

Electronic Supplementary Information for

Reversible multistimuli-responsive vesicles formed by an amphiphilic cationic platinum(II) terpyridyl complex with a ferrocene unit in water

Ling-Bao Xing, Shan Yu, Xiao-Jun Wang, Ge-Xia Wang, Bin Chen, Li-Ping Zhang, Chen-Ho Tung, Li-Zhu Wu*

Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

E-mail: lzhu@mail.ipc.ac.cn

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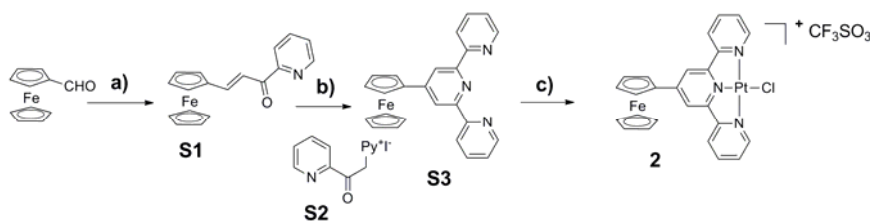
Materials: All chemicals were purchased from Acros or Aldrich and used without further purification, unless otherwise stated. Milli-Q water (18.2 M Ω -cm) was used in aqueous experiments. TEA was distilled with CaH₂ before use.

Instruments: ¹H NMR spectra was recorded on a Bruker Avance dpx 400 MHz instrument using tetramethylsilane as an internal standard. MS spectra were determined with BEFLEX III for TOF-MS and AEI-MS 50 for EI-MS. Elemental analyses (CHN) were performed at FLASH EA1112 Elemental Analyzer. UV-vis spectra were measured with a Shimadzu UV-1601PC spectrophotometer. Dynamic Light Scattering (DLS) data were collected on a DynaPro NanoStar (Wyatt Technology) with a gallium-arsenide diode laser of 658 nm emission. Scanning electron microscopy (SEM) images were obtained on a HITACHI S-4300 instrument operating at 10 kV with Au coated. Cryogenic transmission electron microscopy (cryo-TEM) was performed on FEI Tecnai 20 and JEM 2200FS. Electrochemical experiments were carried out with a Princeton Applied Research potentiostat/galvanostat model 283 in a three-electrode single-compartment cell equipped with a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) reference electrode.

Synthesis of amphiphile **1**

A mixture of platinum(II) 4'-ferrocenyl-2,2':6',2''-terpyridyl chloride **2** (50 mg, 0.063 mmol), triethylene glycol monomethyl ether terminal alkyne **3** (100 mg, 0.126 mmol), CuI (10 mg), DMF (3 mL), and triethylamine (6 mL) were sonicated under argon for 8 h. Thereafter, excess NH_4PF_6 was added. Dark-green precipitate was obtained after stirring for 1 h. The product was filtered and washed with diethyl ether. Subsequent re-crystallization by diffusion of diethyl ether vapor into a solution of the product in acetonitrile gave **1** (75.9 mg, 0.050 mmol, 78 %) as green solids. ^1H NMR (400 MHz, DMSO-d_6) δ 9.17 (s, 2H), 8.82 (d, $J = 7.7$ Hz, 2H), 8.69 (s, 2H), 8.55 (s, 3H), 8.47 (s, 1H), 7.93 (s, 2H), 7.86 (d, $J = 7.9$ Hz, 2H), 7.58 (d, $J = 8.0$ Hz, 2H), 7.20 (s, 2H), 5.43 (s, 2H), 4.81 (s, 2H), 4.22 (s, 5H), 4.15 (t, $J = 4.5$ Hz, 4H), 4.07 (t, $J = 4.5$ Hz, 2H), 3.77 (t, $J = 4.5$ Hz, 4H), 3.67 (t, $J = 4.8$ Hz, 2H), 3.62 – 3.49 (m, 18H), 3.42 – 3.40 (m, 6H), 3.33 (s, 4H), 3.23 (br, 9H), 1.80 (d, $J = 7.0$ Hz, 2H). MALDI-TOF-MS: m/z calcd for $[\text{C}_{65}\text{H}_{78}\text{FeN}_5\text{O}_{14}\text{Pt}]^+$: 1403.45, found: 1403.17 $[\text{M}]^+$. Elemental analysis: calcd (%) for $\text{C}_{65}\text{H}_{78}\text{F}_6\text{FeN}_5\text{O}_{14}\text{PPT}\cdot 2\text{C}_4\text{H}_{10}\text{O}$: C, 51.65; H, 5.82; N, 4.13, found: C, 51.84; H, 5.56; N, 4.58.

Synthesis of compound 2



Scheme S1 The synthetic route to **2**, a) NaOH, H₂O, C₂H₅OH; b) C₂H₅OH, CH₃COONH₄; c) K₂PtCl₄, CH₃CN, H₂O.

S1. Ferrocenecarboxaldehyde (2.15 g, 0.01 mol) in ethanol (15 mL) was added 2-acetylpyridine (1.21 g, 0.01 mol) and NaOH (0.60 g, 0.015 mol). After the addition, the mixture was stirred for 2 h at room temperature. The product was filtered off and washed with water as pH = 7. Subsequent re-crystallization in ethanol gave **S1** (2.9 g 9.15 mmol, 91.5 %) as purplish red crystal. ¹H NMR (400 MHz, CDCl₃) δ 8.74 (s, 1H), 8.19 (d, *J* = 7.6 Hz, 1H), 7.88 (q, *J* = 15.7 Hz, 3H), 7.48 (s, 1H), 4.68 (s, 2H), 4.50 (s, 2H), 4.19 (s, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 188.60, 154.87, 148.87, 147.25, 137.07, 126.63, 123.02, 117.99, 79.60, 71.61, 69.97, 69.55. EI-MS: *m/z* calcd for C₁₈H₁₅FeNO: 317.05, found: 317.05.

S3. The mixture of **S1** (2.536 g, 0.008 mol) and **S2** (2.608 g, 0.008 mol) in ethanol (50 mL) was added ammonium acetate (5 g, 0.065 mol). The mixture was refluxed for 3 h under argon. After cooling to the room temperature, the product was filtered off and washed with water and ethanol. The crude product was purified by silica gel flash column chromatography (petroleum ether/ethyl acetate, 15/1) to give **S3** as brick-red solids (1.766 g, 3.92 mmol, 49%). ¹H NMR (400 MHz, CD₃CN) δ 8.75 (d, *J* = 4.7 Hz, 2H), 8.68 (d, *J* = 7.9 Hz, 2H), 8.57 (s, 2H), 7.97 (td, *J* = 7.8, 1.8 Hz, 2H), 7.46 (dd, *J* = 6.9, 5.3 Hz, 2H), 5.12 – 4.90 (m, 2H), 4.59 – 4.41 (m, 2H), 4.11 (s, 5H). MALDI-TOF-MS: *m/z* calcd for C₂₅H₁₉FeN₃: 417.09, found: 417.09 [M]⁺.

2. A mixture of **S3** (100 mg, 0.24 mmol) and K₂PtCl₄ (99.5 mg, 0.24 mmol) in H₂O (50 mL) and CH₃CN (50 mL) was stirred overnight at 80 °C. After cooling to the room temperature, the product was filtered off and washed with water. Subsequent re-crystallization by diffusion of diethyl ether

vapor into a solution of the product in acetonitrile gave **2** (162.2 mg, 0.20 mmol, 85 %) as dark red solids. ^1H NMR (400 MHz, DMSO) δ 8.90 (d, $J = 5.6$ Hz, 2H), 8.77 (d, $J = 8.0$ Hz, 2H), 8.59 (s, 2H), 8.52 (t, $J = 7.8$ Hz, 2H), 7.98 – 7.87 (m, 2H), 5.41 (s, 2H), 4.82 (s, 2H), 4.21 (s, 5H). MALDI-TOF-MS: m/z calcd for $[\text{C}_{25}\text{H}_{19}\text{ClFeN}_3\text{Pt}]^+$: 647.03, found: 647.24 $[\text{M}]^+$.

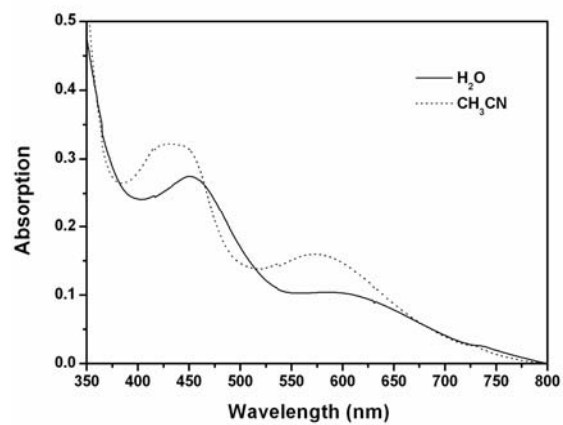


Fig. S1 UV-vis absorption spectrum of **1** (2.58×10^{-5} M) in aqueous and acetonitrile solutions at room temperature.

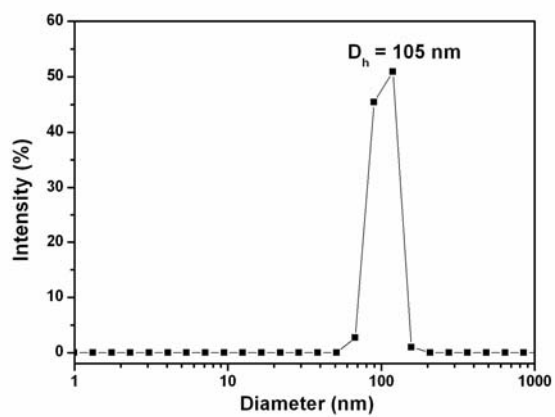


Fig. S2 Size distributions of amphiphilic **1** (1.29×10^{-4} M) measured by DLS in aqueous solution.

The DLS data are shown as the size probability distribution obtained by a CONTIN analysis.

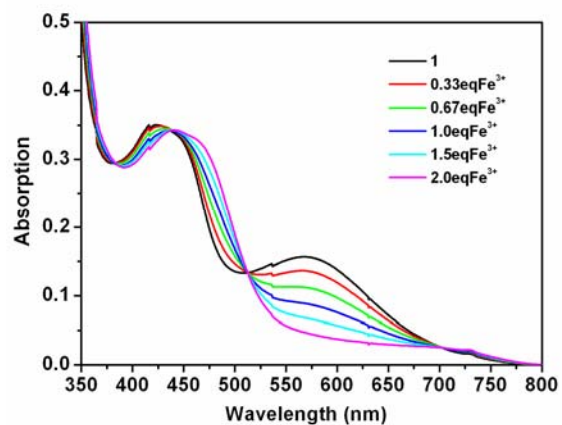


Fig. S3 UV-vis absorption spectral changes of **1** (2.84×10^{-5} M) in acetonitrile with the concentration of $\text{Fe}(\text{ClO}_4)_3$.

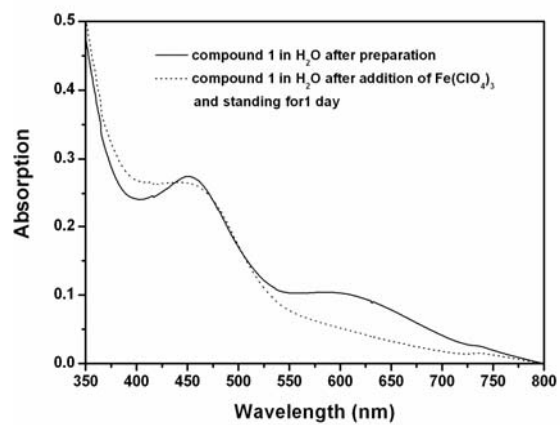


Fig. S4 Absorption spectral changes of **1** (2.84×10^{-5} M) in aqueous solution after preparation and addition of $\text{Fe}(\text{ClO}_4)_3$ and standing for one day.

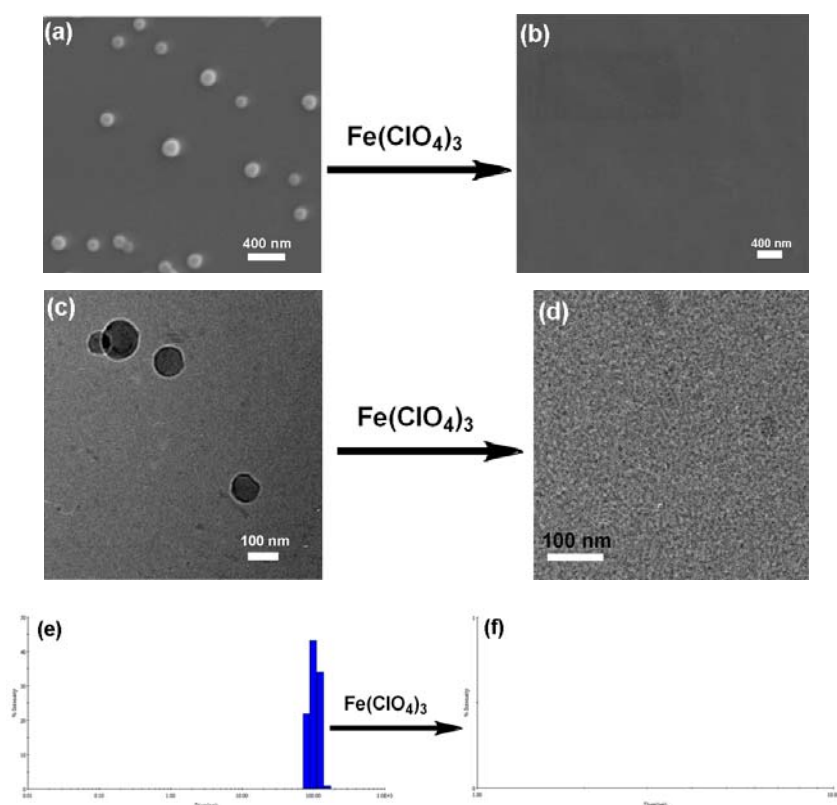


Fig. S5 SEM images, cryo-TEM and size distributions of amphiphilic **1** (1.29×10^{-4} M) measured by DLS in aqueous solution before (a, c, e) and after (b, d, f) addition of $\text{Fe}(\text{ClO}_4)_3$. The DLS data are shown as the size probability distribution obtained by a CONTIN analysis.

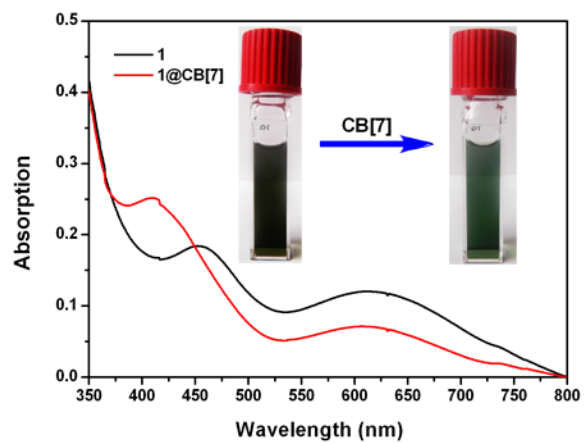


Fig. S6 Absorption spectra of **1** (2.84×10^{-5} M) in the absence and presence of CB[7] (1.0 equiv.) in H₂O.

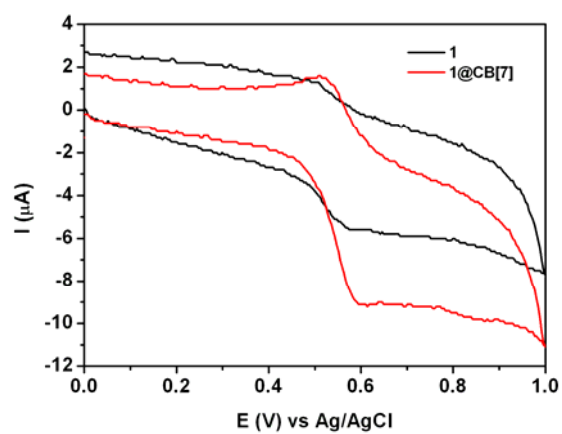


Fig. S7 Cyclic voltammetry of **1** (1 mM) in the absence and presence of CB[7] (1.0 equiv.) in H_2O -DMSO (1:1). The supporting electrolyte is KCl (0.1 M), and the scan rate is 100 mV s^{-1} .

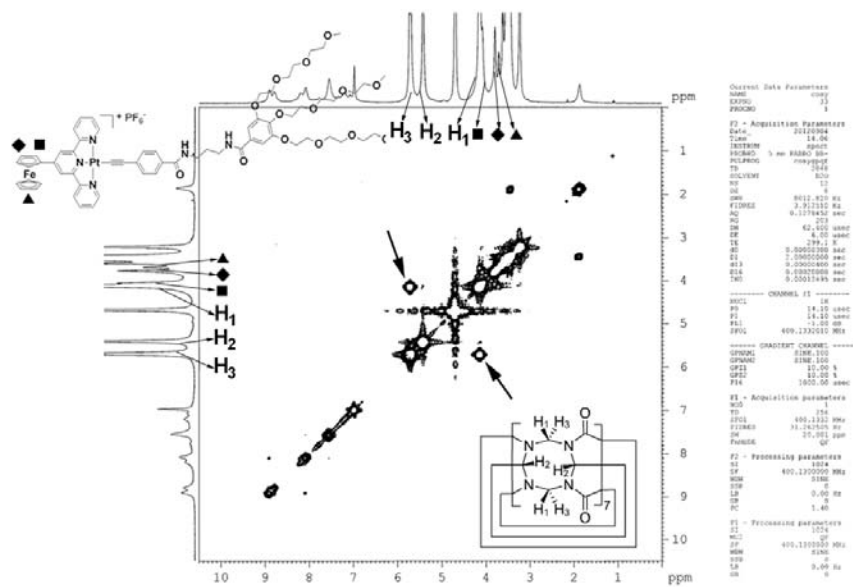


Fig. S8 2D COSY NMR of spectra of **1**@CB[7] in D₂O at 298 K.

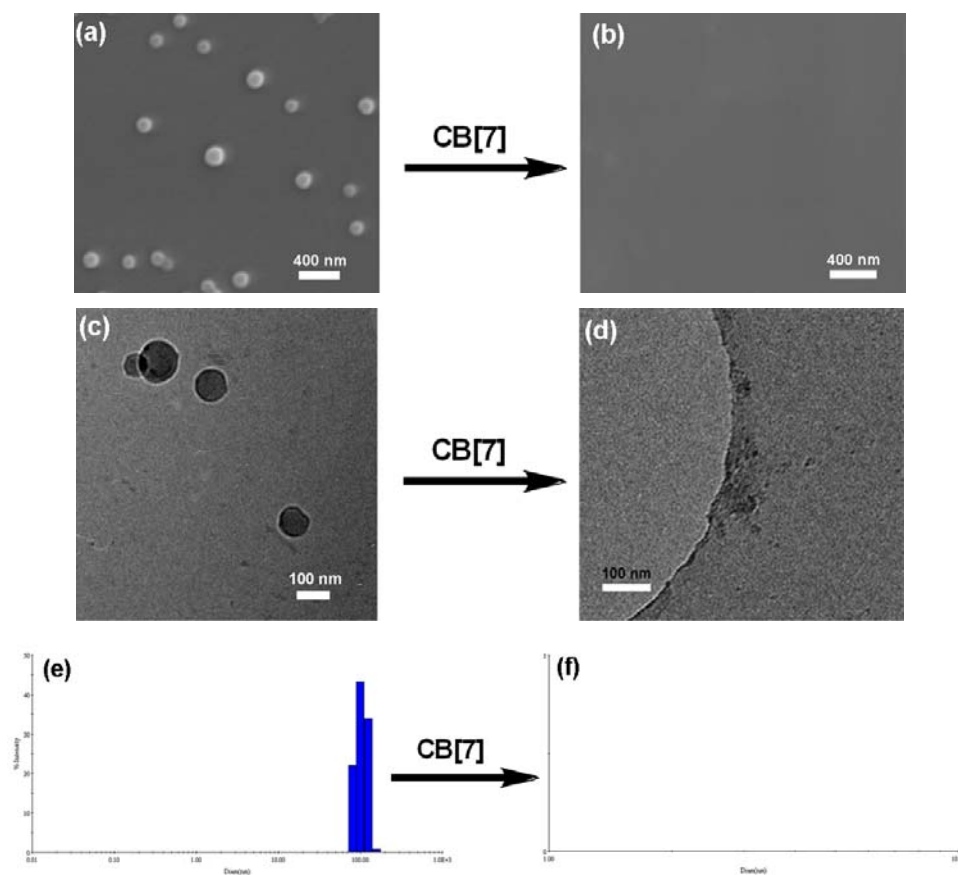


Fig. S9 SEM images, cryo-TEM and size distributions of amphiphilic **1** (1.29×10^{-4} M) measured by DLS in aqueous solution before (a, c, e) and after (b, d, f) addition of 1 equiv. CB[7]. The DLS data are shown as the size probability distribution obtained by a CONTIN analysis.

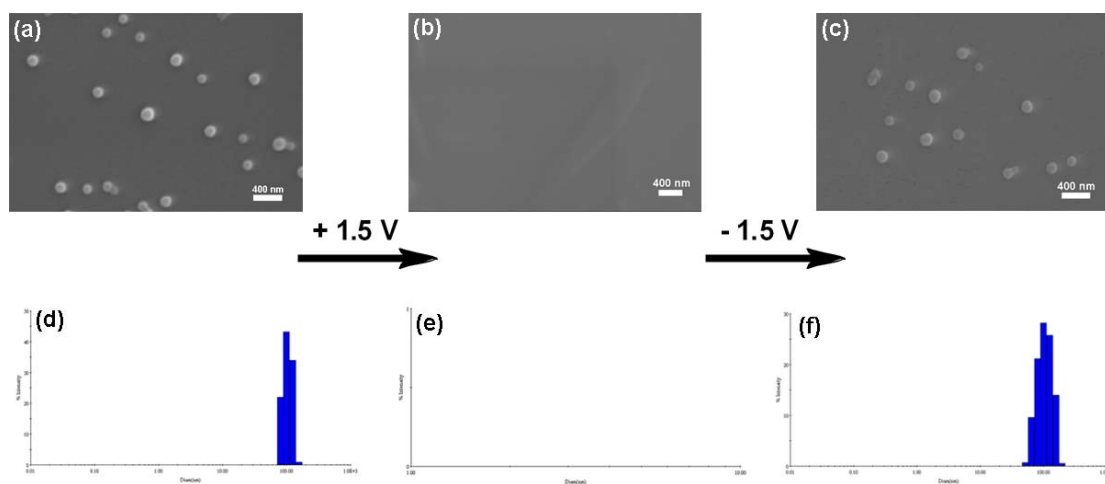


Fig. S10 SEM images and size distributions of amphiphilic **1** (1.29×10^{-4} M) measured by DLS in aqueous solution (a, d) in the presence of a positive (b, e) and reductive voltage (c, f). The DLS data are shown as the size probability distribution obtained by a CONTIN analysis.

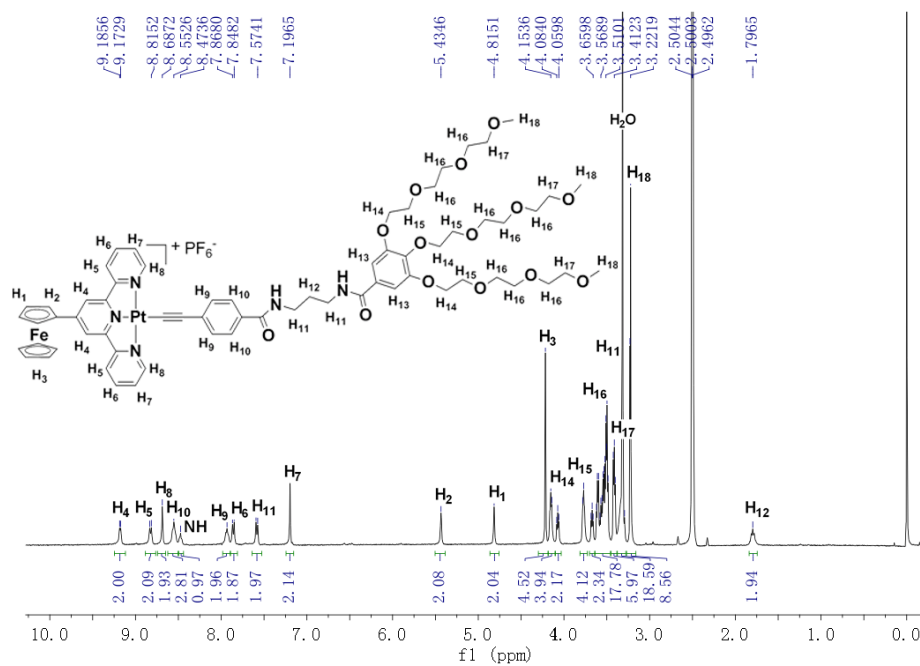


Fig. S11 ¹H NMR spectra of amphiphile **1** in DMSO-d₆.