

Dendrimers Supported by the $[\text{Re}_6\text{Se}_8]^{2+}$ Metal Cluster Core

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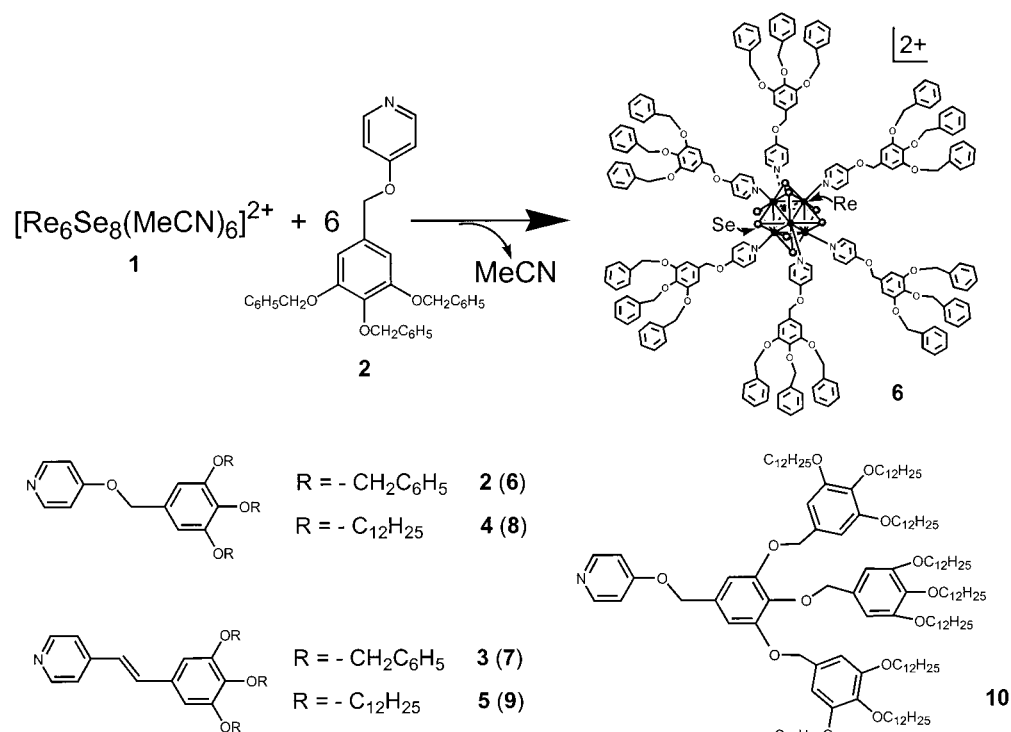
The focus of dendrimer research is currently shifting from mere construction of molecules with dendritic topology to development of materials that have specific functions and show intriguing supramolecular organizational phenomena.¹ One strategy to modify the properties of dendrimers is to introduce metals on the surface, within the branches, or at the interior core.² This approach enables the nanoscopic dimensions of dendrimers to be combined with the rich redox and magnetic properties of metals, thus leading to the formation of materials with unique optical, electrical, magnetic, and catalytic properties. Although dendrimers containing single metal centers are being intensively studied from various perspectives,² a similar design using metal clusters as the focal point to dispose dendritic ligands has barely been addressed.^{2d,3} We expect this chemistry to be even more intriguing because one may find, in addition to properties related to single metal atoms, traits associated with the metal–metal interactions that are intrinsic to clusters.⁴ Toward this goal, we have recently initiated a program to study metal cluster-based dendrimers. Specifically, we are interested in utilizing an octahedral cluster core such as $[\text{Re}_6\text{Se}_8]^{2+}$ as a scaffold to construct a previously unknown class of dendrimers. We report herein our preliminary findings in the design and synthesis of such novel macromolecules with dendritic topologies. Moreover, their interesting and potentially important optical tunability is addressed.

Our approach to a dendrimer supported by an octahedral metal cluster core is generically illustrated in Scheme 1. The fully solvated metal cluster $[\text{Re}_6\text{Se}_8(\text{MeCN})_6](\text{SbF}_6)_2$ (**1**)^{5c} and dendritic

ligands (**2–5**)⁶ are the key precursors to the corresponding dendrimers. Several hexanuclear cluster complexes have been reported with coordinating solvents such as water,¹⁰ acetonitrile,^{5c,11} dimethylformamide,¹² and methanol,^{11a} but their synthetic utilities have received little attention.^{11a} The preliminary results presented here indicate that these cluster derivatives provide a convenient entry into a new class of dendrimers as well as a starting point for an extremely broad range of chemistry.¹³

The preparation of dendrimers (Scheme 1), via a convergent route, takes advantage of the lability of $[\text{Re}_6\text{Se}_8(\text{CH}_3\text{CN})_6](\text{SbF}_6)_2$ in a ligand substitution reaction;^{5d} the loosely ligated acetonitrile molecules can be readily replaced by a variety of pyridyl functionality-bearing dendrons (**2–5**) to give the desired products. A typical synthesis involves the heterogeneous reaction of **1** with individual dendritic ligands (6.5 molar equiv) in refluxing chlorobenzene. A clear solution is obtained after ca. 12 h, indicating the completion of the reaction. Purification by chromatography on alumina (basic) affords the desired products as crystalline solids in excellent yields (80–90%). The solubility of the dendrimers in common organic solvents is very similar to that of their corresponding dendrons. For example, **6** and **7** are only soluble in polar organic solvents, reflecting the solubility of **2** and **3**. In contrast, **8** and **9** are soluble in hydrocarbons but have very limited solubility, if any, in acetone and acetonitrile, resembling the solubility of their constituent dendrons, **4** and **5**, respectively. The formation of dendrimers **6–9** was confirmed by the disappearance of the ¹H signal at 2.69 ppm (CDCl_3) of the coordinated acetonitrile in **1**. Among the most interesting spectroscopic observations is the downfield shift of the ¹H resonances of dendrons upon coordination to the cluster core. For example, the shifts of **8** are displaced by 0.4 and 0.6 ppm (pyridyl), 0.2 ppm (benzyl), and 0.1 ppm (benzene) compared to that of **4**. These chemical shift changes are clearly demonstrated in Figure 1. Other dendrimers reported here show similar ¹H chemical shift changes. Relevant data are provided as Supporting Information. The identity of the dendrimers is further confirmed

Scheme 1



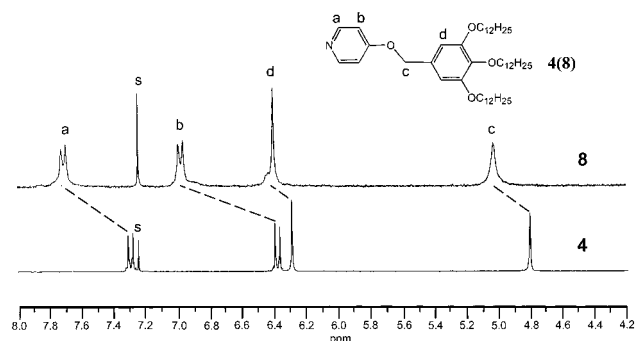


Figure 1. ^1H NMR spectra of dendron **4** and dendrimer **8** in CDCl_3 . The signals marked with an "s" are attributed to residual solvent. The resonances due to the dodecoyl ($-\text{OC}_{12}\text{H}_{25}$) groups in both **4** and **8** are omitted for clarity.

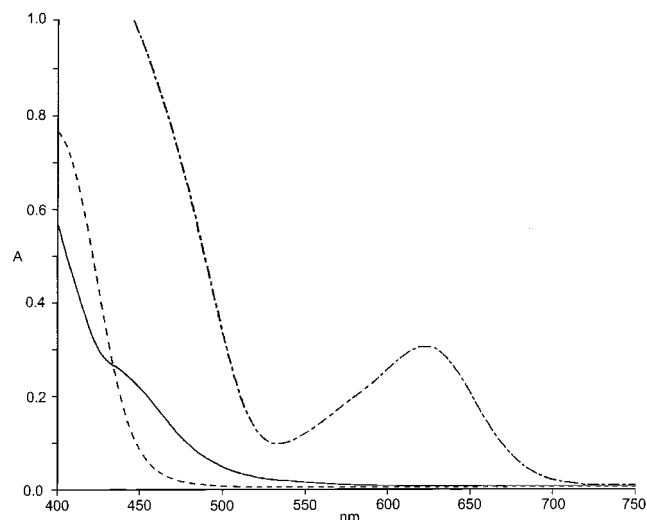


Figure 2. Absorption spectra of **1** (—, 0.5 mM), **6** (---, 0.5 mM), and **7** (- - -, 5.0 μM) in CH_2Cl_2 solutions.

by their electrospray ionization mass spectra (ESI-MS).¹⁴ The interpretation of the results is straightforward because the molecular ion peaks are clearly identified. The mass spectroscopic

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(6) Dendrons **2–5** were prepared by slightly modified literature procedures.^{7–9} See Supporting Information for experimental details.

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studies coupled with the ^1H and ^{13}C NMR evidence lead to our unambiguous conclusion that structurally perfect first-generation dendrimers have indeed been synthesized.

The molecular structure and composition of cluster-based dendrimers such as **6–9** show promises for fabricating advanced materials that are easily processable. Specifically, dramatic color changes were observed when **1** was allowed to react with structurally slightly different ligands: dendrimers **7** (CH_2Cl_2 solution, $\lambda_{\text{max}} = 394$ nm vs 389 nm for **1**) and **9** ($\lambda_{\text{max}} = 394$ nm) are orange-red solids, whereas **6** ($\lambda_{\text{max}} = 624$ nm) and **8** ($\lambda_{\text{max}} = 626$ nm) are emerald-green powders. The UV-vis spectra of **1**, **6**, and **7** are presented in Figure 2. The appearance of the band at ~ 630 nm is probably indicative of the LMCT between the dendritic ligands and the $[\text{Re}_6\text{Se}_8]^{2+}$ core, and it is apparent that a simple modification of the ligands completely shifts the absorption maxima of the resulting dendrimers.¹⁵ These results strongly suggest that changes in molecular architecture and composition can be correlated to their wavelength tunability, absorbance maxima, and reflectivity, allowing fine-tuning and optimization of the optical properties of these novel dendrimers. We are in the course of preparing dendrimers with the second-generation dendron **10** and those of even higher generations. The results will be published in due course.

In conclusion, we have presented the first examples of utilizing solvated metal clusters to construct a novel class of metallo-dendrimers. These dendrimers, supported by the hexanuclear $[\text{Re}_6\text{Se}_8]^{2+}$ cluster core, exhibit dramatic color changes with structurally slightly different component dendrons. It is clear from the preliminary results described herein that polynuclear metal clusters are superb structural and functional scaffolds for dendrimer construction. First, one-pot ligand substitution reaction of the fully solvated hexanuclear clusters leads to the addition of six dendron ligands, thus engendering a globular system, even with low-generation dendrons. Second, octahedral disposal of six metal sites establishes optimal occupation of the cluster coordination sphere by dendrons, thus reducing the structural defects due to steric congestion at higher dendritic generations. Third, the existence of multiple metal sites presents an opportunity for variable degrees of ligand replacement, making it possible to modify the molecular properties with a certain number of dendrons of selected functionality. Finally, the rich varieties of metal clusters coupled with their unique magnetic, electrochemical, and photophysical properties offer abundant opportunities in materials research. We expect many more exciting results to follow.

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Supporting Information Available: Text giving full experimental details and spectroscopic data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(15) The reaction of **1** with pyridine or 4-hydroxypyridine affords a yellow powder that is insoluble in any common organic solvents. The yellow color of these insoluble products indicates that they resemble **1** spectroscopically. Similar low solubility of the pyridine-ligated W_6S_8 complex has been reported independently by McCarley and DiSalvo. See: Zhang, X.; McCarley, R. E. *Inorg. Chem.* **1995**, *34*, 2678. Ehrlich, G. M.; Warren, C. J.; Vennos, D. A.; Ho, D. M.; Haushalter, R. C.; DiSalvo, F. J. *Inorg. Chem.* **1995**, *34*, 4454.