Control of Electron Transport using Redox-Active Core Dendrimers

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SUMMARY: We are constructing a model system to elucidate the molecular structure-property relationships for attenuation of electron transfer (e.g. electron encapsulation). This information is relevant in bio-electron transfer schemes and in emerging molecular electronics schemes such as storage of information using individual molecules. Our system consists of an inorganic cluster surrounded by dendritic ligands which act as an organic coating. Although the electrochemical and photophysical properties of a variety of metal clusters have been established, very little has been described on the chemistry on metal clusters.

Introduction

Encapsulation is a general term that connotes isolation or trapping or a moiety inside an architecture.[1, 2] We and others are particularly interested in the phenomenon of encapsulation with regards to electron transfer rate control. In redox proteins (Figure 1a) metallocenters are surrounded by a poly-peptide structure that often permits fast, vectorially well defined, long range electron transfer. In molecular electronics (Figure 1b) one can envision the necessity of an architecture that attenuates electron transfer as much as possible so that oxidized and reduced molecules (e.g. "on" and "off" states or "1" and "0") in close proximity to one another do not become scrambled.

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Dendrimers may be excellent architectures for encapsulation. Fundamental questions still remain, however, about their conformation and conformational flexibility. A redox active, metal core in a dendrimer can simultaneously be used as a functional element and as a probe of molecular structure. Furthermore, the properties of this core indicate very different tertiary structures for dendrimers with different primary structures. Thus, a relatively complete depiction of molecular structure/function is possible.

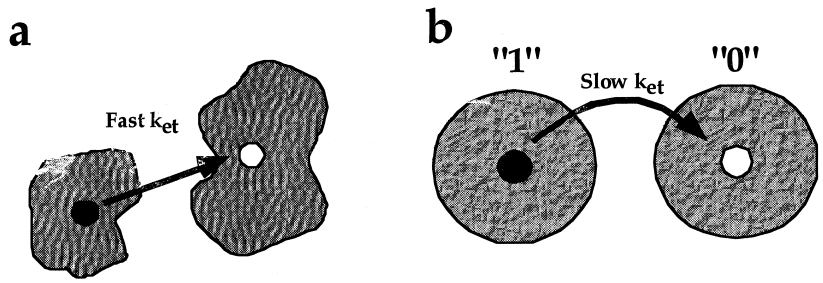

Fig1. Cartoon illustrating roles of encapsulation in electron transfer.

Electrochemistry has been used to characterize quantitatively the size and heterogeneous electron transfer rate attenuation of the iron-sulfur core dendrimers previously reported.[1, 2] Ligand structure has an important effect on electron transfer rate attenuation in these redox-core dendrimers. This effect is likely due to the conformation that the dendrimer molecules adopt.

Furthermore, we have also shown that properties of the cluster can be used as probes of dendrimer conformation.[3] Specifically, the paramagnetic nature of the Fe_4S_4-based cluster has a strong, through-space influence on relaxation rates of protons in the dendron ligands surrounding it. From this influence, information about the average conformation of the arms around the core could be discerned.

Results and Discussion

It was found that ligand exchange reactions originally reported in the early 1970's by Holm et al. were sufficiently facile to prepare Fe_4S_4 core dendrimers (Fig 2).[4] This was, in our minds, an

important step to take as incomplete reaction would form side products (e.g. iron-sulfur core dendrimers with only one, two, or three dendritic arms) that would be difficult or impossible to separate. Ligand exchange could be accomplished by mixing a focally substituted aromatic thiol dendron (ca. 5 eq.) with $(n\text{–}Bu_4N)_2$ $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]$ in dimethyl formamide solution with slight heating and application of vacuum. Generally, the dimethyl formamide and *t*-butyl thiol side product were pumped off slowly overnight at ca. 40-50 °C. Purification generally consisted of one dissolution/precipitation. All compounds gave satisfactory ^1H and ^{13}C NMR spectra, elemental analyses and mass spectra. It is noteworthy that analytically pure materials with high molecular weights could be obtained using such minimal purification techniques. All of these molecules appeared as brown to black solids that were soluble in tetrahydrofuran and methylene chloride but had varying solubility in other solvents.

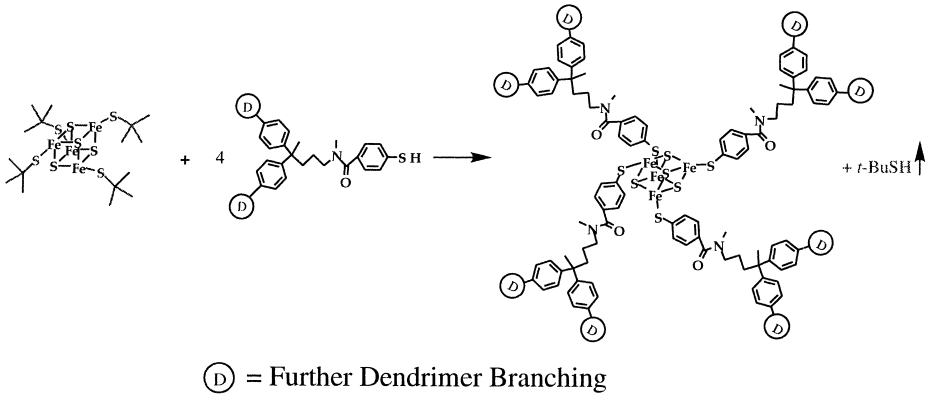

Fig 2. Schematic of the ligand exchange reaction used to prepare the iron-sulfur core dendrimers

Two kinds of iron-sulfur core dendrimers were prepared (Fig 3). These consisted of alternatively flexible and rigid ligands. Diffusion coefficients of these dendrimers in dilute solution were determined using two complementary methods: by pulsed field gradient spin echo proton NMR and electrochemically by chronoamperometry. Heterogeneous electron transfer rate constants (k_0) were determined for these molecules in two ways: (1) via a Nicholson analysis of the cyclic

voltammograms (CVs) of these molecules taken at a number of scan rates and (2) by an iterative fit of their Osteryoung square wave voltammograms (OSWV)

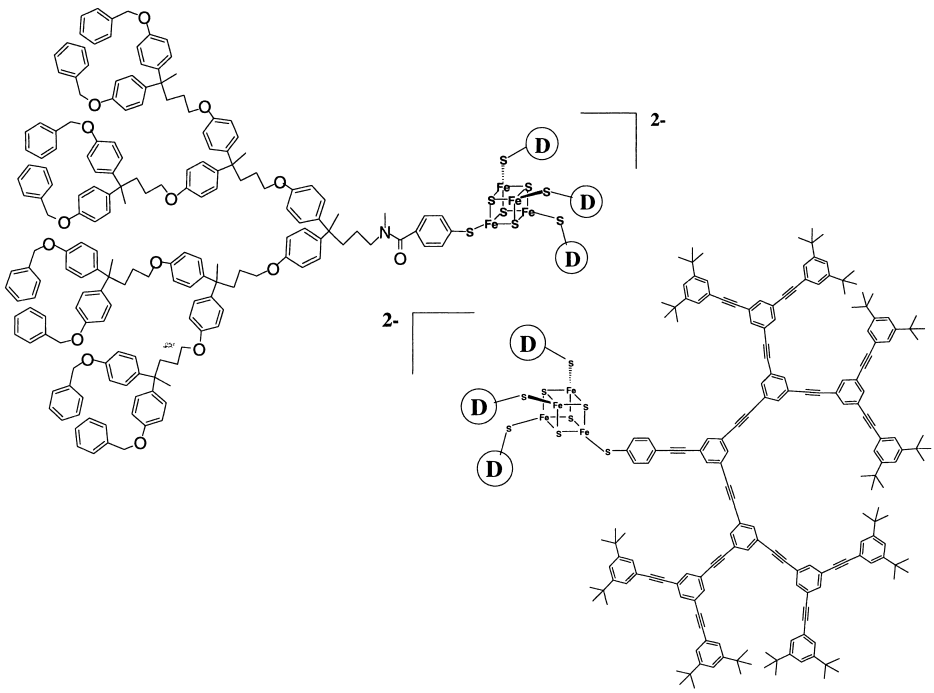

Fig 3. Third generation examples of the two types of dendrimers prepared herein. Dendrimers of these structures of generations 1-4 have been prepared. Circled-Ds represent three additional copies of the dendron arm fully drawn out.

When flexible and rigid dendrimers of similar molecular weights were compared, it was found that the rigid dendrimer architectures attenuated electron transfer more than their flexible counterparts. Molecular modeling suggests that this result is due to a more mobile iron-sulfur core in the flexible dendrimers and a core that is held more resolutely in the center of the molecule in the rigid dendrimers (Fig 4). These results have two important implications. First, macromolecular structure-property relationships exist for electronic encapsulation. Second, although one might initially be tempted to choose the cross-conjugated phenyl acetylene

architecture as the less attenuating architecture due to its primary structure, it turns out that tertiary structure (conformation) is most important in electronic encapsulation.

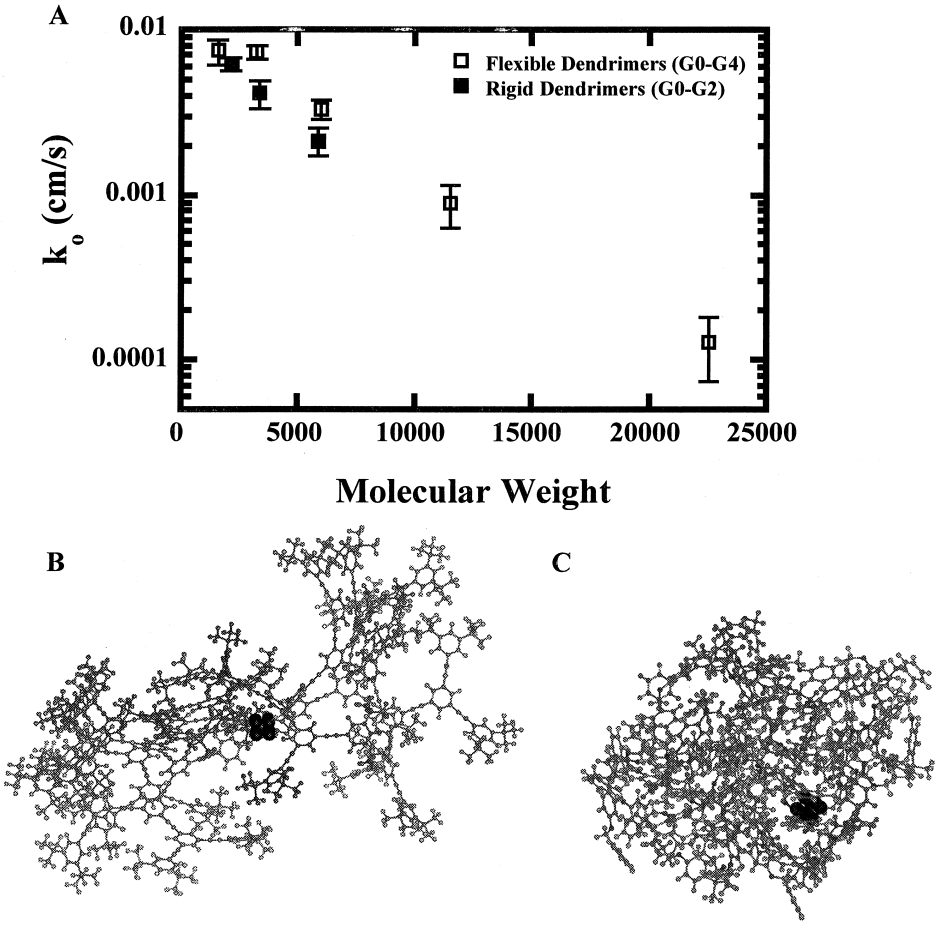

Fig 4. (A) Graph showing electron transfer rate attenuation in flexible and rigid dendrimers. Snapshots of a minimum energy structure found during a conformational search of (B) a third generation rigid dendrimer and (C) a third generation flexible dendrimer.

It was of interest to illustrate the utility of other metal clusters in functional dendrimer synthesis. Metal clusters offer geometries and electronic properties (redox activity, luminescence, etc.) that

are sometimes difficult to build into an architecture using only organic groups. For example, although it would be challenging to construct a six-coordinate organic core for a dendrimer with octahedral symmetry, several inorganic clusters exist with this symmetry. As emphasized above, the question becomes whether some type of efficient ligand exchange reaction can be adapted to the synthesis of these molecules. We have found[5] that, in the case of a $Mo_6(\mu 3\text{-}Cl)_8$ core, dendrons consisting of a focal phenol or phenoxide group could be reacted with clusters of the form $Mo_6(\mu 3\text{-}Cl)_8(OR)_6$ (R = OCH_3 or OSO_2CF_3) respectively. At about the time this work was first reported, Zheng et al. reported similar chemistry using an Re_6S_8 core.[6] These two examples illustrate the first six-arm dendrimers — a new architecture that naturally employs metal clusters as core elements. Examination of the properties of these molecules as well as the exploration of other synthetic reactions on metal clusters to give functional macromolecules is in progress in our group.

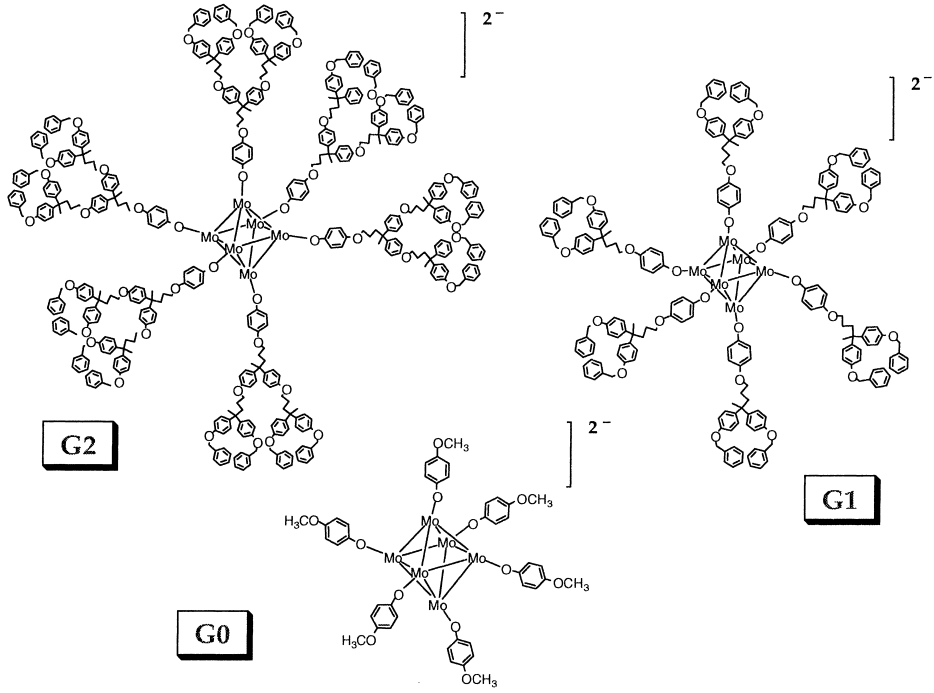

Fig 5. Hexa-arm dendrimers based on a $Mo_6(\mu 3\text{-}Cl)_8$ core (shown as an octahedron of Mo atoms — face capping chloride atoms were omitted for clarity)

References

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