

Encapsulated Electroactive Molecules Based upon an Inorganic Cluster Surrounded by Dendron Ligands

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Encapsulated electroactive molecules are of great importance in understanding biological electron transfer¹ and are of interest for their potential utility in molecular electronics devices (e.g., a molecular redox switch).^{2–4} We sought to design a tailorable model system in which electron transfer to and from a redox center would be attenuated in a rational fashion by groups surrounding it. Such a system is a logical first step in creating a molecule in which the redox state could be kinetically trapped, potentially permitting molecules in different redox states to coexist in small (admittedly as yet undefined) regions of space without facile electron transfer between them. Here, we report the preparation, characterization, and electrochemical properties of a series of encapsulated electroactive molecules. These are composed of dendrons^{5–7} tetrahedrally disposed around an electroactive iron–sulfur core of the form $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$. Symmetric disposition of dendrons around an inorganic core represents, to the best of our knowledge, a new molecular topology and thus is a new example of a hybrid organic/inorganic architecture. When the generation (number of branch points) of the ligands around the core is varied, a simple method for varying the degree of encapsulation is realized.

Molecules in which dendrons surround an electroactive group have been prepared by attaching dendrons around the periphery of a porphyrin core.^{8–11} Electron transfer to/from porphyrin cores has been affected by the dendron due to its bulkiness and by the microenvironment it creates around the core. The iron–sulfur core employed here has much higher (pseudotetrahedral) symmetry and thus enforces a different arrangement of the ligands around it. Using a high-symmetry core should result in a more symmetric placement of the dendrons around it and thus an optimal scheme for encapsulation of the core by the dendron ligands.

Molecules **G0–G4** (Figure 1) were synthesized via a ligand exchange reaction described originally by Holm et al.¹² in which aromatic thiols displace aliphatic thiols in FeS clusters of the form $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$. In this reaction, 4.1 equiv of a thiol-

substituted dendron¹³ and 1 equiv of $(n\text{-Bu}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{S-}t\text{-Bu})_4]^{14}$ were dissolved in a minimum amount of dimethylformamide in an inert atmosphere and heated at 40 °C under partial vacuum for 30 min followed by removal of the solvent at higher vacuum. The resulting black solid was dissolved in methylene chloride and precipitated with the addition of excess diethyl ether. After being filtered and dried, the products appeared as black, shiny, slightly air-sensitive solids. Molecules **G1–G4** were soluble in tetrahydrofuran, methylene chloride, and dimethylformamide. Molecule **G0** was similarly soluble, with the exception of tetrahydrofuran. The solubility differences are presumed to be the result of the differing ligands surrounding the core. Because of their slight air sensitivity, all characterization of these clusters was performed in an inert atmosphere. The ligand exchange reaction could be monitored by the appearance of free *t*-BuSH in the ¹H NMR spectrum and was observed to be complete within 30 min.

Several spectroscopic features were characteristic of these molecules. The substitution of an aromatic thiolate ligand for an alkyl thiolate on the cluster resulted in a red shift of the visible long-wavelength absorption due to the FeS core from 420 nm in $(n\text{-Bu}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{S-}t\text{-Bu})_4]$ to 460 nm in **G0–G4**. This red shift was similar to that observed for electronically similar molecules.¹⁵ Also characteristic was the substantial broadening and change in chemical shifts of the thiolate aromatic ring protons close to the paramagnetic iron–sulfur unit. The protons on this ring were shifted upfield to ~6 ppm and downfield to ~8 ppm upon ligand substitution.¹⁶ Inversion recovery experiments revealed that these protons relaxed very quickly for aromatic ring protons (T_1 values of 5 ms and 40 ms were measured for protons at 6 and 8 ppm, respectively). This behavior was anticipated for protons in close vicinity to a paramagnetic group. Most of the protons in the dendron ligands were found to relax faster when these ligands were attached to the FeS core.¹⁷

Molecules **G0–G4** have large molecular weights, and the measurement of a high molecular weight should be characteristic for complete dendron substitution around the FeS core. Unfortunately, only **G0** and **G1** were found to be amenable to mass spectral characterization (Table 1). Moreover, all of the molecules were found to decompose slightly under thin-layer chromatography (both normal and reverse phase silica gels) and gel permeation chromatography conditions. The molecular weights of these molecules, however, could be determined by vapor phase osmometry (VPO, Table 1) and were found to be similar to that expected for the structures shown in Figure 1. It is interesting that this technique gave molecular weights consistent with the inclusion of two tetrabutylammonium counterions. This result suggests that these salts are tightly associated in the tetrahydrofuran solutions employed. We hope to probe the extent of this association using both T_1 and T_2 ¹H NMR relaxation experiments.

Cores of the form $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ have a well-precedented, quasi-reversible one-electron reduction, and the electromotive force required for this reaction has been shown to be sensitive to the electronic nature of the aromatic thiolate ligands, following Hammett-type behavior.¹⁵ We hypothesized that as the generation of the dendron ligand around the core increased,

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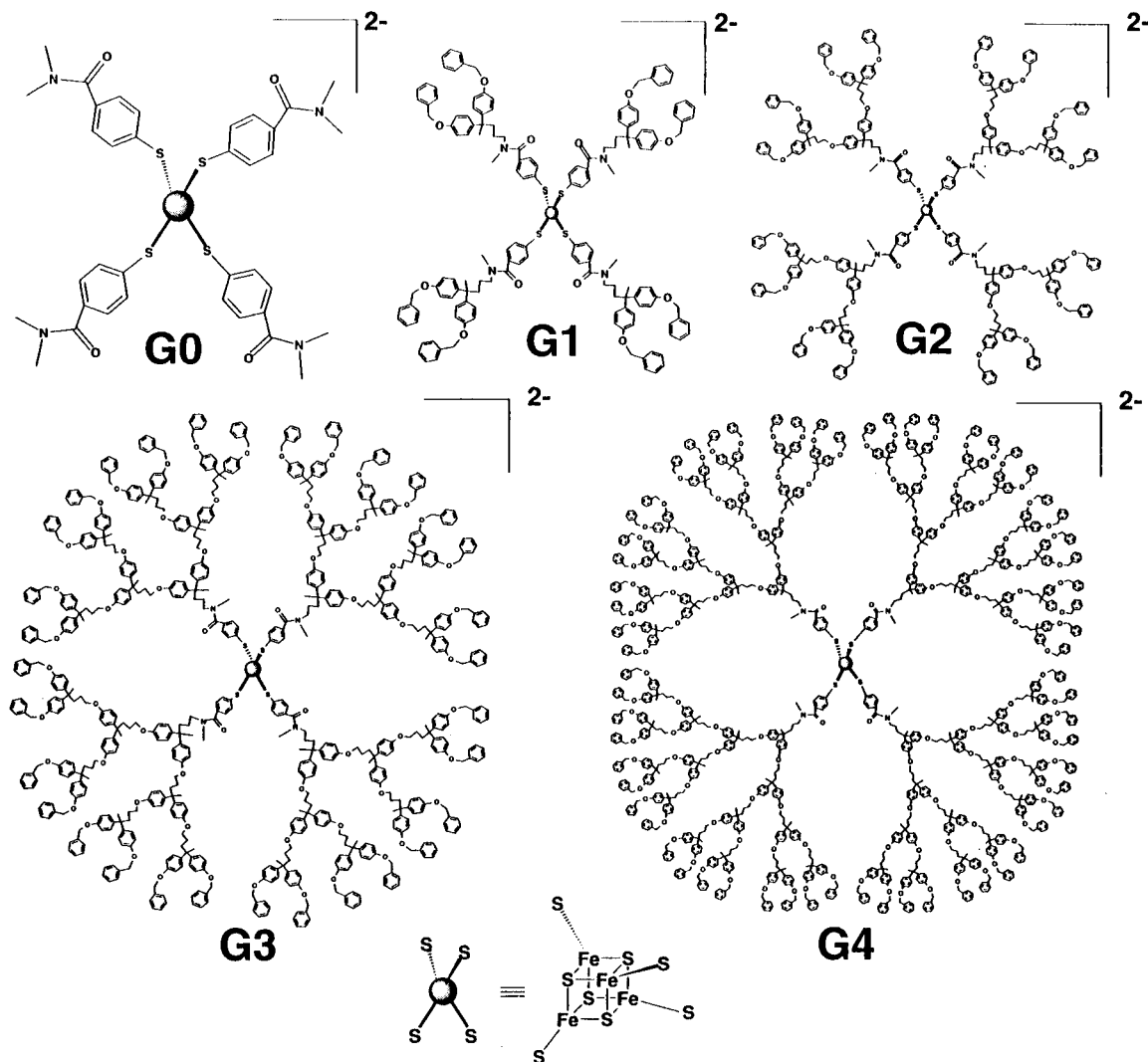


Figure 1. Structures of molecules **G0–G4**.

Table 1. Molecular Weight and Elemental Data on **G0–G4**

molecule	MW (calcd) ^a	Mn (VPO) ^b	$E_{1/2}$ ^c	ΔE ^c
G0	1558	1557 [M] ^{+d}	-970	130
		1799 [M + <i>n</i> -Bu ₄ N] ^{+d}		
G1	3239	3180	-1000	250
		3240 [M + H] ^{+d}		
		3482 [M + <i>n</i> -Bu ₄ N] ^{+d}		
G2	5995	6030	-1030	340
G3	11507	11760	-1080	370
G4	22529	22800	<i>e</i>	<i>e</i>

^a Values based on the molecular formula (*n*-Bu₄N)₂[Fe₄S₄(SR)₄].

^b From vapor phase osmometry unless noted otherwise. VPO was performed under an inert atmosphere at 35 °C in tetrahydrofuran with benzil as a standard. Error in the measurement was estimated to be <15%. ^c From cyclic voltammetry in dimethylformamide solution, 100 mV/s scan rate, tetrabutylammonium hexafluorophosphate supporting electrolyte, Ag/AgCl reference. $E_{1/2}$ is defined as the average of the two voltages at the current maximum/minimum of the reduction and return oxidation waves. ΔE is defined as the difference between these two voltages. Uncertainty in these values is ± 20 mV. ^d From field desorption mass spectrometry. ^e The reduction wave was shifted ca. 50 mV more negative compared to **G3**. No clear return oxidation wave was discernable.

the increased steric bulk of the ligand would render the molecule both kinetically and thermodynamically more difficult to reduce. This behavior was observed by comparing the cyclic voltammograms of these molecules (Table 1). Molecules **G0–G4** were found to have an increasingly more negative reduction potential ($E_{1/2}$), indicative of increasing electromotive force required for reduction. Moreover, molecules **G0–G3** displayed

an increasingly larger voltage difference between the current maxima of the reduction and return oxidation waves (ΔE), indicative of increasing kinetic difficulty of reduction/oxidation. Molecule **G4** did not display a clear return oxidation wave as would be expected for increasing kinetic difficulty of reoxidation. Differences in electrode kinetics in this series were shown not to result from electrode fouling by running these experiments in random order and by verifying that **G0** reduction/oxidation kinetics were not affected by the history of the electrode.

In conclusion, we have reported a route to a novel architecture for the study of encapsulated electroactive molecules based on dendron-encapsulated inorganic, electroactive cores with high symmetry. In addition, the “insulating effects” of increasing generation of the ligand on the electrochemical properties of the core were demonstrated.

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Supporting Information Available: UV-vis absorption spectra for (*n*-Bu₄N)₂[Fe₄S₄(*S-t*-Bu)₄] and **G0–G4**, elemental analysis data, cyclic voltammograms, and assigned ¹H NMR spectra of **G0–G4** (11 pages). See any current masthead page for ordering and Internet access instructions.

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