Published in final edited form as:

J Org Chem. 2008 November 7; 73(21): 8553–8557. doi:10.1021/jo801692v.

Synthesis of a New Family of Hexakisferrocenyl Hexagons and Their Electrochemical Behavior

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Abstract

The design and synthesis of two new hexakisferrocenyl hexagons has been achieved via coordination-driven self-assembly wherein the size and relative distribution of six ferrocene moieties has been precisely controlled. Insight into the structure and electronic properties of these supramolecules was obtained through electrochemical studies.

Introduction

Many naturally occurring systems are observed to exhibit a high degree of symmetry in their patterns, shapes, and general architecture. It is often the case, whether intentionally or accidentally, that unnatural, synthetic systems similarly express architectural symmetries that mirror those of nature. Hexagons, for example, are prevalent throughout nature such as in the honeycomb structure of a beehive or the micrograph of a snowflake.¹ Likewise, in carbon based chemistry, hexagonal shaped structures are familiar from benzene to graphite, polycyclic aromatic hydrocarbons, nanotubes, and fullerenes.² In the last decade we have used coordination driven self-assembly via the directional bonding approach to build supramolecular hexagonal metallacycles by combining appropriately chosen acceptor and donor units in a controllable manner.³ According to the “molecular library” and “symmetry interaction” models,⁴ discrete hexagonal entities of the type $A_6^2L_6^2$ can be rationally assembled via the combination of six shape-defining and directing corner units A^2 (offering two coordination sites oriented 120° from each other) with six complementary linear units L^2 . An alternative route⁵ for the assembly of hexagonal systems involves the combination of two complementary ditopic building blocks A^2 and X^2 , wherein coordination sites of each building-block are oriented at a 120° angle, allowing for the construction of hexagonal systems of the type $A_3^2X_3^2$.

With the goal of incorporating materials properties into such hexagons we have designed 120° building-blocks functionalized with dendrimer, crown ether, and ferrocene moieties, from which various multifunctional hexagons have been prepared via coordination-driven self-assembly.⁶ In each case the underlying rigid supramolecular hexagons have proven to act as well-defined scaffolds upon which the various functional groups can be attached through covalent bonds. Furthermore, metal acceptors and organic donors are mixed in precise stoichiometric ratios allowing for unambiguous control over the exact number of functional groups appended to a given supramolecular assembly. These desirable aspects of functional group control are augmented, synthetically, by the very process of using coordination-driven self-assembly, which significantly reduces synthetic costs.

The design and synthesis of macromolecules that contain multiple redox-addressable centers has attracted considerable attention over the past few decades given the potential of such systems for use as electroluminescent, information storage, and photochemical devices.⁷ Ferrocene – a stable, well-studied, and readily oxidizable organometallic subunit – has been extensively employed in the construction of molecular and supramolecular architectures that possess desirable magnetic, optical, and electrochemical properties.⁸ To date, much of the effort put forth in the design and synthesis of multiferrocenyl systems has been devoted to the preparation of ferrocene-functionalized dendrimers and polymers.⁹ Utilizing traditional covalent strategies to prepare functionalized dendritic and polymeric architectures, however, often requires considerable synthetic effort and results in relatively unsatisfactory yields. In addition, dendritic and polymeric macromolecules often possess large, flexible, and/or globular structures that are not well-defined, potentially limiting their use in a materials setting. Recently, the implementation of coordination bonds¹⁰ in the synthesis of multiferrocenyl complexes, especially hexakisferrocenyl systems,¹¹ has been explored and has proven to be a highly efficient approach to the construction of such architectures. Nevertheless, it is still a challenge to design and synthesize well-defined hexakisferrocenyl compounds while exhibiting precise control over the location of incorporated ferrocene moieties.

We have shown that the combination of 120° ferrocenyl donor precursor **1** (Figure 1) with 180° di-Pt acceptor units in a ratio of 1:1 gives rise to hexakisferrocenyl hexagon with precise control over the size (5.3 nm) and distribution of the ferrocene moieties.^{6d} In an extension to our earlier studies, a new ferrocenyl 120° di-Pt(II) acceptor building block has been designed and prepared, from which a novel family of hexakisferrocenyl hexagons can be constructed via two alternative methods. Additionally the structural and electrochemical behavior of two hexakisferrocenyl assemblies is discussed.

Results and Discussions

Synthesis of 120° Ferrocenyl di-Pt(II) Acceptor

The 120° ferrocenyl di-Pt(II) acceptor **2** can be synthesized as indicated in Scheme 1. The redox-active ferrocene moiety was introduced by a coupling reaction of **3** with ferrocene carboxylic acid. Compound **4** was then reacted with an excess of *trans*-PtI₂(Et₃)₂ to give diiodo metal complex **5**. Subsequent halogen abstraction with AgOTf resulted in the isolation of bistriflate salt **2** in 58% overall yield. The ³¹P {¹H} NMR spectrum of diplatinum acceptor **2** displayed a singlet at 22.7 ppm, accompanied by flanking ¹⁹⁵Pt satellites. Unfortunately, all attempts to grow single crystals for X-ray diffraction studies of **2** have proven unsuccessful to date; therefore the distance between the two platinum centers of **2** was estimated using molecular modeling force field (OPLS) simulations and shown to be ~1.0 nm (See Supporting Information). It is worth noting that the new ferrocenyl 120° di-Pt(II) acceptor is a heterobimetallic compound with two Pt(II) centers, which can coordinate a variety of donor ligands, as well as a redox addressable ferrocene moiety.

Self-assembly of Hexakisferrocenyl Hexagons

Preparation of a hexakisferrocene assembly via Method A (Scheme 2) utilizes three 120° donor units (**1**) and three 120° acceptor units (**2**), from which the [3+3] hexagon **6** can be self-assembled. Stirring a mixture of acceptor and donor precursors in a 1:1 ratio in CD₂Cl₂ for 30 min resulted in a homogeneous clear orange solution. Analysis of the reaction solution using ³¹P {¹H} NMR spectroscopy (Figure 2B) shows a single peak at 16.4 ppm, consistent with the formation of highly symmetric species, shifted upfield by $\Delta J = -6.3$ ppm relative to **2**. The ¹H NMR spectrum (Figure 3C) displays significant downfield shifts of the pyridyl signals ($\Delta\delta = 0.05$ and 0.43 ppm for α and β protons, respectively), which are associated with the loss of electron density upon coordination by the nitrogen lone pair to platinum metal centers. ESI mass spectra exhibited two charge states at $m/z = 1366.8$ and $m/z = 1063.6$, corresponding to [M-4OTf]⁴⁺ and [M-5OTf]⁵⁺ (See Supporting Information). These peaks were isotopically resolved, and they agree well with the theoretical distribution.

An alternative self-assembly protocol (Scheme 2, Method B) calls for the combination of six 120° angular acceptors and six 180° linear building blocks. The combination of 120° ferrocene derivatized acceptor **2** and 180° donor 4,4'-bipyridyl **7** in a 1:1 ratio results in a homogeneous orange solution. Multinuclear NMR (¹H and ³¹P {¹H}) analysis (Figure 2C and 3E) of the reaction mixture revealed the formation of a single, discrete, highly symmetric species. The ³¹P {¹H} NMR spectra of **8** displayed a sharp singlet (16.3 ppm) shifted upfield from the starting platinum acceptor **2** by approximately 6.4 ppm. In the ¹H NMR spectrum of **8**, only one sharp set of peaks was found and the signals display characteristic shifts associated with Pt(II)-pyridyl metal-ligand coordination. This observation, as well as the significant downfield shifts of the pyridyl proton signals (for α proton, $\Delta\delta = 0.10$ ppm; for β proton, $\Delta\delta = 0.94$ ppm) supports the efficient self-assembly of the hexakisferrocenyl hexagon **8**. ESI mass spectra provide further evidence for the formation of the new hexakisferrocenyl complex. Two peaks at $m/z = 2353.4$ and $m/z = 1852.9$, attributable to [M-4OTf]⁴⁺ and [M-5OTf]⁵⁺, respectively, were observed and their isotopic patterns are in good agreement with the theoretical distributions (See Supporting Information).

Molecular Force-field Study

All attempts to grow X-ray quality single crystals of hexaferrocenyl complexes have so far been unsuccessful. Therefore, molecular force-field simulations were used to gain further insight into the structural characteristics of assemblies **6** and **8**. A 1.0 ns molecular dynamics simulation (OPLS force field) was used to equilibrate supramolecules **6** and **8**, followed by energy minimization of the resulting structures to full convergence. The model structures of both hexakisferrocenyl hexagons **6** and **8** feature well-defined cavities with approximate cavity sizes of 3.0 nm and 4.6 nm respectively (Figure 4). In addition to the previously reported^{6d} hexakisferrocenyl complexes these methods provide three different means to introduce six ferrocene units onto the periphery of a molecular hexagon as well as a direct means of varying the cavity size of these multi-redox active complexes while retaining the efficiency of coordination-driven self-assembly.

Electrochemical Study of Hexakisferrocenyl Hexagons

Electrochemical oxidation of hexakisferrocenyl complexes **6** and **8** was performed at a 0.009 cm² Pt electrode (0.2 mM in CH₂Cl₂, 0.15 M *n*-Bu₄NPF₆ supporting electrolyte). The cyclic voltammograms of all complexes, obtained at various scan rates (Figure 5), showed cathodic/anodic peak current ratios of $i_c/i_a \approx 1$, indicating that the oxidized complexes are chemically stable on the voltammetric timescale. The potential difference between the anodic and cathodic peak potentials (ΔE_p) was found to be 108 mV, larger than the theoretical value for a reversible redox system (59 mV).¹² The large non-ideal ΔE_p values are partially due to the large ohmic resistance of the CH₂Cl₂ solution. Previous electrochemical studies revealed that this family

of multiferrocenyl complexes lacks strong intramolecular electronic coupling between ferrocene groups, i.e., the multiple ferrocene groups react independently, producing a single voltammetric wave, although more than one electron is transferred in the overall reaction. In addition to the peak splitting due to ohmic resistance, the statistical nature of the multielectron transfer process causes the voltammetric peak to broaden as well.^{13, 14} The half-wave potentials, $E_{1/2}$, measured from the average of voltammetric waves are presented in Table 1.

Quantitative evaluation of the voltammograms provides an estimation of the diffusion coefficient (D) of ferrocene as well as complexes **6** and **8**.¹³ Diffusion coefficients were calculated from the peak current values recorded at different scan rates (See supporting information for details) and are summarized in Table 1. The measured value for ferrocene ($1.9 \times 10^{-5} \text{ cm}^2/\text{s}$) is in good agreement with those reported in the literature.¹⁵ Values of D are expected to be inversely proportional to size.¹³ It has been found that the ratio of D between ferrocene, **6** and **8** is 6.9:1.5:1, consistent with outer diameters of 0.7, 3.0, 4.6 nm for ferrocene, **6** and **8**, respectively, obtained from molecular modeling.

Voltammograms were also obtained using 30 nm and 140 nm Pt disk electrodes. The fabrication and characterization of these nanoelectrodes have been discussed previously.¹⁶ A diffusion-limited response was obtained for compound **8** and the limiting current i_{lim} was used to calculate a diffusion coefficient, D , of $2.6 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$, in good agreement with the value obtained using the larger electrodes (Table 1). Strong adsorption of compound **6** was observed at both electrodes. Analysis of the adsorption peak current shown in Figure 5C yielded an adsorbed amount of $2.2 \times 10^{-18} \text{ mol}$, corresponding to a surface coverage of $4.7 \times 10^{16} \text{ molecules/cm}^2$ (See Supporting Information). Assuming an outer diameter of 3 nm for **6** yields a predicted monolayer surface coverage of $\sim 1.4 \times 10^{13} \text{ molecules/cm}^2$, demonstrating that the current peak in Figure 5C is associated with a multilayer redox film.

Conclusion

In summary, we have provided two new approaches to generate hexakisferrocenyl hexagons via coordination-driven self-assembly from a new ferrocenyl 120° di-Pt(II) acceptor and either a 120° or 180°^{off} bipyridyl 120° ferrocenyl donor unit while exhibiting precise control of size and the distribution of ferrocene moieties. The work presented here provides a simple yet highly efficient approach to the construction, via coordination-driven self-assembly, of ferrocene-derivatized metallacyclic hexagons containing well-defined cavities of varying diameter. Simple covalent attachment of ferrocene to both a 120° di-Pt(II) acceptor and a 120° bispyridyl donor provides easy access to such functional hexakisferrocenyl supramolecules by self-assembly under mild conditions and in near quantitative yields.

The increased size of the hexagonal assemblies has a pronounced effect on their electrochemical properties: a decrease in the diffusion coefficient and increase in their half-wave potential. These results provide an enhanced understanding of the influence of structural factors on the electrochemistry of multifunctional electro-active supramolecular metallacycles, which will help to extend this investigation to other structures and to explore their potential applications in electronic devices.

Experimental Section

Synthesis of **4**

To a solution of ferrocene carboxylic acid (162 mg, 0.7 mmol) in 5 mL of anhydrous dichloromethane were added a catalytic amount (10 %) of DMAP and **3**, 5-diethynyl-phenol **3** (100 mg, 0.7 mmol). DCC (0.146mg, 0.7 mmol) was then added to the reaction mixture at 0 °C, followed by stirring for 5 min at 0 °C and 3 h at room temperature. Precipitated urea was

then filtered off, and the filtrate was evaporated under vacuum. The residue was taken up in 25 mL of CH_2Cl_2 , washed twice with 0.5N HCl and with saturated NaHCO_3 solution, and then dried over MgSO_4 . The residue was purified by column chromatography on silica gel (acetone/hexane: 1/4) to give compound **4** as a pale yellow liquid. Yield: 0.20g, 81%. $R_f = 0.5$ (Hexane/acetone : 4/1), ^1H NMR (CDCl_3 , 300 MHz): δ 7.50 (m, 1H), 7.30 (m, 2H), 4.95 (m, 2H), 4.53 (m, 2H), 4.30 (m, 5H), 3.13 (s, 2H) ^{13}C NMR (CDCl_3 , 75 MHz) δ 155.3, 128.8, 123.9, 119.8, 82.7. HR-TOF-MS Calculated for $\text{C}_{21}\text{H}_{14}\text{O}_2\text{Fe}$, 354.0343, found: 354.0335.

Synthesis of 5

To a 50 mL round-bottom Schlenk flask were added *trans*-diiodobis(triethylphosphine) platinum (1.33 g, 1.94 mmol) and **4** (180 mg, 0.49 mmol). Then 15 mL of toluene and 7 mL of dry diethylamine were added under nitrogen. The solution was stirred for 10 min at room temperature before 15 mg of cuprous iodide was added in one portion. After 12 h at room temperature, a small amount of diethylammonium iodide started precipitating out of solution. The solvent was removed under vacuum, the resulting yellow residue was separated by column chromatography on silica gel with a solvent mixture of hexane/DCM (2/1) yielded of **5** as a yellow powder. Yield: 0.49g, 70%. Mp 149–150°C. $R_f = 0.45$ (2/1 : Hexane/ DCM). ^1H NMR (CDCl_3 , 300 MHz): δ 7.07 (m, 1H), 6.87 (s, 2H), 4.96 (m, 2H), 4.50 (m, 2H), 4.29 (m, 5H), 2.25 (m, 24H), 1.21 (m, 36H). ^{13}C (CDCl_3 , 75 MHz) 170.6, 151.2, 130.6, 129.9, 121.5, 99.6, 91.9, 72.6, 71.1, 70.5, 17.3, 8.7. ^{31}P { ^1H } NMR (CDCl_3 , 121.4 MHz): δ 9.41 (s, $^1J_{\text{Pt-P}} = 2864.1$ Hz). MS (ESI) m/z : 1341.22 ($[\text{M}+1]^+$), 1313.6 ($[\text{M}-\text{I}]^+$). Anal. Calcd for $\text{C}_{45}\text{H}_{72}\text{FeI}_2\text{O}_2\text{P}_4\text{Pt}_2$, C 37.24; H, 4.94; found: C, 37.64; H, 5.13.

Synthesis of 2

A 50 ml round bottom Schlenk flask was charged with 0.12 mg (0.08 mmol) of **5** and 15 ml of dichloromethane. To the solution, 0.046 mg (0.16 mmol) of AgOTf was added at once, resulting in a yellowish precipitate of AgI . After 4 h at room temperature the suspension was filtered through a glass fiber filter and the volume of the solution reduced to 5 ml. Subsequent addition of diethylether resulted in the precipitation of the bistriflate salt **2** as a slightly yellow powder. Yield: 0.117g, 95%. Mp 110–111°C. ^1H NMR (CD_2Cl_2 , 300 MHz): δ 6.93 (s, 1H), 6.78 (s, 2H), 4.93 (m, 2H), 4.54 (m, 2H), 4.31 (m, 5H), 2.06 (m, 24H), 1.27 (m, 36H). ^{31}P { ^1H } NMR (CD_2Cl_2 , 121.4 MHz): δ 22.7 (s, $^1J_{\text{Pt-P}} = 2935.8$ Hz). MS (ESI) m/z : 1364.7 ($[\text{M}-\text{OTf}]^+$). Anal. Calcd for $\text{C}_{47}\text{H}_{72}\text{F}_6\text{FeO}_8\text{P}_4\text{Pt}_2\text{S}_2$, C 37.31; H, 4.80; found: C, 37.73; H, 4.94.

General procedure for the preparation of hexagonal assemblies 6 and 8

To a 0.5mL dichloromethane- d_2 solution of triflate **2** (4.61 mg for **1**, 0.003 mmol; 9.014 mg for **7**, 0.006 mmol) was added a 0.5 mL dichloromethane- d_2 solution of the appropriate donors **1** (1.55 mg, 0.003 mmol) or **7** (0.93 mg, 0.006 mmol) drop by drop with continuous stirring (10 min). The reaction mixture was stirred 30 minutes at room temperature. The solution was evaporated to dryness, and the product was collected.

6. 5.92 mg (orange solid). Yield: 96%. ^1H NMR (CD_2Cl_2 , 300 MHz): δ 8.66 (d, $J = 5.7$ Hz, 12H, $\text{H}_\alpha\text{-Py}$), 7.89 (s, 3H), 7.84 (d, $J = 5.7$ Hz, 12H, $\text{H}_\beta\text{-Py}$), 7.56 (s, 6H, ArH), 7.04 (s, 3H, ArH), 6.89 (s, 6H, ArH), 5.00 (m, 6H), 4.96 (m, 6H), 4.60 (m, 6H), 4.57 (m, 6H), 4.37 (m, 15H), 4.34 (m, 15H), 1.84 (m, 72H, PCH_2CH_3), 1.27 (m, 108H, PCH_2CH_3). ^{31}P { ^1H } NMR (CD_2Cl_2 , 121.4 MHz): δ 16.4 (s, $^1J_{\text{Pt-P}} = 2850.6$ Hz). Anal. Calcd for $\text{C}_{342}\text{H}_{480}\text{N}_{12}\text{O}_{48}\text{Fe}_6\text{F}_{36}\text{P}_{24}\text{Pt}_{12}\text{S}_{12}$: C, 41.01; H, 4.83; N, 1.68. Found: C, 41.36; H, 4.97; N, 1.66.

8. 9.65 mg (yellow solid). Yield: 97%. ^1H NMR (CD_2Cl_2 , 300 MHz): δ 8.83 (d, $J = 5.7$ Hz, 12H, $\text{H}_\alpha\text{-Py}$), 8.49 (d, $J = 5.7$ Hz, 24H, $\text{H}_\beta\text{-Py}$), 7.06 (s, 6H, ArH), 6.90 (s, 12H, ArH), 4.95 (m, 12H), 4.56 (m, 12H), 4.34(m, 30H), 1.81(m, 144H, PCH_2CH_3), 1.15–1.26 (m, 216H,

PCH_2CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 121.4 MHz): δ 16.3 (s, $^1J_{\text{Pt-P}} = 2820.4$ Hz). Anal. Calcd for $\text{C}_{234}\text{H}_{276}\text{Fe}_6\text{N}_6\text{O}_{30}\text{F}_{18}\text{P}_{12}\text{Pt}_6\text{S}_6$: C, 46.35; H, 4.59; N, 1.39. Found: C, 45.93; H, 4.69; N, 1.40.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgment

P.J.S. thanks the NIH (Grant GM-057052) and the NSF (Grant CHE-0306720) for financial support. B.H.N. thanks the NIH (Grant GM-080820) for financial support. H.S.W. thanks the NSF (Grant CHE-0616505) for financial support.

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FIGURE 1.
Schematic and molecular structure of 120° ferrocenyl donor **1** and acceptor **2**.

FIGURE 2.

The ^{31}P NMR spectra of the ferrocenyl acceptor **2** (A) and hexakisferrocenyl hexagons **6** (B) and **8** (C).

FIGURE 3.

Partial ^1H NMR spectra of ferrocenyl acceptor **2** (A), ferrocenyl donor **1** (B), small hexakisferrocenyl hexagon **6** (C), linear donor **7** (D), and large hexakisferrocenyl hexagon **8** (E).

FIGURE 4.
Molecular force field models of hexakisferrocenyl hexagons **6** (A) and **8** (B).

FIGURE 5.

Cyclic voltammetric response on a Pt electrode (0.009 cm²) of 0.20 mM **6** (A) and **8** (B) at a scan rate of 25–250 mV/s. Steady-state response on a Pt nanodiskelectrode with radius of 30 nm at a scan rate of 20 mV/s for 0.20 mM **6** (C) and 0.20 mM **8** (D) in CH₂Cl₂ containing 0.15 M *n*-Bu₄NPF₆.

SCHEME 1. Synthesis of 120° Ferrocene Containing Di-Pt(II) Acceptor Subunit **2**.

SCHEME 2.
Self-assembly of Different Sized Hexakisferrocenyl Hexagons.

TABLE 1

Results of Electrochemical Studies (CH_2Cl_2 with 0.15 M $\text{n-Bu}_4\text{NPF}_6$, 298K) of Free Ferrocene, Hexakisferrocenyl Hexagons **6**, and **8**.

Compound	M.W. (g/mol)	$E^{1/2}$ (V vs Ag/AgCl)	$10^{-6}D$ ($\text{cm}^2 \cdot \text{s}^{-1}$)
ferrocene	186	0.453 ± 0.001	18.7 ± 0.1
6	6,061	0.74 ± 0.01	4.1 ± 0.2
8	10,009	0.91 ± 0.01	2.7 ± 0.3