

Facile Self-Assembly of Supramolecular Hexakisferrocenyl Triangles via Coordination-Driven Self-Assembly and Their Electrochemical Behavior

Guang-Zhen Zhao^a, Quan-Jie Li^b, Li-Jun Chen^a, Hongwei Tan^{*,b}, Cui-Hong Wang^a,

Danielle A. Lehman^c, David C. Muddiman^c, Hai-Bo Yang^{*,a}

hbyang@chem.ecnu.edu.cn

^a Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, 3663 N. Zhongshan Road, Shanghai, 200062, P. R. China. Fax: +86-21-62235137; Tel: +86-21-62235137; E-mail: hbyang@chem.ecnu.edu.cn;

^b Department of Chemistry, Beijing Normal University, Beijing 100050, P. R. China.

^c W. M. Keck FT-ICR Mass Spectrometry Laboratory and Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695, United States.

Electronic Supplementary Information

Table of Contents:

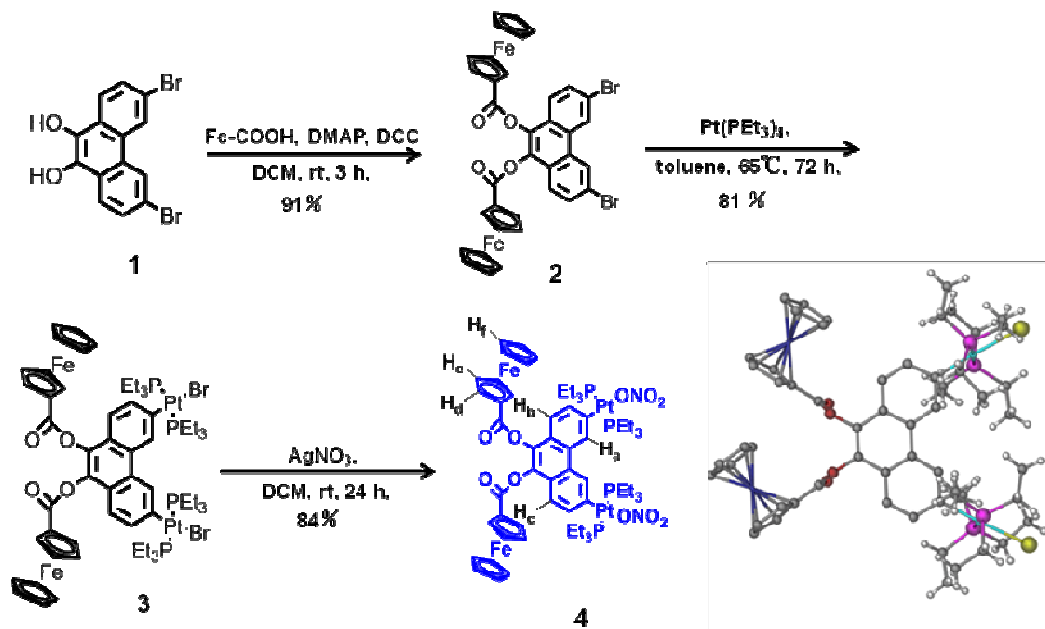
1. General Information	S2
2. Synthetic Procedures and Characterizations	S3
3. ¹ H, ³¹ P and ¹³ C NMR Spectra of New Compounds.....	S5
4. Cyclic Voltammetry.....	S12
5. The model structures of 6b and 6c	S12

1. General Information

All solvents were dried according to standard procedures and all of them were degassed under N_2 for 30 minutes before use. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. ^1H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on Bruker 400 MHz Spectrometer (^1H : 400 MHz; ^{13}C : 100 MHz; ^{31}P : 161.9 MHz) at 298 K. The ^1H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals, and ^{31}P NMR resonances are referenced to an internal standard sample of 85% H_3PO_4 (δ 0.0). Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet, br = broad.

2. Synthetic Procedures and Characterizations

Scheme S1. Synthesis of 60° ferrocenyl building block **4**



Synthesis of compound 2: To a solution of ferrocene carboxylic acid (435 mg, 1.89 mmol) in 15 ml anhydrous dichloromethane was added catalytic amount (10 %) of DMAP and 2,9-dibromo-5,6-dihydroxyphenanthrene (**1**) (349 mg, 0.945 mmol). DCC (429 mg, 2.10 mmol) was then added to the reaction mixture at 0 °C, followed by stirring for 5 min at 0°C and 3h at room temperature. Precipitated urea was then filtered off and the filtrate was evaporated under vacuo. The residue was taken up in 100 ml CH₂Cl₂, washed twice with 0.5 N HCl and with saturated NaHCO₃ solution, and then dried over MgSO₄. The residue was purified by column chromatography on silica gel (acetone/hexane: 1/2) to give compound **2**. Yield: 0.54 g, 91% (orange solid). *R_f* = 0.40 (1/1: acetone/hexane). Mp >300 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.80 (s, 2H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 5.08 (s, 4H), 4.54 (s, 4H), 4.27 (s, 10H), ¹³C NMR (CDCl₃, 167.6 MHz): δ 169.1, 136.4, 131.0, 129.9, 126.6, 125.9, 124.0, 121.7, 72.1, 70.9, 70.0, 69.4. MALDI Mass: 792.9 [M+H]⁺, 814.9 [M+Na]⁺.

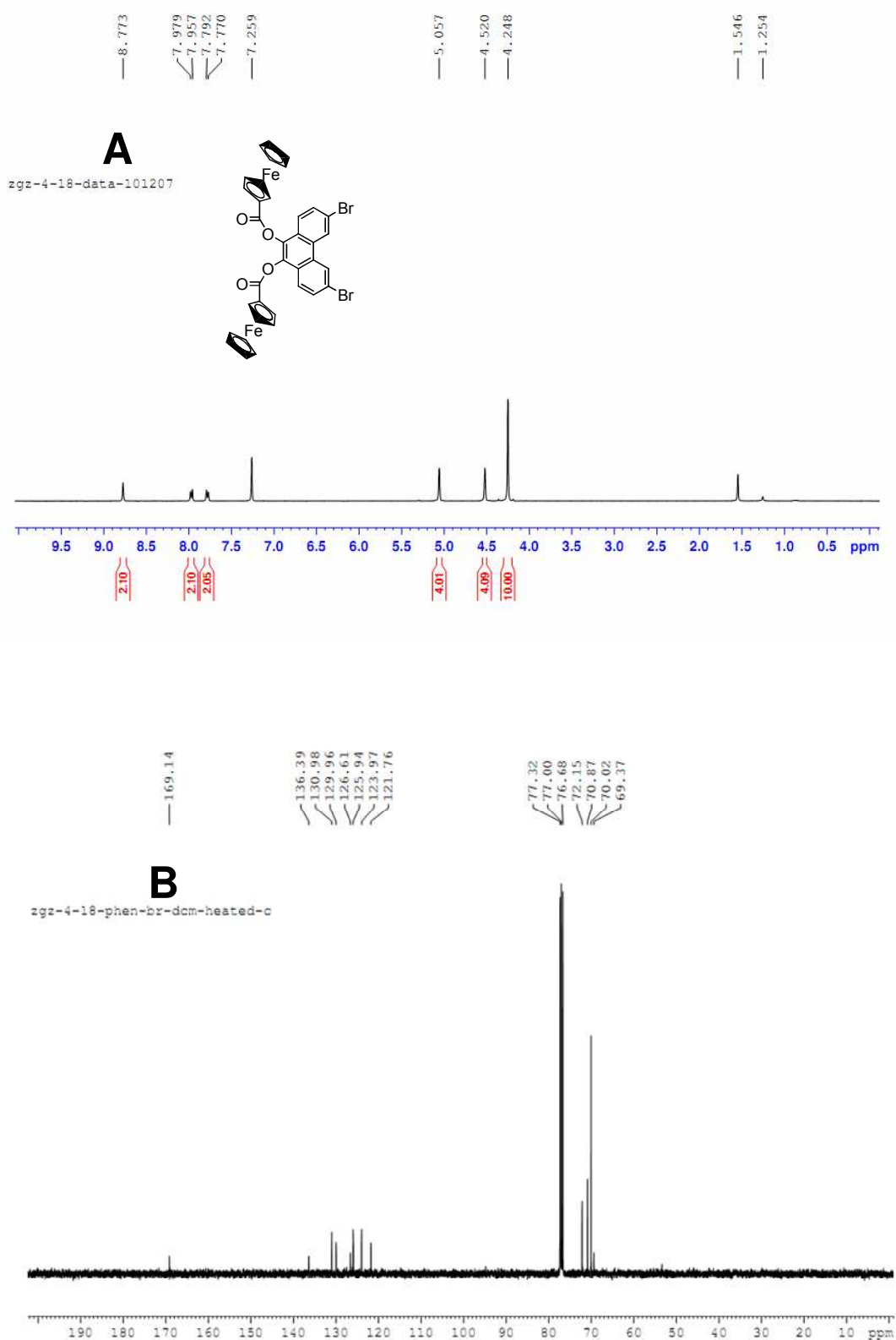
Synthesis of compound 3: A 50-mL Schlenk flask was charged under nitrogen with **2**

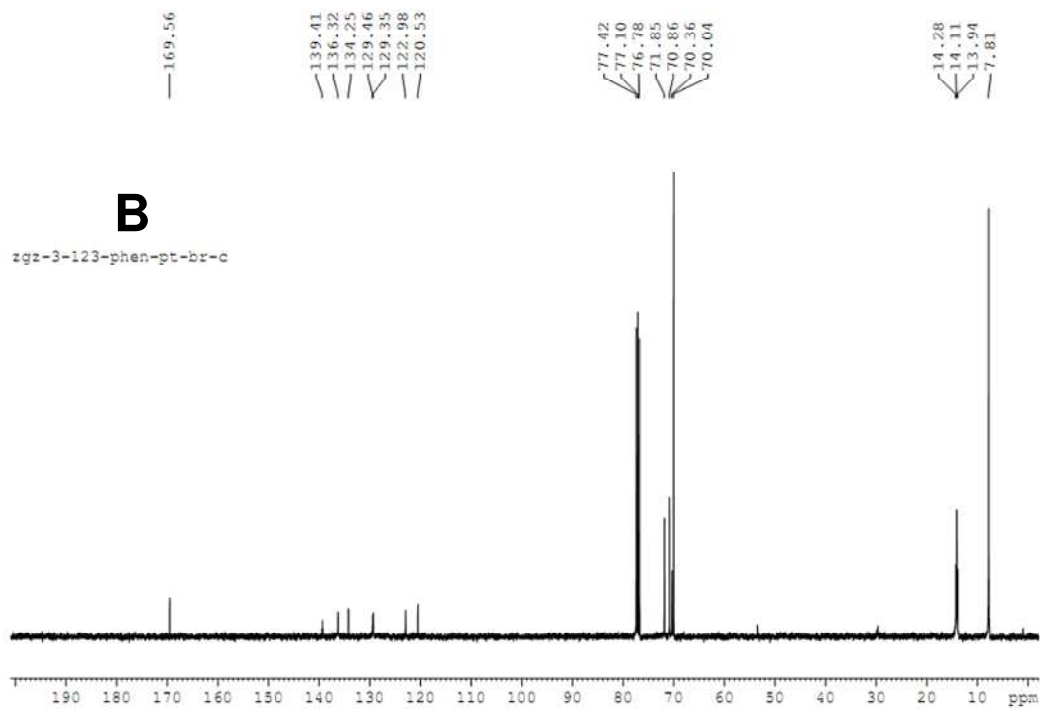
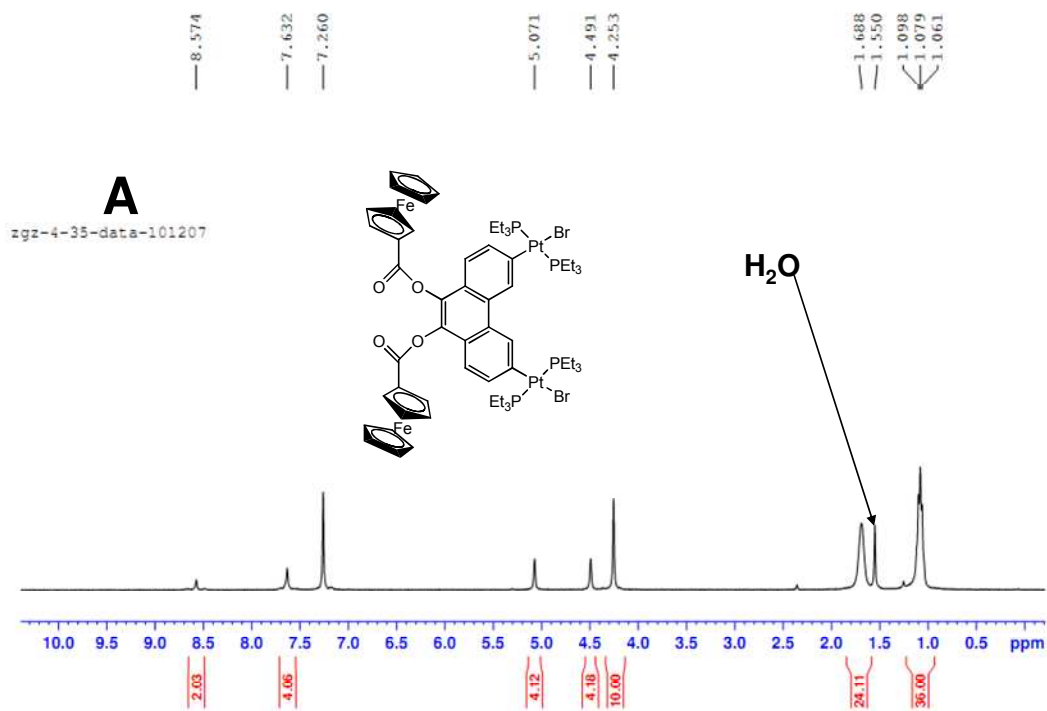
(100 mg, 0.126 mmol) and Pt(PEt₃)₄ (336 mg, 0.504 mmol). Freshly distilled toluene (10 mL) was added to the flask under nitrogen by syringe, and the resulting bright red solution was stirred for 72 h at 65 °C. The solvent was then removed in vacuo. The orange solid was washed with methanol (3 × 10 mL) and dried in vacuo. Yield: 0.31 g, 81%; mp 269-270 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.57 (s, 2H), 7.63 (s, 4H), 5.07 (s, 4H), 4.49 (s, 4H), 4.25 (s, 10H), 1.68 (s, 24H), 1.06-1.10 (m, 36H). ¹³C NMR (CDCl₃, 167.6 MHz): δ 169.6, 139.4, 136.3, 134.2, 129.4, 129.3, 122.9, 120.5, 71.8, 70.8, 70.3, 70.0, 14.1, 7.8. ³¹P{¹H}NMR (CDCl₃, 161.9 MHz): δ 12.7 (s, ¹J_{Pt-P} = 2741.0 Hz).

Synthesis of compound 4: Dibromide complex **3** (156 mg, 0.093 mmol) and AgNO₃ (157 mg, 0.93 mmol) were placed in a 2-dram vial followed by 3 mL of dichloromethane. The reaction was stirred in the dark at room temperature for 24 h. A clear solution with a heavy creamy precipitate resulted, the precipitate was filtered off, and the solvent was removed under a flow of nitrogen. The residue was redissolved in a minimal amount of dichloromethane, and then *n*-pentane was carefully added to precipitate the residual AgNO₃, but not the product. The cloudy solution was filtered through a glass fiber filter, and the product was then precipitated by the addition of more *n*-pentane. The supernatant was decanted, and the product was obtained as orange solid and dried in vacuo overnight. Yield: 126 mg, 84%; mp 194-195 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.50 (s, 2H), 7.64(s, 4H), 5.07 (s, 4H), 4.50 (s, 4H), 4.24 (s, 10H), 1.53 (s, 24H), 1.13-1.18 (m, 36H). ³¹P{¹H} NMR (CDCl₃, 161.9 MHz): δ 19.06 (s, ¹J_{Pt-P} = 2867.2 Hz). MALDI Mass: 1557.1 [M-NO₃]⁺

3. ^1H , ^{31}P and ^{13}C NMR Spectra of New Compounds

Figure S1. A) ^1H and B) ^{13}C NMR Spectra of Complex **2** in CDCl_3





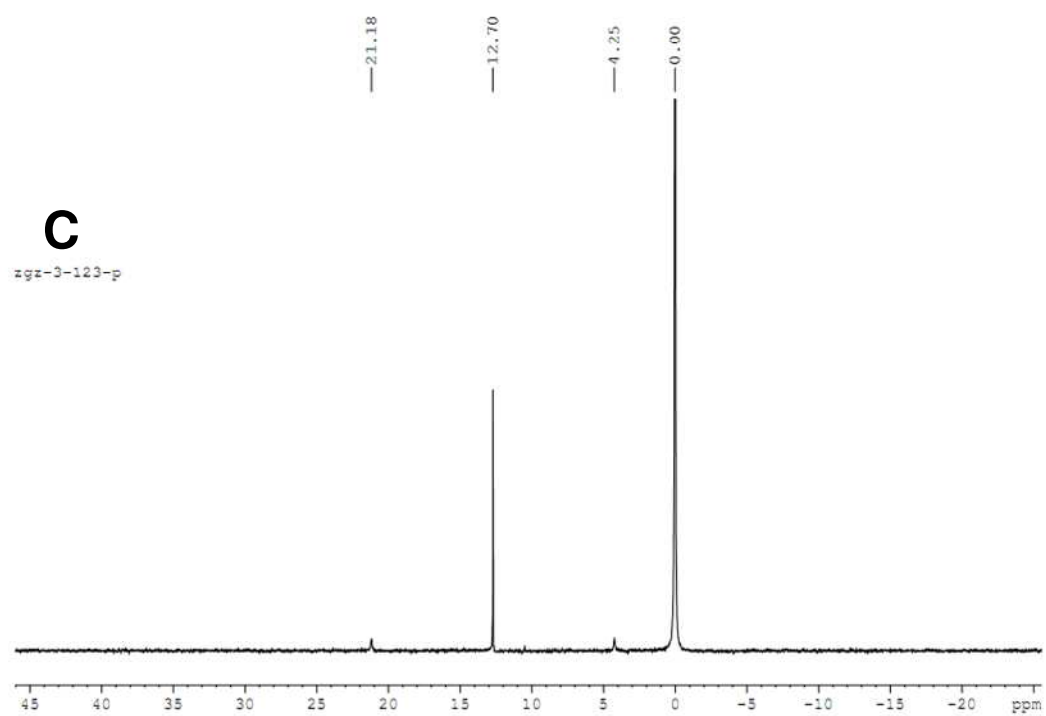


Figure S3. A) ^1H and B) ^{31}P NMR Spectra of Complex **4** in CDCl_3

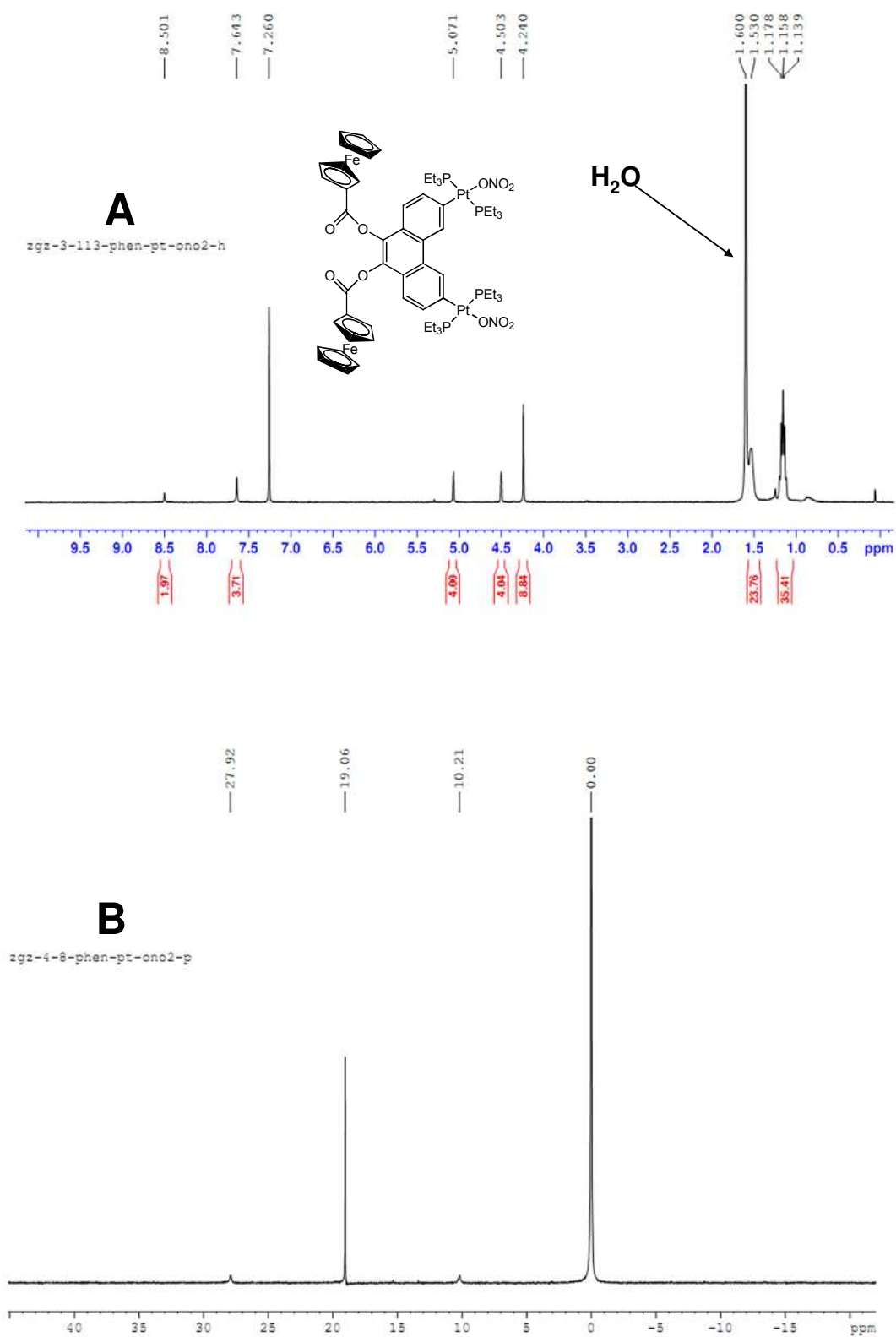


Figure S4. A) ^1H and B) ^{31}P NMR Spectra of Complex **6a** in CD_2Cl_2

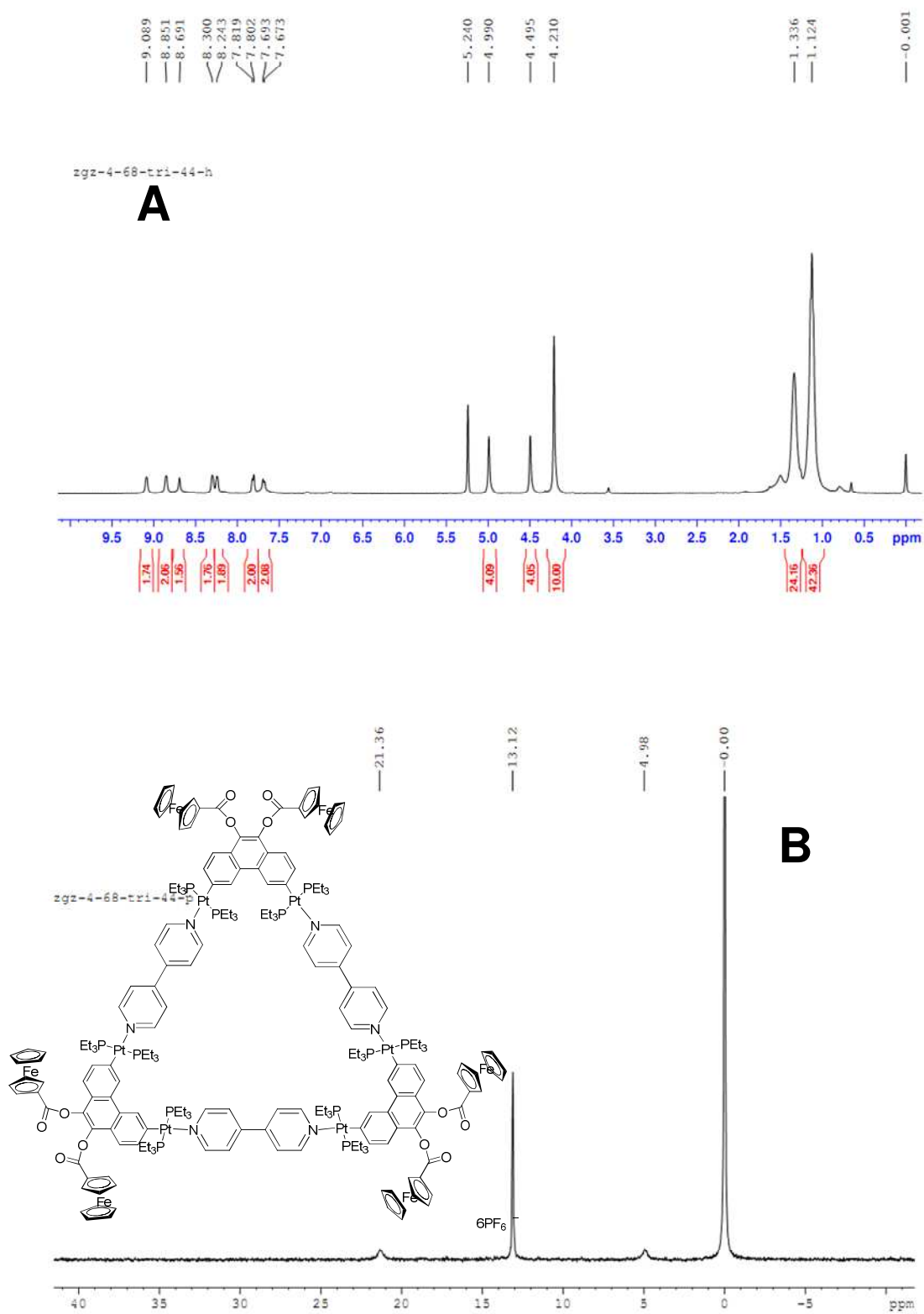


Figure S5. A) ^1H and B) ^{31}P NMR Spectra of Complex **6b** in CD_2Cl_2

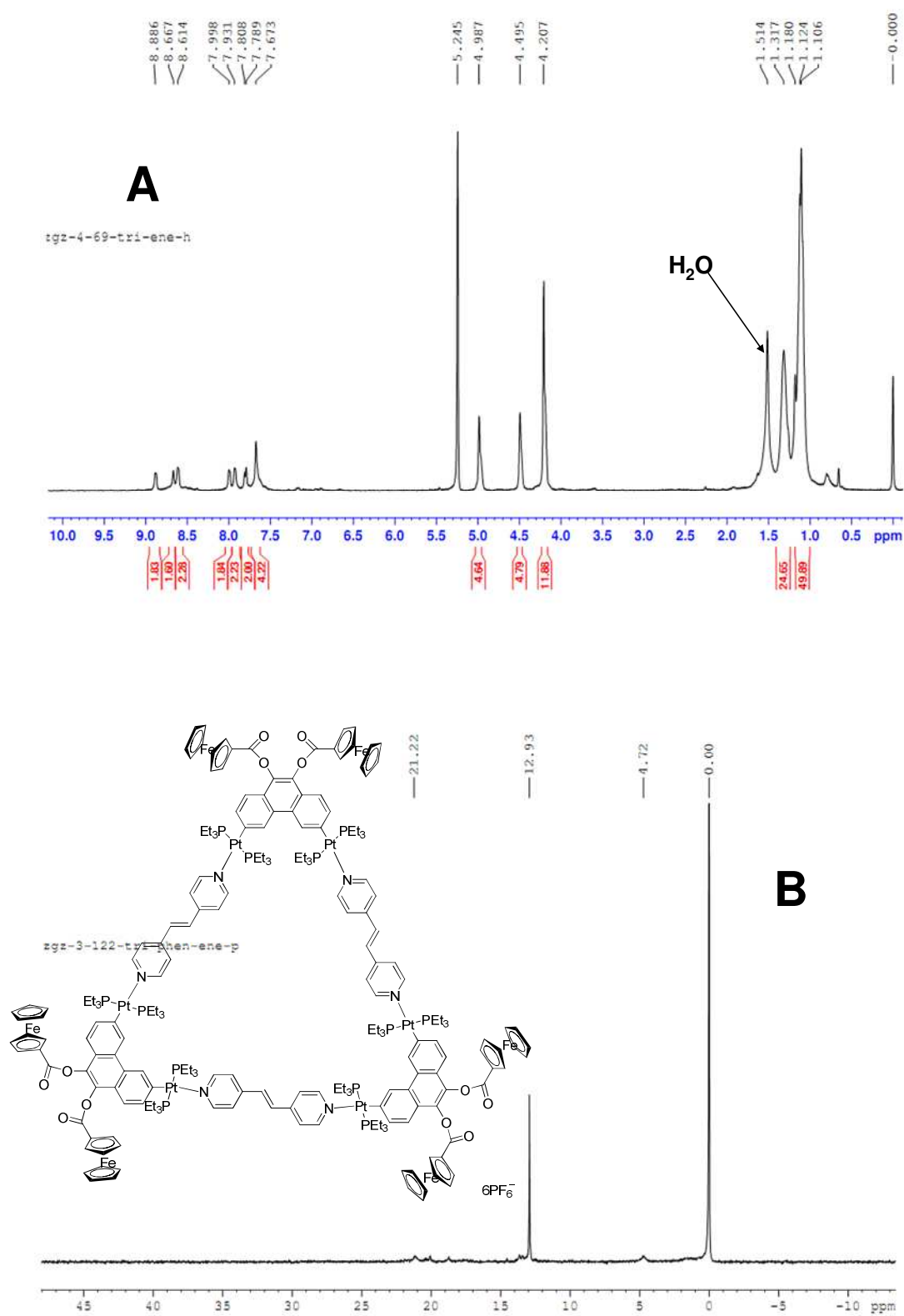
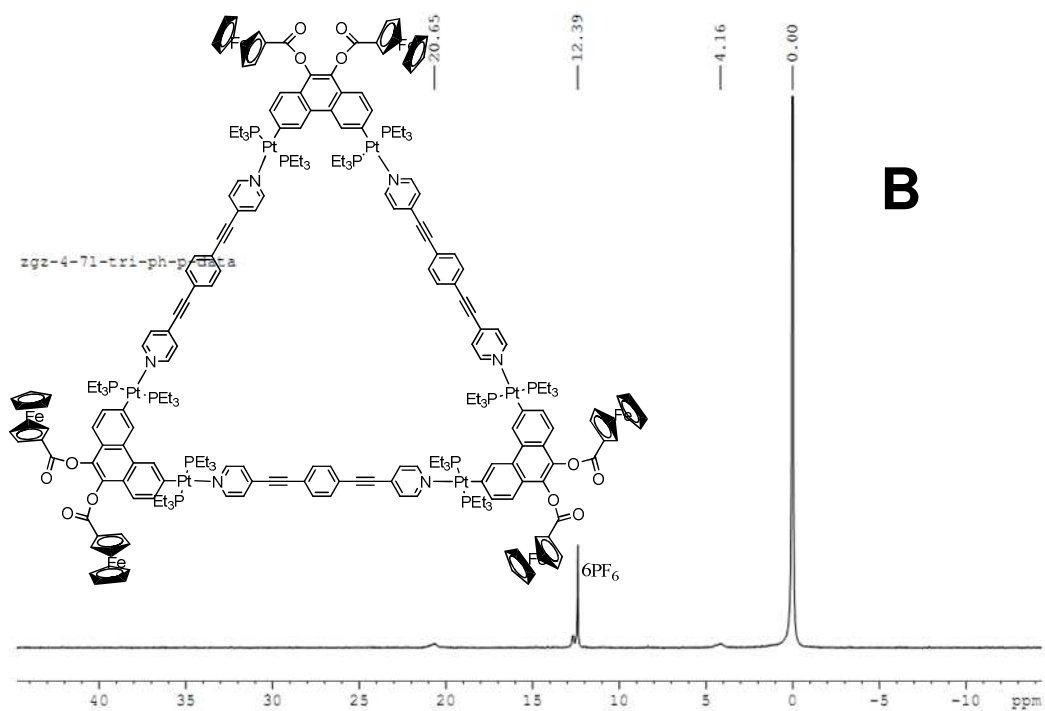
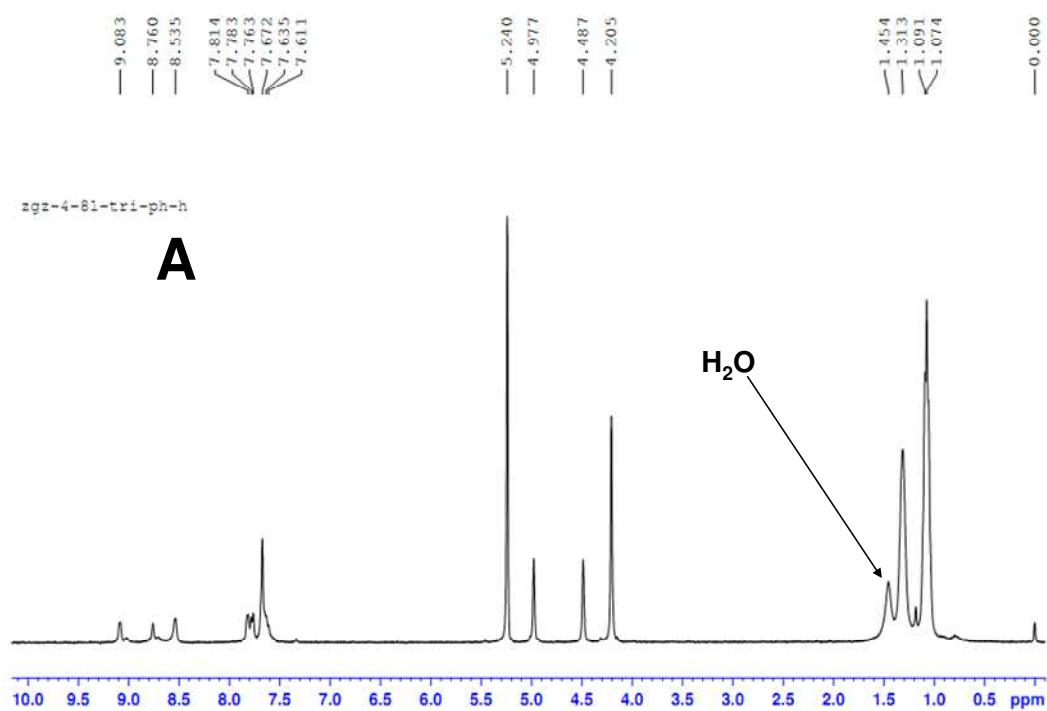


Figure S6. A) ^1H and B) ^{31}P NMR Spectra of Complex **6c** in CD_2Cl_2



4. Cyclic Voltammetry

Cyclic voltammetry (CV) was performed using a 3-electrode cell and a RST electrochemical work station. The working electrode was a glassy carbon disk with surface area of about 7.0 mm². A SCE electrode was used as reference electrode and a Pt wire as the counter electrode.

The CV measurements were carried out in a dichloromethane solution containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (*n*-Bu₄NPF₆). The concentration of redox molecule in solution was: (1) triangle **6a**, 1.99×10⁻⁴ M, (2) triangle **6b**, 1.99×10⁻⁴ M, (3) triangle **6c**, 2.00×10⁻⁴ M. The results of electrochemical studies are summarized in the Table 1 of the main text and shown in Figure S4. Scan rates are indicated in the figures.

In reversible system, the peak current (*i*) with respect to the scanning speed (*v*) can be expressed as: $i = 0.463 \times n^{3/2} F^{3/2} A (RT)^{-1/2} D^{1/2} C v^{1/2}$. Where the $F^{3/2} (RT)^{-1/2}$ is a constant which has a value of 5.81×10⁵; *n* is the mole of electrons transferred per mole of electroactive species (in our system, *n*=1); *A* is the area of the electrode in cm²; *D* is the diffusion coefficient in cm²/s; *C* is the concentration of samples in mol/mL; and *v* is the scan rate of the potential in volt/s.

A plot of *i* vs $v^{1/2}$ should give a straight line, the slope of which can be used to determine the diffusion coefficient, if *n*, *A*, and *C* are known. Thus by plotting *i* vs $v^{1/2}$, *D* can be evaluated from the slope. The results are outlined in Table1 of main text. The errors of slopes were estimated by fitting the data with two reasonable lines with a maximum slope and a minimum slope and taking one-half of the difference between the max and min slopes.

Figure S7. Cyclic voltammograms of 0.199 mM **6a** (A1), 0.199 mM **6b** (A2), and 2.00 mM **6c** (A3) at a scan rate of 25-250 mV/s and plot of the experimental ratio i vs $v^{1/2}$ at a scan rate of 25-250 mV/s (B1-B3 for **6a-c**).

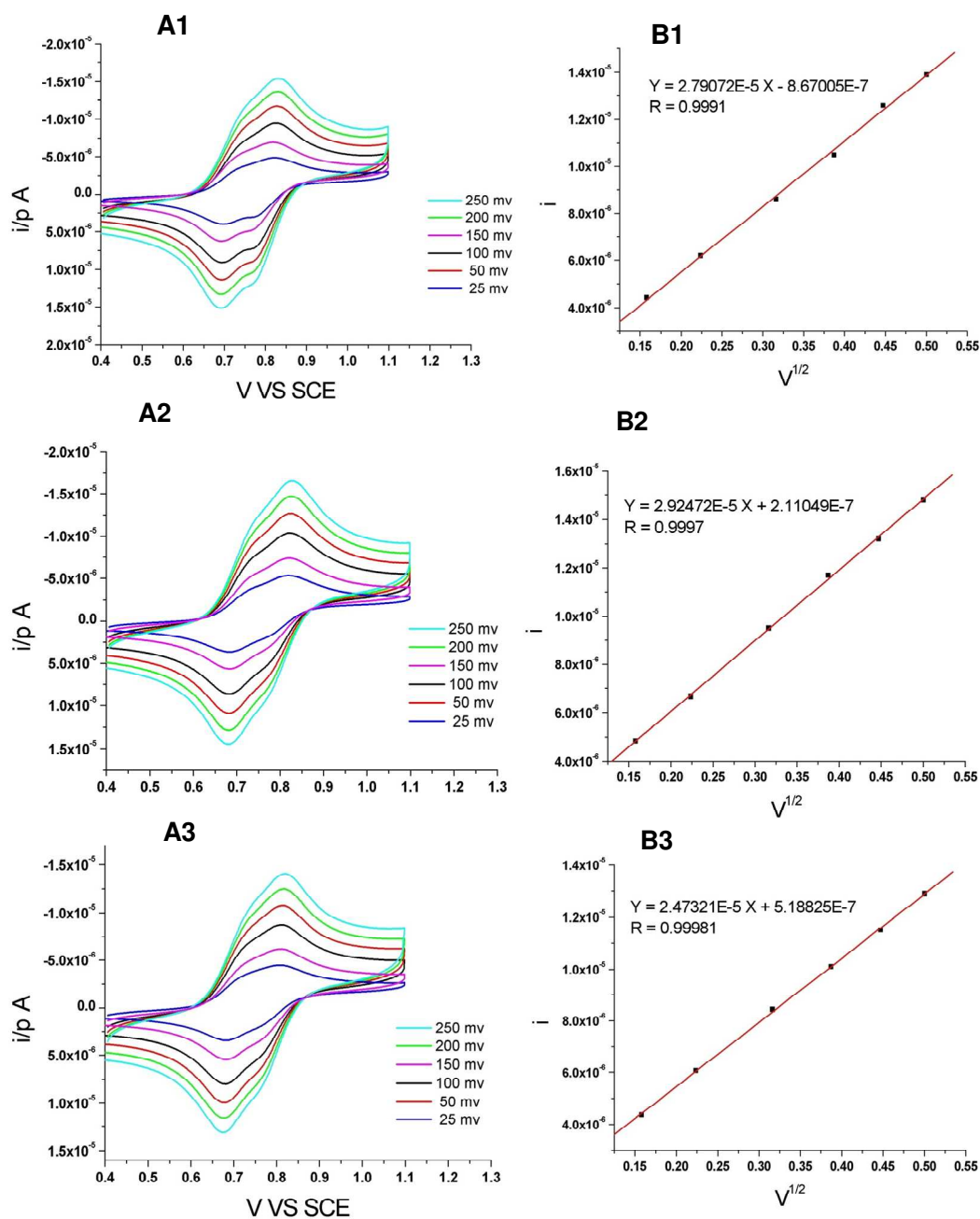


Figure S8. The geometry structures of the **6b** (A) and **6c** (B) optimized by PM6 semiempirical molecular orbital method.

