

A New Family of Multiferrocene Complexes with Enhanced Control of Structure and Stoichiometry via Coordination-Driven Self-Assembly

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Synthesis of Donor 1

To a solution of ferrocene-1-carboxylic acid (156 mg, 0.60 mmol) in 5 ml anhydrous dichloromethane was added catalytic amount (10 %) of DMAP and 3, 5-bis-pyridin-4-ylethynyl-phenol (200 mg, 0.60 mmol). DCC 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 50 ml CH₂Cl₂, washed twice with 0.5N HCl and with sat. NaHCO₃ solution, and then dried over MgSO₄. The residue was purified by column chromatography on silica gel (acetone/hexane: 2/1) to give compound **1**. Orange crystals suitable for single-crystal X-ray analysis were grown by slow evaporation of a hexane/dichloromethane solution.

Yield: 0.32 g, 90% (orange solid). *R*_f = 0.40 (1/1: acetone/hexane). Mp 152-153 °C. ¹H NMR (CD₂Cl₂, 300 MHz): δ 8.61 (d, *J* = 4.8 Hz, 4H), 7.67 (s, 1H), 7.41-7.43 (m, 6H), 4.97 (t, *J* = 1.8 Hz, 2H), 4.57 (t, *J* = 1.8 Hz, 2H), 4.34 (s, 5H). ¹³C NMR (CDCl₃, 75MHz) δ 170.2, 151.0, 150.1, 132.5, 130.9, 126.1, 125.8, 124.1, 92.0, 88.3, 72.5, 70.9, 70.3. MS (CI) *m/z*: 509.9 (M+1)⁺. Anal. Calcd for C₃₁H₂₀FeN₂O₂: C, 73.24; H, 3.97; N, 5.51. Found: C, 73.05; H, 4.02; N, 5.62.

Synthesis of Ferrocene Rhomboid 5

The donor **1** (2.87 mg, 0.0056 mmol) and nitrate **2**¹ (6.56 mg, 0.0056 mmol) were placed in a 2-dram vial. 0.75 mL of a mixture of solvent (acetone-*d*₆/D₂O : 2/1) was added. The vial was sealed with Teflon tape and immersed in an oil bath at 55-60 °C for 12 h. After no further changes to the NMR spectra, excess KPF₆ and H₂O were added to precipitate the assemblies as hexafluorophosphate salts, which were collected by vacuum filtration as an orange solid.

Yield: 9.98 mg, 97%. ¹H NMR (CD₂Cl₂, 300 MHz): δ 9.15 (d, *J* = 5.7 Hz, 4H, H_α-Py), 8.75 (s, 4H, H_{4,5}), 8.63 (d, *J* = 5.7 Hz, 4H, H_α-Py), 7.95 (d, *J* = 5.7 Hz, 4H, H_{1,8}), 7.90 (s, 2H, ArH), 7.76 (d, *J* = 5.7 Hz, 4H, H_{2,7}), 7.59-7.62 (m, 16H, H_β-Py, H_{9,10}, and ArH), 5.00 (t, *J* = 2.1 Hz, 4H, H_{Fc}), 4.62 (t, *J* = 2.1 Hz, 4H, H_{Fc}), 4.38 (s, 10H, H_{Fc}), 1.36 (m, 48H, PCH₂CH₃), 1.09 -1.19 (m, 72H, PCH₂CH₃). ³¹P {¹H} NMR (CD₂Cl₂, 121.4 MHz): δ 12.2 (s, ¹*J*_{Pt-P} = 2687.1 Hz). Anal. Calcd for C₁₃₈H₁₇₆F₂₄Fe₂N₄O₄P₁₂Pt₄·H₂O: C, 44.89; H, 4.86; N, 1.52. Found: C, 44.62; H, 4.94; N, 1.69.

General Procedure for the Preparation of Ferrocene Hexagon 6 and 7

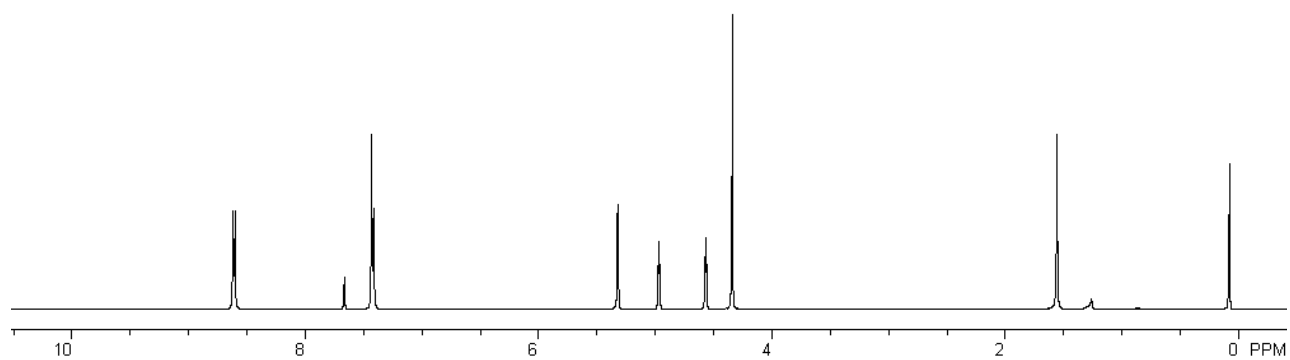
To a 0.5 mL CD_2Cl_2 solution triflate (for **3**², 5.0 mg, 0.0037 mmol; for **4**³, 3.95mg, 0.0037 mmol) was added a 0.5 mL acetone-*d*₆ solution of the appropriate donor precursor **1** drop by drop with continuous stirring (10 min). The reaction mixture was stirred for 30 min at room temperature. The solution was evaporated to dryness, and the product was collected.

6. Yield: 6.54 mg (orange solid), 95%. ¹H NMR (CD_2Cl_2 /acetone-*d*₆: 1/1, 300 MHz): δ 8.83 (d, *J* = 6.3 Hz, 12H, H _{α} -Py), 7.79 (d, *J* = 6.3 Hz, 12H, H _{β} -Py), 7.74 (s, 3H, ArH), 7.49-7.52 (m, 18H, ArH), 7.43 (d, *J* = 7.8 Hz, 12H, ArH), 4.97 (s, 6H, H_{Fc}), 4.50 (s, 6H, H_{Fc}), 4.24 (s, 15H, H_{Fc}), 1.31 (m, 72H, PCH_2CH_3), 1.00-1.10 (m, 108H, PCH_2CH_3). ³¹P{¹H} NMR (CD_2Cl_2 /acetone-*d*₆: 1/1, 121.4 MHz): δ 13.53 (s, ¹*J*_{Pt-P} = 2650.5 Hz). Anal. Calcd for C₂₁₀H₂₆₄F₁₈Fe₃N₆O₂₇P₁₂Pt₆S₆: C, 45.46; H, 4.80; N, 1.51. Found: C, 45.75; H, 5.15; N, 1.66.

7. Yield: 5.71 mg (orange solid), 98%. ¹H NMR (CD_2Cl_2 /acetone-*d*₆: 1/1, 300 MHz): δ 8.88 (d, *J* = 6.6 Hz, 24H, H _{α} -Py), 7.71-7.73 (m, 30H, H _{β} -Py and ArH), 7.48 (s, 12H, ArH), 6.98 (s, 24H, ArH), 4.88 (t, *J* = 1.8 Hz, 6H, H_{Fc}), 4.52 (t, *J* = 1.8 Hz, 6H, H_{Fc}), 4.26 (s, 15H, H_{Fc}), 1.05-1.17 (m, 216H, PCH_3). ³¹P {¹H} NMR (CD_2Cl_2 /acetone-*d*₆: 1/1, 121.4 MHz): δ -14.55 (s, ¹*J*_{Pt-P} = 2729.31 Hz). Anal. Calcd for C₃₀₆H₃₆₀F₃₆Fe₆N₁₂O₄₈P₂₄Pt₁₂S₁₂: C, 38.84; H, 3.83; N, 1.78. Found: C, 38.89; H, 4.22; N, 1.97.

Figure S1. A) ^1H and B) ^{13}C NMR Spectra of Donor Precursor **1** in CD_2Cl_2

A



B

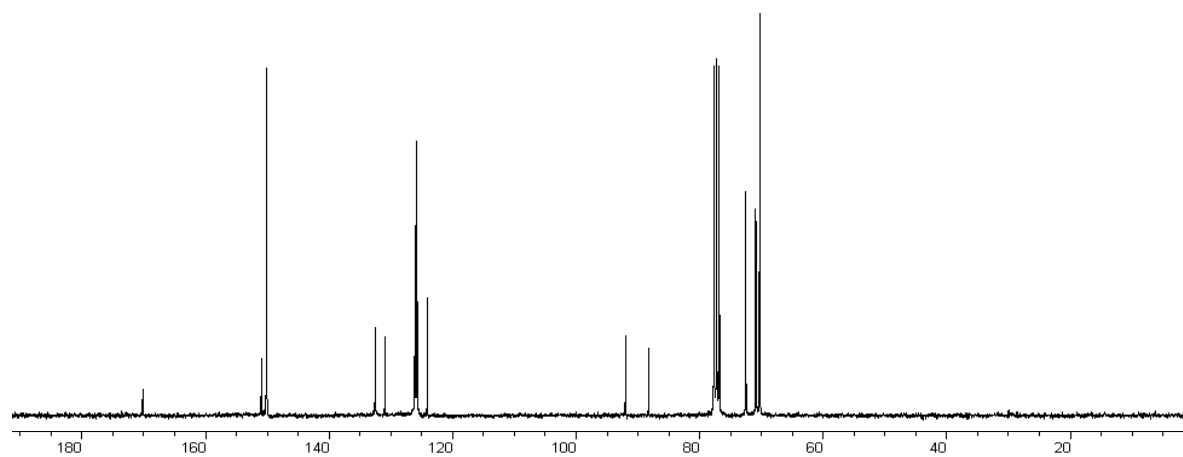


Figure S2. A) ^1H and B) ^{31}P NMR Spectra of Rhomboid **5** in CD_2Cl_2

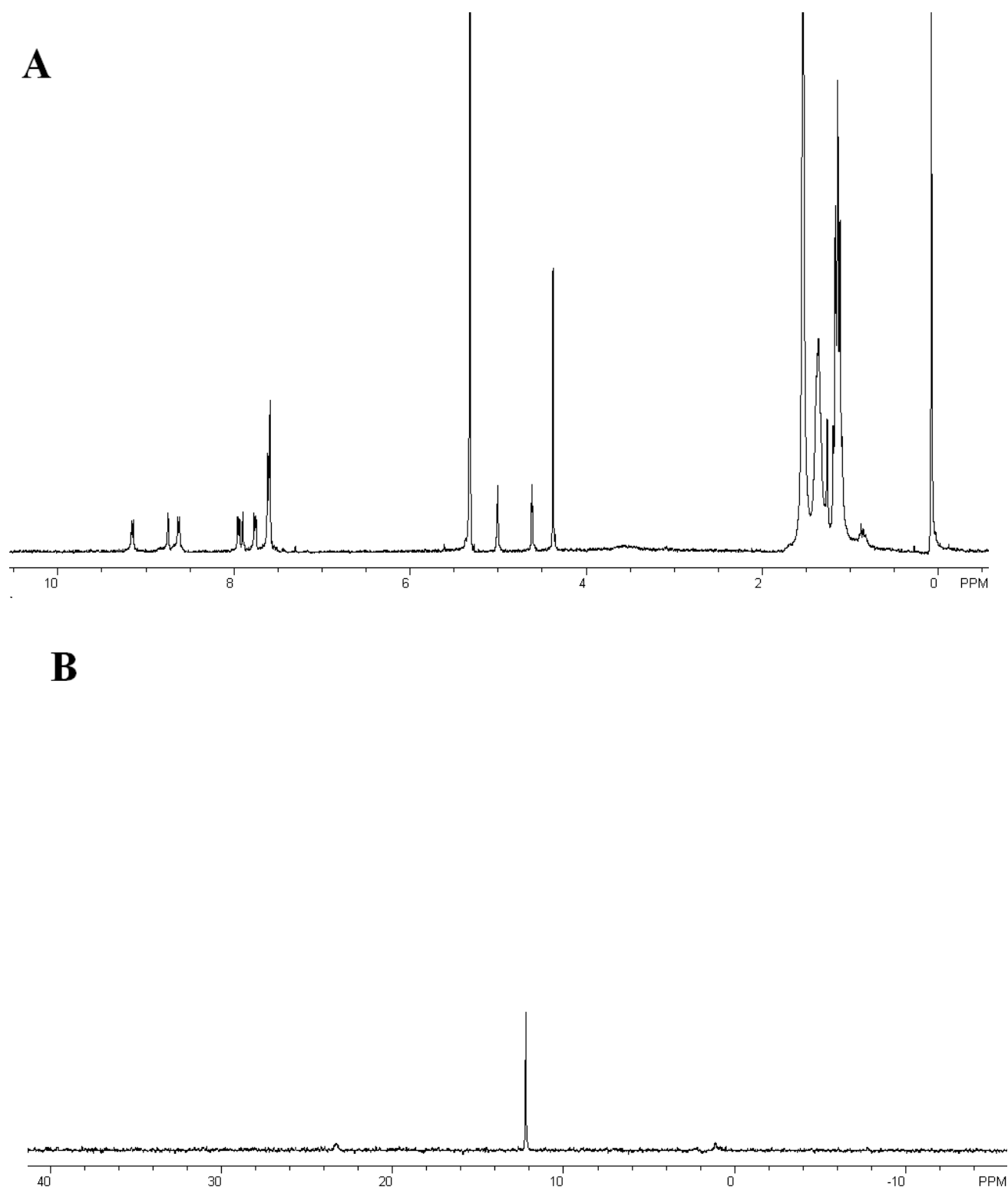
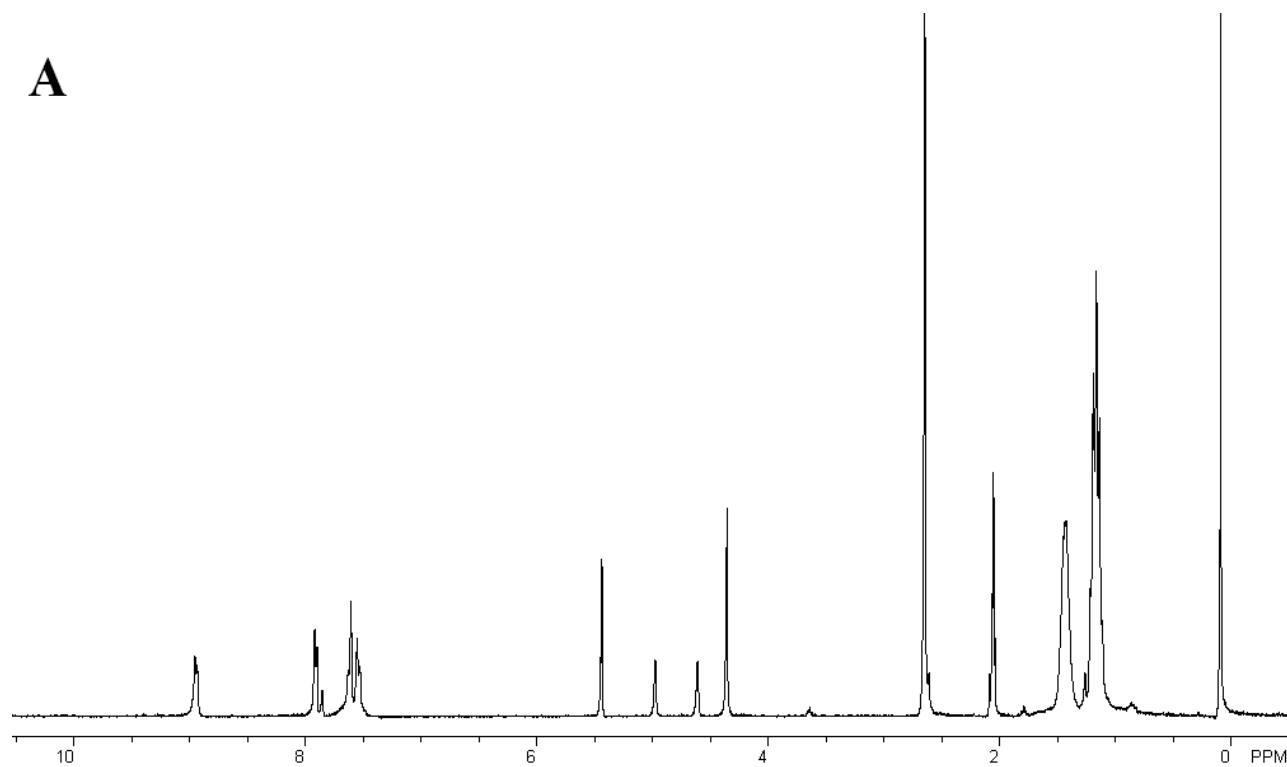


Figure S3. A) ^1H and B) ^{31}P NMR Spectra of Hexagon **6** in CD_2Cl_2

A



B

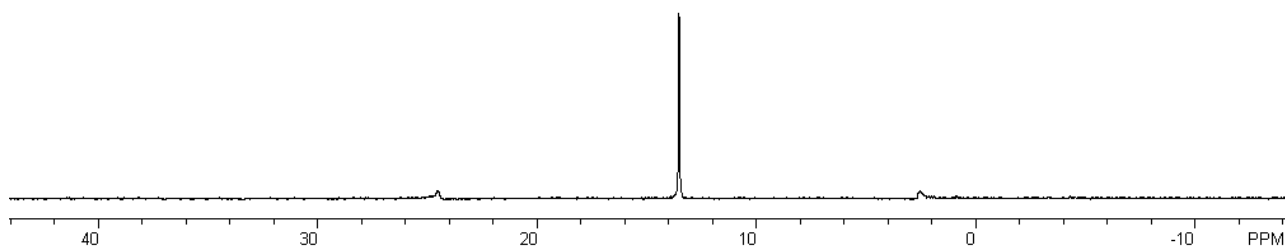
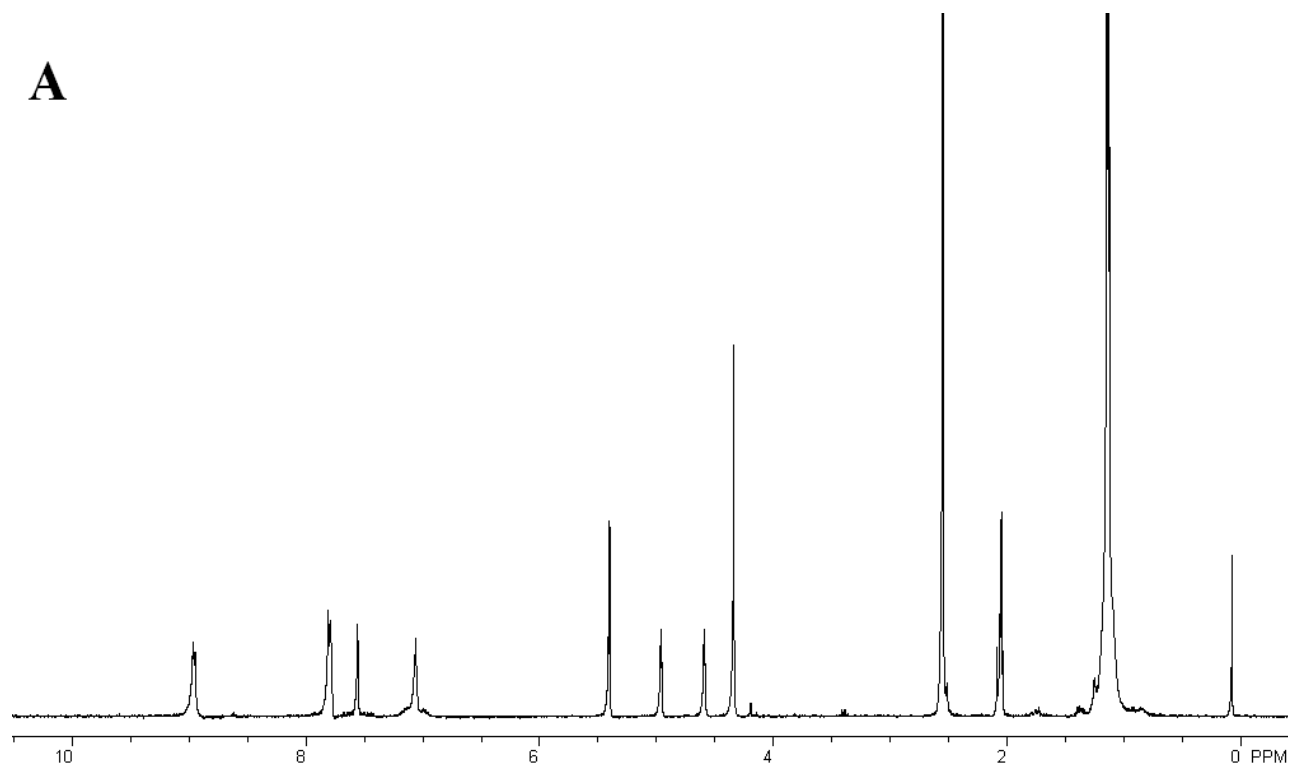
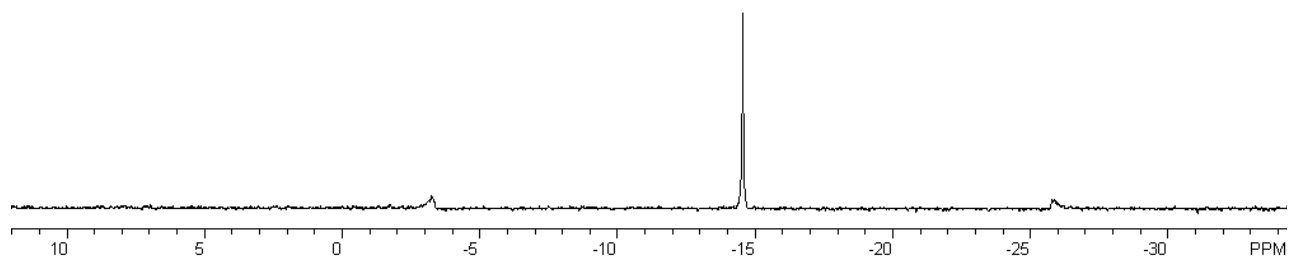


Figure S4. A) ^1H and B) ^{31}P NMR Spectra of Hexagon **7** in CD_2Cl_2

A



B



Cyclic Voltammetry.

Cyclic voltammetry (CV) was performed in a Faraday cage using a 3-electrode cell and a potentiostat (Pine Instrument Co., RDE4). The working electrode was a platinum disk embedded in glass with surface area of about 1 mm². A Ag/AgCl electrode was used as reference electrode and a Pt wire as the counter. Voltammetric data were recorded using in-house virtual instrumentation written in LabVIEW 8.0 (National Instrument).

The CV measurements were carried out in a dichloromethane solution containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (*n*-Bu₄NPF₆). The concentration of redox molecule in solution was: (1) ferrocene, 2.15×10⁻⁴ M, (2) donor **1**, 2.04×10⁻⁴ M, (3) rhomboid **5**, 1.98×10⁻⁴ M, (4) hexagon **6**, 2.02×10⁻⁴ M, (5) hexagon **7**, 2.06×10⁻⁴ M. See Figures S7 and S8 for the voltammetric results of **1** and **5** (results for **6** and **7** are in Figure 4 of the main text). Scan rates are indicated in the figures.

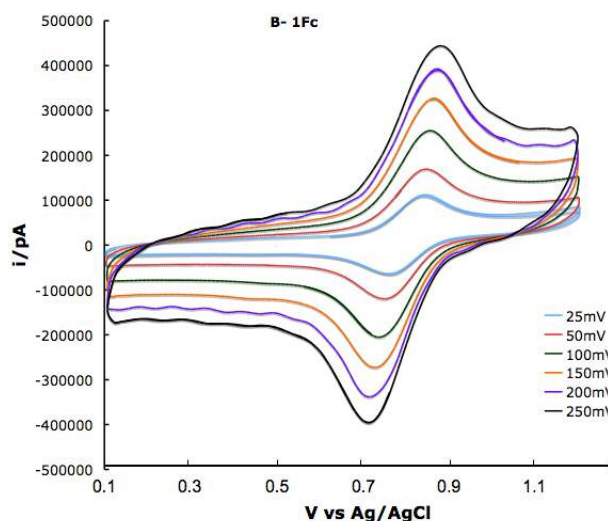


Figure S5. Cyclic voltammetric response of 2.04×10⁻⁴ M donor **1** in dichloromethane containing 0.1M *n*-Bu₄NPF₆.

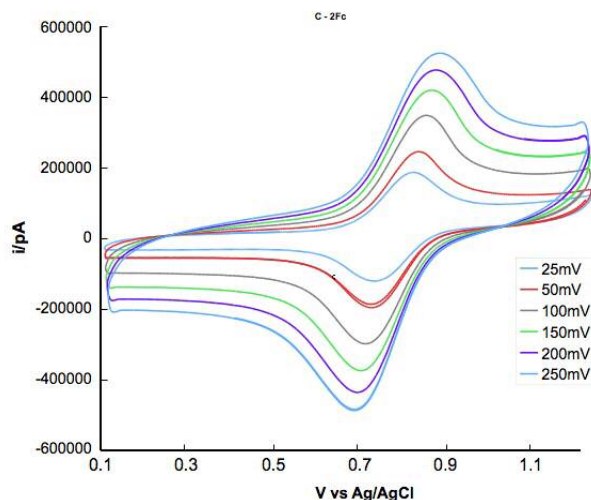


Figure S6. Cyclic voltammetric response of 1.98×10^{-4} M rhomboid **5** in dichloromethane containing 0.1M *n*-Bu₄NPF₆.

Chronoamperometry Measurements

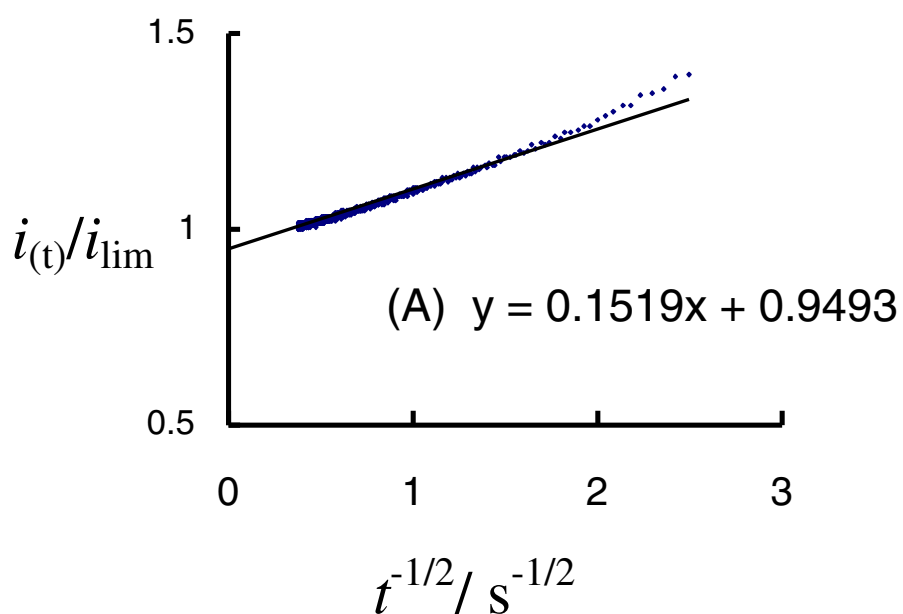
Chronoamperometry was performed by stepping the electrode potential from a value where no electron transfer occurred to a value where the oxidation of the redox molecule was diffusion limited.

The normalized time-dependent current with respect to the steady-state limiting current (i_{lim}) of a microdisk can be expressed as:⁵

$$\frac{i(t)}{i_{\text{lim}}} = 1 + (2/\pi^{3/2})a(Dt)^{-1/2}$$

Thus, by plotting $i(t)/i_{\text{lim}}$ vs $t^{-1/2}$, D can be evaluated from the slope when a is known. Figure S7 shows two examples of $i(t)/i_{\text{lim}}$ vs $t^{-1/2}$ plots. The linear region of the plots at long times were used to calculate D . At short times, upward curvature observed in $i(t)/i_{\text{lim}}$ vs $t^{-1/2}$ plots is apparent and is presumed due to loss of potential control

associated with the ohmic potential drop in the dichloromethane solution. Calculated values of D for each compound are presented in Table 1 of the 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.



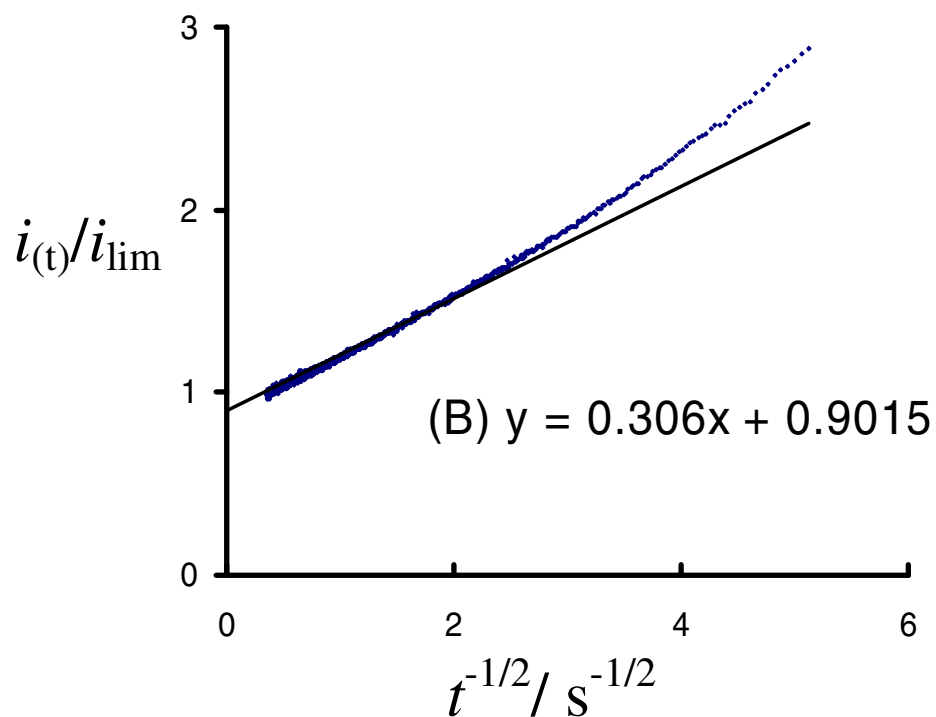


Figure S7 Plot of the experimental ratio $i(t)/i_{\text{lim}}$ vs $t^{-1/2}$ for the oxidation of 3.5mM ferrocenyl donor **1** (A) and 2.5mM of rhomboid **5** (B) in CH_2Cl_2 containing 0.1M $n\text{-Bu}_4\text{NPF}_6$ using a 12.5 μm microelectrode.

Steady-State Measurements using Pt microdisk electrodes.

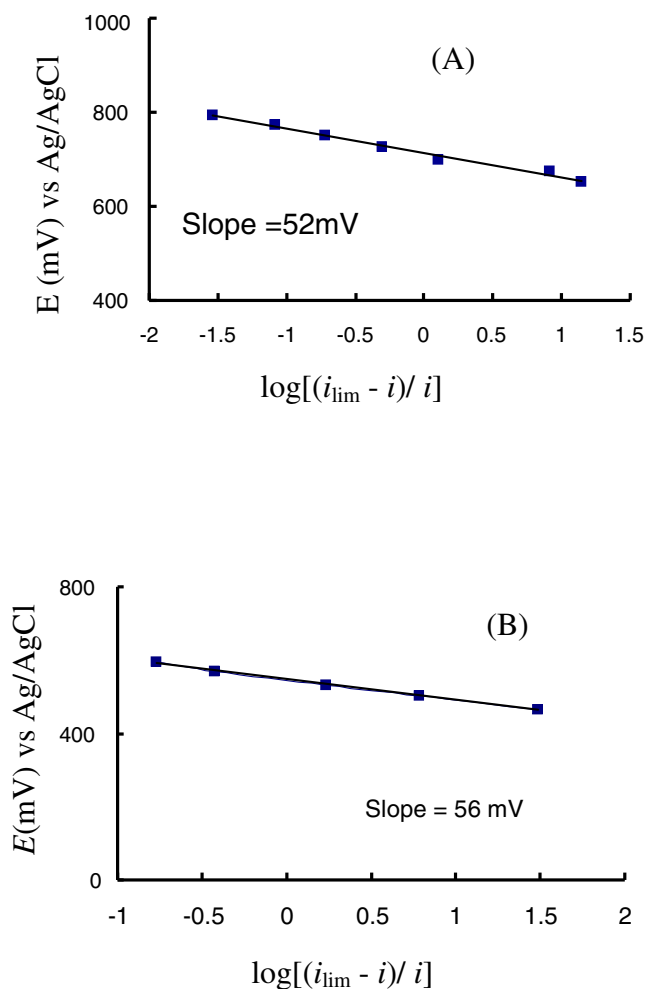
Steady-state voltammetric measurements were made using the same cell and instrument as described previously. The limiting current can be calculated from the equation:

$$i_{\text{lim}} = 4nFDaC\theta_{\text{sites}} \quad (1)$$

where n is the number of electrons transferred per ferrocene ($=1$), F is the Faraday constant C is the bulk concentration, θ_{sites} is the number of reacting ferrocenyl sites per the redox molecule, and a is the radius of the electrode. An acetonitrile solution

containing 5.1 mM ferrocene and 0.2M TBAPF₆ was used to determine the radius of the Pt microdisk ($a = 21 \mu\text{m}$).

To determine if the oxidation of the compounds correspond to independent serial electron transfer reactions, the current function $\log[(i_{\text{lim}}-i)/i]$ from the steady-state voltammograms was plotted vs E , Figure S8. For each compound, the slope corresponded closely to the one-electron value, (59 mV for $n = 1$) supporting the conclusion that oxidation of the ferrocenyl groups occur independently of one another.



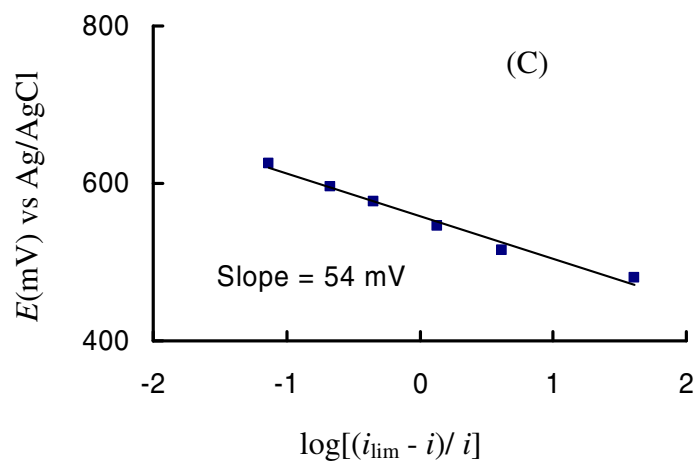


Figure S8. Plot of $\log[(i_{\text{lim}}-i)/i]$ vs E from the steady-state measurements using a Pt microelectrode: (A) rhomboid **5**, (B) hexagon **6**, (C) hexagon **7**. Blue dots are the experimental data and black lines represent best fit lines to the data.

Molecular Modeling Procedures:

The molecular structures of multiferrocene complexes **5** - **7** were each constructed within the input mode of the program⁴ Maestro v8.0.110 with the OPLS force-field.⁶ A 1.0 ns molecular dynamics simulation (0.05 fs timestep) at a simulation temperature of 300 K was used to equilibrate each structure. Following each molecular dynamics simulation a full energy minimization was used to obtain the final optimized structures.

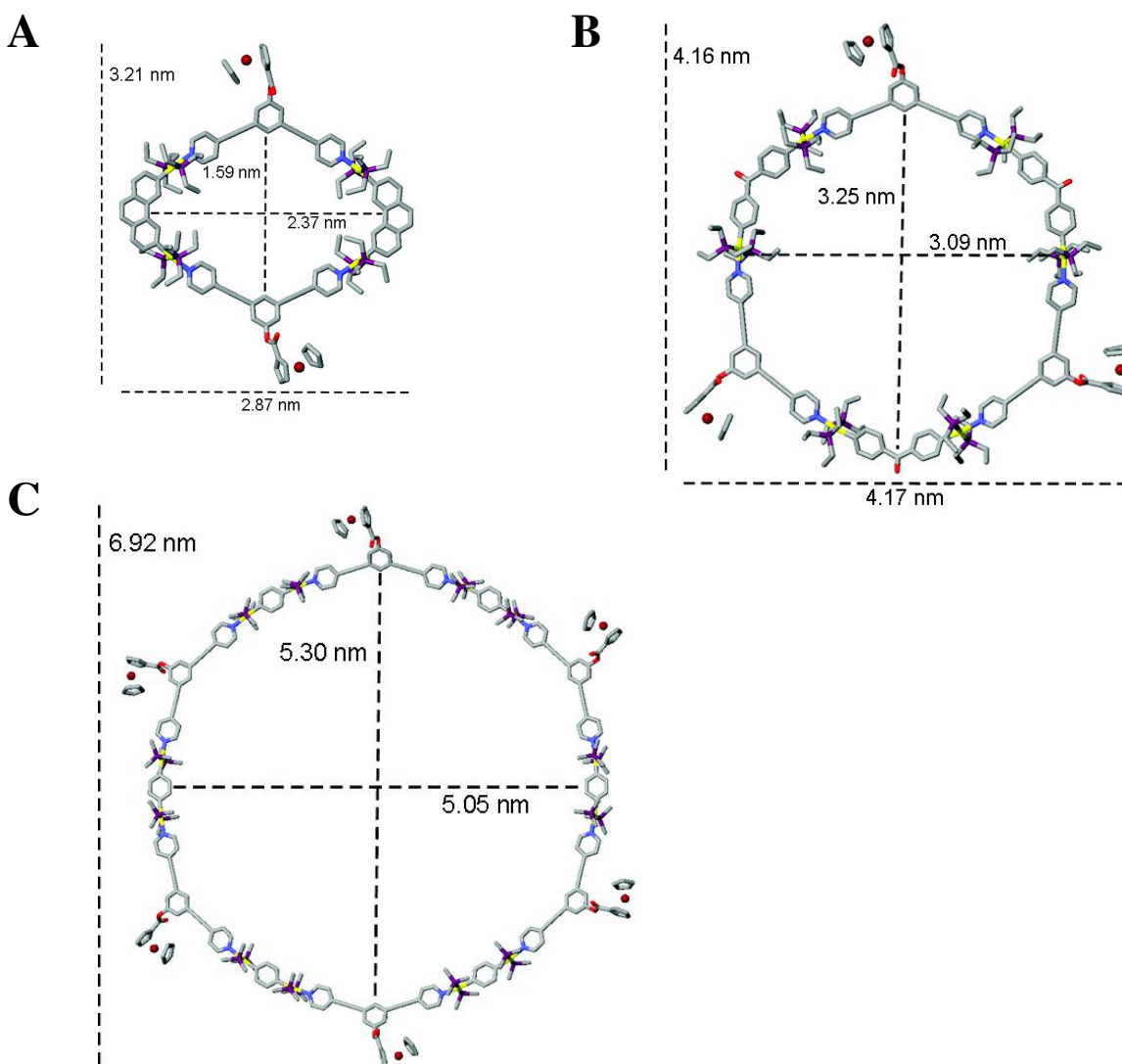


Figure S9. Simulated molecular model of rhomboid **5** (A), hexagon **6** (B), and hexagon **7** (C) optimized with the OPLS force-field. All other hydrogen atoms have been removed for clarity.

References:

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