

Supporting Information

Design and synthesis of a fused porphyrin dimer for enhanced visible-to-near-infrared-driven photocatalytic hydrogen evolution

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Experimental Section

Materials and Methods

All commercial reagents were purchased from Dieckmann Chemical Company, China. Solvents were dried by distilling over suitable dehydrating agents according to the standard

procedures. Purification of the compounds was performed by column chromatography with 100-200 mesh silica gel. ^1H 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 solvent chloroform (CDCl_3) at δ 7.26 ppm for ^1H NMR spectra and δ 77.0 ppm for ^{13}C NMR spectra. 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 tetrahydrofuran (THF) solutions (10 μM) at room temperature by using UV-Vis spectrophotometer and spectrofluorimeter, respectively. Cyclic voltammetry (CV) experiments were conducted on an electrochemical workstation (CHI660C Instruments, China) with standard three-electrode cell. A glassy carbon working electrode, a non-aqueous Ag/Ag^+ reference electrode, and a platinum wire counter electrode were used for the measurements. CV experiments were measured at room temperature in THF solution (200 μM). Tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte and ferrocene (100 μM) was added as the internal reference. Powder X-ray diffraction (PXRD) patterns were recorded with a Bruker D8 Advance X-Ray Diffractometer equipped with a non-monochromated $\text{Cu K}\alpha$ radiation (40 kV and 40 mA; $\lambda = 1.5406 \text{ \AA}$). 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. Gas adsorption-desorption isotherms were recorded on a Quantachrome Autosorb-1 system at 77 K (N_2). Samples were activated under reduced pressure at 75°C prior to gas uptake experiments. TGA analyses were performed on a TA Instruments Q50 analyzer using high purity N_2 carrier gas in the range of $25\text{--}800^\circ\text{C}$. A ramp rate of $5.00^\circ\text{C s}^{-1}$ was applied between $25\text{--}800^\circ\text{C}$.

Scanning Electron Microscopy (SEM)

The samples were prepared by drying a solvent-based dispersion on silica substrates, followed by gold sputtering, and then transferred to a flat aluminum sample holder for SEM analysis. These samples were analyzed using a field emission scanning electron microscope (FESEM) (Tescan MAIA3) under an accelerating voltage of 5.0 kV.

Preparation of Photocatalytic Systems

A multichannel photochemical reaction system equipped with LED white light (full spectrum, PCX50B, 148.5 mW/cm²) was used as the light source. The PHE evolution experiments were performed in a quartz vial reactor (20 mL) sealed with a rubber septum in a gas-closed system at ambient temperature and pressure. Initially, 0.1 mM of porphyrins in a THF/water (1:1, v/v) solution was sonicated for 5 minutes, and 0.4 M of ascorbic acid (AA) was added. Subsequently, 3 wt% of the Pt cocatalyst was loaded by the in situ photoreduction deposition method under light irradiation for 30 minutes, using aqueous H₂PtCl₆ (chloroplatinic acid) as the Pt source.^{1, 2} The resulting solution was purged with argon gas for 15 minutes to ensure anaerobic conditions and then placed in the multichannel photochemical reaction system. After 1 hour of irradiation, the released gas (400 μL) was collected by syringe from the headspace of the reactor and analyzed by gas chromatography (Shimadzu, GC-2014, Japan, with ultrapure Ar as the carrier gas), equipped with a TDX-01 (5 Å molecular sieve column) and a thermal conductivity detector (TCD). Finally, the total amount of hydrogen evolved was calculated according to the standard curve.

The apparent quantum yield (AQY) was measured under similar photocatalytic reaction conditions except that LED light sources with wavelengths of 420, 630, and 810 nm were used. The illuminated area of the LED lights was 9.04 cm², and the focused intensities of the white LED light at each wavelength were as follows: 68 mW/cm² at 420 nm, 49 mW/cm² at 630 nm, and 46 mW/cm² at 810 nm. The AQE was calculated using the following equation:

$$\text{AQE} = \left(\frac{2 \text{ \AA} - \text{number of hydrogen molecules}}{\text{number of incident photons}} \right) \text{ \AA} - 100\%$$

Transient Photocurrent Measurements

The transient photocurrent-time response (i-t curves) studies were performed using an electrochemical workstation (CHI660C Instruments, China) with a Pt wire (counter electrode), a non-aqueous Ag/AgNO₃ (reference electrode) and a fluorine-doped tin oxide (FTO) glass coated with 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 mm². Typically, the working electrode was prepared by drop-casting a 100 μM solution of porphyrins on the conductive surface of the FTO glass. A 5 mL volume of 0.5 M Na₂SO₄ aqueous solution acted as the electrolyte. The open-circuit voltages were set as the initial bias voltages in the transient photocurrent response tests.

Photoluminescence Quantum Yields (Φ_{PL}).

The Φ_{PL} of the porphyrins in degassed THF solution were calculated by comparing with that of 5,10,15,20-tetraphenylporphyrin (TPP). TPP was used as photoluminescence standard (λ_{exc} = 552 nm) with Φ_{PL} = 0.12 in degassed toluene. The absorbance of the sample and reference solutions was measured by keeping at 0.1 and the emission of the sample and reference solutions was recorded at 552 nm excitation wavelength. The Φ_{PL} was calculated according to the following equation:

$$\Phi_{PL}^{sample} = \Phi_{PL}^{ref} \left(\frac{S_{sample}}{S_{ref}} \right) \left(\frac{A_{ref}}{A_{sample}} \right) \left(\frac{n_{sample}}{n_{ref}} \right)$$

Where A_{ref} , S_{ref} , n_{ref} and A_{sample} , S_{sample} , n_{sample} represent the absorbance at the excited wavelength, integrated area under the photoluminescence curves and the solvent refractive index of the standard and the sample solutions.

Density Functional Theory Calculations

All the geometries of the compounds were optimized by using DFT with B3LYP/6-31G(d) level for C, H, N, S and O atoms and LANL2DZ for heavy atoms. The excitation energy and energy gaps between the S_0 state and excited singlet/triplet states of the compounds were computed using time-dependent density functional theory (TDDFT), which is based on the optimal ground-state geometry. These calculations were performed with the Gaussian 16 Rev B01 program package.

Synthesis

The porphyrin scaffold, **1** was synthesized and characterized according to the previous report.³

2:

A solution of **1** (1.1 g, 1.0 mmol) and NBS (0.18 g, 1.0 mmol) in 200 mL of dichloromethane (DCM) was stirred at 0 °C for 4 hours, and the reaction was monitored by TLC. The reaction was quenched with 5 mL of acetone, and the solvent was removed. The residue was purified via chromatography on silica gel using DCM/hexane (2:5, v/v) as the eluent to yield a mono-brominated compound, **2**, as a dark purple solid. Yield: 85%; 0.8 g. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.05 (s, $J = 4.0$ Hz, 1 H, Ar-H), 9.84 (m, $J = 3.9$ Hz, 2 H, Ar-H), 9.83-9.54 (m, $J = 3.9$ Hz, 4 H, Ar-H), 9.28 (m, $J = 3.7$ Hz, 2 H, Ar-H), 5.09 (m, 2 H, alkyl-H), 2.91-2.82 (m, $J = 6.0$ Hz, 4 H, alkyl-H), 2.70-2.62 (m, $J = 6.0$ Hz, 4 H, alkyl-H) 1.47 (m, 5 H, alkyl-H), 1.18 (m, 5 H, alkyl-H), 1.16-1.10 (m, 49 H, alkyl-H), 0.77-0.68 (m, 12 H, alkyl-H), -2.50 (s, 2 H, NH). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 193.08 (Ar-C), 167.52 (Ar-C), 154.42 (Ar-C), 152.84 (Ar-C), 128.23 (Ar-C), 116.02 (Ar-C), 111.75 (Ar-C), 69.72 (alkyl-C), 46.20 (alkyl-C), 45.99 (alkyl-C), 41.53 (alkyl-C), 41.32 (alkyl-C), 31.89 (alkyl-C), 31.80 (alkyl-C), 29.94 (alkyl-C), 29.61 (alkyl-C), 29.48 (alkyl-C), 29.29 (alkyl-C), 22.69 (alkyl-C), 22.62 (alkyl-C), 14.16 (alkyl-C), 14.03 (alkyl-C).

3:

Compound **2** (1.0 mmol) and Zn(OAc)₂·2H₂O (1.1 g, 5.0 mmol) were refluxed in chloroform (CHCl₃) (200 mL) for 4 hours in a 500 mL round-bottom flask, and the reaction was monitored by TLC. After the reaction was completed, the solvent was removed, and the residue was purified via chromatography on silica gel using DCM/hexane (1:1, v/v) as the eluent, yielding the product in a quantitative yield of **3**. Yield: 82%; 0.9 g. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.06 (s, 1 H, Ar-H), 9.84 (m, *J* = 4.8 Hz, 4 H, Ar-H), 9.78 (d, *J* = 4.8 Hz, 2 H, Ar-H), 9.73 (d, *J* = 4.8 Hz, 2 H, Ar-H), 5.22 (m, 2 H, alkyl-H), 2.93 (d, *J* = 6.0 Hz, 4 H, alkyl-H), 2.74 (d, *J* = 6.0 Hz, 4 H, alkyl-H) 1.53 (m, 4 H, alkyl-H), 1.52-1.51 (m, 11 H, alkyl-H), 1.49-1.20 (m, 44 H, alkyl-H), 1.19-0.68 (m, 13 H, alkyl-H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 152.56 (Ar-C), 152.49 (Ar-C), 150.27 (Ar-C), 150.22 (Ar-C), 149.75 (Ar-C), 149.49 (Ar-C), 147.76 (Ar-C), 147.51 (Ar-C), 143.99 (Ar-C), 133.55 (Ar-C), 132.64 (Ar-C), 131.82 (Ar-C), 131.57 (Ar-C), 130.99 (Ar-C), 130.22 (Ar-C), 126.22 (Ar-C), 122.06 (Ar-C), 104.54 (Ar-C), 47.20 (alkyl-C), 42.99 (alkyl-C), 31.89 (alkyl-C), 31.74 (alkyl-C), 29.94 (alkyl-C), 29.61 (alkyl-C), 29.48 (alkyl-C), 29.18 (alkyl-C), 22.60 (alkyl-C), 22.62 (alkyl-C), 14.06 (alkyl-C), 14.01 (alkyl-C).

4:

A mixture of compound **3** (0.2 g, 1.0 mmol), DDQ (5.0 mmol), and Sc(OTf)₃ (5.0 mmol) was dissolved in freshly distilled toluene (20 mL) and heated at 50 °C under a N₂ atmosphere for 3 hours. The solvent was evaporated, and the solid was purified by silica gel chromatography using DCM/hexane (1:1, v/v) as the eluent to give compound **4** as a green solid. Yield: 46%; 0.1 g. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.89-9.77 (m, *J* = 4.9 Hz, 8 H, Ar-H), 9.38-9.29 (m, *J* = 4.8 Hz, 4 H, Ar-H), 5.23-5.07 (dd, *J* = 6.0 Hz, 4 H, alkyl-H), 2.92-2.62 (m, 17 H, alkyl-H), 1.35-1.24 (m, 9 H, alkyl-H), 0.75-0.69 (m, 147 H, alkyl-H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 143.99 (Ar-C), 133.55 (Ar-C), 132.64 (Ar-C), 131.82 (Ar-C), 131.57 (Ar-C), 123.17 (Ar-C), 122.53 (Ar-C), 122.26 (Ar-C), 111.01 (Ar-C), 46.20 (alkyl-C), 45.99 (alkyl-C), 41.53 (alkyl-C), 41.32 (alkyl-C), 31.89 (alkyl-C), 31.80 (alkyl-C), 29.94 (alkyl-C), 29.61

(alkyl-C), 29.48 (alkyl-C), 29.29 (alkyl-C), 22.69 (alkyl-C), 22.62 (alkyl-C), 14.16 (alkyl-C), 14.10 (alkyl-C). MALDI-TOF (m/z) calculated for **4** (C₁₁₆H₁₆₈N₈Br₂Zn₂): 1965.2440; found: 1965.0941.

5:

A mixture of **4** (1.0 mmol) and 4-ethynyl-2,5-bis(hexyloxy)benzaldehyde (0.98 g, 2.5 mmol) in THF (40 mL) and TEA (20 mL) was purged with nitrogen for 20 minutes. Then, Pd(PPh₃)₄ (140 mg, 0.106 mmol) and CuI (20 mg, 0.106 mmol) were added to the mixture, which was stirred at 50 °C for 12 hours under nitrogen conditions. The solvent was removed under vacuum, and the resulting solid residue was purified by preparative thin-layer chromatography using a CHCl₃/hexane (3:1, v/v) mixture as the eluent and recrystallized from CHCl₃/methanol to give compound **5** as a green solid. Yield : 69%; 0.22 g. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.59 (s, 2 H, CHO), 9.73-9.72 (m, 4 H, Ar-H), 9.72 (d, *J* = 4.8 Hz, 4 H, Ar-H), 9.45 (d, *J* = 4.8 Hz, 2 H, Ar-H), 9.44 (d, *J* = 4.8 Hz, 2 H, Ar-H), 7.55 (d, *J* = 5.8 Hz, 4 H, Ar-H), 4.50-4.79 (m, 4 H, alkyl-H), 4.37-4.28 (m, 8 H, alkyl-H), 2.90-2.21 (m, 18 H, alkyl-H), 1.97-1.82 (m, 11 H, alkyl-H), 1.60-1.59 (m, 15 H, alkyl-H), 1.41-1.39 (m, 27 H, alkyl-H), 1.37-0.91 (m, 89 H, alkyl-H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 189.81 (CHO-C), 189.29 (CHO-C), 155.56 (Ar-C), 154.49 (Ar-C), 133.55 (Ar-C), 132.64 (Ar-C), 132.64 (Ar-C), 131.95 (Ar-C), 131.57 (Ar-C), 130.99 (Ar-C), 128.22 (Ar-C), 125.05 (Ar-C), 124.76 (Ar-C), 123.77 (Ar-C), 123.17 (Ar-C), 122.88 (Ar-C), 121.12 (Ar-C), 121.08 (Ar-C), 116.90 (Ar-C), 114.38 (Ar-C), 110.79 (Ar-C), 109.41 (Ar-C), 104.54 (Ar-C), 69.60 (alkyl-C), 69.49 (alkyl-C), 32.03 (alkyl-C), 31.89 (alkyl-C), 31.74 (alkyl-C), 31.62 (alkyl-C), 29.94 (alkyl-C), 29.61 (alkyl-C), 29.48 (alkyl-C), 29.18 (alkyl-C), 29.31 (alkyl-C), 29.11 (alkyl-C), 22.60 (alkyl-C), 22.78 (alkyl-C), 22.62 (alkyl-C), 22.56 (alkyl-C), 22.23 (alkyl-C), 14.24 (alkyl-C), 14.14 (alkyl-C), 14.10 (alkyl-C), 14.04 (alkyl-C). MALDI-TOF m/z, [M]⁺, calculated for **5** (C₁₅₈H₂₂₆N₈Zn₂O₆): 2464.3560; found: 2464.0717.

F-C19ZnP:

Compound **5** (110 mg, 0.034 mmol) was dissolved in a solution of dry CHCl₃, with 2-3 drops of piperidine, and then 3-ethylrhodanine (70 mg, 0.34 mmol) was added. The resulting solution was refluxed and stirred for 24 hours under argon conditions. The reaction was quenched with water (30 mL). The aqueous layers were extracted with CHCl₃ (3 × 20 mL). The organic layer was dried over Na₂SO₄. After removal of the solvent, the product was purified by chromatography on a silica gel column using CHCl₃ as the eluent and further purified by preparative thin-layer chromatography using CHCl₃ as the eluent. The crude solid was then recrystallized from a mixture of CHCl₃ and methanol to afford **F-C19ZnP** as a gray-green solid. Yield: 65%; 75 mg. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.04-10.02 (m, 4 H, Ar-H), 9.77 (d, *J* = 4.8 Hz, 4 H, Ar-H), 9.20 (d, *J* = 4.8 Hz, 2 H, Ar-H), 8.24 (d, *J* = 4.8 Hz, 2 H, Ar-H), 7.91-7.50 (m, 6 H, Ar-H), 5.22-5.01 (m, 4 H, alkyl-H), 4.28-4.26 (m, 12 H, alkyl-H), 2.92-2.59 (m, 24 H, alkyl-H), 1.92-1.80 (m, 52 H, alkyl-H), 1.71-1.42 (m, 32 H, alkyl-H), 1.11-0.92 (m, 69 H, alkyl-H), 0.80-0.70 (m, 33 H, alkyl-H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 193.09 (Ar-C), 167.51 (Ar-C), 154.43 (Ar-C), 152.81 (Ar-C), 132.13 (Ar-C), 128.30 (Ar-C), 123.77 (Ar-C), 123.35 (Ar-C), 123.17 (Ar-C), 122.87 (Ar-C), 122.60 (Ar-C), 117.67 (Ar-C), 116.19 (Ar-C), 111.85 (Ar-C), 98.53 (Ar-C), 69.74 (alkyl-C), 46.14 (alkyl-C), 41.29 (alkyl-C), 39.92 (alkyl-C), 32.09 (alkyl-C), 31.84 (alkyl-C), 31.81 (alkyl-C), 31.74 (alkyl-C), 31.62 (alkyl-C), 29.94 (alkyl-C), 29.66 (alkyl-C), 29.59 (alkyl-C), 29.50 (alkyl-C), 29.30 (alkyl-C), 29.24 (alkyl-C), 29.11 (alkyl-C), 25.86 (alkyl-C), 22.79 (alkyl-C), 22.63 (alkyl-C), 22.62 (alkyl-C), 22.56 (alkyl-C), 22.23 (alkyl-C), 14.25 (alkyl-C), 14.15 (alkyl-C), 14.09 (alkyl-C), 14.37 (alkyl-C). MALDI-TOF *m/z*, [M]⁺, calculated for **F-C19ZnP** (C₁₆₈H₂₃₆N₁₀O₆S₄Zn₂): 2750.8000; found: 2750.6400.

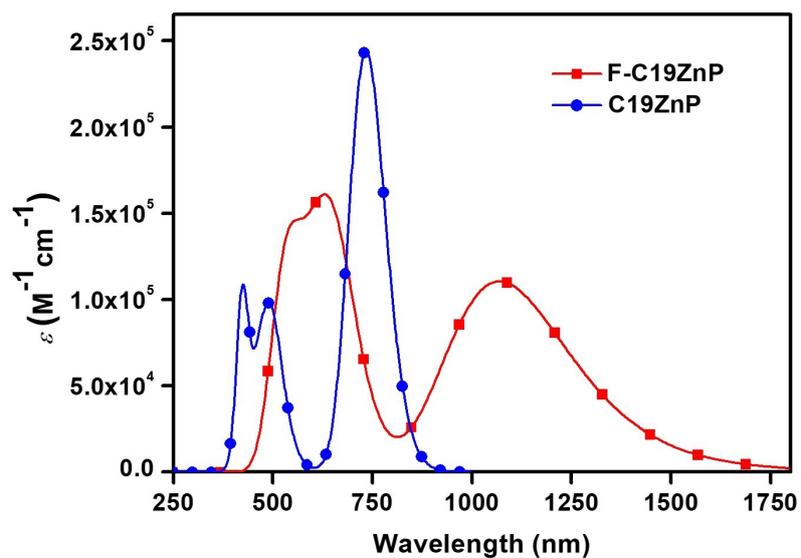


Fig. S1. Calculated UV-Vis absorption spectra of **F-C19ZnP** and **C19ZnP** by DFT at B3LYP/GENECP/LANL2DZ level with Gaussian 16.

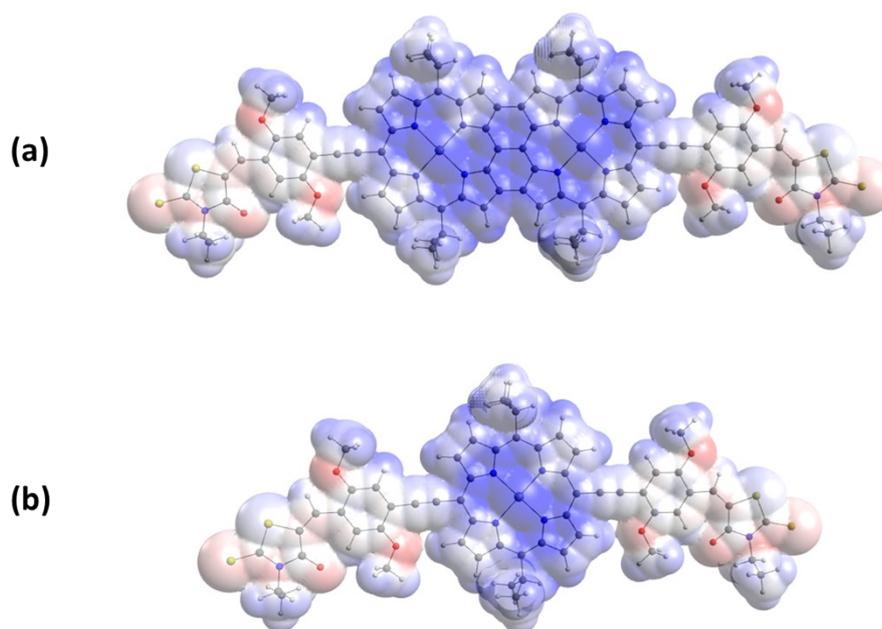


Fig. S2. ESP of (a) **F-C19ZnP** and (b) **C19ZnP** (the blue color region is electron rich while the red color is electron deficient).

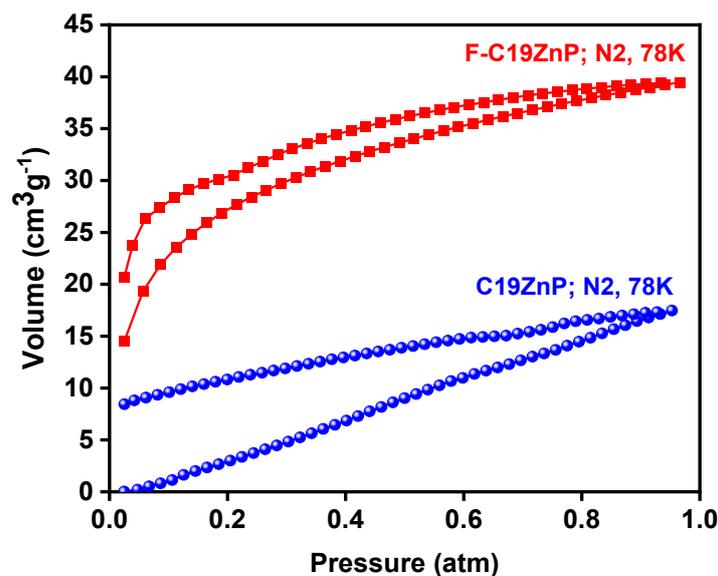


Fig. S3. Comparison of BET isotherms of N₂ adsorption-desorption measurements for **C19ZnP** and **F-C19ZnP**.

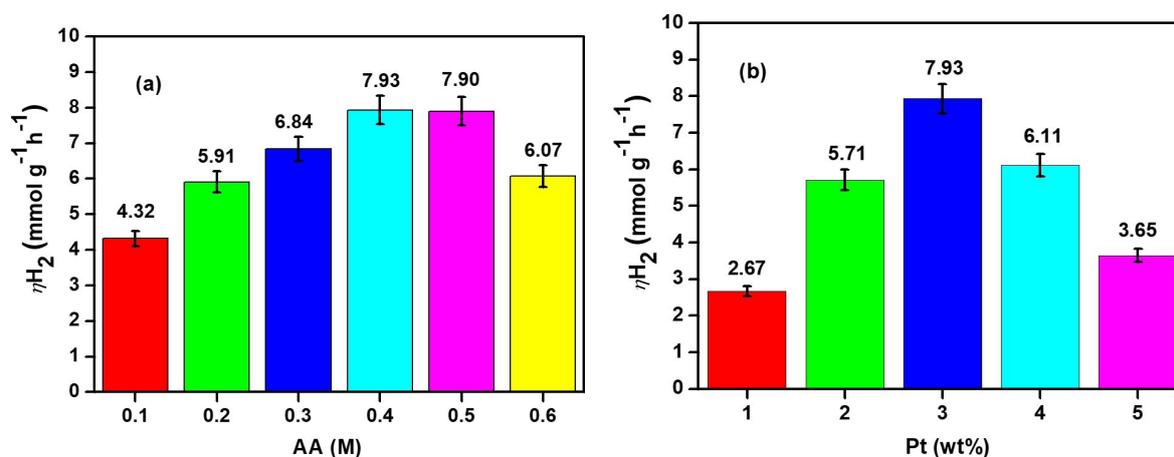


Fig. S4. (a) η_{H_2} of photocatalytic systems of **F-C19ZnP** under irradiation for 5 h: **F-C19ZnP** (0.1 mM) + AA (0.1-0.6 M) + THF/water (1:1, v/v) + Pt (3 wt%) and (b) η_{H_2} of photocatalytic systems of **F-C19ZnP** under irradiation for 5 h: **F-C19ZnP** (0.1 mM) + AA (0.4 M) + THF/water (1:1, v/v) + Pt (1-5 wt%).

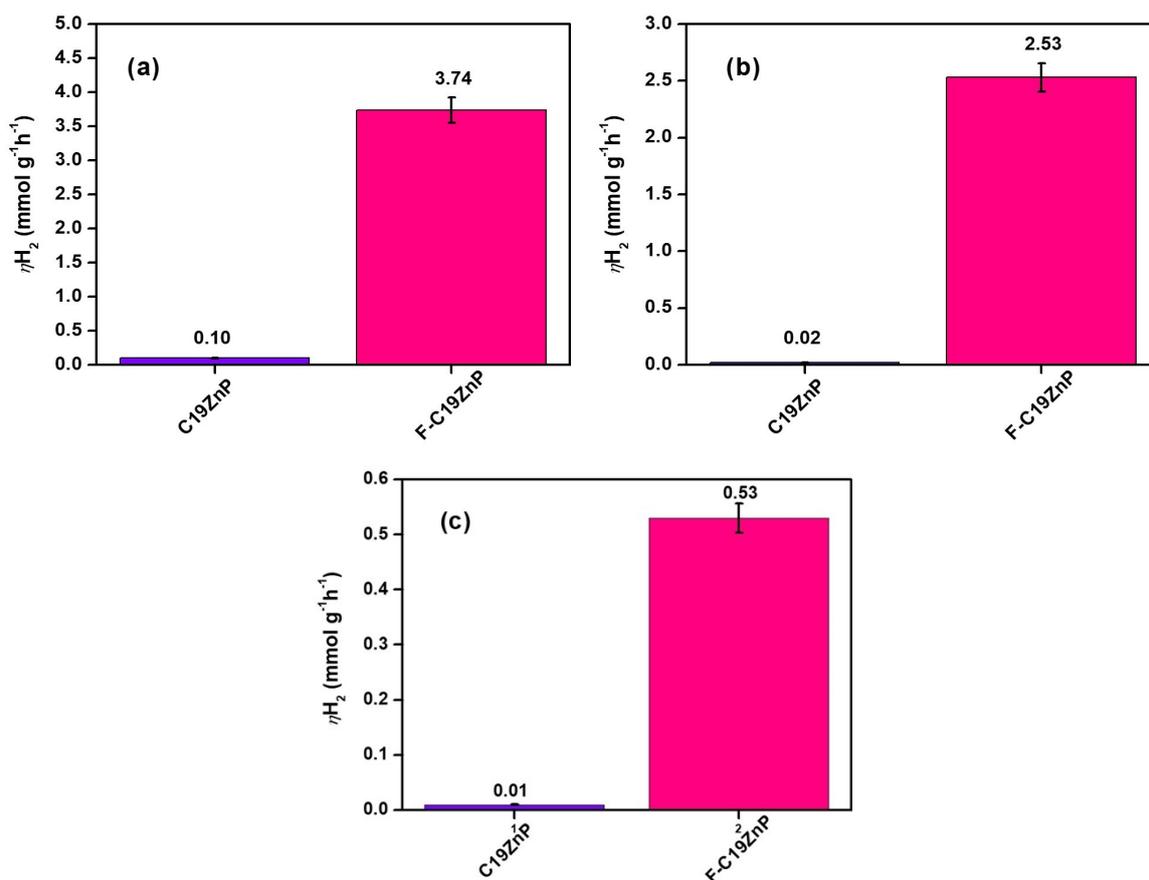


Fig. S5. η_{H_2} of photocatalytic systems of C19ZnP and F-C19ZnP under irradiation for 5 h: C19ZnP/F-C19ZnP (0.1 mM) + SED (0.4 M) + THF/water (1:1, v/v) + Pt (3 wt%); (a) TEA, and (b) TEOA and (c) EDTA.

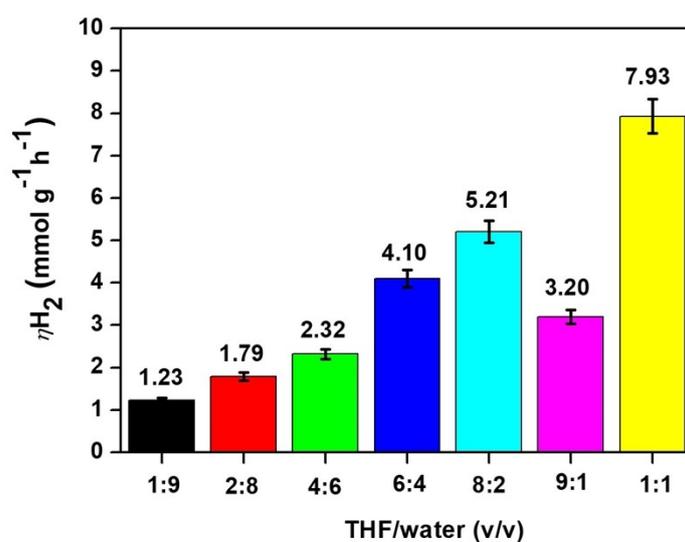


Fig. S6. η_{H_2} of of photocatalytic systems of F-C19ZnP under irradiation for 5 h: F-C19ZnP (0.1 mM) + AA (0.4 M) + THF/water + Pt (3 wt%).

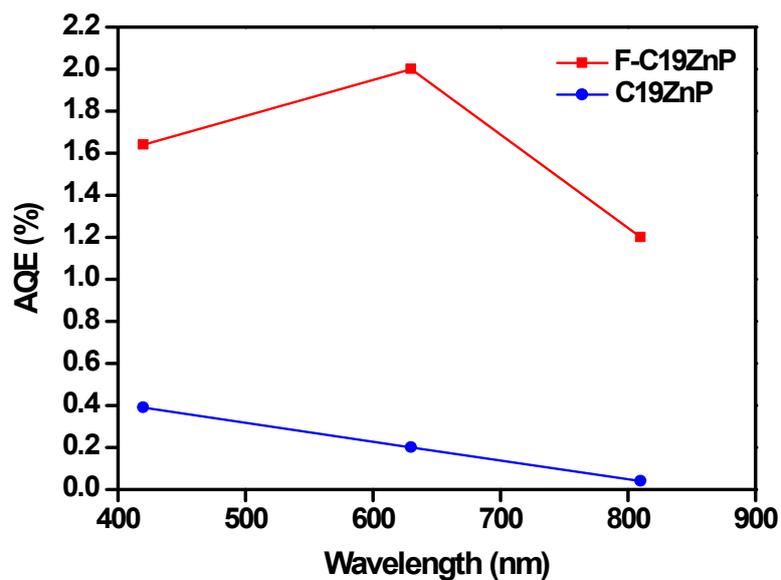


Fig. S7. AQY of the porphyrins measured at monochromatic wavelengths of 420, 630, and 810 nm.

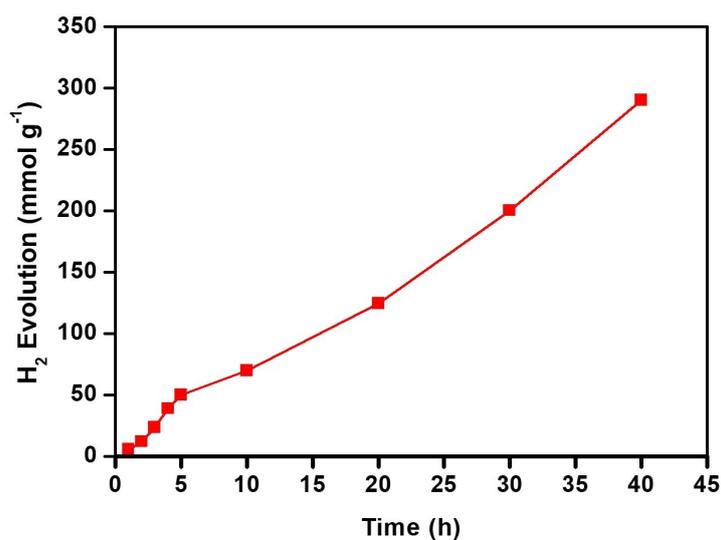


Fig. S8. H₂ evolution of photocatalytic systems of **F-C19ZnP** under irradiation for 40 h: **F-C19ZnP** (0.1 mM) + AA (0.4 M) + THF/water (1:1, v/v) + Pt (3 wt%).

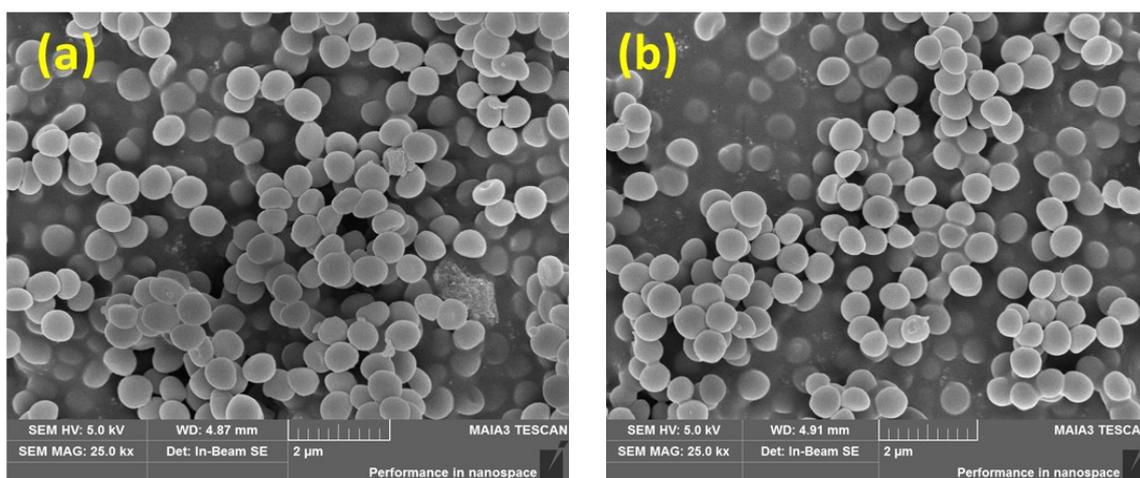


Fig. S9. Typical SEM images of photocatalytic system of F-C19ZnP (a) before light irradiation and (b) after 20 h light irradiation.

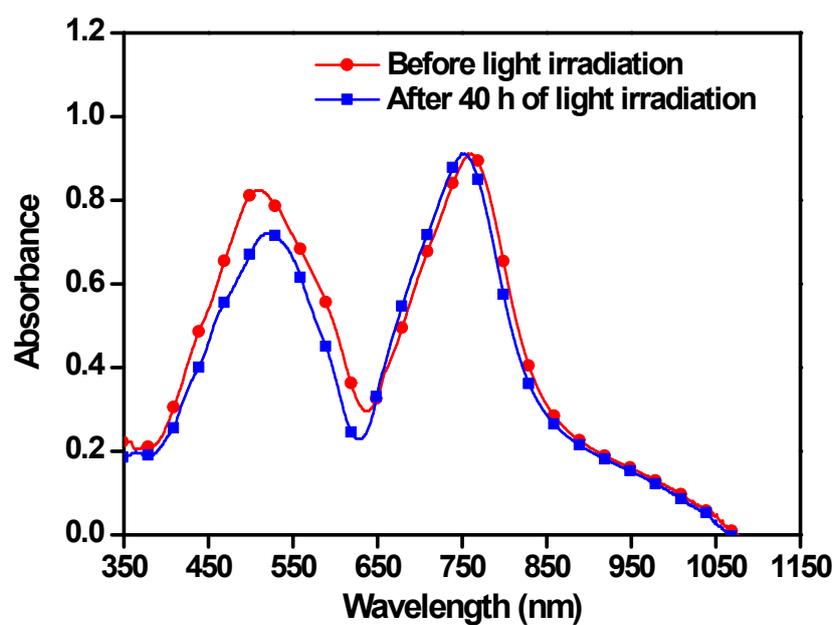


Fig. 10. Photocatalytic system F-C19ZnP before and after light irradiation.

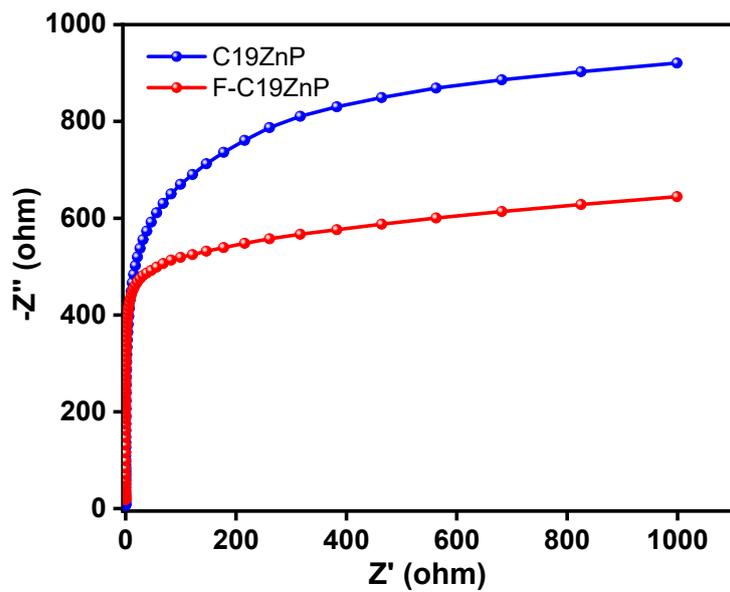


Fig. S11. Nyquist plots of **C19ZnP** and **F-C19ZnP** under illumination conditions.

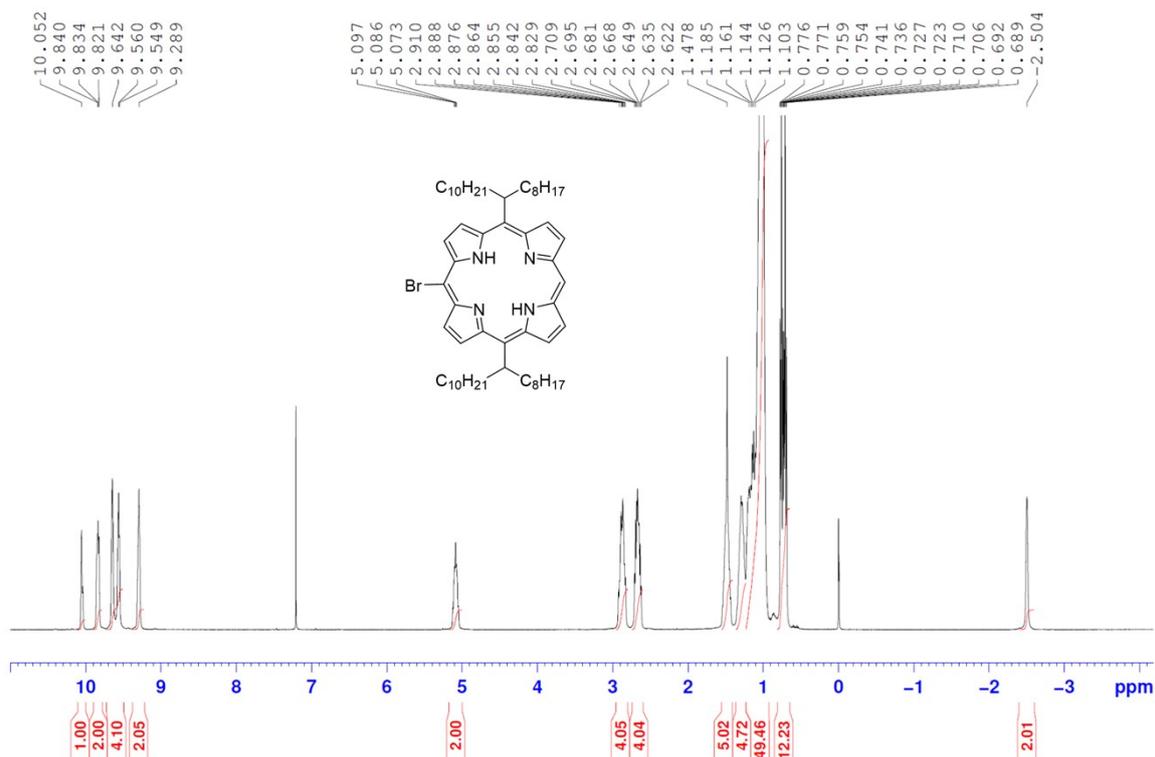


Fig. S12. ^1H NMR spectrum of **2** recorded in CDCl_3 .

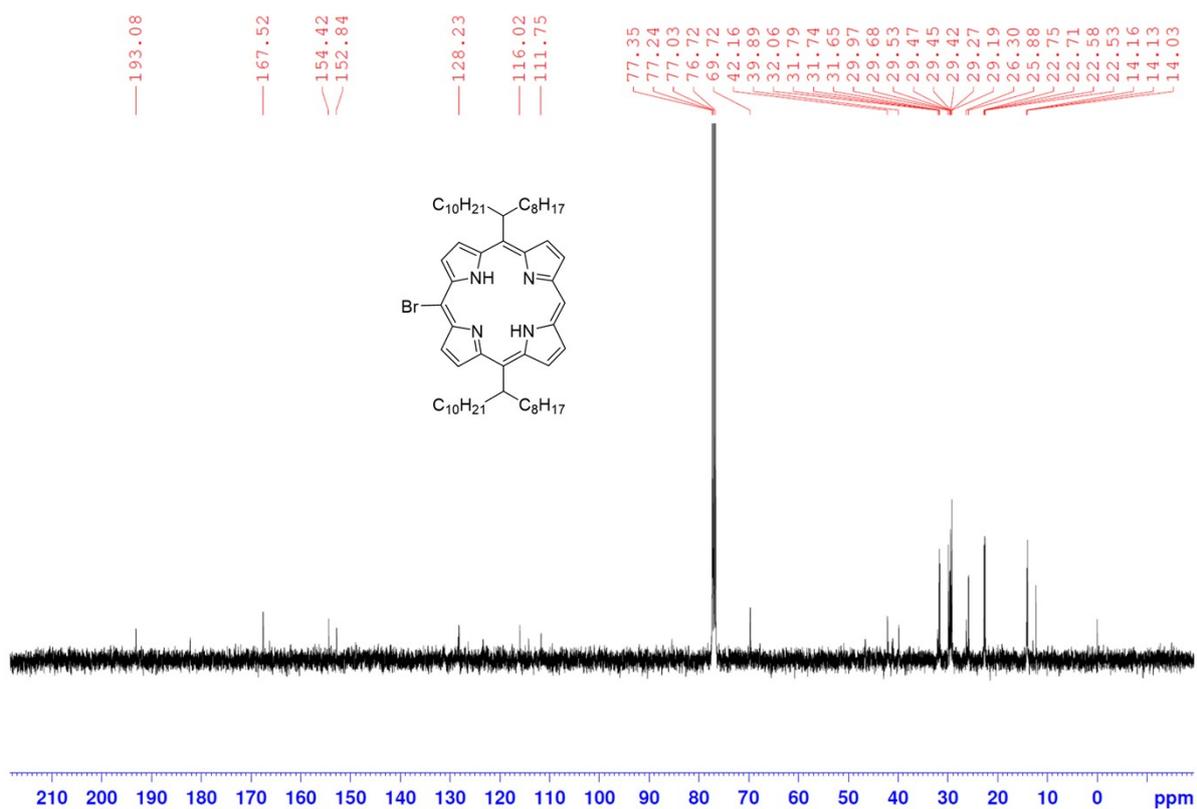


Fig. S13. ^{13}C NMR spectrum of **2** recorded in CDCl_3 .

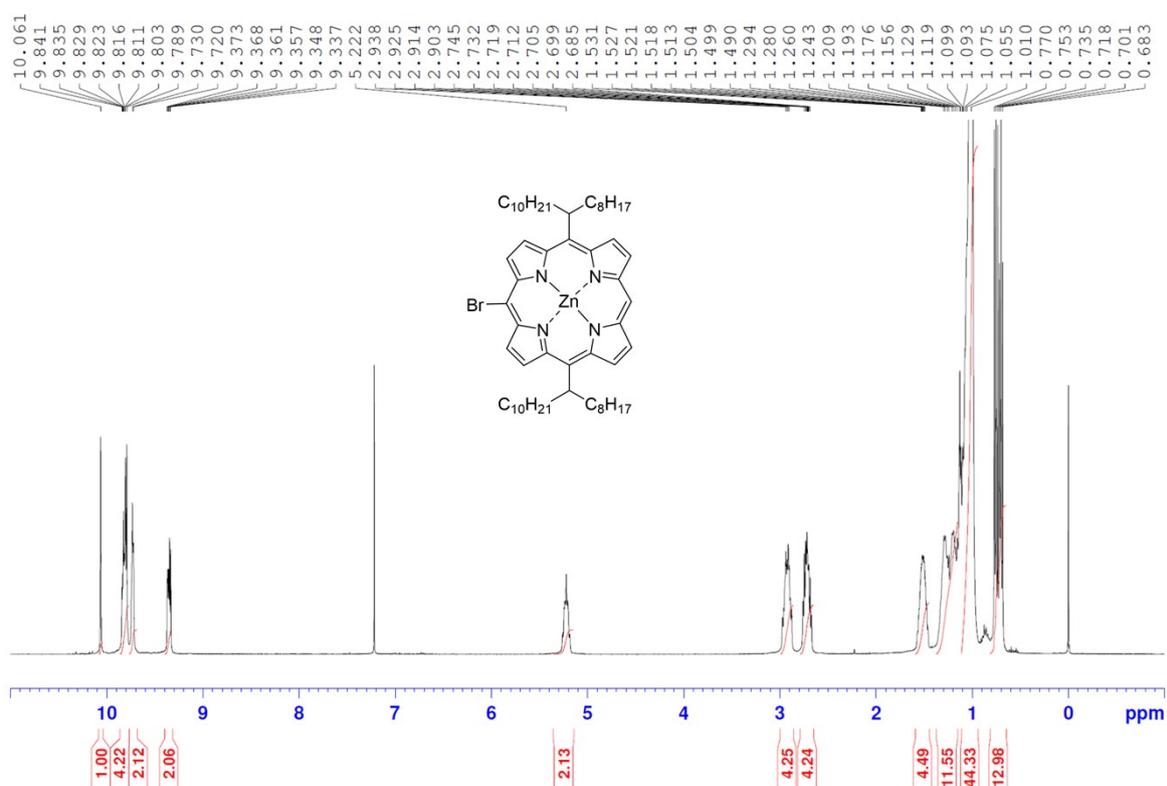


Fig. S14. ^1H NMR spectrum of **3** recorded in CDCl_3 .

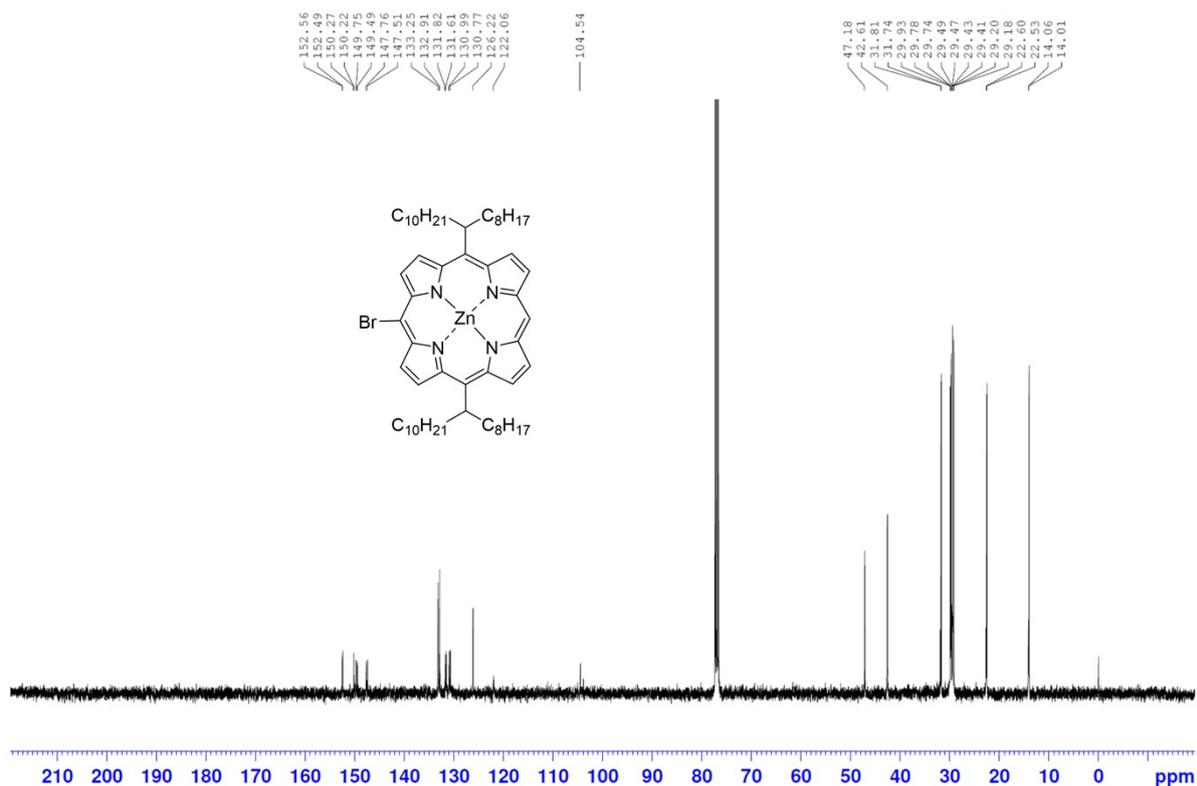


Fig. S15. ¹³C NMR spectrum of 3 recorded in CDCl₃.

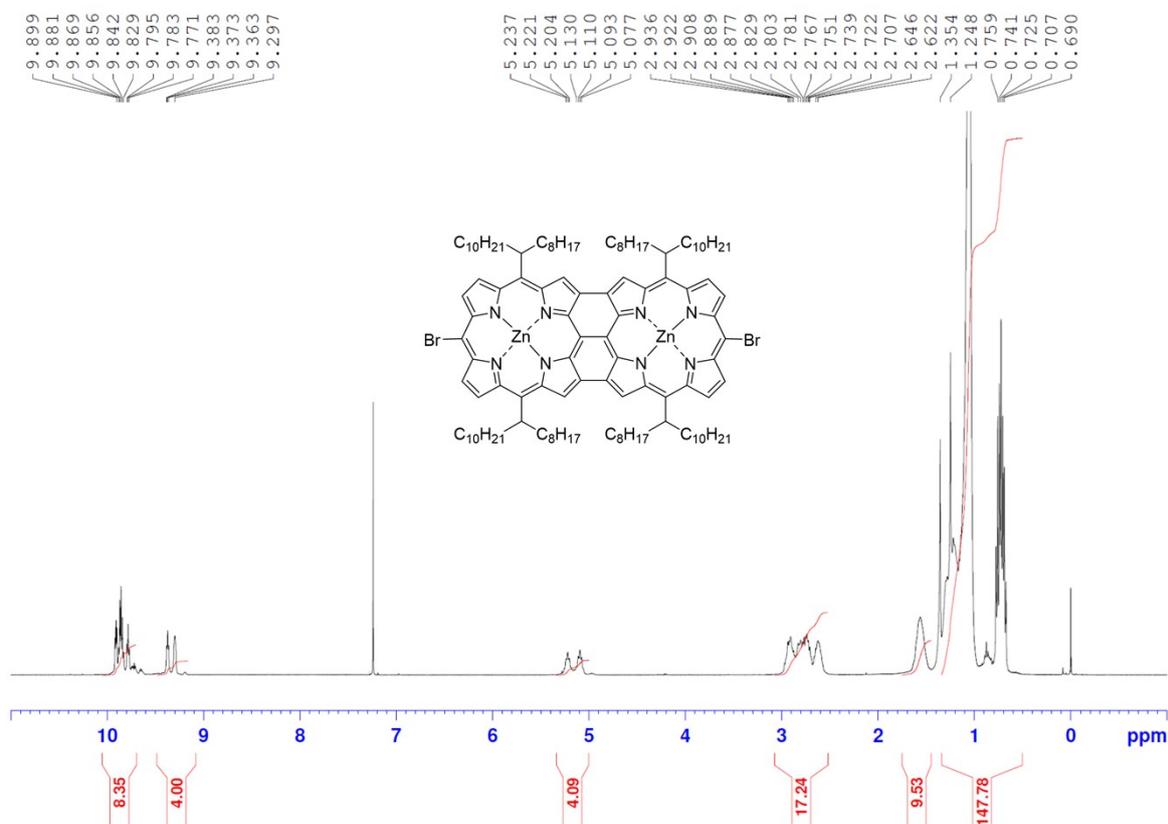


Fig. S16. ¹H NMR spectrum of 4 recorded in CDCl₃.

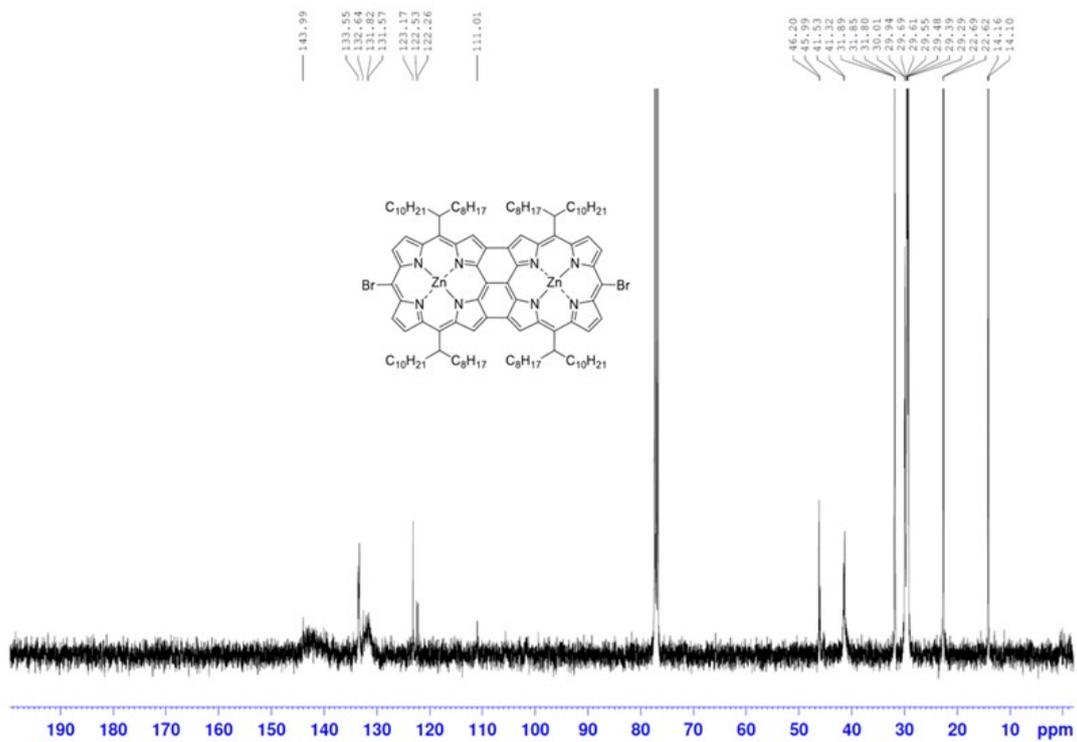


Fig. S17. ¹³C NMR spectrum of **4** recorded in CDCl₃.

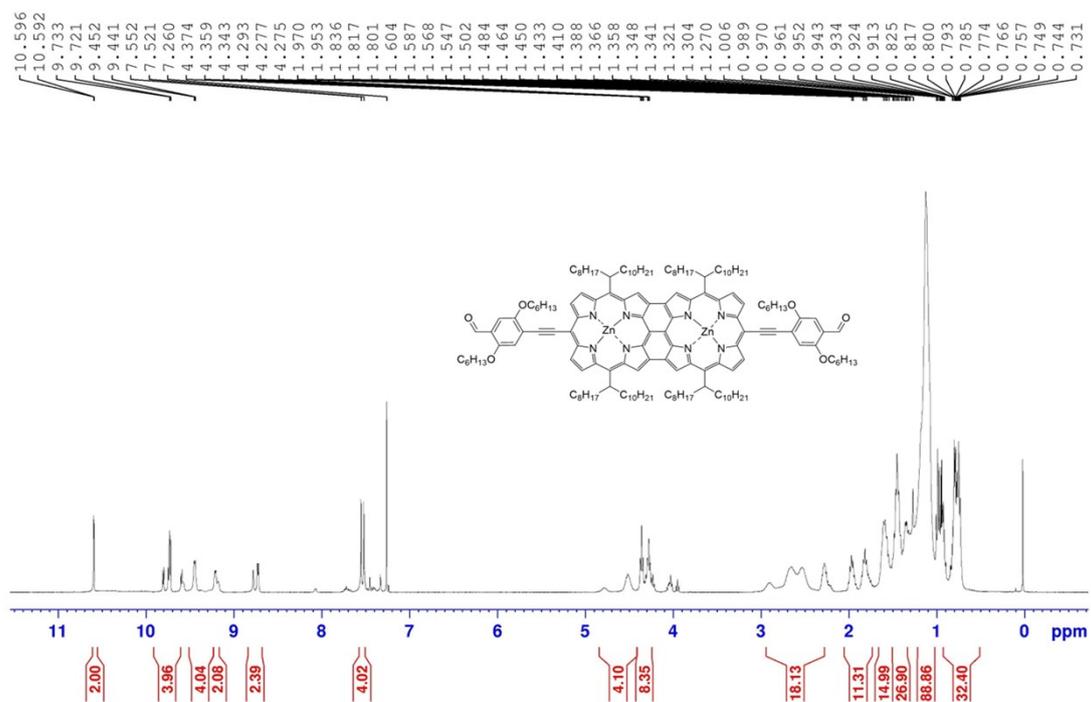


Fig. S18. ¹H NMR spectrum of **5** recorded in CDCl₃.

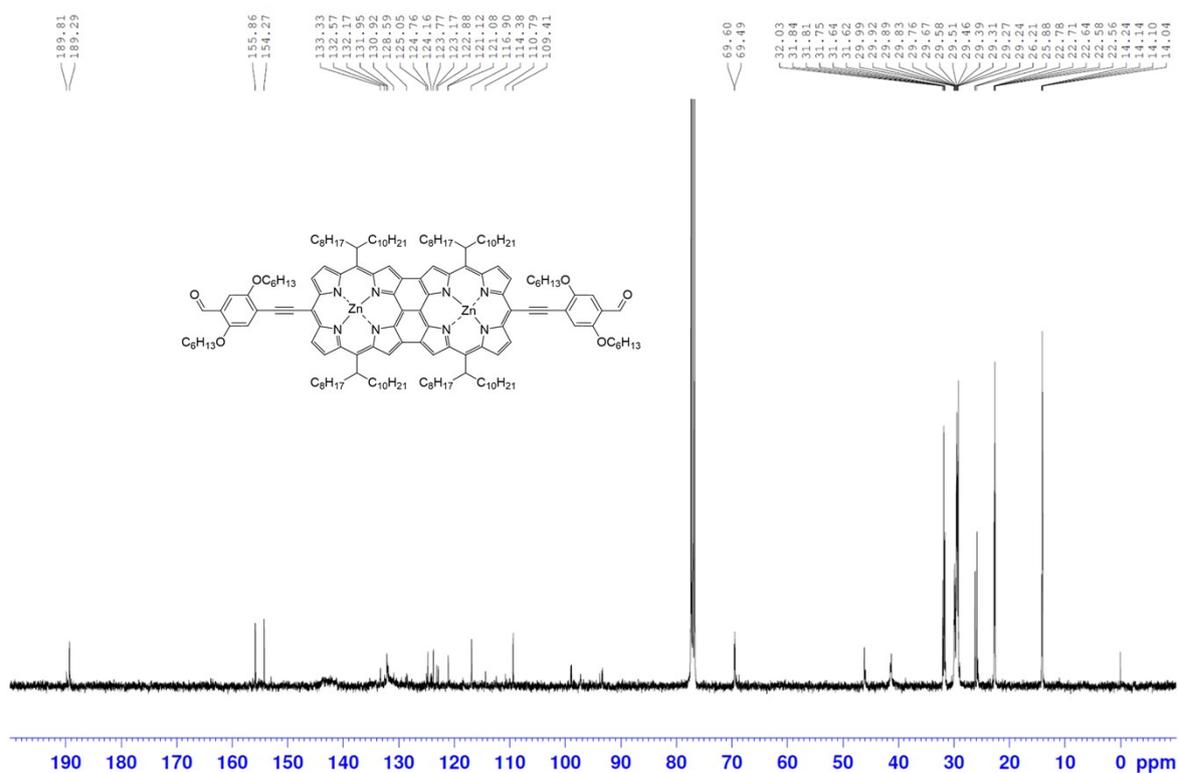


Fig. S19. ¹³C NMR spectrum of **5** recorded in CDCl₃.

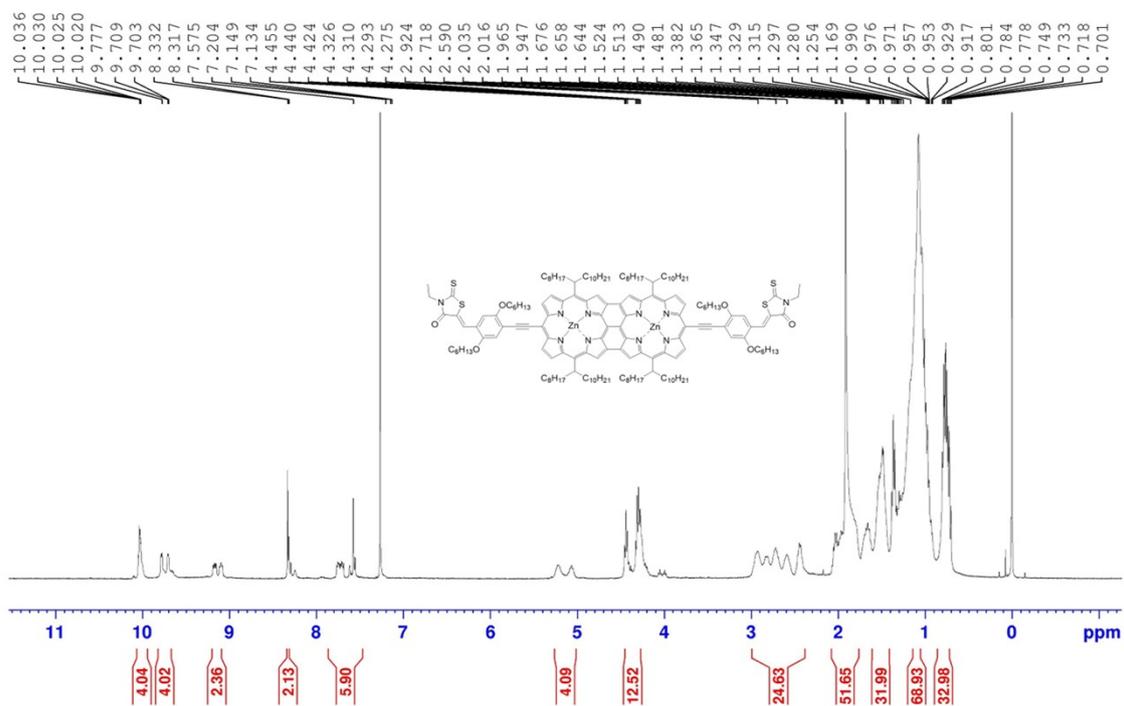


Fig. S20. ¹H NMR spectrum of F-C19ZnP recorded in CDCl₃.

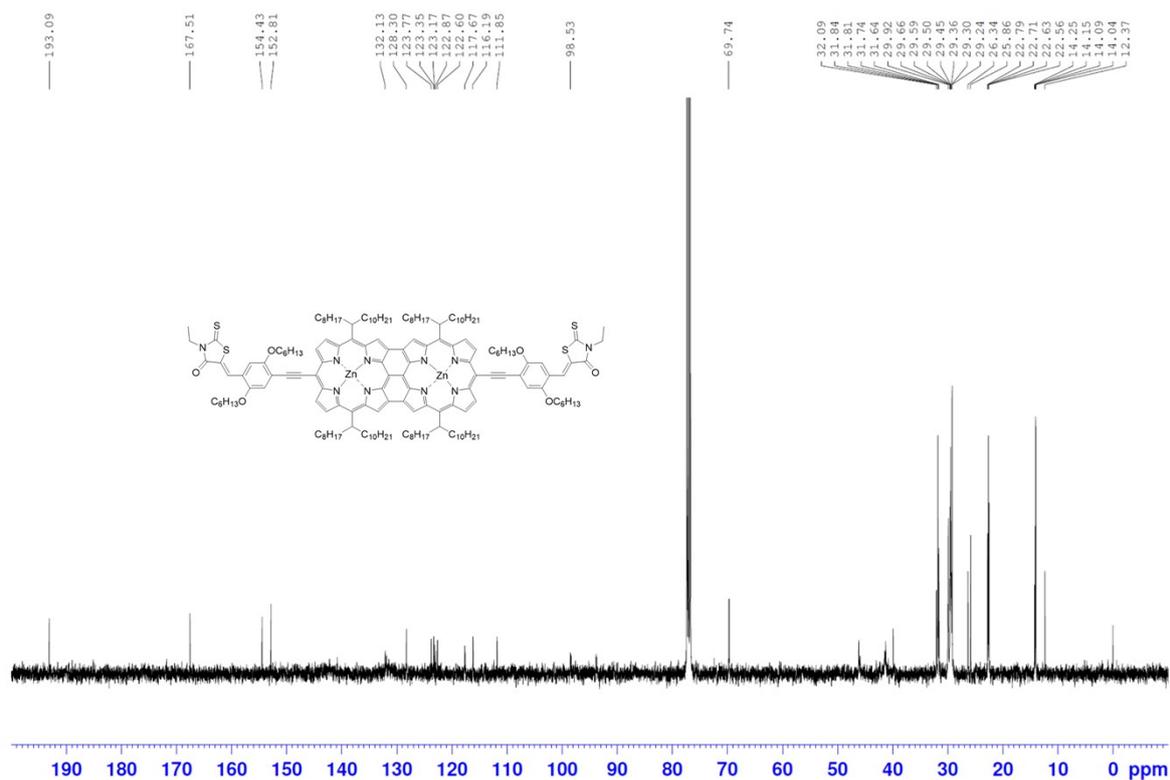


Fig. S21. ^{13}C NMR spectrum of F-C19ZnP recorded in CDCl_3 .

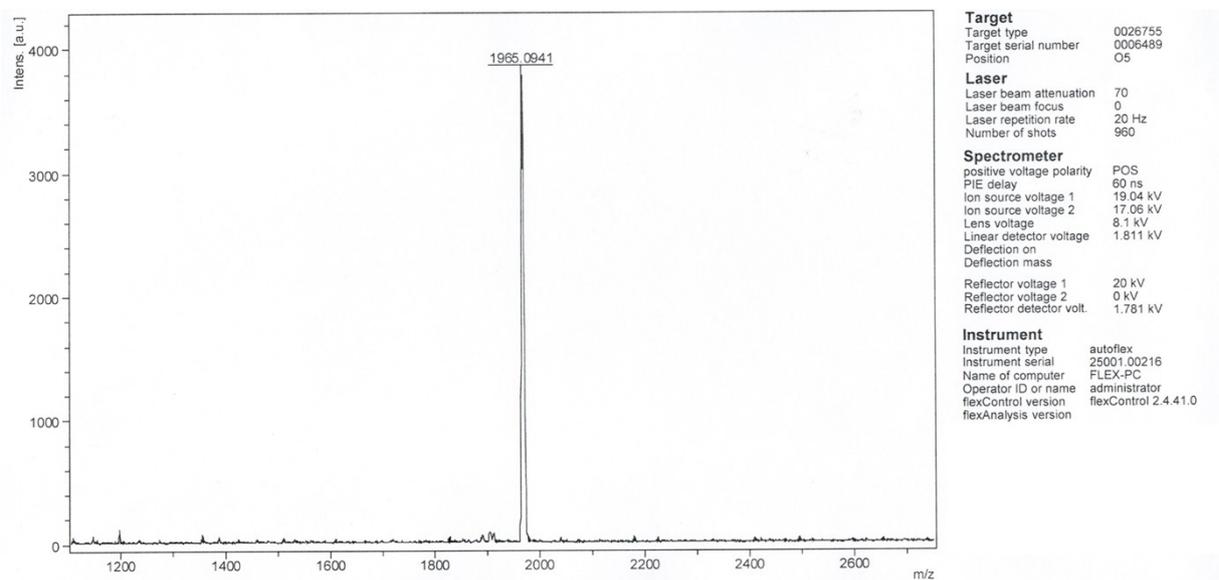


Fig. S22. MALDI-TOF spectrum of 4.

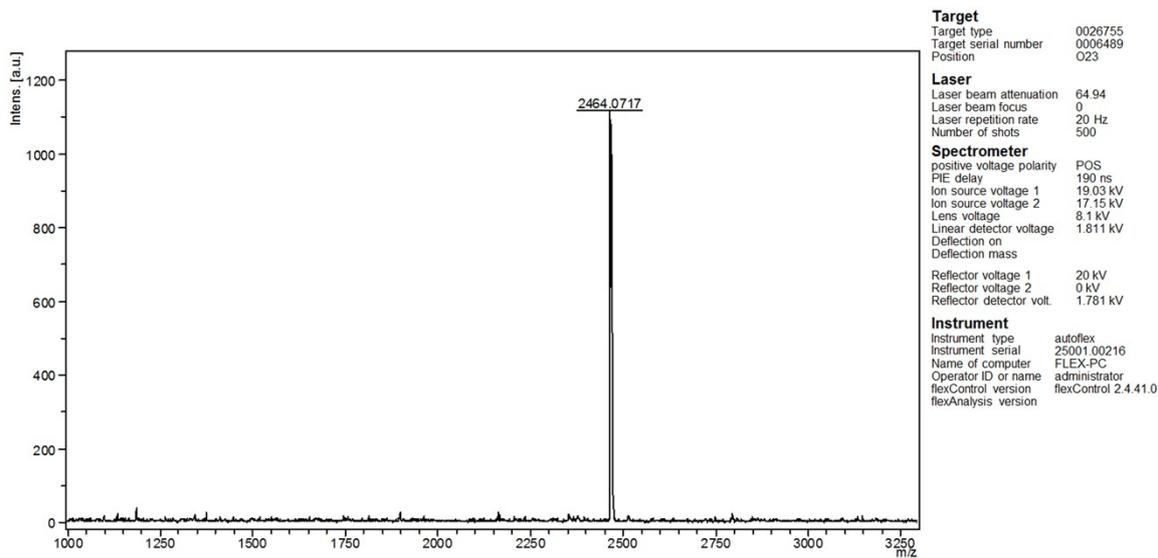


Fig. S23. MALDI-TOF spectrum of **5**.

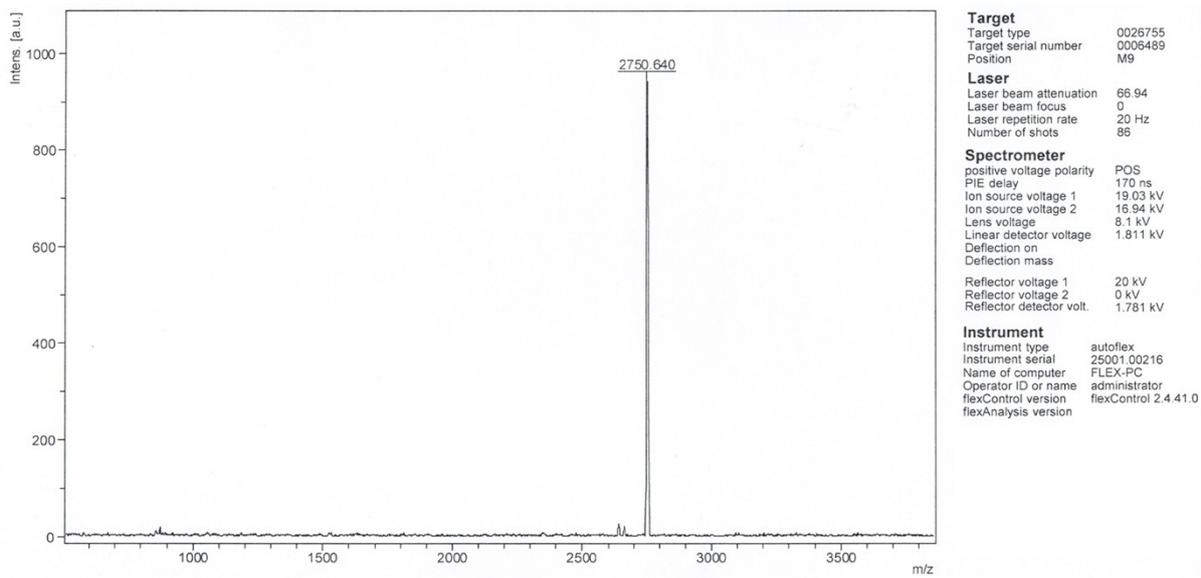


Fig. S24. MALDI-TOF spectrum of **F-C19ZnP**.

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