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Simultaneous Ejection of Six Electrons at a Constant Potential by Hexakis(4-ferrocenylphenyl)benzene

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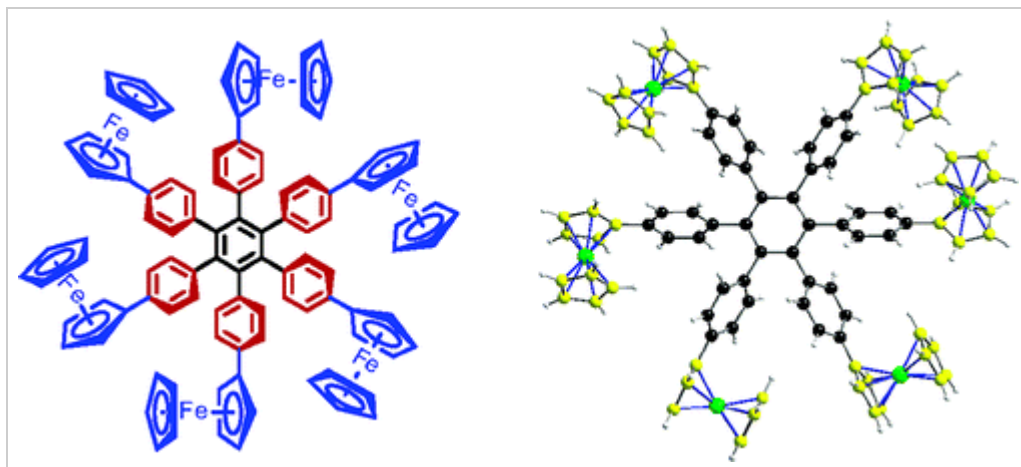
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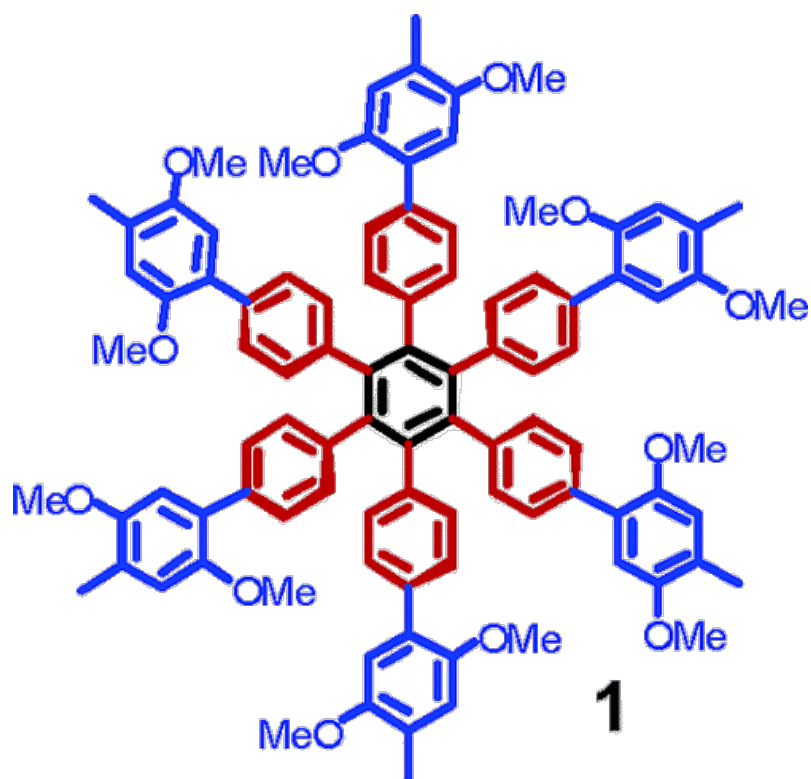
Abstract



A simple synthesis of a dendritic hexaferrocenyl electron donor (**5**) is described in which six ferrocene moieties are connected at the vertices of the propeller of the hexaphenylbenzene core. The molecular structure of **5** is confirmed by X-ray crystallography. An electrochemical analysis along with redox titrations (which are tantamount to coulometry) confirmed that it ejects six electrons at a single potential.

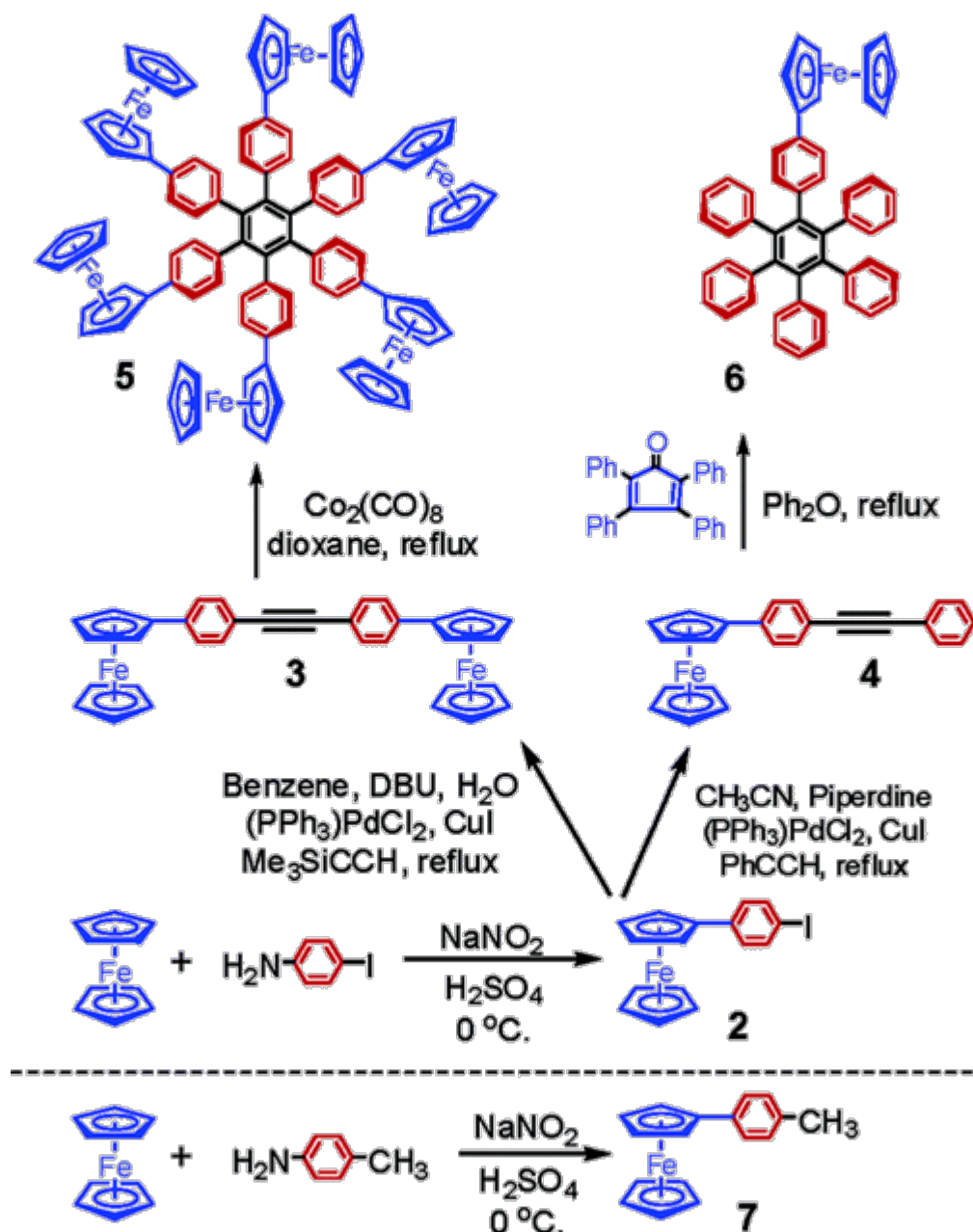
Design and synthesis of organic dendritic molecules containing multiple redox-active chromophores are of importance not only for the preparation of materials with novel light-emitting and charge-transport properties but also as multielectron redox catalysts.^{1,2} Interestingly, a simple $\text{Co}_2(\text{CO})_8$ -catalyzed trimerization of the diarylacetylenes allows an easy access to a variety of hexaarylbenzene (**HAB**) derivatives where the vertices of the hexaphenylbenzene core can be decorated with the desirable electro-active chromophores.^{3,4}

Accordingly, herein, we now report the utilization of the hexaphenylbenzene core as a platform for the preparation of a multicentered electron donor that bears six redox-active ferrocenyl moieties at its vertices (see structure **5**). Moreover, this hitherto unknown macromolecular electron donor **5** undergoes the loss of six electrons in a single step (at a constant potential) to afford a highly charged hexacationic salt which is readily soluble in common organic solvents, such as dichloromethane, chloroform, etc. The simultaneous extraction of six electrons from hexaferrocenyl donor **5** will be delineated (i) with the aid of redox titrations using robust cation-radical salts as aromatic oxidants and (ii) by cyclic voltammetry and comparison with an internal standard, hexakis(4-methyl-2,5-dimethoxybiphenyl)benzene (**1**)⁴ – a donor of similar size and shape that also ejects all of its six electrons at a potential of 1.15 V vs saturated calomel electrode (SCE).



Furthermore, the cyclic voltammeter studies presented herein allows us to emphasize⁵ as well as provide a solution to the problem that is often encountered when determining the number of electrons in a given cyclic voltammetric (CV) wave by using an equimolar amount of internal standards of dissimilar sizes.

As shown in Scheme 1, the synthesis of **5** was accomplished via a standard three-step route. Thus, bis(4-ferrocenylphenyl)acetylene (**3**) was obtained by a Pd-catalyzed coupling⁶ of the readily available 4-ferrocenyliodobenzene⁷ (**2**) with trimethylsilylacetylene in a one-pot procedure in a 75% yield. The resulting acetylene **3** was trimerized in refluxing dioxane in the presence of a catalytic amount of $\text{Co}_2(\text{CO})_8$ to the previously unknown hexakis(4-ferrocenylphenyl)benzene (**5**) in >80% isolated yield.



Scheme 1. Synthesis of Polychromophoric Donor **5** and Model Monoferrocenyl Donors **6** and **7**

Similarly, the monoferrocenyl analogue **6** was prepared by a Diels–Alder reaction of 4-ferrocenyltolan (**4**) with tetraphenylcyclopentadienone in refluxing diphenyl ether. The structures of these macromolecular electron donors **5** and **6** as well as tolylferrocene (**7**) were readily established by $^1\text{H}/^{13}\text{C}$ NMR spectroscopy as well as by correct elemental analysis and FAB mass spectrometry (see the Supporting Information for the experimental details).

The molecular structure of hexaferrocenyl donor **5** was further confirmed by X-ray crystallography as shown in Figure 1. The following structural features of **5** are noteworthy. The propeller formed by six 4-ferrocenylphenyl arms around the central benzene ring

in **5** showed that the dihedral angles between the planes of the central benzene ring and the six peripheral phenyls varied between 54.1 and 66.1° (avg 60.4°) and are similar to those observed in other hexaarylbenzene derivatives.⁸ Interestingly, however, the orientations of the ferrocenyl groups with respect to the peripheral phenyls are much more varied as well as the dihedral angles between the planes of phenyl and adjacent cyclopentadienyl groups, i.e., 4.3–31.2°. It is noteworthy that the cyclopentadienyl moieties of the ferrocene groups generally lie coplanar with the aryl rings in various arylferrocene derivatives; e.g., see Figure S3 and S4 in the Supporting Information.⁸ As such, the reason for substantial deviation from phenylcyclopentadienyl coplanarity in **5** can be attributed to effective C–H··· π interactions⁹ among the ferrocenyl rings of different molecules in the crystals, as shown in the packing diagram in Figure 1.

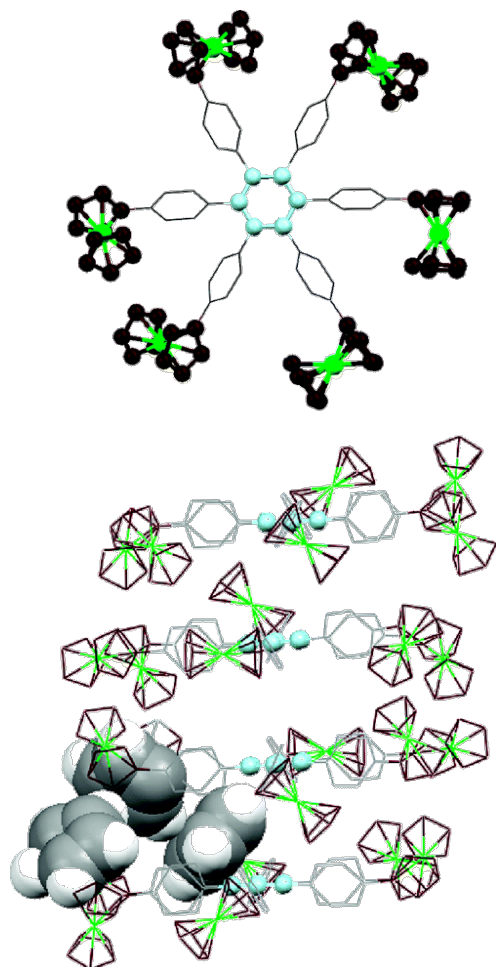


Figure 1 (Top) X-ray structure of **5** showing the varied orientations of the ferrocenyl groups. (Bottom) Packing of **5** in the crystal due to effective CH– π interactions that are exemplified by the partial space-filling representations of three cyclopentadienyl moieties from two different molecules.

The hexaferrocenyl donor **5** and hexakis(4-methyl-2,5-dimethoxybiphenyl)benzene (**1**) were next subjected to the electrochemical oxidation at a platinum electrode as a 2×10^{-4} M solution

in a (4:1) dichloromethane–acetonitrile mixture containing 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte. The cyclic voltammograms of **5** and **1** consistently met the reversibility criteria at various scan rates of 25–400 mV s⁻¹ (see Figure 2), as they all showed cathodic/anodic peak current ratios of $i_a/i_c = 1.0$ (theoretical) as well as the differences between anodic and cathodic peak potentials of $p_a - p_c = 68 \pm 5$ mV at 22 °C. The reversible oxidation potentials of **5** and **1** were calibrated with internal standards (vide infra) and were found to be 0.47 and 1.15 V vs SCE for **5** and **1**, respectively.

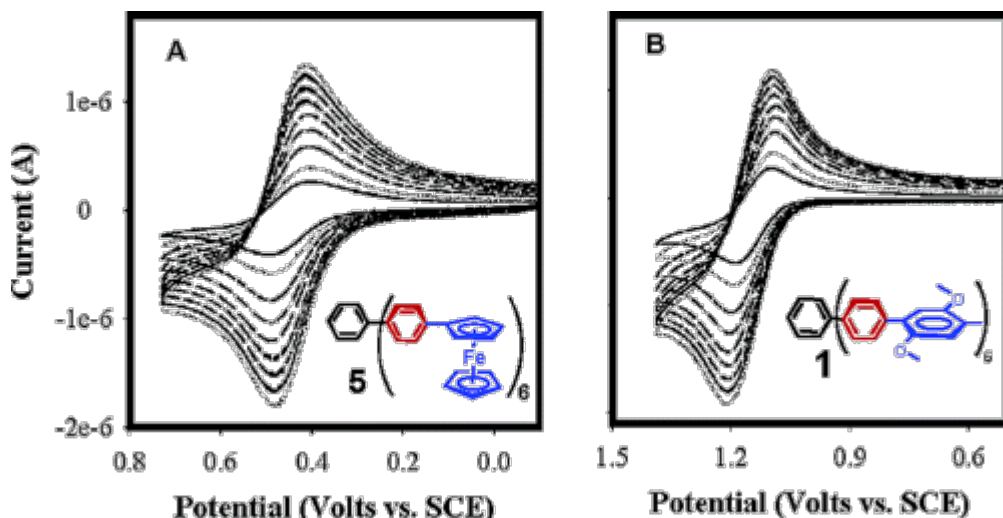


Figure 2 Cyclic voltammograms of 0.2 mM hexakis(4-ferrocenylphenyl)benzene **5** (A) and hexaarylbenzene donor **1** (B) in CH₂Cl₂ containing 0.2 M *n*-Bu₄NPF₆ at a scan rate of 25–400 mV s⁻¹ at 22 °C.

It is interesting to note that irrespective of the number of the electro-active ferrocenyl (FeCp₂) groups (i.e., 6 FeCp₂ groups in **5** and one each in model compounds **6** and **7**), these electron donors showed only a single reversible (CV) wave at a potential of 0.47 ± 0.01 V vs SCE (see Figures S1 and S2 in the Supporting Information), thus suggesting that *the ferrocenyl groups in 5 are not electronically coupled*.

In order to evaluate the number of electrons being ejected in the cyclic voltammetric peaks of **5** and **1** in Figure 2, we employed 4-methyl-2,5-dimethoxytoluene (**8**, $E_{1/2} = 1.15$ V vs SCE) and ferrocene ($E_{1/2} = 0.45$ V vs SCE) as internal standards. For example, the square wave voltammogram of a 1:6 mixture of **5** and **8** (Figure 3A) and **1** and ferrocene (Figure 3B) were recorded in a dichloromethane–acetonitrile solution under conditions identical to those employed in Figure 2. Expectedly, both internal standards (i.e., **8** and ferrocene) showed identical currents, whereas **5** and **1** showed substantially reduced magnitudes of currents (which corresponded to the ejection of roughly 2.4 electrons from **1** and **5**) in comparison to the internal standards. As such, the dissimilarity in the magnitudes of the currents in Figure 3A,B is

readily reconciled by the fact that the difference in the sizes and shapes of **5** vs ferrocene and **1** vs **8** contributes to the difference in diffusion coefficients of the donors.⁵ Indeed, when a square-wave voltammogram of a 1:1 mixture of the two hexaphenylbenzene-based donors **5** and **1** were recorded under identical conditions as above (Figure 3C), it clearly showed identical magnitudes of currents for both **1** and **5**. Such an observation confirms that both **5** and **1** eject six electrons at their respective potentials.

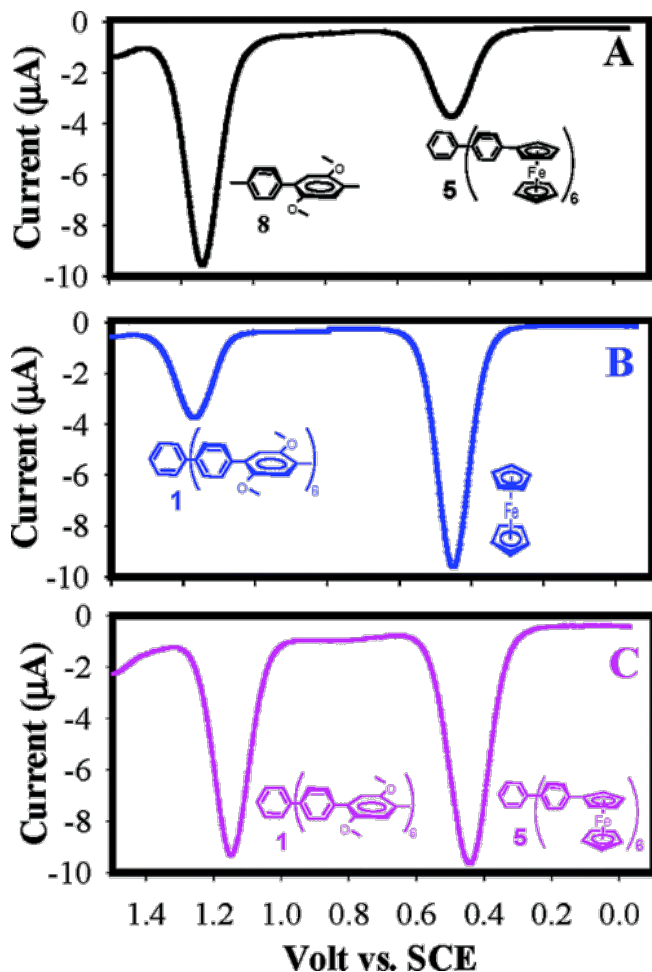
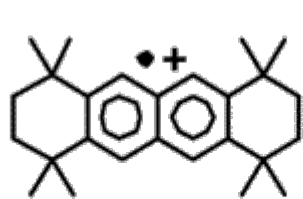


Figure 3 Square-wave voltammograms of mixtures of 0.25 mM **5** and 1.5 mM **8** (A), 0.25 mM **1** and 1.5 mM ferrocene (B), and 0.25 mM each of **1** and **5** (C) in CH_2Cl_2 containing 0.2 M $n\text{-Bu}_4\text{NPF}_6$ at 22 °C.

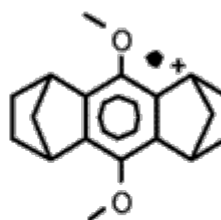
In order to confirm the multiple electron-transfer processes involved in the CV peaks of **1** and **5**, we carried out redox titrations (which are tantamount to coulometry) using a hindered naphthalene (**NAP**)⁴ and a hydroquinone ether (**MA**)¹⁰ cation radicals as robust one-electron oxidants (see below).

Efficient Aromatic Oxidants



NAP⁺

E_{red} (V vs. SCE) = 1.34



MA⁺

1.11

Thus, Figure 4A showed the spectral changes attendant upon the reduction of a dark-blue solution of **NAP⁺** SbCl₆⁻ (λ_{max} = 672, 616, 503, and 396 nm; ϵ_{672} = 9300 M⁻¹ cm⁻¹) by an incremental addition of 1/6 equiv of neutral **1** to afford a bright green hexacation radical **1⁶⁺** (λ_{max} = 415, 550, and 1105 nm, ϵ_{1105} = 1400 M⁻¹ cm⁻¹) in dichloromethane at 22 °C, i.e., eq 1. **NAP⁺** + 1/6 **1** → 1/6 **1⁶⁺** + **NAP** (1)

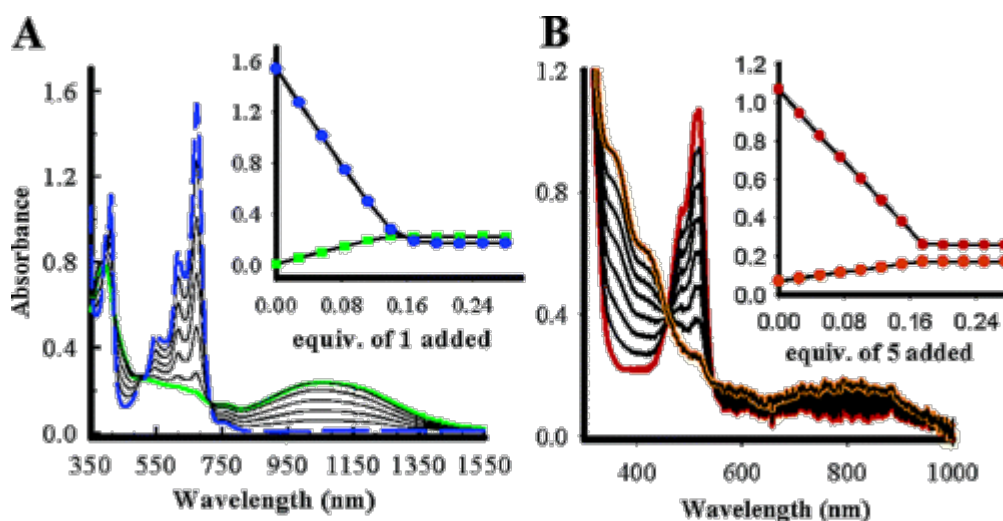


Figure 4 (A) Spectral changes attendant upon the reduction of 1.7×10^{-4} M **NAP⁺**SbCl₆⁻ (blue) by incremental addition of 1.2×10^{-3} M **1** to its hexacation radical **1⁶⁺** (green) in CH₂Cl₂ at 22 °C. **Inset.** A plot of depletion of absorbance of **NAP⁺** (blue circles, at 672 nm) and an increase of the absorbance of **1⁶⁺** (green squares, at 1100 nm) against the equivalent of added **1**. (B) Spectral changes attendant upon the reduction of 1.3×10^{-4} M **MA⁺** BF₄⁻ (red) by incremental addition of 1.3×10^{-3} M **5** to its hexacation **5⁶⁺** (yellow-orange) in CH₂Cl₂ at 22 °C. Inset: plot of depletion of absorbance of **MA⁺** (red circles, at 518 nm) and an increase of the absorbance of **5⁶⁺** (orange circles, at 800 nm) against the equivalent of added **5**.

The presence of well-defined isosbestic points at λ_{max} = 388, 520, and 714 nm in Figure 4 established the clean electron transfer from **1** to **NAP⁺**. Furthermore, a plot of the depletion of **NAP⁺** and formation of **1⁶⁺** against the increments of added **1** in Figure 4A (inset),

established that **NAP⁶⁺** was completely consumed after the addition of 1/6 equiv of **1**; and the resulting absorption spectrum of **1⁶⁺** remained unchanged upon further addition of neutral **1** (i.e., eq 1).

A similar redox titration of hexaferrocenyl donor **5** with **MA⁶⁺** BF₄⁻ ($\lambda_{\text{max}} = 518$ and 486 (sh) nm; $\epsilon_{518} = 7300 \text{ M}^{-1} \text{ cm}^{-1}$) yielded **5⁶⁺** ($\lambda_{\text{max}} = 360, 415, 512, 600,$ and 800 nm; $\epsilon_{800} = 1180 \text{ M}^{-1} \text{ cm}^{-1}$) according to the eq 2. $11\text{MA}^{6+} + 1/6 \text{5} \rightarrow 1/6 \text{5}^{6+} + \text{MA}$ (2)

Moreover, the presence of well-defined isosbestic points at $\lambda_{\text{max}} = 460$ and 547 nm in Figure 4B as well as a plot of the depletion of **MA⁶⁺** and formation of **5⁶⁺** against the increments of added **5** in Figure 4B (inset) established that **MA⁶⁺** was completely consumed after the addition of 1/6 equiv of **5**, and the resulting absorption spectrum of **5⁶⁺** remained unchanged upon further addition of neutral **5** (i.e., eq 2). Furthermore, the stability of both **1⁶⁺** and **5⁶⁺** is attested by the fact that their reduction with zinc dust regenerated the neutral **1** and **5** in quantitative yield.

In summary, we have accomplished a simple synthesis of hitherto unknown (dendritic) hexakis(4-ferrocenylphenyl)benzene (**5**) and confirmed its structure by X-ray crystallography. We have also demonstrated that both hexaaryl- and hexaferrocenylbenzene donors (i.e., **1** and **5**) undergo reversible six-electron oxidation at a constant potential by cyclic and square-wave voltammetry. The ejection of six electrons by **1** and **5** was further confirmed by redox titrations (which are tantamount to coulometry) using stable aromatic oxidants. We are currently exploring the potential applications of these materials and a variety of other hexaarylbenzene derivatives for the preparation of photonic devices.

Acknowledgment

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