prepared air equilibrated solutions at room temperature by using UV-Vis spectrophotometer and spectrofluorimeter, respectively. The self-assembled (SA) porphyrins coated silica substrate were prepared by drop-casting the solution of dispersed porphyrins (100 μM) in water on the silica substrate followed by drying overnight. The morphology of the porphyrins was characterized by field-emission scanning electron microscopy (FESEM, LEO 1530) equipped with an energy-dispersive X-ray (EDX, Oxford) spectrometer and Tecnai G2 20 S-TWIN. X-ray diffraction (XRD) patterns were recorded with a Bruker D8 Advance X-Ray Diffractometer equipped with a non-monochromated Cu Kα radiation (40 kV and 40 mA; λ = 1.5406 Å). Both Soller slits (primary and secondary) of 2.5° are set on incident and diffracted beams; divergence slit fixed to 0.6 mm; anti-scatter slit to 8.08 mm; no receiving slit with an opening of 12.37 mm. Diffraction patterns were collected from 10° to 90° (continuous mode) at a rate of 1.6° per second with a step size of 0.02° (2θ) using a LynxEye 1D detector. The Mott-Schottky plots of SA porphyrins were performed using an electrochemical workstation (CHI660C Instruments, China) with Pt wire (counter electrode), a non-aqueous $Ag/AgNO_3$ (reference electrode) and fluorine-doped tin oxide (FTO) glass coated with SA porphyrins on the conductive surface (working electrode). The working electrode was prepared by drop-casting 100 μM of SA porphyrins on the conductive surface of FTO glass. A 5 mL volume of 0.5 M Na_2SO_4 aqueous solution acted as the electrolyte.

Preparation of photocatalytic systems

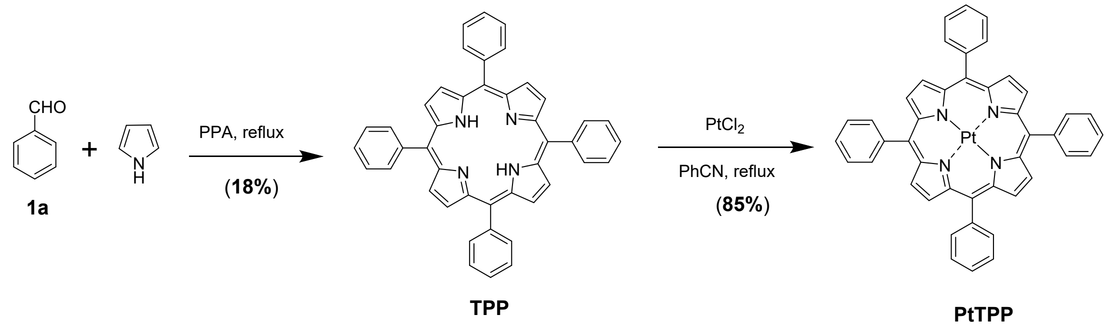
A multichannel photochemical reaction system fixed with LED white light (PCX50B, 148.5 mW/cm^2) was used as the light source. The PHE evolution experiments were performed in a quartz vial reactor (20 mL) sealed with a rubber septum, gas-closed system, at ambient temperature and pressure. Firstly, 5 mL of purple aqueous solution containing SA porphyrins was taken in a quartz vial reactor and to this solution, 0.8 M of TEA was added. The resulting suspension was further purged with argon gas for 15 min to ensure an anaerobic conditions and then it was placed in a multichannel photochemical reaction system. After 1 h of irradiation, the released gas (400 μL) was collected by syringe from the headspace of the reactor and was analyzed by gas chromatography (Shimadzu, GC-2014, Japan, with ultrapure Ar as a carrier gas) equipped with a TDX-01(5 Å molecular sieve column) and a thermal conductivity detector (TCD). Eventually, the total content of PHE was calculated according to the standard curve. Continuous stirring was applied to the whole process to keep the photocatalyst particles in a SA state and to achieve uniform irradiation.

Photoelectrochemical measurement

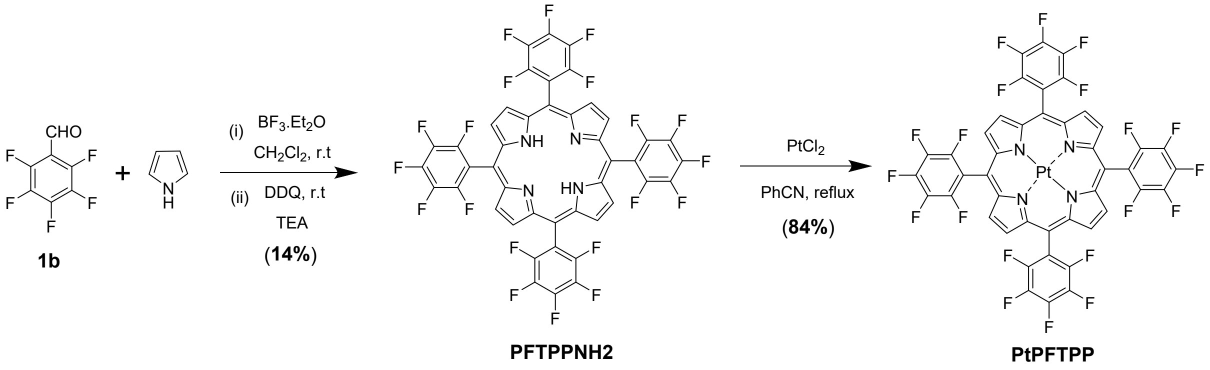
The transient photocurrent-time response (i–t curves) studies were performed using an electrochemical workstation (CHI660C Instruments, China) with Pt wire (counter electrode), a non-aqueous Ag/AgNO$_3$ (reference electrode), and FTO glass coated with SA porphyrins on the conductive surface (working electrode) upon irradiation of LED monochromatic point lamp (3 W, 420 nm). The light spot effective area on the working electrode was set as 28.26 mm^2. Typically, the working electrode was prepared by drop-casting 500 μL of a purple aqueous solution containing SA Pt(II)-porphyrins on the conductive surface of FTO glass and air-dried overnight. A 5 mL volume of 0.5 M Na$_2$SO$_4$ aqueous solution acted as the electrolyte. The open-circuit voltages were set as the initial bias voltages in the transient photocurrent responses tests..

Synthesis

The Pt(II)-porphyrins, **PtPFTPP** and **PtTPP** used in this study were synthesized according to the procedures described in Schemes S1 & S2.



Scheme S1. Synthesis of **PtTPP**.



Scheme S2. Synthesis of **PtPFTPP**.

TPPNH2:

A mixture of **1a** (1.0 g, 9.42 mmol) in propionic acid (PPA) (30 mL) was refluxed for 30 min. To this mixture pyrrole (0.72 mL, 10.4 mmol in PPA (5 mL) was added dropwise for 5-10 min. Then the reaction mixture was stirred for 2 h. After completion of the reaction, the resulting black solid was washed with methanol and purified by column chromatography (100-200 silica mesh) using dichloromethane (DCM)/hexane (2:8 v/v) as eluent. Yield: 1.0 g

(18%). ^{1}H NMR ($CDCl_3$, 400.00 MHz) δ – 2.76 (s, 2 H), 7.74-7.78 (m, 12 H), 8.23-8.26 (m, 8 H), 8.87 (s, 8 H).

PFTPPNH2:

To the solution of **1b** (1.26 mL or 2.0 g, 10.2 mmol) in dried DCM (500 mL), pyrrole (0.740 mL, 10.71 mmol) was added dropwise and the mixture was bubbled with N_2 for 20 min. Then after $BF_3.Et_2O$ (0.16 mL) was added dropwise for 1-2 min, the reaction continued up to 7 hours. After that DDQ (4.63 g, 20.4 mmol) was added in one portion and the reaction mixture was vigorously stirred for 30 min. The reaction was quenched by the addition of TEA (1 mL). The resulting reaction crude product was purified by column chromatography (100-200 silica mesh) using DCM/hexane (2:8 v/v) as eluent. Yield: 1.4 g (14%). ^{1}H NMR ($CDCl_3$, 400.00 MHz) δ – 2.92 (s, 2 H), 8.92 (s, 8 H).

PtTPP:

$PtCl_2$ (324 mg, 1.22 mmol) was dissolved in 9 mL of purified benzonitrile and the suspension was purged with N_2 for 15 min followed by preheating at 100 ˚C for 1 h under a N_2 atmosphere. Free-base porphyrin **TPP** (150 mg, 0.244 mmol) was added to the previous solution and the mixture was refluxed at 190 ˚C until the free-base porphyrin disappeared (12 h). After completion of the reaction, benzonitrile was removed under hot condition by reduced pressure. The resulting red color solid was purified by column chromatography (100-200 silica mesh) using DCM/hexane (1:1 v/v) as eluent. Yield: 167 mg (85%). ^{1}H NMR ($CDCl_3$, 400.00 MHz) δ 7.71-7.77 (m, 12 H), 8.14-8.17 (m, 8 H), 8.76 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100.00 MHz) δ 122.35, 126.83, 127.85, 130.59, 130.74, 130.89, 133.90, 140.87, 141.40. MALDI–TOF, m/z) calculated for $C_{44}H_{28}N_4Pt$: 807.1959 found 807.0256.

PtPFTPP:

$PtCl_2$ (111 mg, 0.42 mmol) was dissolved in 6 mL of purified benzonitrile and the suspension was purged with N_2 for 15 min followed by preheating at 100 ˚C for 1 h under a N_2 atmosphere. Free-base porphyrin **PFTPP** (100 mg, 0.10 mmol) was added to the previous solution and the mixture was refluxed at 100 ˚C until the free-base porphyrin disappeared (72 h). After completion of the reaction, benzonitrile was removed under hot condition by reduced pressure. The resulting red color solid was purified by column chromatography (100-200 silica mesh) using DCM/hexane (1:1 v/v) as eluent. Yield: 98 mg (84%). ^{1}H NMR ($CDCl_3$, 400.00 MHz) δ 8.83 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100.00 MHz) δ 106.37, 114.62, 114.78, 114.81, 114.97, 131.08, 136.40, 136.53, 138.82, 138.94, 139.07, 141.30, 143.66, 145.16, 147.64. MALDI–TOF, m/z) calculated for $C_{44}H_8F_{20}N_4Pt$: 1167.0075 found 1167.0062.

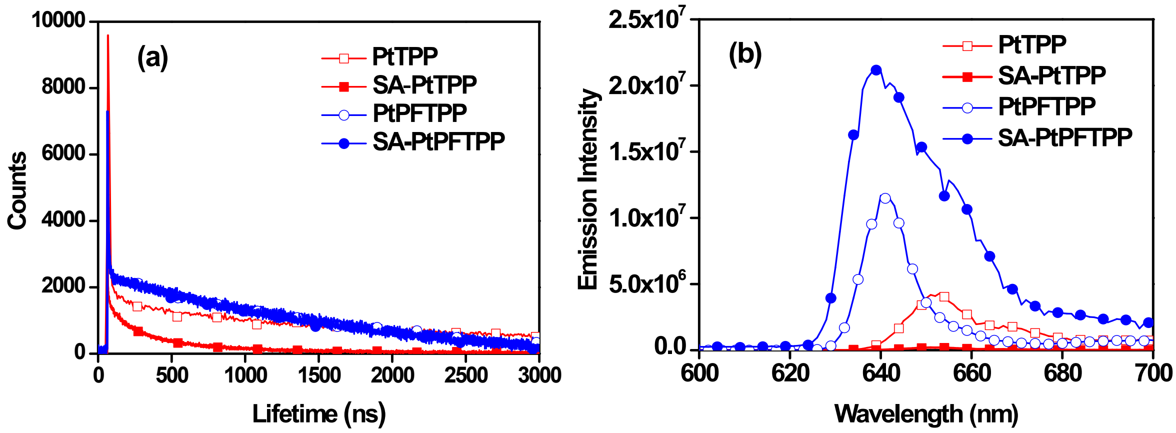


Fig. S1 (a) Photoluminescence lifetime decay spectra of Pt(II)-porphyrins recorded in THF (10 µM) and SA Pt(II)-porphyrins recorded in H_2O at room temperature under argon and (d) emission spectra of Pt(II)-porphyrins in THF (10 µM) and SA Pt(II)-porphyrins in H_2O recorded at 77 K under argon.

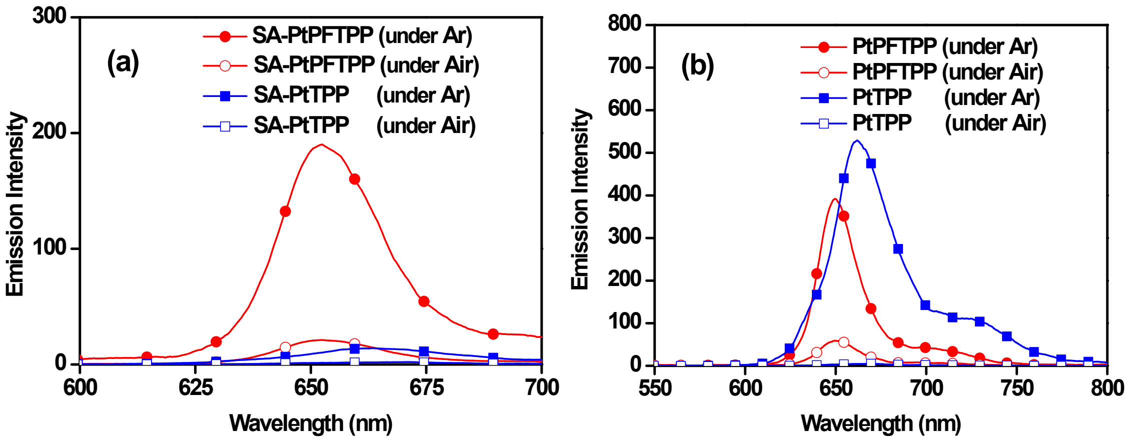


Fig. S2 (a) Emission spectra of SA Pt(II)-porphyrins recorded in H_2O (100 μM) at room temperature under argon (Ar) and air (Air) atmosphere and (b) emission spectra of Pt(II)-porphyrins recorded in THF (10 μM) at room temperature under argon (Ar) and air (Air) atmosphere

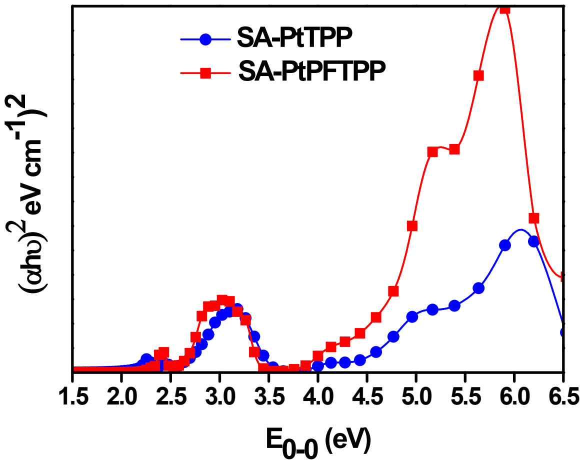


Fig. S3 Tauc plots of SA-PtPFTPP and SA-PtTPP.

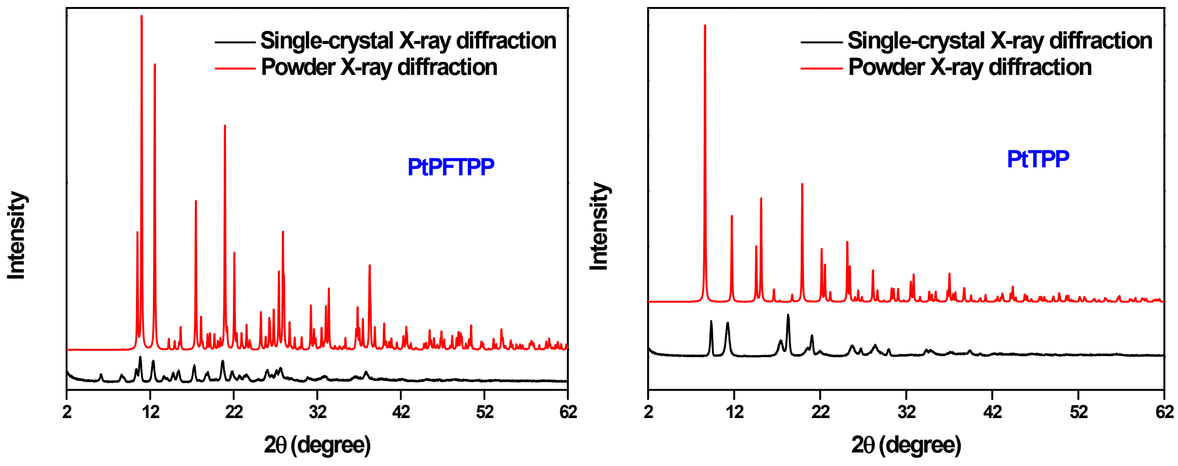


Fig. S4 Comparison of powder X-ray diffraction and single-crystal X-ray diffraction patterns of the Pt(II)-porphyrins.

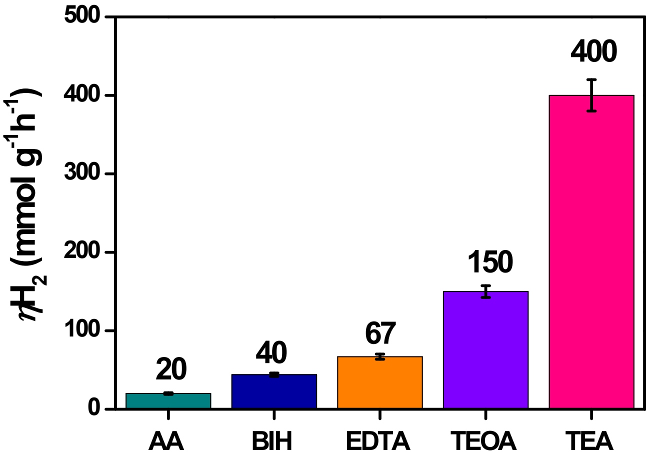


Fig. S5 ηH_2 of photocatalytic systems of **SA-PtPFTPP** under irradiation for 5 h: **SA-PtPFTPP** (100 μM), TEA/TEOA/AA (0.8 M) and H_2O.

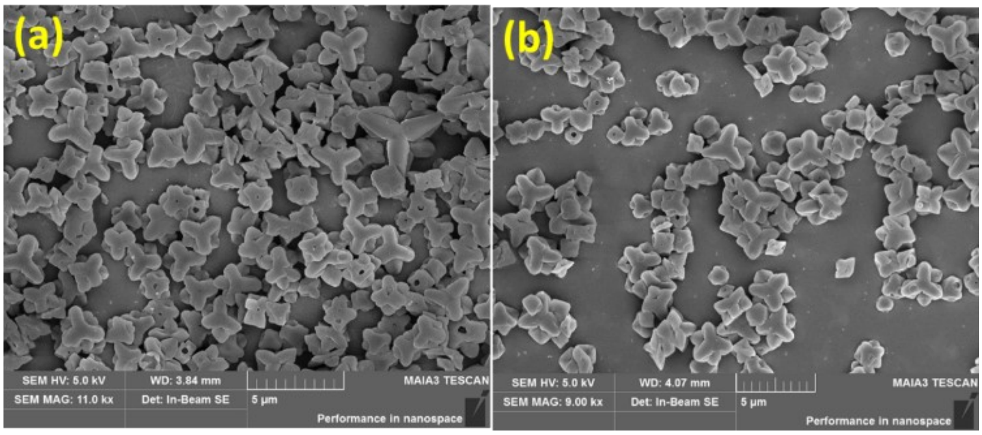


Fig. S6 Typical SEM images of photocatalytic system of **SA-PtPFTPP** (a) before light irradiation and (b) after 20 h light irradiation.

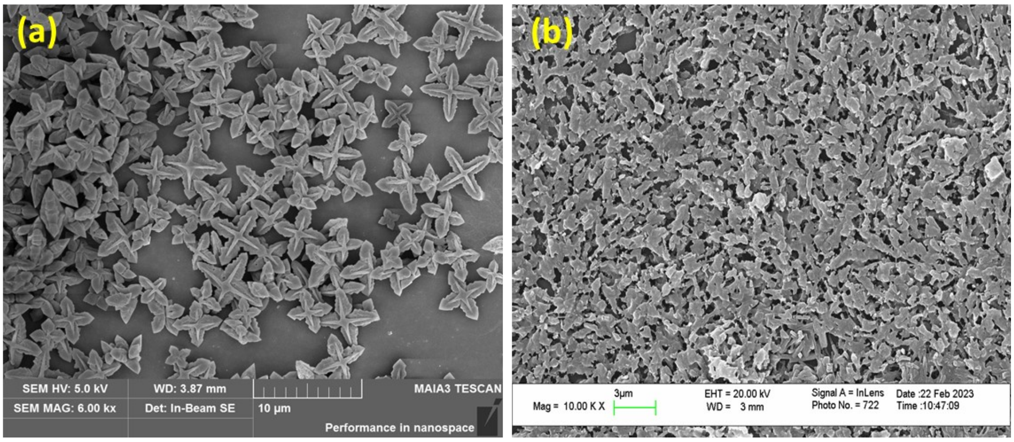


Fig. S7 Typical SEM images of the photocatalytic system of **SA-PtTPP** (a) before light irradiation and (b) after 20 h of light irradiation.

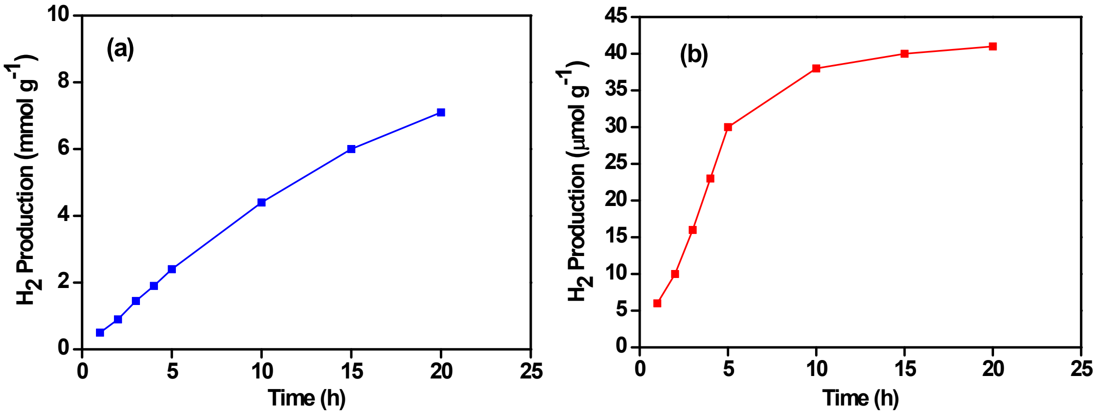


Fig. S8 Time dependent H_2 production of photocatalytic systems of (a) **SA-PtPFTPP** and (b) **SA-PtTPP** for 20 h of light irradiation.

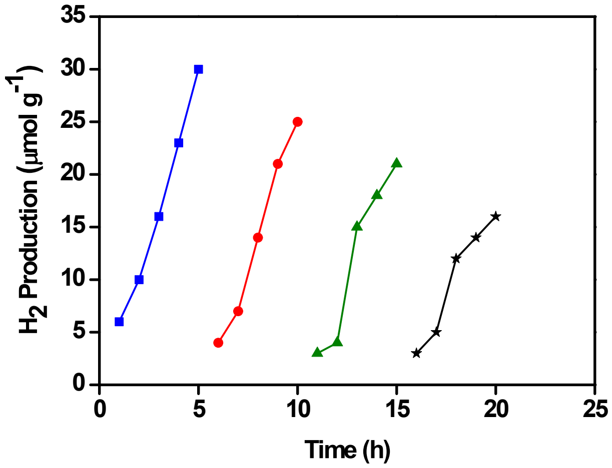


Fig. S9 H_2 production of different cycles of **SA-PtTPP** photocatalytic system.

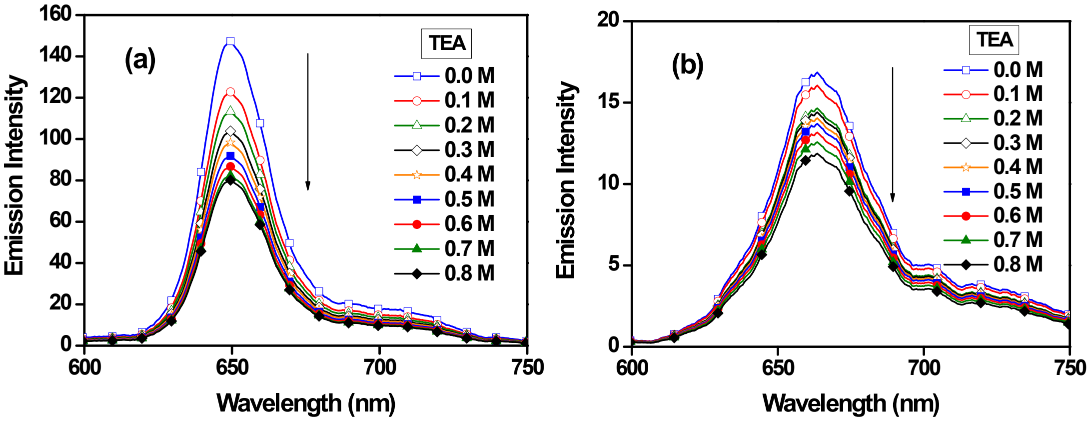


Fig. S10 Photoluminescence quenching of (a) **SA-PtPFTPP** and (b) **SA-PtTPP** with TEA quencher.

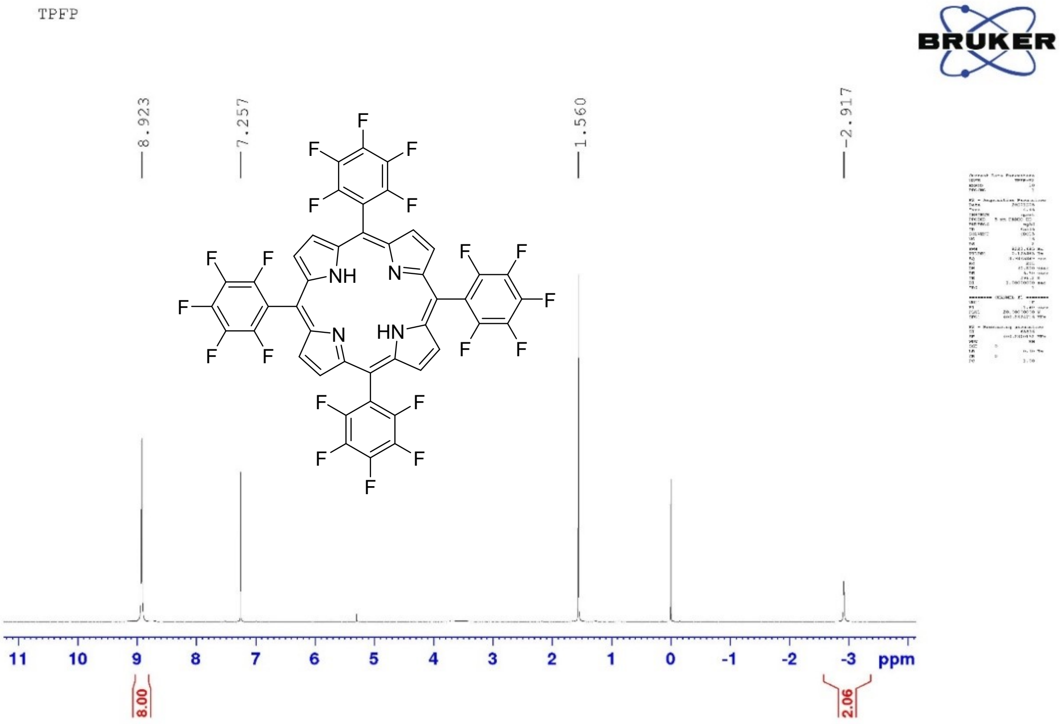


Fig. S11 ^{1}H NMR spectrum of **PFTPPNH2** recorded in CDCl$_3$.

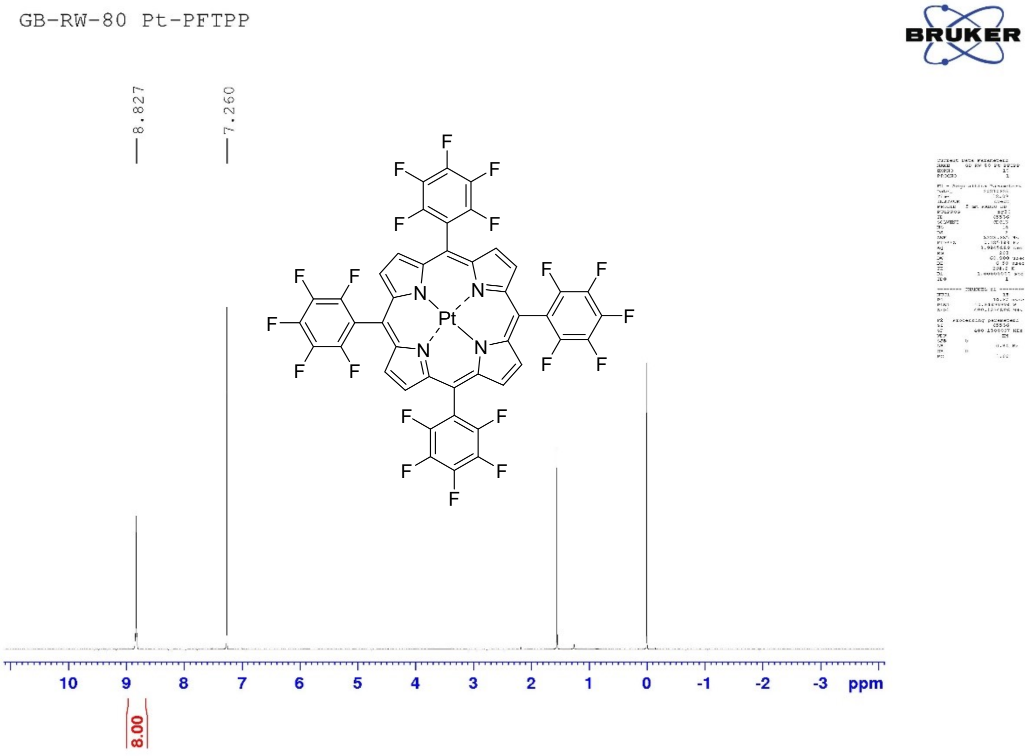


Fig. S12 ^{1}H NMR spectrum of **PtPFTPP** recorded in $CDCl_3$.

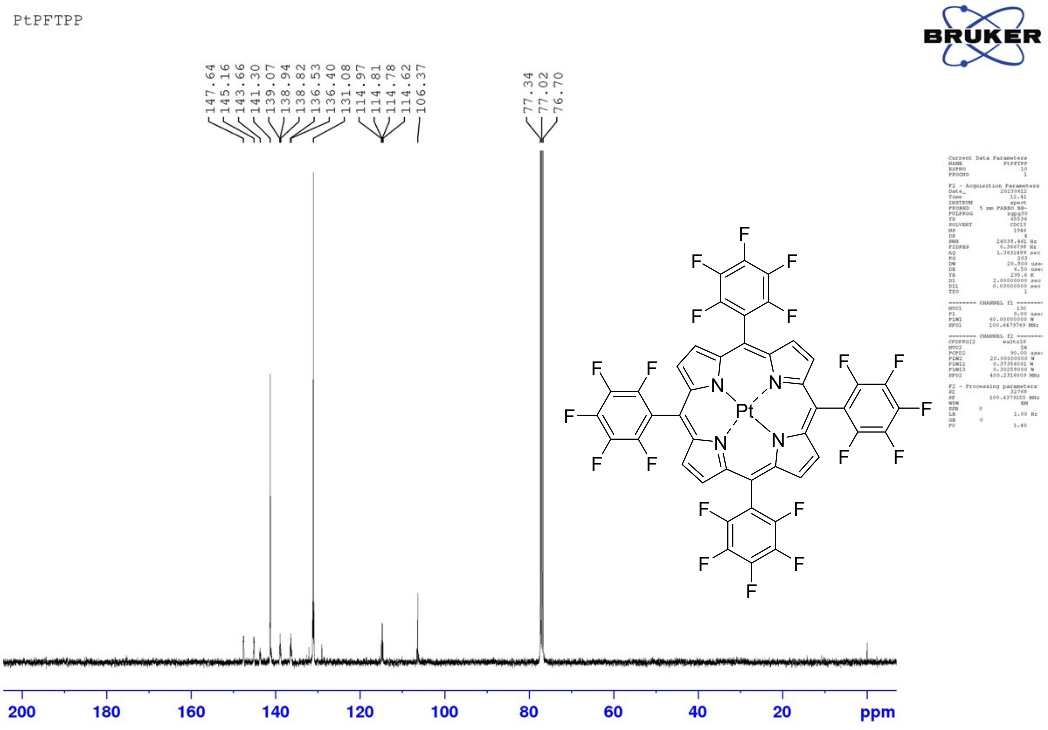


Fig. S13 ^{13}C NMR spectrum of **PtPFTPP** recorded in $CDCl_3$.

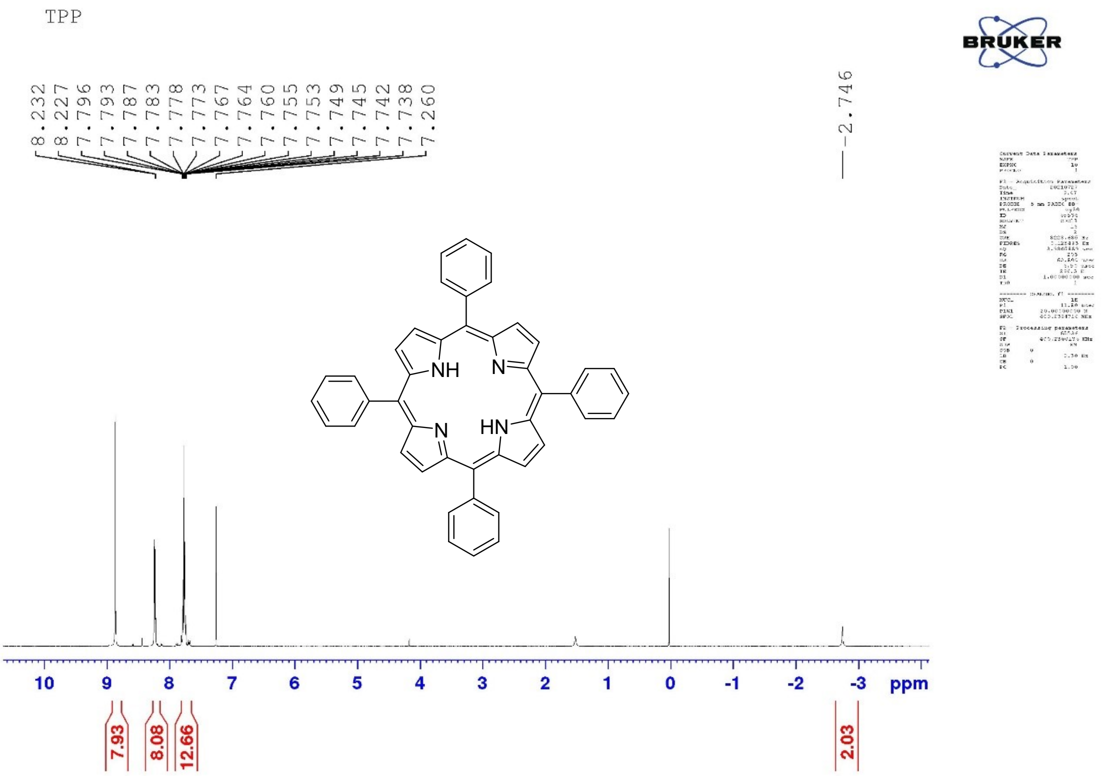


Fig. S14 ^{1}H NMR spectrum of **TPPNH2** recorded in CDCl$_3$.

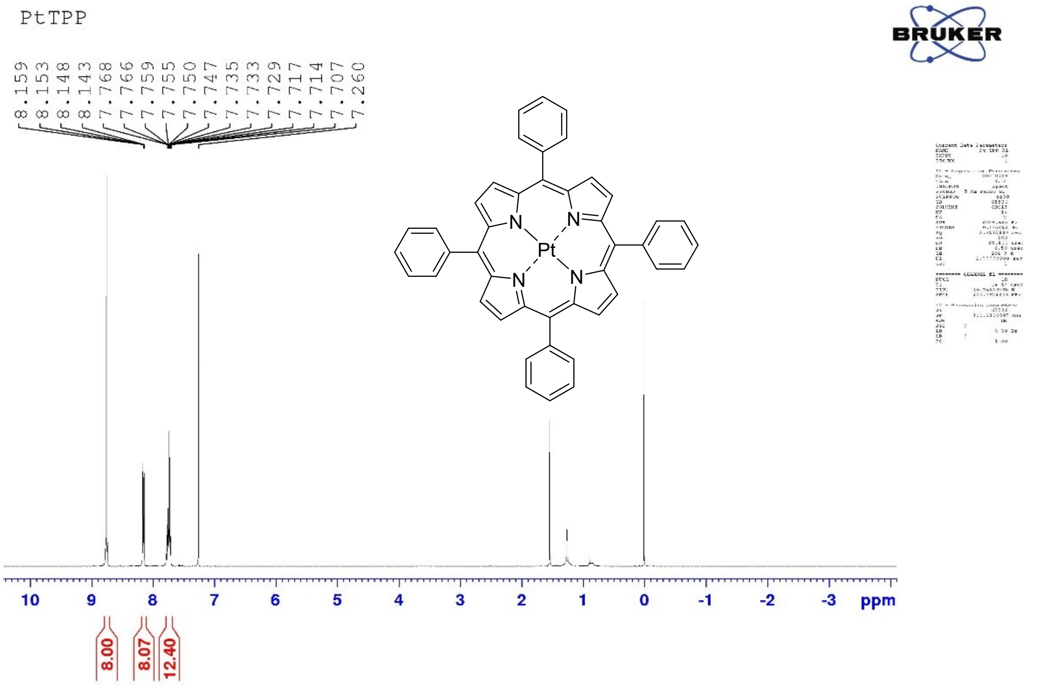


Fig. S15 ^{1}H NMR spectrum of **PtTPP** recorded in CDCl$_3$.

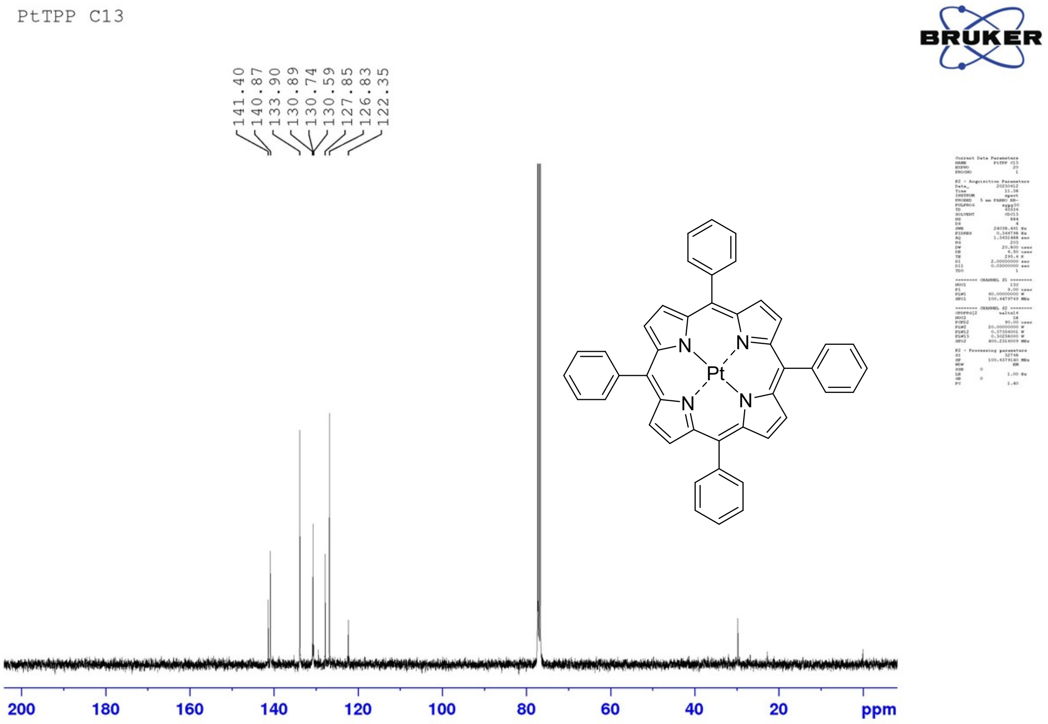
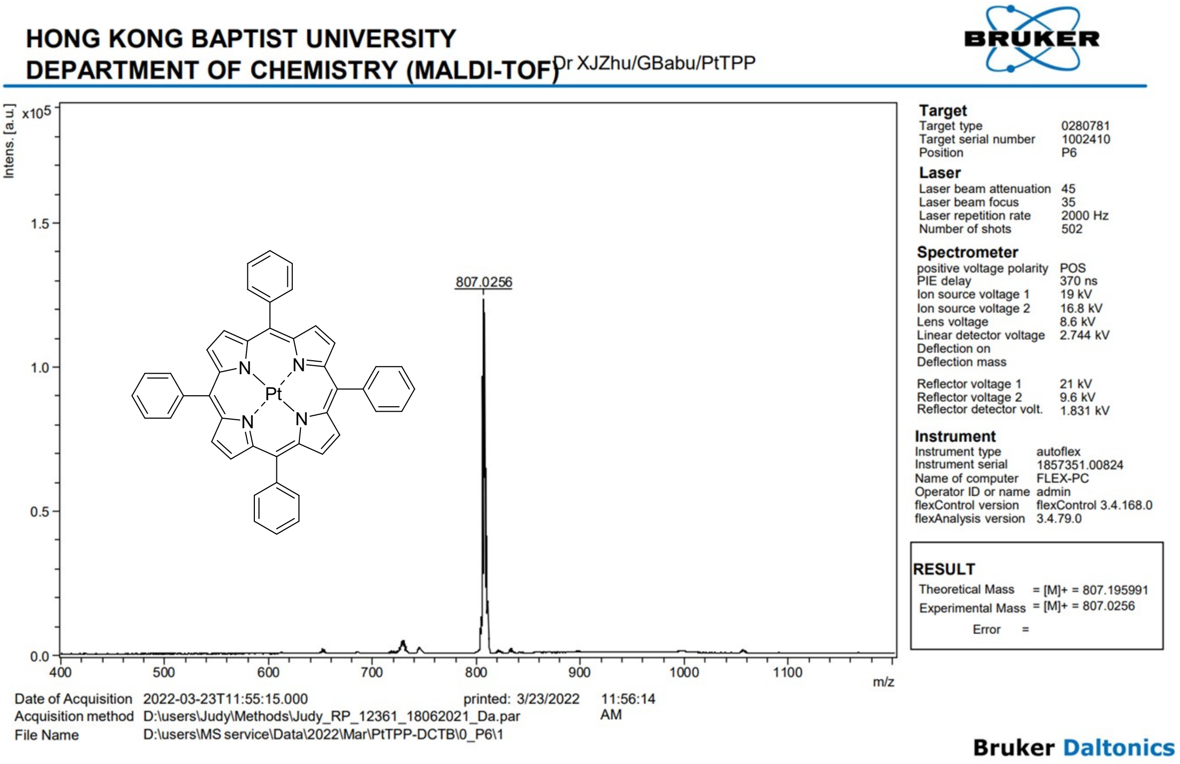


Fig. S16 ^{13}C NMR spectrum of **PtTPP** recorded in CDCl$_3$.



HONG KONG BAPTIST UNIVERSITY
DEPARTMENT OF CHEMISTRY (MALDI-TOF) Dr XJZhu/GBabu/PtTPP

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Spectrometer

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Lens voltage	8.6 kV
Linear detector voltage	2.744 kV
Deflection on	
Deflection mass	
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Instrument

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Operator ID or name	admin
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flexAnalysis version	3.4.79.0

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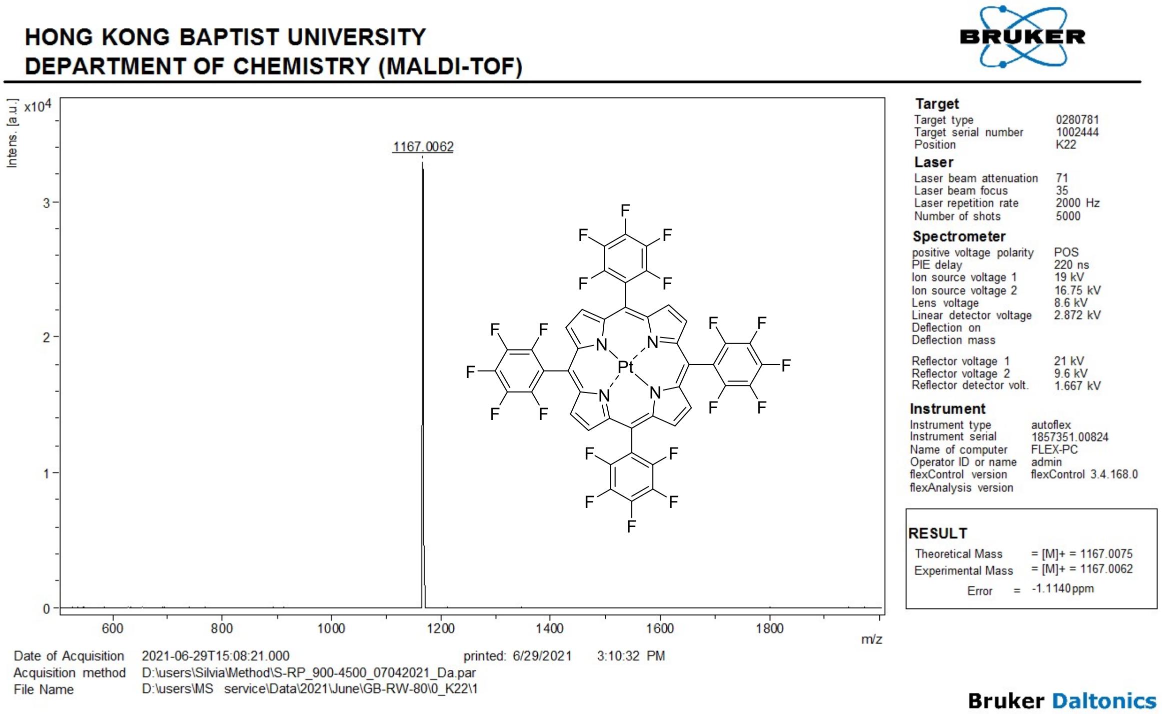
Fig. S17 MALDI–TOF spectrum of **PtTPP**.



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DEPARTMENT OF CHEMISTRY (MALDI-TOF)

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Spectrometer

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RESULT

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Bruker Daltonics

Fig. S18 MALDI–TOF spectrum of **PtPFTPP**.