

**Post-Self-Assembly Covalent Chemistry of Discrete Multicomponent**

**Metallosupramolecular Hexagonal Prisms**

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## Experimental Section

Hexakis-[4-(4-pyridylphenyl)]benzene **1** was prepared according to a reported method.<sup>1</sup> Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). NMR spectra were recorded on a Varian Unity 300 MHz spectrometer. <sup>1</sup>H NMR chemical shifts are reported relative to residual proteo solvent signals, and <sup>31</sup>P{<sup>1</sup>H} NMR chemical shifts are referenced to an external unlocked sample of 85% H<sub>3</sub>PO<sub>4</sub> (δ 0.0). Mass spectra for the self-assemblies were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system. Molecular modeling of tetragonal prisms was performed using the program Maestro v 8.0.110 with MMFF methods. Platinum was modeled using the force field of carbon restrained to have a planar geometry and typical platinum-nitrogen, platinum-oxygen, and platinum-phosphorus bond lengths. For the models of **10**, ferrocenes were replaced with cyclopentadiene groups.

**Synthesis and Characterization of (9-methylene anthracenyl)-1-ferrocenoate:** Ferrocene carboxylic acid (350 mg, 1.52 mmol), 9-anthracenemethanol (348 mg, 1.67 mmol), and 4-dimethylaminopyridine (40 mg, 0.33 mmol) were mixed in 30 mL of dry dichloromethane at 0 °C. To the mixed solution was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (320 mg, 1.67 mmol) gradually, and the resulting mixture stirred overnight at room temperature. After removing all solvents, the residue was purified by flash chromatography on silica gel (eluent: dichloromethane/hexane, v:v = 2:1) to afford (9-methylene anthracenyl)-1-ferrocenoate as reddish solid. Yield: 81%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298K, ppm) δ = 8.53, 8.02, 7.63, 7.51 (m, 9H, H<sub>anthracene</sub>), 6.29 (s, 2H, CH<sub>2</sub>O); 4.75, 4.30, 3.82 (s, 9H, ferrocene); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 298K, ppm) δ = 172.2, 131.7, 131.2, 129.4, 129.3, 127.2, 126.7, 125.4, 124.5, 71.6, 71.1, 70.4, 69.8, 58.9.

**Synthesis and Characterization of 5:** Hexakis-[4-(4-pyridylphenyl)]benzene **1** (1.24 mg, 1.25  $\mu\text{mol}$ ),  $(\text{PEt}_3)_2\text{Pt}(\text{OTf})_2$  **2** (5.49 mg, 7.50  $\mu\text{mol}$ ), and 5-amine-isophthalate **3** (0.84 mg, 3.75  $\mu\text{mol}$ ) were mixed in 0.9 mL of acetone/ $\text{H}_2\text{O}$  (v:v = 8:1), followed by 2 h of stirring at 70  $^\circ\text{C}$ . After removing all solvent *in vacuo*, the residue was redissolved in neat nitromethane-*d*3, which was followed by 3 h of stirring at 70  $^\circ\text{C}$ . Hexagonal prism **5** was isolable from the resulting colorless solution by removing the solvent *in vacuo*. Yield: 95%.  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.4 MHz, acetonitrile-*d*3, ppm):  $\delta = 6.73$  (d,  $^2J_{\text{P-P}} = 21.3\text{Hz}$ ,  $^{195}\text{Pt}$  satellites  $^1J_{\text{Pt-P}} = 3157\text{ Hz}$ ), 0.88 (d,  $^2J_{\text{P-P}} = 21.3\text{Hz}$ ,  $^{195}\text{Pt}$  satellites  $^1J_{\text{Pt-P}} = 3413\text{ Hz}$ );  $^1\text{H}$  NMR (300 MHz, acetonitrile-*d*3, ppm):  $\delta = 8.61$  (m, 24H,  $\text{H}_{\alpha\text{-Py}}$ ), 7.64 (m, 24H,  $\text{H}_{\beta\text{-Py}}$ ), 7.39, 7.21 (m, 48H, Ar-H), 7.19 (s, 6H,  $\text{H}_{2\text{-isophthalate}}$ ), 7.11 (s, 12H,  $\text{H}_{4,6\text{-isophthalate}}$ ), 4.25 (m, 12H, amine), 1.70 (m, 144H,  $\text{PCH}_2\text{CH}_3$ ), 1.18 (m, 216H,  $\text{PCH}_2\text{CH}_3$ ); ESI-MS for **5** ( $\text{C}_{348}\text{H}_{486}\text{F}_{36}\text{N}_{18}\text{O}_{60}\text{P}_{24}\text{Pt}_{12}\text{S}_{12}$ ): m/z: 2358.4  $[\text{M}-4\text{OTf}]^{4+}$ , 1856.7  $[\text{M}-5\text{OTf}]^{5+}$ , 1522.6  $[\text{M}-6\text{OTf}]^{6+}$ , 1157.8  $[\text{M}-7\text{OTf}]^{7+}$ , 1104.7  $[\text{M}-8\text{OTf}]^{8+}$ , 854.2  $[\text{M}-10\text{OTf}]^{10+}$ .

**Synthesis and Characterization of 6:** Hexakis-[4-(4-pyridylphenyl)]benzene **1** (0.87 mg, 0.87  $\mu\text{mol}$ ),  $(\text{PEt}_3)_2\text{Pt}(\text{OTf})_2$  **2** (3.82 mg, 5.23  $\mu\text{mol}$ ), and 5-maleimideisophthalate **4** (0.80 mg, 2.62  $\mu\text{mol}$ ) were mixed in 0.9 mL of acetone/ $\text{H}_2\text{O}$  (v:v = 8:1), followed by 2 h of stirring at 70  $^\circ\text{C}$ . After moving all solvent *in vacuo*, the residue was redissolved in neat nitromethane-*d*3, which was followed by 3 h of stirring at 70  $^\circ\text{C}$ . Hexagonal prism **6** was isolable from the resulting colorless solution by removing the solvent *in vacuo*. Yield: 90%.  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.4 MHz, acetonitrile-*d*3, ppm):  $\delta = 6.57$  (d,  $^2J_{\text{P-P}} = 21.5\text{Hz}$ ,  $^{195}\text{Pt}$  satellites  $^1J_{\text{Pt-P}} = 3179\text{ Hz}$ ), 1.07 (d,  $^2J_{\text{P-P}} = 21.6\text{Hz}$ ,  $^{195}\text{Pt}$  satellites  $^1J_{\text{Pt-P}} = 3475\text{ Hz}$ );  $^1\text{H}$  NMR (300 MHz, acetonitrile-*d*3, ppm):  $\delta = 8.57$  (m, 24H,  $\text{H}_{\alpha\text{-Py}}$ ), 7.87 (m, 6H,  $\text{H}_{2\text{-isophthalate}}$ ), 7.81 (m, 12H,  $\text{H}_{4,6\text{-isophthalate}}$ ), 7.62 (m, 24H,  $\text{H}_{\beta\text{-Py}}$ ), 7.37 (d, 24H,  $J = 8.3\text{ Hz}$  Ar-H), 7.16 (d, 24H,  $J = 8.3\text{ Hz}$  Ar-H), 6.92 (s, 12H, maleimide-olefin), 1.88-1.70 (m, 144H,  $\text{PCH}_2\text{CH}_3$ ), 1.24-1.02 (m, 216H,  $\text{PCH}_2\text{CH}_3$ ); ESI-MS for **6** ( $\text{C}_{372}\text{H}_{486}\text{F}_{36}\text{N}_{18}\text{O}_{72}\text{P}_{24}\text{Pt}_{12}\text{S}_{12}$ ): m/z: 2478.8  $[\text{M}-4\text{OTf}]^{4+}$ , 1952.7  $[\text{M}-5\text{OTf}]^{5+}$ , 1602.4  $[\text{M}-6\text{OTf}]^{6+}$ , 1164.7  $[\text{M}-8\text{OTf}]^{8+}$ , 902.0  $[\text{M}-10\text{OTf}]^{10+}$ .

**General procedure for the covalent post-modification of 5:** Hexagonal prism **5** (6.0 mg, 0.59  $\mu\text{mol}$ ) and isocyanate or maleic anhydride was mixed in a 1:10 ratio in a nitromethane-*d*3 solution, followed by 12 h of stirring at 90 °C. Then all solvent was removed *in vacuo*, the residue was redissolved in neat acetone and precipitated with diethyl ether to afford post-modified hexagonal prisms **7-9**.

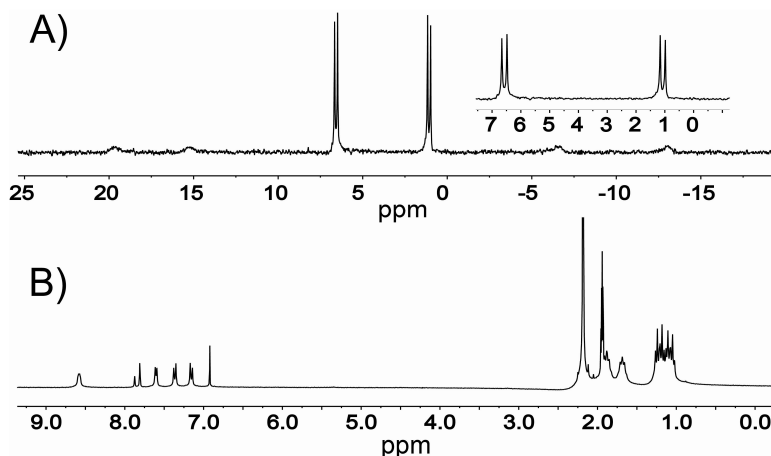
**Synthesis and Characterization of 7:** Yield: 73%.  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.4 MHz, acetonitrile-*d*3, ppm):  $\delta = 6.74$  (d,  $^2J_{\text{P-P}} = 21.5\text{Hz}$ ,  $^{195}\text{Pt}$  satellites  $^1J_{\text{Pt-P}} = 3200$  Hz), 0.95 (d,  $^2J_{\text{P-P}} = 21.5\text{Hz}$ ,  $^{195}\text{Pt}$  satellites  $^1J_{\text{Pt-P}} = 3464$  Hz);  $^1\text{H}$  NMR (300 MHz, acetonitrile-*d*3, ppm):  $\delta = 8.62$  (m, 24H,  $\text{H}_{\alpha\text{-Py}}$ ), 8.49 (m, 6H,  $\text{H}_{\text{urea}}$ ), 7.92 (s, 12H,  $\text{H}_{4,6\text{-isophthalate}}$ ), 7.64 (m, 24H,  $\text{H}_{\beta\text{-Py}}$ ), 7.52 (s, 6H,  $\text{H}_{2\text{-isophthalate}}$ ), 7.41, 7.19 (m, 48 H, Ar-H), 5.91 (m, 6H,  $\text{CH}=\text{CH}_2$ ), 5.54 (m, 6H,  $\text{H}_{\text{urea}}$ ), 5.18 (m, 12H,  $\text{CH}=\text{CH}_2$ ), 3.79 (m, 12H,  $\text{CH}_2\text{CH}=\text{CH}_2$ ), 1.89 (m, 144H,  $\text{PCH}_2\text{CH}_3$ ), 1.16 (m, 216H,  $\text{PCH}_2\text{CH}_3$ ); ESI-MS for **7** ( $\text{C}_{372}\text{H}_{516}\text{F}_{36}\text{N}_{24}\text{O}_{66}\text{P}_{24}\text{Pt}_{12}\text{S}_{12}$ ): 2482.6  $[\text{M}-4\text{OTf}]^{4+}$ , 1956.3  $[\text{M}-5\text{OTf}]^{5+}$ , 1605.4  $[\text{M}-6\text{OTf}]^{6+}$ , 1166.7  $[\text{M}-8\text{OTf}]^{8+}$ , 808.5  $[\text{M}-11\text{OTf}]^{11+}$ .

**Synthesis and Characterization of 8:** Yield: 71%.  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.4 MHz, acetonitrile-*d*3, ppm):  $\delta = 6.75$  (d,  $^2J_{\text{P-P}} = 21.5\text{Hz}$ ,  $^{195}\text{Pt}$  satellites  $^1J_{\text{Pt-P}} = 3198$  Hz), 0.94 (d,  $^2J_{\text{P-P}} = 21.5\text{Hz}$ ,  $^{195}\text{Pt}$  satellites  $^1J_{\text{Pt-P}} = 3418$  Hz);  $^1\text{H}$  NMR (300 MHz, acetonitrile-*d*3, ppm):  $\delta = 8.61$  (m, 24H,  $\text{H}_{\alpha\text{-Py}}$ ), 8.49 (m, 6H,  $\text{H}_{\text{urea}}$ ), 7.91 (s, 12H,  $\text{H}_{4,6\text{-isophthalate}}$ ), 7.64 (m, 24H,  $\text{H}_{\beta\text{-Py}}$ ), 7.50 (s, 6H,  $\text{H}_{2\text{-isophthalate}}$ ), 7.41, 7.19 (m, 48H, Ar-H), 5.41 (m, 6H,  $\text{H}_{\text{urea}}$ ), 3.20 (m, 12H,  $\text{NHCH}_2\text{CH}_3$ ), 1.88 (m, 144H,  $\text{PCH}_2\text{CH}_3$ ), 1.15 (m, 216H,  $\text{PCH}_2\text{CH}_3$ ); ESI-MS for **8** ( $\text{C}_{366}\text{H}_{516}\text{F}_{36}\text{N}_{24}\text{O}_{66}\text{P}_{24}\text{Pt}_{12}\text{S}_{12}$ ): 2456.2  $[\text{M}-4\text{OTf}]^{4+}$ , 1942.4  $[\text{M}-5\text{OTf}]^{5+}$ , 1593.5  $[\text{M}-6\text{OTf}]^{6+}$ , 1012.7  $[\text{M}-9\text{OTf}]^{9+}$ .

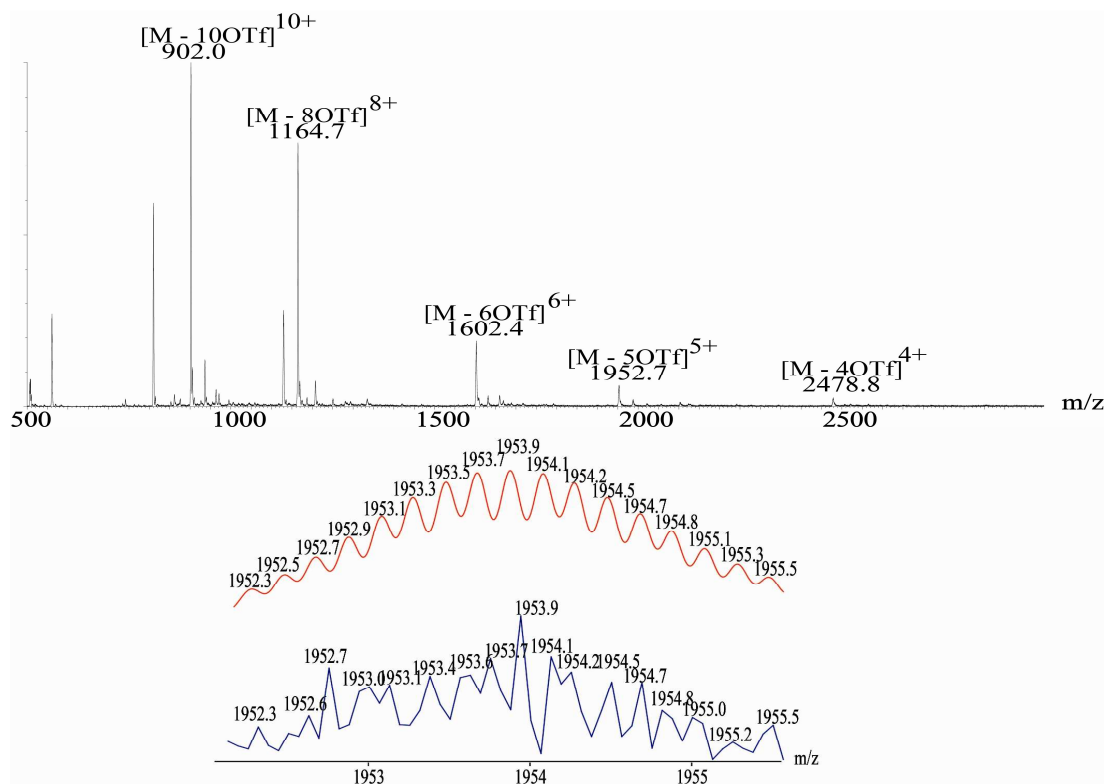
**Synthesis and Characterization of 9:** Yield: 78%.  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.4 MHz, acetonitrile-*d*3, ppm):  $\delta = 6.75$  (d,  $^2J_{\text{P-P}} = 21.5\text{Hz}$ ,  $^{195}\text{Pt}$  satellites  $^1J_{\text{Pt-P}} = 3209$  Hz), 1.16 (d,  $^2J_{\text{P-P}} = 21.5\text{Hz}$ ,  $^{195}\text{Pt}$  satellites  $^1J_{\text{Pt-P}} = 345$  Hz);  $^1\text{H}$  NMR (300 MHz, acetonitrile-*d*3, ppm):  $\delta = 9.69$  (s, 6H, amide), 8.62 (m, 16H,  $\text{H}_{\alpha\text{-Py}}$ ), 8.16 (s, 12H,  $\text{H}_{4,6\text{-isophthalate}}$ ), 7.75 (s, 6H,  $\text{H}_{2\text{-isophthalate}}$ ), 7.62 (m, 16H,  $\text{H}_{\beta\text{-Py}}$ ), 7.38, 7.18 (m,

32H, Ar-H), 6.63, 6.40 (d, 12H, olefin), 1.78 (m, 144H, PCH<sub>2</sub>CH<sub>3</sub>), 1.21 (m, 216H, PCH<sub>2</sub>CH<sub>3</sub>); ESI-MS for **9** (C<sub>372</sub>H<sub>498</sub>F<sub>36</sub>N<sub>18</sub>O<sub>78</sub>P<sub>24</sub>Pt<sub>12</sub>S<sub>12</sub>): 2505.1[M-4OTf]<sup>4+</sup>, 1974.4 [M-5OTf]<sup>5+</sup>, 1620.4 [M-6OTf]<sup>6+</sup>, 1178.1 [M-8OTf]<sup>8+</sup>.

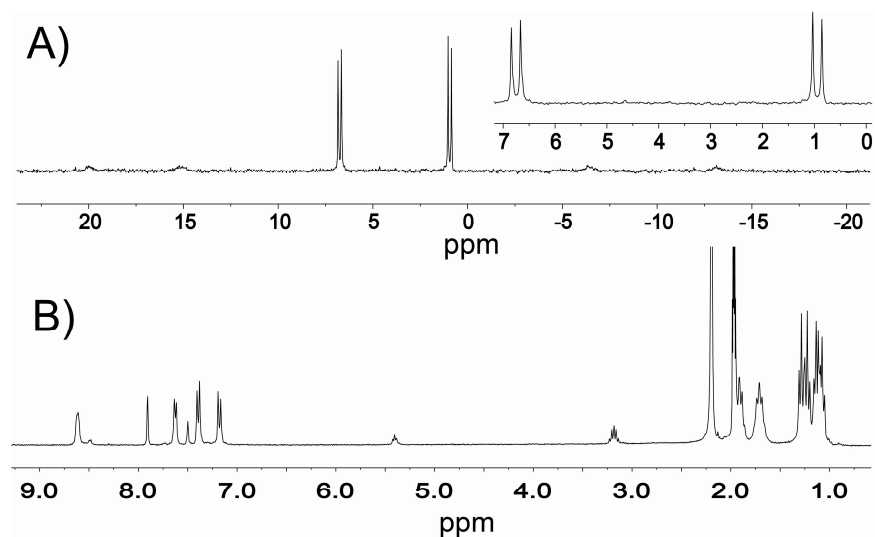
**Synthesis and Characterization of 10:** Hexagonal prism **6** (6.0 mg, 0.59 μmol) and (9-methylene anthracenyl)-1-ferrocenoate was mixed in a nitromethane-*d*<sub>3</sub> solution, followed by 12 h of stirring at 90 °C. Then, all solvent was removed *in vacuo* and the residue was redissolved in neat acetone and precipitated with diethyl ether to afford post-modified hexagonal prisms **10** in a 75% yield. <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, acetonitrile-*d*<sub>3</sub>, ppm): δ = 6.51 (d, <sup>2</sup>J<sub>P-P</sub> = 21.5 Hz, <sup>195</sup>Pt<sub>satellites</sub> <sup>1</sup>J<sub>Pt-P</sub> = 3205 Hz), 1.13 (d, <sup>2</sup>J<sub>P-P</sub> = 21.5 Hz, <sup>195</sup>Pt<sub>satellites</sub> <sup>1</sup>J<sub>Pt-P</sub> = 3456 Hz); <sup>1</sup>H NMR (300 MHz, acetonitrile-*d*<sub>3</sub>, ppm): δ = 8.49 (m, 24H, H<sub>α-Py</sub>), 7.81 (m, 6H, H<sub>2-isophthalate</sub>), 7.56 (m, 36H, H<sub>4,6-isophthalate</sub>, H<sub>β-Py</sub>), 7.36, 7.06 (m, 72H, cycloadduct of anthracene and Ar-H), 7.19 (d, 24H, Ar-H), 5.59 (m, 12H, OCH<sub>2</sub>-anthracene), 4.92 (m, 6H, anthracene-H<sub>9</sub>), 4.83-4.36 (m, 54H, ferrocene), 3.59 (m, 12H, cycloadducts of maleimide), 1.86-1.69 (m, 144H, PCH<sub>2</sub>CH<sub>3</sub>), 1.27-1.02 (m, 216H, PCH<sub>2</sub>CH<sub>3</sub>); ESI-MS for **10** (C<sub>528</sub>H<sub>606</sub>F<sub>36</sub>Fe<sub>6</sub>N<sub>18</sub>O<sub>84</sub>P<sub>24</sub>Pt<sub>12</sub>S<sub>12</sub>): m/z: 2456.8[M-5OTf]<sup>5+</sup>, 2022.5 [M-6OTf]<sup>6+</sup>, 1479.7[M-8OTf]<sup>8+</sup>, 1154.0 [M-10OTf]<sup>10+</sup>, 936.8 [M-12OTf]<sup>12+</sup>



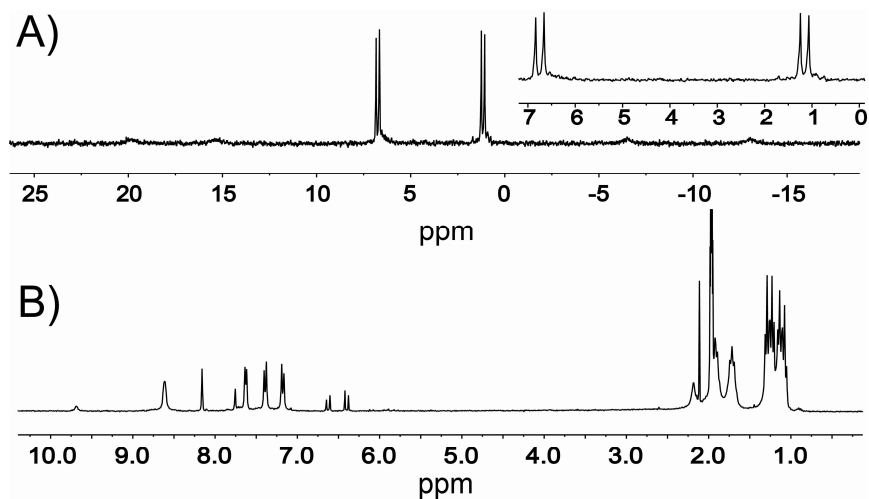
**Figure S1.** <sup>31</sup>P{<sup>1</sup>H} NMR (A, 122.14 MHz, 298 K) and <sup>1</sup>H NMR (B, 300 MHz, 298 K) spectra of hexagonal prisms **6** in acetonitrile-*d*<sub>3</sub>.



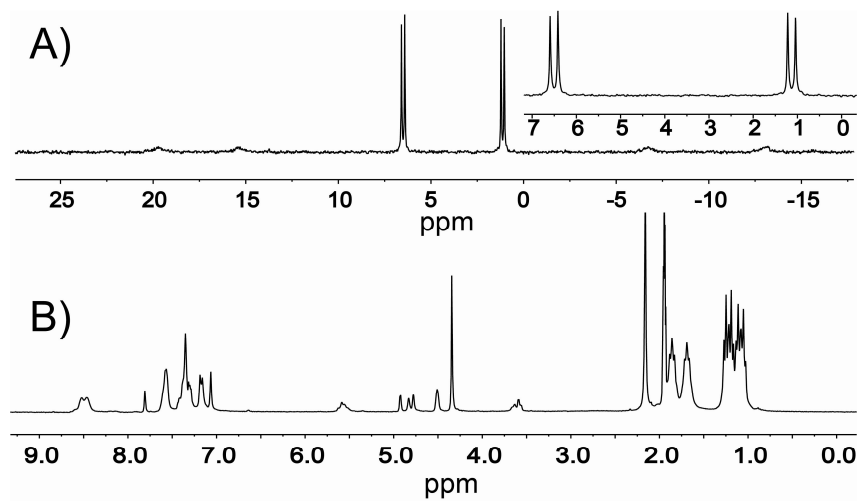
**Figure S2.** ESI-MS spectra of hexagonal prism **6**: *top*) full MS spectra of **6**; *bottom*) calculated (red) and experimental (blue) mass spectra corresponding to the  $[M-5OTf]^{5+}$  peak of **6**.



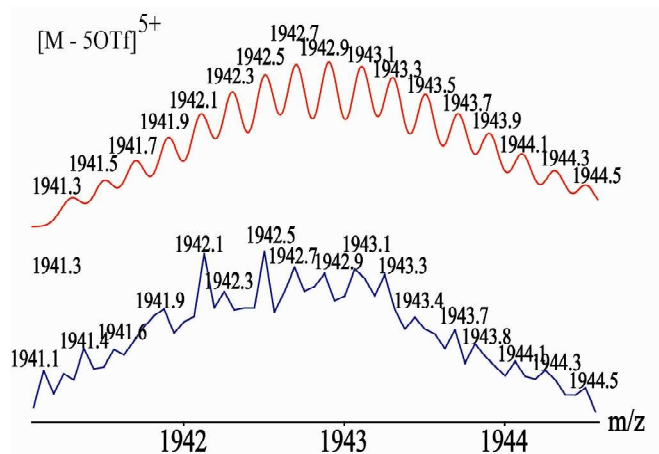
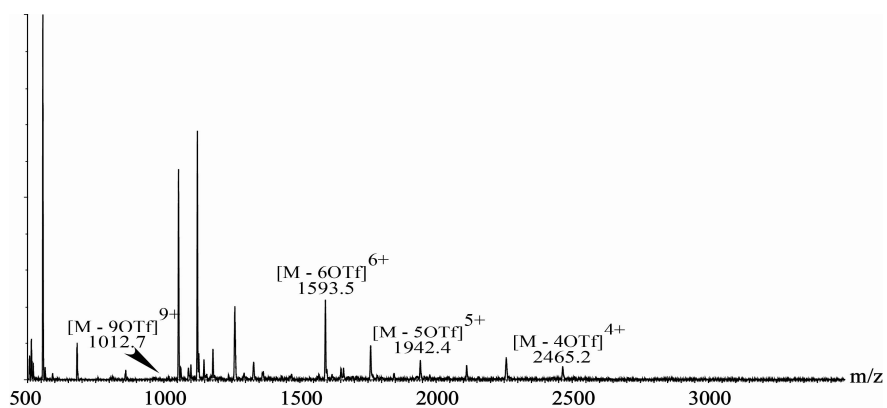
**Figure S3.**  $^{31}P\{^1H\}$  NMR (A, 122.14 MHz, 298 K) and  $^1H$  NMR (B, 300 MHz, 298 K) spectra of hexagonal prisms **8** in acetonitrile- $d_3$ .



**Figure S4.** <sup>31</sup>P{<sup>1</sup>H} NMR (A, 122.14 MHz, 298 K) and <sup>1</sup>H NMR (B, 300 MHz, 298 K) spectra of hexagonal prisms **9** in acetonitrile-*d*<sub>3</sub>.

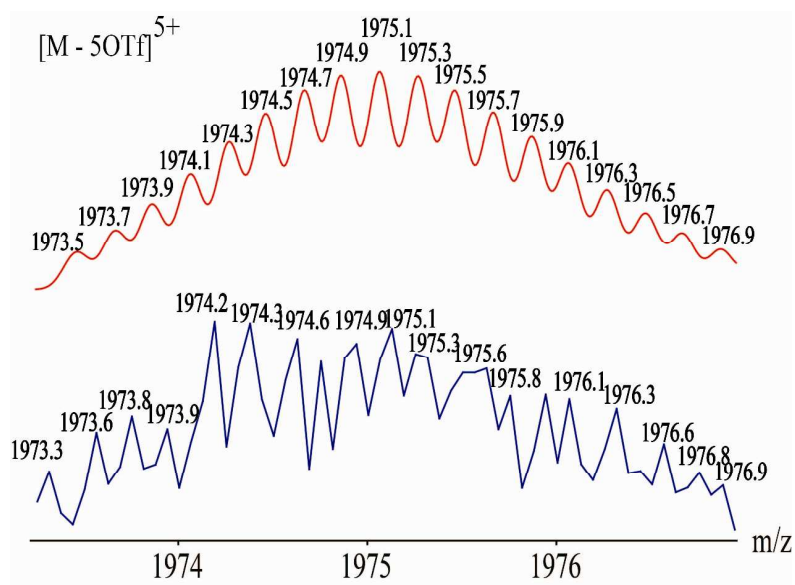
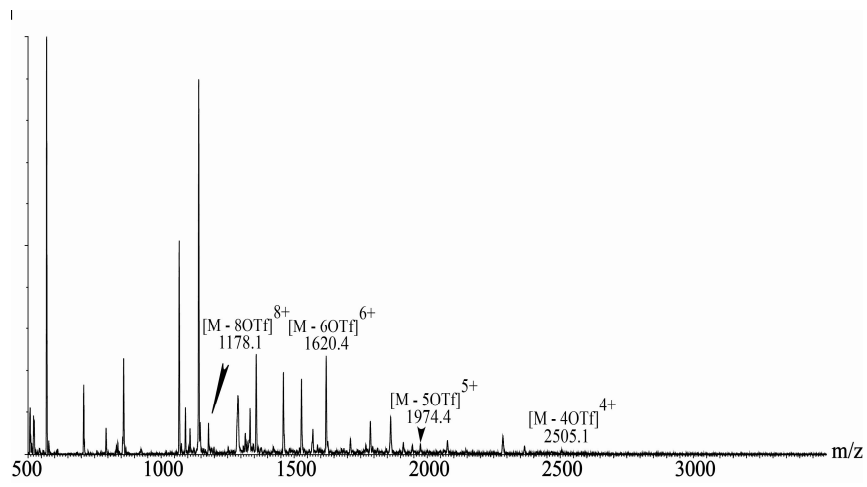


**Figure S5.** <sup>31</sup>P{<sup>1</sup>H} NMR (A, 122.14 MHz, 298 K) and <sup>1</sup>H NMR (B, 300 MHz, 298 K) spectra of hexagonal prisms **10** in acetonitrile-*d*<sub>3</sub>.

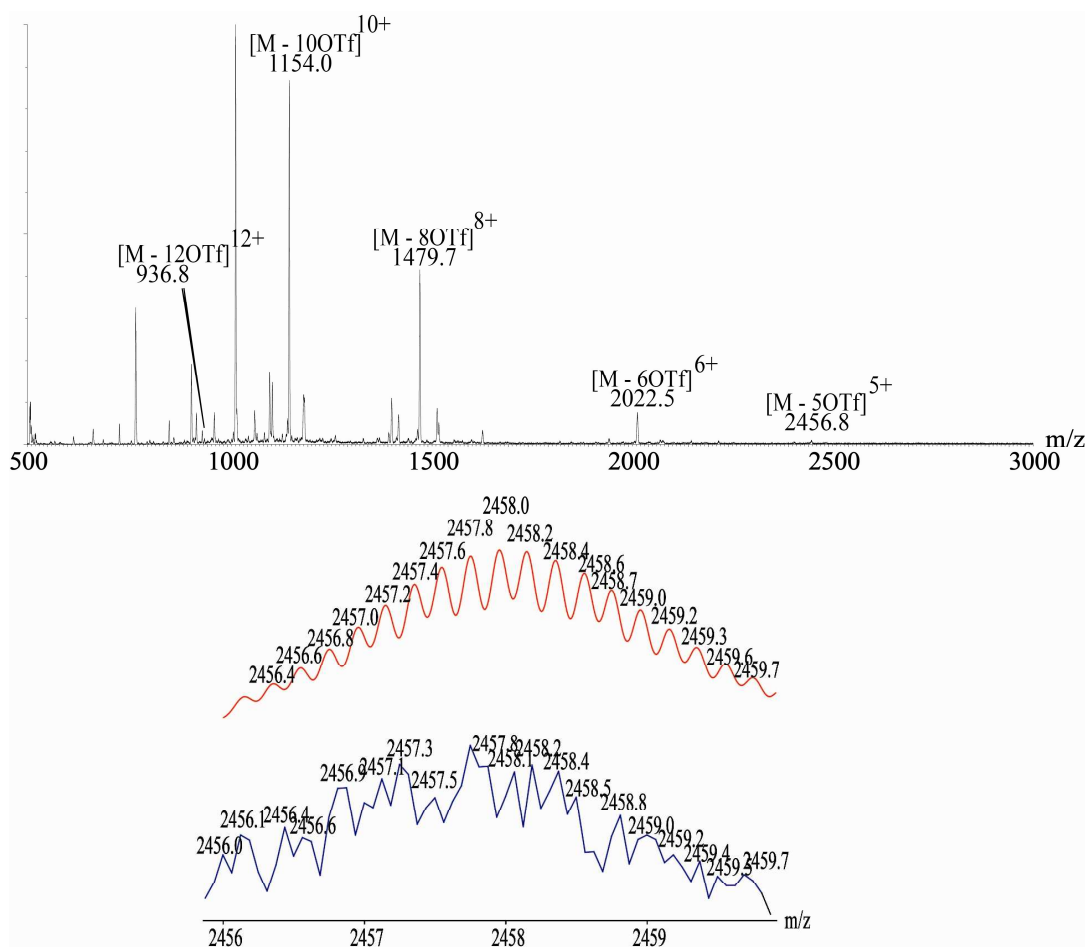


**Figure S6.** ESI-MS spectra of **8**: *top*) Full spectrum; *bottom*) Theoretical (*red*) and experimental (*blue*) mass spectra corresponding to the  $[M - 5OTf]^{5+}$  peak of **8**.





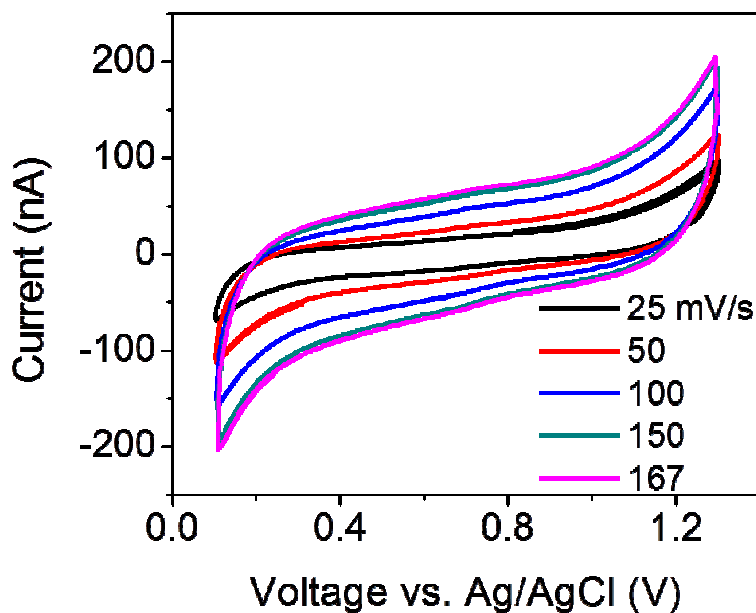
**Figure S7.** ESI-MS spectra of **9**: *top*) Full spectrum; *bottom*) Theoretical (*red*) and experimental (*blue*) mass spectra corresponding to the  $[M - 5OTf]^{5+}$  peak of **9**.



**Figure S8.** ESI-MS spectra of **10**: *top*) Full spectrum; *bottom*) Theoretical (*red*) and experimental (*blue*) mass spectra corresponding to the  $[M-5OTf]^{5+}$  peak of **10**.

## Cyclic Voltammetry.

Cyclic voltammetry (CV) was performed in a Faraday cage using a 3-electrode cell and a potentiostat (Pine Instrument Co., RDE3) interfaced to a computer through a PCI 6251 data acquisition board (National Instruments) for potential and current measurements. Voltammetric data were recorded using in-house virtual instrumentation written in LabVIEW 8.0 (National Instrument). The working electrode was a Pt disk embedded in glass with surface area of  $\sim 0.5 \text{ mm}^2$ . A Ag/AgCl electrode was used as the reference electrode, and a Pt wire was used as the counter.



**Figure S9.** Cyclic voltammetry of **6** at different scan rates (25-167 mV/s) at a  $\sim 0.5 \text{ mm}^2$  Pt electrode. Solution: 0.2 mM **6** in acetonitrile containing 0.1 M *n*-BuN<sub>4</sub>PF<sub>6</sub>.

## Steady-State Electrochemical Measurements.

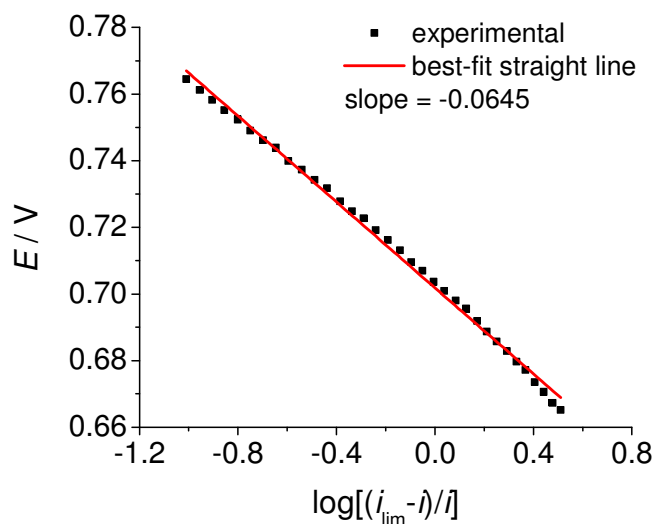
Steady-state voltammetric measurements were made in the same solution, but with a two electrode compartment using a 25- $\mu\text{m}$ -diameter Pt disk as the working and a Ag/AgCl electrode as the counter and reference. A Dagan Cornerstone Chem-Clamp potentiostat was also used in combination with RDE3. The area of Pt electrode was measured by voltammetric measurement in a 5.0 mM ferrocene acetonitrile solution containing 0.1 M  $n\text{-BuN}_4\text{PF}_6$ .

The limiting current for electroactive compound **10**:<sup>2</sup>

$$i_{\text{lim}} = 4nFDca\theta_{\text{sites}} \quad (\text{SI1})$$

where  $n$  is the number of electrons transferred per ferrocene ( $= 1$ ),  $F$  is the Faraday constant,  $D$  is the diffusion coefficient,  $c$  is the bulk concentration,  $a$  is the electrode radius, and  $\theta_{\text{sites}}$  is the number of ferrocenyl sites, respectively.

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.  $E$ .<sup>2</sup>



**Figure S10.** Plot of  $\log[(i_{\text{lim}}-i)/i]$  vs.  $E$  from the steady-state voltammetric response.

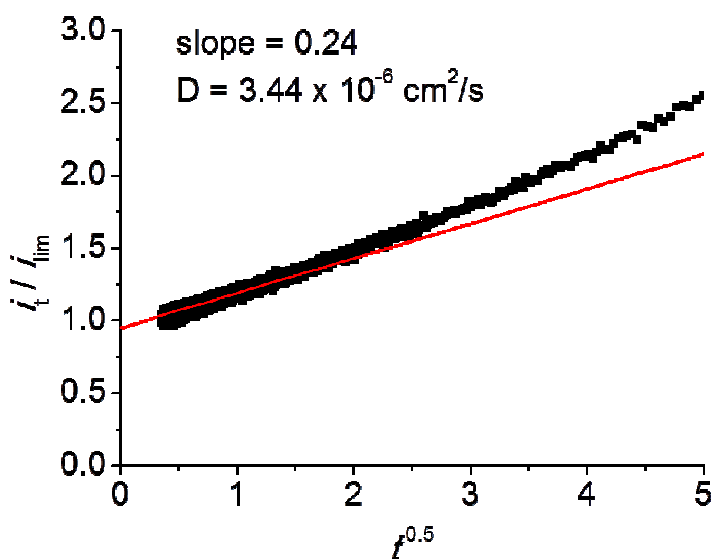
## Chronoamperometry Measurements

Chronoamperometry was performed by stepping the electrode potential from a non-reaction value to a diffusion-limited value.

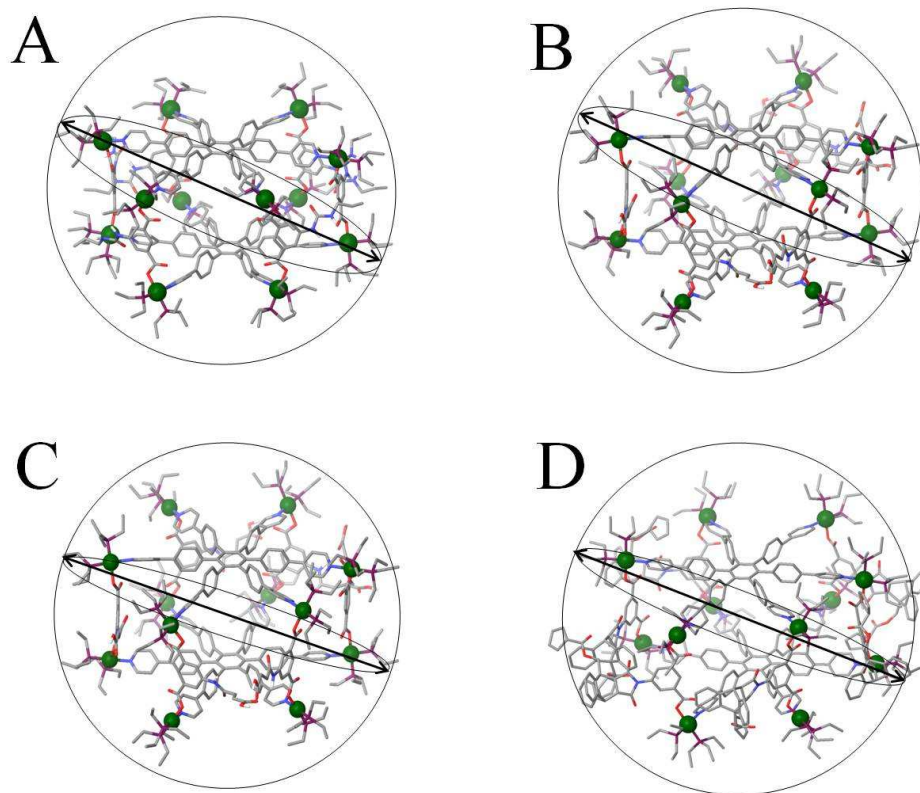
The normalized time-dependent current can be expressed as<sup>3</sup>:

$$\frac{i_t}{i_{\text{lim}}} = 1 + \frac{2}{\pi^{1.5}} a(Dt)^{-0.5} \quad (\text{SI2})$$

Thus, by plotting  $i_t/i_{\text{lim}}$  vs  $t^{0.5}$ ,  $D$  can be evaluated from the slope when  $a$  is known. This method was applied on ferrocene and the calculated  $\theta_{\text{sites}}$  of ferrocene is very close to 1. Figure S11 shows one example of  $i_t/i_{\text{lim}}$  vs  $t^{0.5}$  plots. The fitted slope value is 0.24.  $D$  is then calculated from eq SI2, and  $\theta_{\text{sites}}$  can be further obtained by eq SI1.



**Figure S11.** Plot of the experimental ratio  $i_t/i_{\text{lim}}$  vs.  $t^{0.5}$  for the oxidation of **10** in acetonitrile containing 0.1 M  $n\text{-BuN}_4\text{PF}_6$  using a 25- $\mu\text{m}$ -diameter Pt disk electrode.



**Figure S12.** Molecular modeling of hexagonal prisms **6, 8-10 (A-D)**.

## Reference

1. Zhao, Z.; Zheng, Y.-R.; Wang, M.; Pollock, J. B.; Stang, P. J. *Inorg. Chem.* **2010**, *49*, 8653.
2. Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; 2nd ed.; John Wiley & Sons: New York, 2001.
3. (a) Denault, G.; Mirkin, M.; Bard, A. J. *J. Electroanal. Chem.* **1991**, *308*, 27. (b) Biondi, C.; Bellugi, L. *J. Electroanal. Chem.* **1970**, *24*, 263. (c) Amatore, C.; Azzali, M.; Calas, P.; Jutand, A.; Lefrou, C.; Rollin, Y. *J. Electroanal. Chem.* **1990**, *288*, 45. (d) Mirkin, M. V.; Nilov, A. P. *J. Electroanal. Chem.* **1990**, *283*, 35. (e) Nowinski, S. A.; Anjo, D. M. *J. Chem. Eng. Data* **1989**, *34*, 265.