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Dendritic Arrays of $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ Core-Containing Clusters: Exploratory Synthesis and Electrochemical Studies

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Abstract: The reaction between the previously reported site-differentiated cluster solvate $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(MeCN)](SbF_6)_2$ (**1**) with pyridyl-based ditopic ligands 4,4′-trimethylenedipyridine (**2**), 1,2-bis(4-pyridyl)ethane (**3**), and (*E*)-1,2-bis(4-pyridyl)ethene (**4**) afforded cluster complexes of the general formula $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(L)](SbF_6)_2$ (**5**−**7**), where L represents one of the pyridyl-based ligands. Reacting these cluster complex-based ligands with the fully solvated cluster complex $[Re_6(\mu_3\text{-}Se)_8(MeCN)_6](SbF_6)_2$ (**8**) produced dendritic arrays of the general formula $\{Re_6(\mu_3\text{-}Se)_8[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(L)]_6\}(SbF_6)_{14}$ (**9**−**11**), each featuring six circumjacent $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5]^{2+}$ units bridged to a $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core cluster by the pyridyl-based ligands. Electrochemical studies using a thin-layer electrochemical cell revealed cluster-based redox events in these cluster arrays. For **9** (L = **2**), one reversible oxidation event corresponding to the removal of 7 electrons was observed, indicating noninteraction or extremely weak interactions between the clusters. For **10** (L = **3**), two poorly resolved oxidation waves were found. For **11** (L = **4**), two reversible oxidation events, corresponding respectively to the removal of 1 and 6 electrons, were observed with the 1-electron oxidation event occurring at a potential 150 mV more positive than the 6-electron oxidation. These electrochemical studies suggest intercluster coupling in **11** via through-bond electronic delocalization, which is consistent with electronic spectroscopic studies of this same molecule.

Introduction

Dendrimers are highly branched, monodisperse macromolecules emanating from a central core.[1,2] A dendritic architecture features three distinct structural components, the core or focal point, the branching units, and the periphery. The unique structure, combined with the possibility of incorporating functional groups into each of these structural modules, offers great potential for making useful new materials.[3] Understandably, tremendous interest has been generated ever since the genesis of this novel class of macromolecules. Earlier efforts have focused on the development of synthetic methodologies, most notably the now well-established divergent and convergent syntheses.[4] Although interest in seeking creative synthesis of dendrimers remains, the focus has shifted from the mere construction of dendritic molecules to the realization of functional materials. This may be achieved either by making use of the overall globular structure[5] and the voids[6] formed between the branching units or, more straightforwardly, by introducing functional groups into a dendritic architecture. By controlling where the functional groups are positioned, possibilities arise for structure manipulation and property modification, possibly leading to new substances with useful applications.

One strategy in this context is incorporation of metallic units to generate metal-containing dendrimers, that is, metallodendrimers.[7] The combination of the inherently interesting electronic, magnetic, or catalytic properties of metal elements with the unique and often nanoscopic dendritic architecture offers great prospects of discovering novel functional materials. A large number of metallodendrimers have thus been synthesized, some of which promise to be useful in catalysis,[8] sensor development,[9] nanoelectronics,[10] nanooptics,[11] and biomedical imaging.[12]

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The synthesis of metallodendrimers has been dominated by the use of mononuclear metal units. However, many of the synthetic methodologies should be readily extendable to metal clusters. These unique chemical species have in most cases predictable and well-defined coordination geometries. They display inherently interesting physical properties as a result of metal−metal bonding interactions.[13] As such, metal cluster-containing dendrimers represent a distinct subgroup of metallodendrimers, likely offering fascinating research challenges with potentially important ramifications.

The first cluster-containing metallodendrimers, sinalol dendrimers featuring dinuclear cluster motifs on their peripheries, were reported in 1995 by Seyferth and co-workers.[14] More examples have since appeared in the literature,[15,16] among which are the first cluster-cored metallodendrimers, reported by Gorman and co-workers, featuring a biologically significant $[\mathrm{Fe}_4\mathrm{S}_4]^{2+}$ cluster encapsulated by dendron-functionalized aromatic thiolato ligands.[16] The dendritic ligands are shown to regulate both the kinetics and the potential of the cluster-based redox processes, a property possibly useful for applications of such materials in information storage.[16b]

Our efforts in this vein utilize the hexarhenium cluster $[\mathrm{Re}_6(\mu_3\text{-Q})_8]^{2+}$, whose structure is shown in Figure 1 with the terminal ligands (L). The cluster core is an octahedron of metal−metal bonded Re atoms face-capped with chalcogen atoms Q (S or Se).[17] Recognized first in extended solids, this cluster system has generated significant recent interest[18−22] due to its high-yield synthesis,[23] facile chemical transformations,[24,25] and interesting electrochemical and luminescent properties.[26−28]

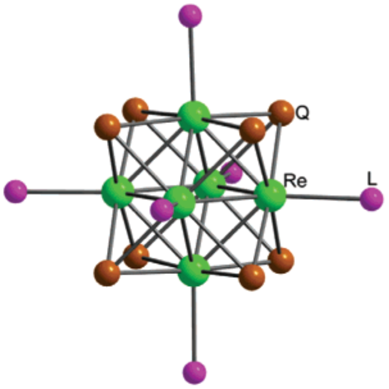

Figure 1. Structure of the $\mathrm{Re}_6(\mu_3\text{-Q})_8$ (Q = S, Se) cluster core shown with terminal ligands (L).

The iodide-terminated cluster $[\mathrm{Re}_6(\mu_3\text{-Se})_8\mathrm{I}_6]^{4-}$, prepared by high-temperature solid-state synthesis,[23] has been used in our work as the starting material. Substitution of the terminal ligands is facile, and a variety of cluster derivatives have been produced, wherein L is triethylphosphine, acetonitrile, a pyridyl-based ligand, or a mixed set of triethylphosphine and one of the other two ligand types.[22,24,25] Phosphine ligands are particularly useful in stabilizing the Re sites, affording a set of site-differentiated clusters available for further chemical transformations at the remaining metal sites.

The superior synthetic utility of these clusters has been demonstrated through the realization of a great variety of super/

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supramolecular constructs,[29] including metallodendrimers cored by this octahedral cluster.[30] It has been shown that the electronic structure of the cluster can be modulated with the use of Fréchet-type dendrons featuring different focal cluster-coordinating moieties; dramatic color changes have been observed for the resulting cluster-core metallodendrimers.

Encouraged by these initial findings, we extended our efforts to the synthesis and property investigation of even more sophisticated metallodendrimers.[31] Our synthetic goal is to generate the first bona fide metal cluster dendrimers that are characterized by the presence of clusters at the core, within the branches, and on the periphery. In terms of interesting and potentially useful properties, the cluster is redox-active with a potential tunable by its coordination environment. Furthermore, the parent and oxidized forms of the cluster exhibit drastically different absorption characteristics, which occur in the UV region, and both states are luminescent (broad emission, 600−1200 nm).[28] Thus, generating dendritic arrays with multiple such cluster units is expected to be of fundamental scientific interest as well as practical significance in developing molecular electronic and optical devices.[32] In this report, we discuss the details of the synthesis, characterization, and spectroscopic and electrochemical studies of these uniquely designed metallodendrimers.

Results and Discussion

For convenience of discussion, pertinent compounds are designated as follows: $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(MeCN)](SbF_6)_2$, **1**; 4,4′-trimethylenedipyridine, **2**; 1,2-bis(4-pyridyl)ethane, **3**; (*E*)-1,2-bis(4-pyridyl)ethene, **4**; $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(\mathbf{2})](SbF_6)_2$, **5**; $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(\mathbf{3})](SbF_6)_2$, **6**; $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(\mathbf{4})](SbF_6)_2$, **7**; $[Re_6(\mu_3\text{-}Se)_8(MeCN)_6](SbF_6)_2$, **8**; $\{Re_6(\mu_3\text{-}Se)_8[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(\mathbf{2})]_6\}(SbF_6)_{14}$, **9**; $\{Re_6(\mu_3\text{-}Se)_8[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(\mathbf{3})]_6\}(SbF_6)_{14}$, **10**; and $\{Re_6(\mu_3\text{-}Se)_8[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(\mathbf{4})]_6\}(SbF_6)_{14}$, **11**. The heptacluster arrays, having the general formula $\{Re_6(\mu_3\text{-}Se)_8[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(L)]_6\}(SbF_6)_{14}$ (**9**, L = **2**; **10**, L = **3**; **11**, L = **4**), were synthesized by reacting the previously reported acetonitrile solvated complex $[Re_6(\mu_3\text{-}Se)_8(MeCN)_6](SbF_6)_2$ (**8**)[24] with 6 equiv of one of the site-differentiated cluster complexes of the general formula $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(L)](SbF_6)_2$ (**5**, L = **2**; **6**, L = **3**; **7**, L = **4**) (Figure 2); the cluster complex ligands (**5**−**7**) were prepared by reacting the previously reported mononitrile complex $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(MeCN)](SbF_6)_2$ (**1**)[24] with one of the pyridyl-based bridging ligands L (**2**, **3**, or **4**). All new compounds (**5**−**7** and **9**−**11**) were characterized by multinuclear (^{1}H, ^{31}P, and ^{77}Se) NMR and elemental analysis (CHN). In addition, the molecular structure of **6** was established by single-crystal X-ray diffraction. Details of the syntheses, spectroscopic characterization, and crystallographic studies can be found in the Supporting Information.

It is worth noting that the reaction between **8** and $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(4,4'\text{-dipyridyl})](SbF_6)_2$[22b] failed to produce an analogous heptacluster dendrimer.

Electronic Spectroscopic Studies. Spectroscopic studies of the cluster complex ligands and corresponding dendrimers were carried out to probe the effect(s) of bridging ligand on the electronic structure of the cluster arrays. The mono-cluster ligands (**5**−**7**) all show similar featureless absorbances in the UV region, attributable to ligand-to-metal cluster charge transfer (a, Figure 3). The electronic spectra of the corresponding metallodendrimers are also shown (b, Figure 3). The cluster dendrimers **9** and **10** have absorbance spectra nearly identical to their respective cluster complex ligands (**5** and **6**), suggesting that attachment of these cluster-ligand “arms” to the central cluster has virtually no influence on the electronic energies of the cluster-ligand pairs. Dendrimer **11**, however, exhibits new and substantially “red-shifted” bands in the UV, presumably due to the presence of a conjugated system, with which electrical charges are delocalized and the energy of the excited electronic state is lowered.[33] The possibility of electronic communications between the peripheral and core clusters arises, a suggestion further supported by electrochemical studies detailed below.

Electrochemical Studies. Voltammetric studies of the oxidation/reduction behavior for molecules **9**−**11** (ca. 0.2 mM solutions) were carried out using a special thin-layer electrochemical cell (TLE, see Supporting Information).[34] This cell provides the opportunity to voltammetrically characterize small quantities of material and voltammetrically resolve sequential electron-transfer events with better resolution and sensitivity than conventional linear sweep or pulse voltammetries.

Dendrimer **9**, with its nonconjugated propyl linkers, gives a response comparable to those observed for the oligomers of the same cluster type;[22b,c,i] all clusters on the molecule (even the core cluster) are rapidly oxidized at nearly the same potential, yielding a measured value of 7.1 e^- (Figure 4). Such a voltammetric response suggests that all clusters sit in essentially energy-equivalent environments, both with respect to the loss of an electron and with respect to the ability of the solution counterions to compensate the change in charge density of the whole molecule.[34−39]

For molecule **10**, the first voltammetric oxidation wave is extended over a larger potential window, and a second and much broader oxidation process is barely resolved above the background current (Figure 4). Upon scan reversal, the reduction wave is better defined and coulometric analysis of this wave shows a 6.6-e^- process. These results suggest that oxidation of the first few peripheral clusters (5−6 clusters) causes the oxidation of the final clusters to become energetically more difficult. What is not clear from these measurements, however, is whether this change in electrochemical behavior is due to a through-space interaction between closely spaced, but nonconjugated clusters (e.g., coulomb repulsion effects) and/or whether counterion compensation during the oxidation event, which, because of the close spacing of these redox centers, slows the attainment of a stable, fully oxidized state for this molecule.

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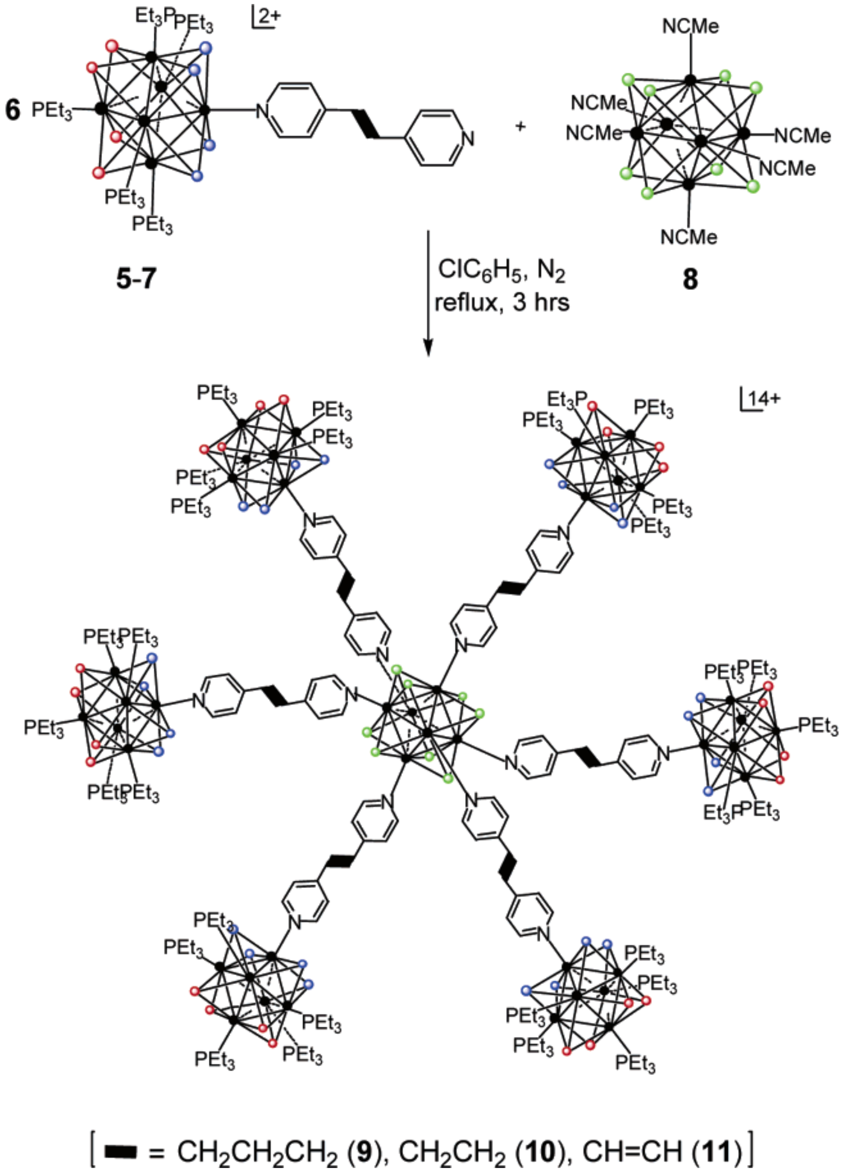

Figure 2. Synthesis of cluster dendrimers **9**−**11**.

Once full oxidation has been completed, at ca. +1.0 V, it appears that reduction of all seven oxidized centers occurs at a single potential.

For **11**, two resolved voltammetric oxidation events are observed, where the areas correspond to 5.8 e^- for the first oxidation at a midpoint potential of 0.73 V and 1.1 e^- for the second oxidation at a midpoint potential of 0.88 V (Figure 4). The stepwise oxidation is more conspicuous when shown in a more expanded form (Figure 5). Both peaks remain separated on the reverse sweep and, after correction for background charging currents, show the same charge on the oxidation sweep as on the reduction sweep. This observation suggests that oxidation of the core cluster is made energetically more costly once the six outer clusters have been oxidized, as expected for truly interacting redox centers.[35−38] Although the coulomb repulsion effects and the kinetics of counterion compensation may still be effective, as in the case of **10**, the distinct stepwise redox events observed suggest strongly through-bond electronic delocalization, which is consistent with the shifts in the absorbance band of **11** versus those seen for **9** and **10** (Figure 3).

The coulometric analysis of each voltammetric wave showed a total of 7-electron oxidation for each molecule, but the uncertainty in these calculations was larger for **10**, because the second oxidation wave was too broad. Cluster oxidation potentials, collected in Table 1, were determined from the midpoint potentials in these voltammograms (the mean of anodic and cathodic peak potentials). Careful characterization of these molecules by normal cyclic voltammetry, and by differential pulse voltammetry, did not indicate any additional spurious electrochemical processes, such as surface adsorption of either reactant or product, which would have complicated the thin-layer voltammetric characterization.[34]

The electrochemical properties of molecular and supramolecular systems containing multiple redox centers have been a topic of great interest, largely due to their potential use in designing new molecular electronic materials.[35−38,41−43] When

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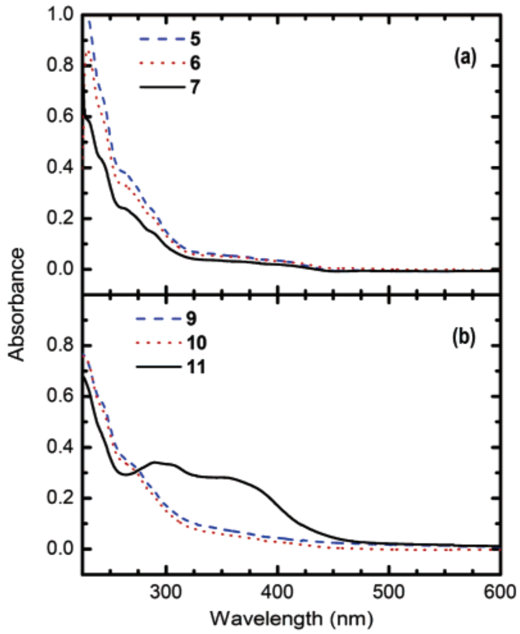

Figure 3. UV−vis spectra of **5**, **6**, and **7** and the corresponding dendrimers **9**, **10**, and **11**.

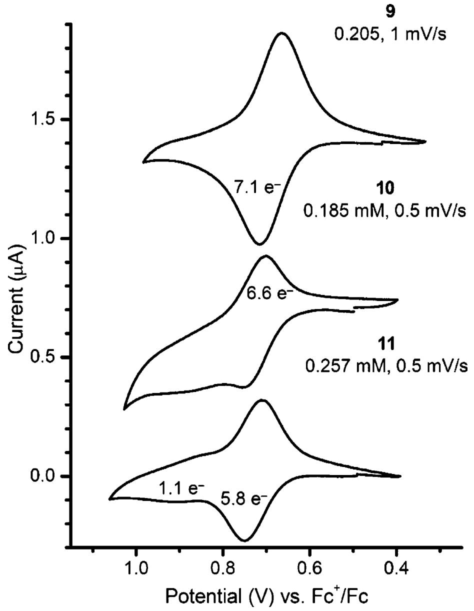

Figure 4. Thin-layer cyclic voltammograms of heptacluster dendrimers **9**, **10**, and **11**.

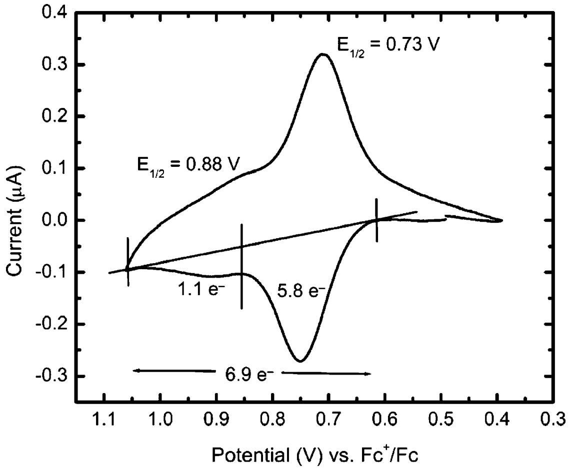

Figure 5. Thin-layer cyclic voltammogram of **11** in expanded form.

Table 1. Oxidation Potentials and the Number of Electrons Transferred for **9**−**11**[a]

dendrimer	$E_{0\times1}$ vs Fc$^+$/Fc (V)	electrode volume (mL)	Q/C (mC/mM)	n
9	0.69	0.373	255	7.1
10	0.71	0.373	237	6.6 (cathodic)
11	0.73, 0.88	0.373	207, 39	5.8, 1.1

[a] The total amount of charge passed (Q) in exhaustively oxidizing/reducing the contents of such a thin-layer cell can be related to the number of electrons transferred per redox event (n) by formalism $Q = nFCV$, where F is Faraday's constant, C is the bulk analyte concentration, and V is the cell volume.[40]

interaction between centers is weak, oxidation/reduction occurs for all of the redox-active centers at the same potential, whereas when such interaction is strong, oxidation or reduction of these centers leads to resolved voltammetric peaks; that is, oxidation or reduction of one class of centers alters the oxidation or reduction potential of nearby centers. The importance of the bridging ligand in determining such interactions is well recognized. Electronic communications may be mediated by through-bond interaction, for which superexchange theory provides a theoretical basis.[43] Such interactions may also be through-space whereby the bridging ligands control the distance and orientation of the metal-containing units.

Molecules **9**, **10**, and **11** appear to span the aforementioned range of interactions, and, at first glance, the observations seem to be consistent with what one would expect on the basis of the ligand structure. Specifically, clusters in **9** are well-spaced, not linked through conjugation, and provide additional space for counterions to enter/exit and compensate the change in cluster charge during redox events. Extremely weak interactions between the component clusters are expected. The change of electrochemical behavior in **10**, while certainly not due to conjugation in the linker units, may result from steric hindrance to oxidation (and counterion incorporation) in the central cluster. Strong interactions in **11** can be rationalized by the conjugation in the linker, in addition to coulomb repulsion effects and the kinetics of counterion compensation.

The above rationalization of electrochemical behavior in terms of ligand structure (length, conjugation, or lack thereof), although intuitive and seemingly reasonable, is inadequate as it fails to reconcile with our previous observations made for oligomeric cluster arrays composed of two, three, or four clusters of this same type bridged by conjugated ligands; these cluster arrays show no evidence of coupled cluster oxidations or increased/decreased oxidation potentials.[22b,c,i] On the basis of these previous findings, it can be concluded that the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ cluster is predominantly capable of sustaining the charge associated with an oxidized state without substantially polarizing neighboring moieties/clusters even when conjugated linkers exist. Nevertheless, coupled oxidations are displayed by a

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dicluster featuring two $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ units intimately fused via a rhombic Re_2Se_2 bridge,[22a] suggesting that the cluster may not be entirely efficient in sustaining charge buildup and that the additive effect of this may still result in appreciable polarization of neighboring moieties/clusters, depending on how compact is a cluster array's structure. In the present case, it is the unique dendritic architecture that provides a structural and functional platform where various effects possibly influencing the intercluster electronic interactions, the electronic properties of the cluster, the bulk (length) and degree of conjugation of the bridging ligand, and the overall compactness of the multicluster array, intertwine. An analogous cluster dendrimer featuring 4,4′-bypyridyl, a shorter conjugated bridging ligand, if realized, should display a more pronounced intercluster coupling than **11**. However, although sterically feasible, this dendrimer failed to materialize, suggesting an energetically insurmountable charge buildup as a result of the highly compact structure, and further manifesting the critical role of the dendritic architecture in subtly disposing the redox-active clusters for the intriguing electrochemical properties to be observed.

Summary

Three novel metallodendrimers, each composed of one central and six peripheral $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core-containing clusters linked by pyridyl-based bridging ligands, have been synthesized. They represent the first bona fide cluster-supported metallodendrimers featuring cluster units at the core, within the branch, and on the periphery of a dendritic architecture. The structures of these nanoscopic multicluster arrays have been established, and their electrochemical properties have been studied by voltammetry and coulometric analysis in a special thin-layer cell. It has been found that individual clusters behave independently of one another within the same dendritic structure when adequately long nonconjugated bridging ligands are utilized, whereas in the case of a conjugated linking group, the clusters are appreciably coupled. The coupled oxidation is attributable to the additive effects of the polarization of the core cluster by the oxidized peripheral clusters. Both through-space and though-bond interactions are possible, and the kinetics of counterion compensation during the redox processes may have also played an important role, depending on the size and nature of the bridging ligands. However, on the basis of our previous and present findings, it is clear that the dendritic architecture is critically important for the unique electrochemical behavior to be observed. On the basis of the response of the materials presented here, it is anticipated that sequential increases in dendrimer generation, especially with the use of conjugated ligands, would result in further splitting of the oxidative waves. If this strategy were viable, it would suggest that the electrochemical properties of these materials might be controlled by controlling the supramolecular structure.

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Supporting Information Available: Synthetic and characterization details; development of a thin-layer cell electrode and hypothetical models rationalizing variations observed in the voltammetry of the heptacluster dendrimers. This material is available free of charge via the Internet at http://pubs.acs.org.

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