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Dendritic encapsulation-roles of cores and branches

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Abstract—Examples of new dendrimers are presented. In the first, the effect on electron transfer rate attenuation is investigated for two dendrimer isomers that differ only in the linkage (*ortho*- versus *meta*-linked) of the phenyl ether units within one generation of the structure. Second, the effect of encapsulation on electrochemical and luminescence behavior of a new type of rhenium selenide cluster core dendrimer is illustrated.

1. Introduction

The phenomenon of encapsulation manifests itself across the realms of materials science and life science. The need to separate, to contain and to release under controlled conditions is found in structures both natural and artificial. These include cells, micelles/liposomes, host–guest complexes, and core-shell structures. The effect of the encapsulation can be shielding (e.g. steric protection from the outer environment) and/or engulfing (e.g. partitioning into an inner environment). At the molecular level, the mode of encapsulation can be either covalent or non-covalent.

Dendrimers have been explored extensively as molecular scale encapsulants. This area has been discussed critically in the literature by both us[1] and by Fréchet et al.[2] Small molecule encapsulation may have utility in catalysis,[3] efficient binding in macromolecular host structures,[4–10] and molecular scale imprinting.[11] In covalent encapsulation, the dendrimer serves to sterically shield and/or protect a moiety typically found at its core. This type of dendritic shielding has been used to mimic metalloproteins[12–17] and in electron transfer rate attenuation which is potentially important in molecular electronics.[18,19]

Recently, we have reported several types of metal cluster core dendrimers.[1,12,18,20–23] The properties of these clusters have been exploited to probe dendrimer conformation and to understand the effects of encapsulation on electronic properties of the molecules. An open question is how differing structures of dendrimers and differing environments into which they have been placed influence the conformation of the dendrimer, its concomitant ability to shield sterically the core moiety and how this shielding is manifest in the physical properties of the molecule. To this end, we have embarked on several investigations of dendrimer structure–property relationships relevant to this question. Results of several approaches are reported here.

2. Results and discussion

Our general strategy is to prepare cluster core dendrimers in which (1) the effect of dendrimer encapsulation on the electrochemical, magnetic and/or photophysical properties can be observed and (2) the structure of the dendron arms is modified so as to maximize the encapsulating effect. One might imagine that the ideal scenario for this is to find the cluster at the geometric center of the dendrimer with the arms somehow uniformly disposed around the cluster. This general architecture is shown in Figure 1. Thus, it is of interest to vary both the structure of the arms and of the

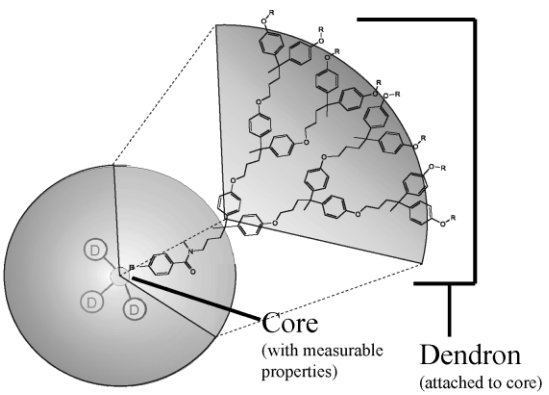

Figure 1. Generic encapsulation scheme highlighting the roles of the core (to be encapsulated) and the dendrons (to affect the encapsulation).

Keywords: dendrimer; encapsulation; isomers; conformation; rhenium; selenide; iron sulfer.

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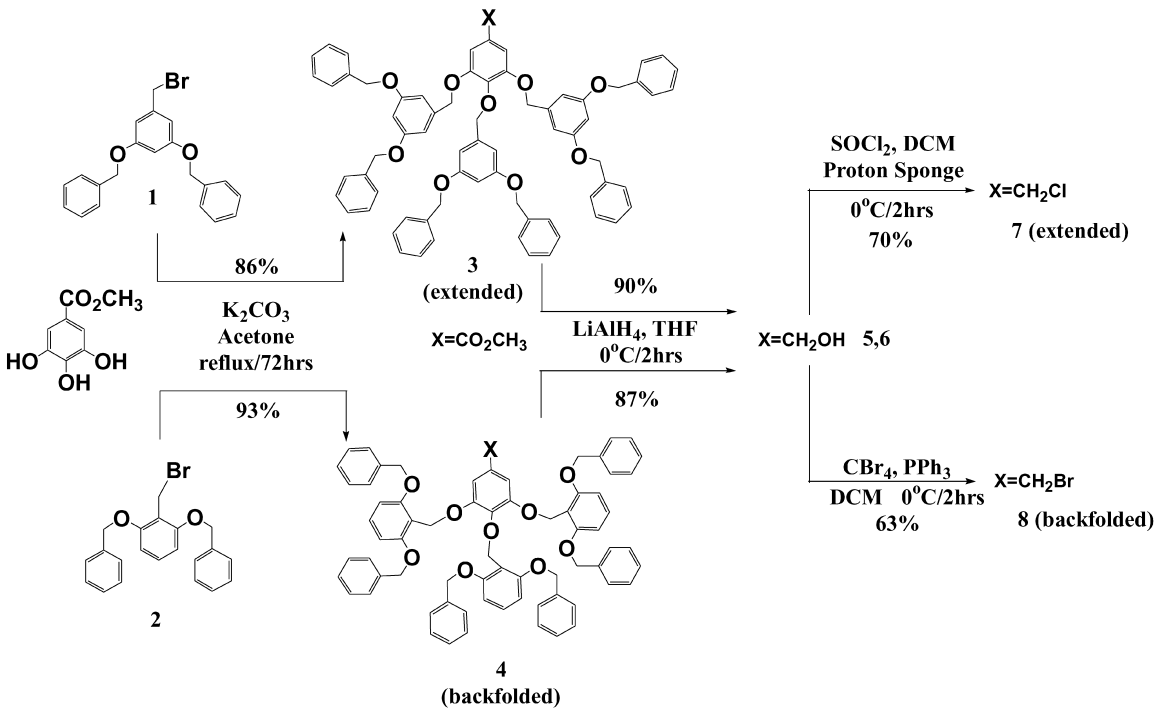
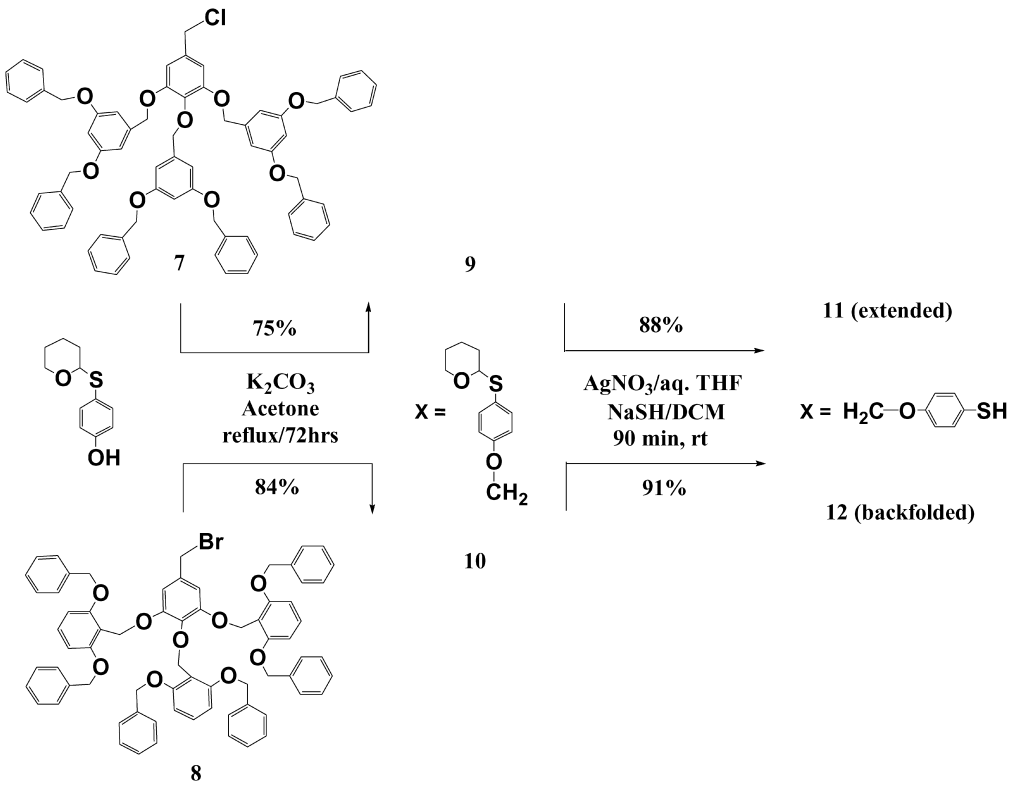


Scheme 1.

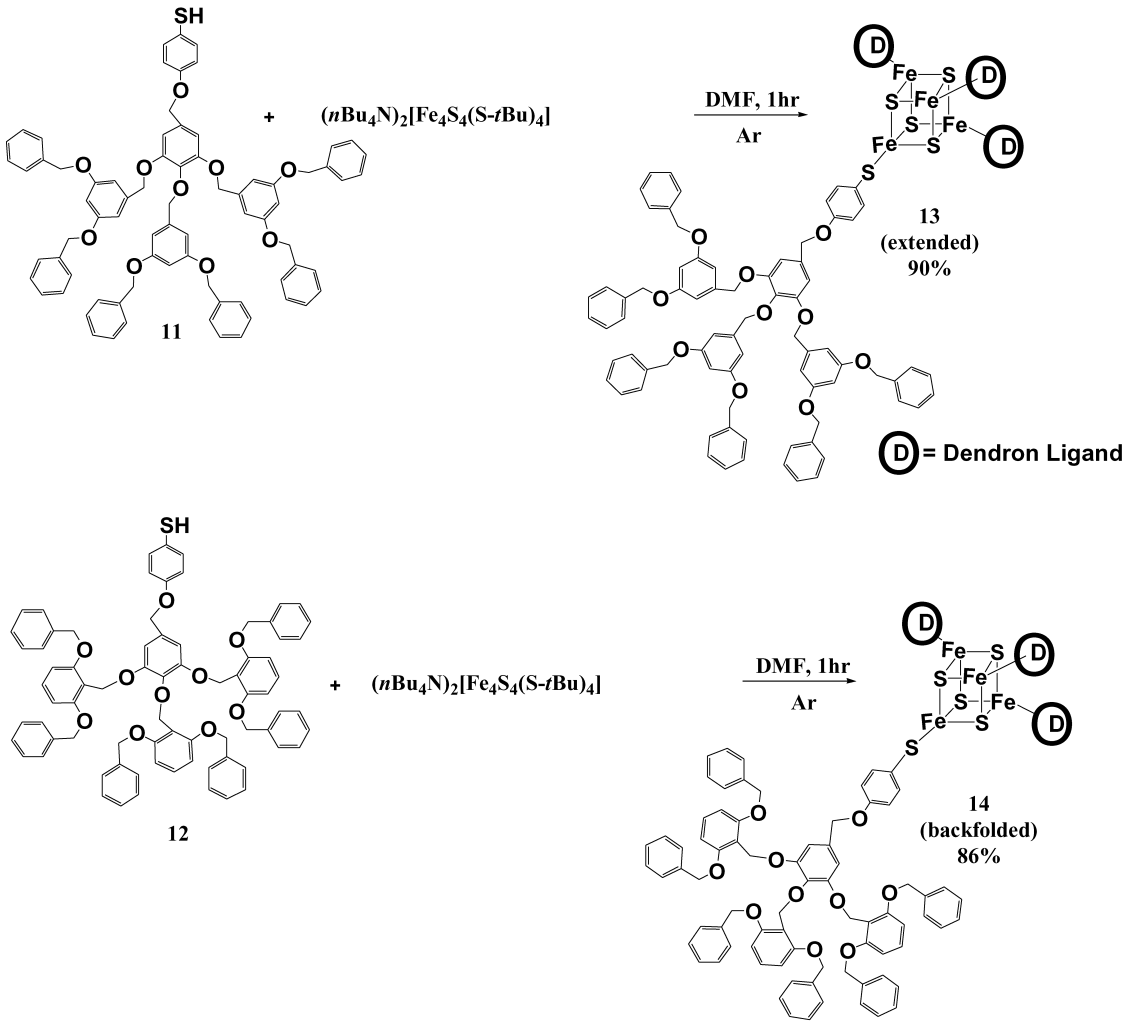
encapsulated cluster. Approaches for both types of variation are described here.

2.1. Dendrimer isomers

The primary structure of the dendrimer influences conformation, which, in turn, influences encapsulation behaviors. We recently showed this in a simple way by comparing redox active, iron–sulfur cluster core dendrimers that had alternatively stiff and flexible repeat units.[1,23] An aesthetically satisfying way to probe the influence of structure on encapsulation via conformation is through the study of constitutional isomers. The synthesis[24] and study of dendrimer isomers has had some precedent including the



Scheme 2.



Scheme 3.

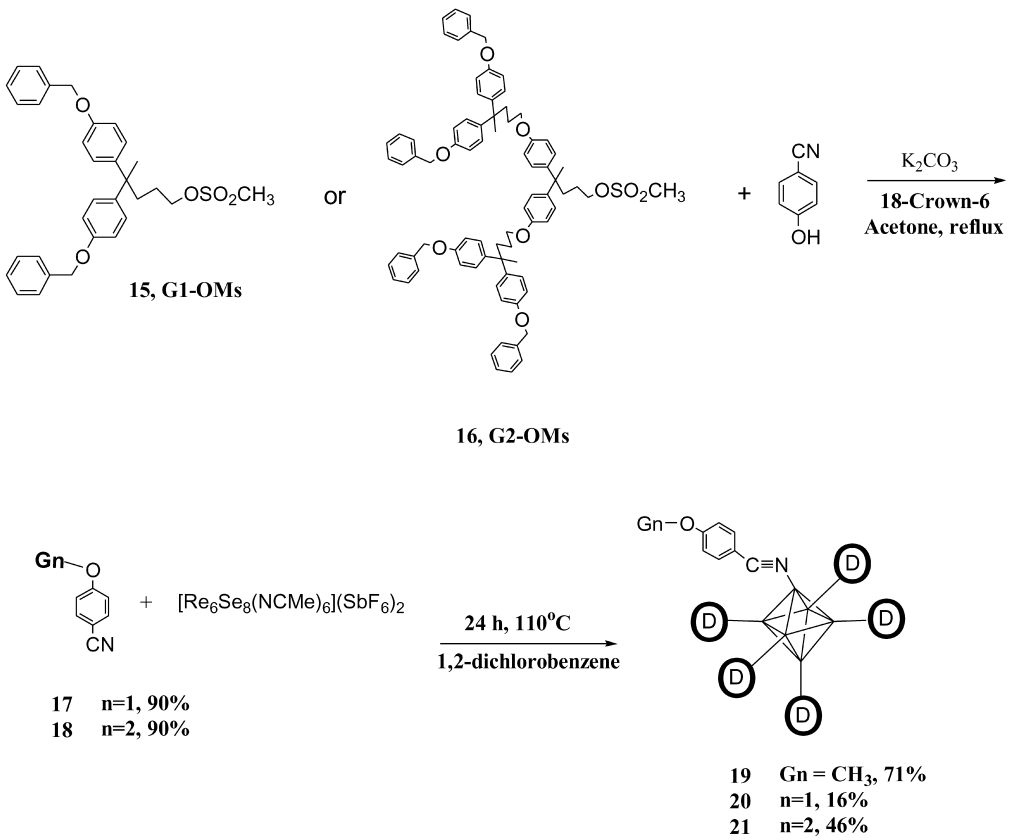
study of linear versus hyperbranched structures,[25,26] supramolecular organization of different dendrimer isomers,[27] stereoisomers in dendrimers (e.g. *cis* versus *trans* azobenzene linkages in dendrimers)[28] and isomeric metallodendrimers.[29] Ideal dendrimer isomers differ only in their primary structure. Changes in the primary structure of the dendrimer can result in a change in its conformation (e.g. the disposition of the arms around the core and the relative degree to which the core is buried in the dendrimer). This change in conformation could be reflected in a change in the measured degree of encapsulation of the core. For example, in the case of an electroactive core (such as is discussed here), a change in the kinetics and/or thermodynamics of electron transfer to/from that core is expected.

The question emerges as to what primary structural elements in dendrimers might be most efficacious at influencing the conformation of these molecules. We and others[30–33] have hypothesized that primary structural elements that enforce backfolding should increase the

Table 1. Electrochemical data obtained for dendrimer isomers

Structure	CA[a]		CV[b]	OSWV[c]	
	D_o ($\times 10^6$ cm^2/s)[d]	R_H (Å)[e]	$E_{1/2}$[f]	k_o ($\times 10^3$ cm/s)	α
13 (extended)	2.78(0.05)	11.86(0.34)	−1494(4)	4.79(0.92)	0.48(0.03)
14 (backfolded)	4.26(0.17)	7.57(0.32)	−1618(2)	0.64(0.15)	0.50(0.005)

Values in parentheses represent the magnitude of the 90% confidence intervals of these values.
[a] Data determined from chronoamperometry.
[b] Data determined from cyclic voltammetry.
[c] Data determined from Osteryoung square wave voltammetry.
[d] Diffusion coefficient.
[e] Stokes–Einstein radius calculated from the diffusion coefficient.
[f] Thermodynamic redox potential.



Scheme 4.

degree of steric congestion around the core moiety of the dendrimer. This behavior should lead to more effective encapsulation. To probe this hypothesis experimentally, two redox-active cluster core dendrimer isomers were prepared as illustrated in Schemes 1–3. Using a combination of cyclic voltammetry, chronoamperometry and Osteryoung square wave voltammetry as described previously,[23] diffusion coefficients and heterogeneous electron transfer rate constants for these molecules were determined and are reported in Table 1.

Several observations can be made from these data that are consistent with our hypothesis that units in the outer generation that were backfolded (in this case *ortho*-linked) resulted in better encapsulation than units that were more extended (in this case *meta*-linked). A lower rate of electron transfer is observed for the backfolded isomer compared to the more extended isomer. Moreover, the backfolded isomer is more difficult to reduce (e.g. it has a more negative redox potential) than the more extended isomer, consistent with the core being found in a more compact, hydrophobic dendrimer environment. As the reduction of interest here is the conversion of a di-anion to a tri-anion, this increase in effective charge is expected and found to be impeded by the hydrophobic dendrimer environment compared to the more polar solvent (DMF). This process has been discussed previously by us relative to several redox cluster core dendrimers.[1]

Estimating the hydrodynamic radius of these two molecules from their diffusion coefficients using the Stokes–Einstein equation, the backfolded isomer is also found to be smaller than the more extended-isomer. This observation is consistent with the hypothesis that backfolding results in more steric congestion. Interestingly, it is the smaller molecule that has the lower rate of electron transfer. This perhaps counterintuitive observation can be rationalized by suggesting that it is the relative degree to which the redox active iron–sulfur cluster is buried within the molecule, rather than the overall size of the molecule that is most relevant to the attenuation of the rate of electron transfer.

2.2. Octahedral cluster core dendrimers

Discrete clusters offer a variety of interesting and potentially useful electrochemical, luminescent and magnetic properties. To harness these properties in new materials, efficient synthetic protocols are required to functionalize them appropriately. We have, for example, described ligand exchange chemistry that can be used to prepare Mo_6Cl_8 cluster core dendrimers.[22]

Zheng et al. have reported the efficient synthesis of dendrimers composed of Re_6Se_8 units.[34–36] Given our interest in electroactive encapsulation, we performed cyclic voltammetry on these molecules. However, only irreversible electrochemistry was observed. Postulating that the focal group moiety bonding to the cluster could have a significant effect on its electrochemical kinetics, and that the pyridyl linkage employed by Zheng et al. might be non-ideal in this regard, we explored the synthesis and electrochemistry of Re_6Se_8 cluster core dendrimers that

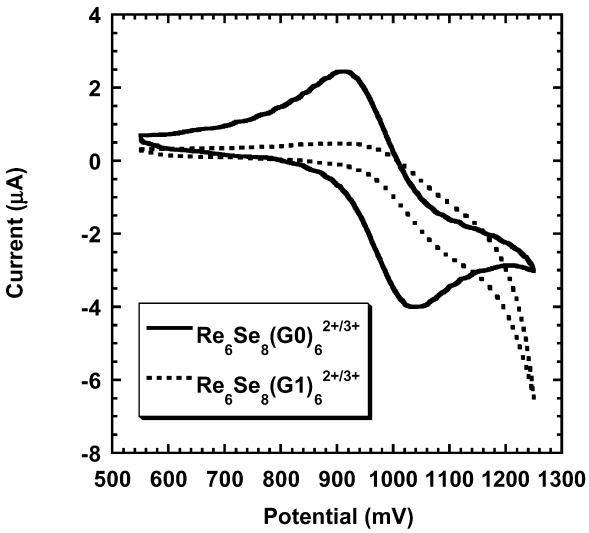


Figure 2. Cyclic voltammograms of rhenium selenide cluster core molecules. Conditions: 100 mV/s scan rate, 2 mM solution in propylene carbonate containing 300 mM tetrabutyl ammonium tetrafluoroborate supporting electrolyte. Potentials are referenced to Ag/100 mM $AgNO_3$/MeCN.

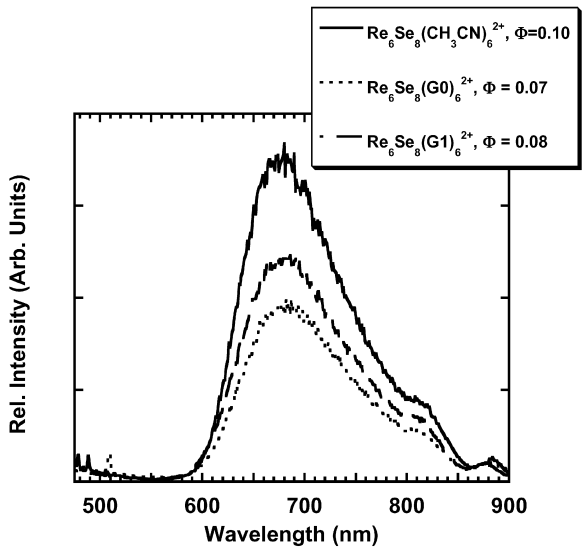


Figure 3. Fluorescence spectra of rhenium selenide cluster core molecules using an excitation wavelength of 436 nm. The zero and first generation dendrimer spectra were recorded in dichloromethane solution and the hexa-acetonitrile complex was recorded in acetonitrile solution.

employed different linkages between the dendron and the cluster core.

We determined synthetically that a benzonitrile linking group provided efficient ligand exchange chemistry and retained quasi-reversible electrochemical kinetics for the $Re_6Se_8L_6$ moiety (L=*para*-methoxy benzonitrile). Dendrimer versions of these clusters were prepared to determine the encapsulating effect of six dendritic arms octahedrally disposed around an inorganic cluster. The synthesis of the dendrons and the ligand exchange to form the Re_6Se_8-cluster core dendrimers are shown in Scheme 4. Conditions for the ligand exchange involved longer reaction times and higher temperatures than were necessary for the analogous ligand exchange reactions around iron–sulfur clusters. Yields of the resulting dendrimers were modest, mostly as the result of repeated precipitations to ensure the purity of these molecules

A preliminary investigation of the electrochemical behavior of these dendrimers was performed using cyclic voltammetry. The results of these experiments are shown in Figure 2 One can observe the quasi-reversible electrochemical behavior (ΔE=125 mV at 100 mV/sec scan rate for Re_6Se_8(*p*-methoxy benzonitrile)$_6^{2+/3+}$) for the "zero generation" compound. In contrast, essentially irreversible electrochemical behavior is observed for the analogous "first generation" molecule.

Rhenium selenide clusters of this type are known to photoluminesce efficiently.[37] Using the compound $Re_6Se_8(CH_3CN)_6^{2+}$ as an actinometer, the relative quantum yields of the G0 and G1 ligated molecules were obtained by exciting at 436 nm and observing the relative fluorescence.[37] The data are presented in Figure 3. The similarity of the three fluorescence spectra indicates that the *para*-alkoxy benzonitrile linkage in the molecules under study did not affect the relative luminescence efficiency or color of the rhenium selenide moiety.

3. Conclusions

Overall, these results indicate several intriguing properties of metal cluster core dendrimers. First, the structure of the dendron ligands around the cluster has a measurable effect on encapsulation behaviors such as electron transfer rate attenuation. This effect is illustrated in two dendrimer isomers in which the structure of the linkage is alternatively backfolded and extended. Second, a variety of metal cluster cores can be incorporated into dendrimer architectures provided efficient ligand exchange chemistry can be effected. This chemistry has allowed us to probe electronic encapsulation and luminescence behaviors in rhenium selenide cluster core dendrimers.

4. Experimental

Instrumentation for routine characterization. NMR and FAB-MS were used as previously reported.[38] Fluorescence experiments were carried out on an ISS PC1 photon counting spectrofluorimeter with and ILC PS300-1 25 D.C. ampere illuminator power supply. UV–Vis spectra were recorded using a Hewlett Packard 8452A diode array spectrometer.

Electrochemical apparatus. Electrochemical experiments were carried out on a Bioanalytical Systems CV-50W Voltammetric Analyzer. The three-electrode cell consisted of a Pt disk working electrode (geometric area of 0.0201 cm^2), a Pt auxiliary electrode, and a homemade, non-aqueous $Ag/AgNO_3$ reference electrode (Ag wire contacting a DMF solution of 0.01 M $AgNO_3$ and 0.1 M supporting electrolyte, tetraethylammonium tetrafluoroborate, $TEAF_4B$). All electrochemical experiments were carried out in a nitrogen-filled Vacuum Atmospheres controlled atmosphere box at room temperature. Millimolar concentrations of the analytes were dissolved in DMF, which contained 0.1 M $TEAF_4B$ supporting electrolyte.

Cyclic voltammetry. Potential sweep rates ranged from 25 to 400 mV/s for analytes displaying quasireversible electrochemical behavior at these scan rates

Osteryoung square wave voltammetry. Osteryoung square wave voltammetry was performed using a step height of 4 mV, sweep width amplitude of 25 mV, and a frequency of 5, 10, 15, and 20 Hz. Difference current was iteratively fit using FSQPLT software (provided by J. J. O'Dea of the J. Osteryoung Group)

Chronoamperometry. Chronoamperometry was carried out using a pulse width of 900, 1000, and 1500 ms and a potential step height of 800 mV centered about $E_{1/2}$ for each molecule studied.

4.1. Synthesis of dendrimer isomers

Reagents were purchased from Aldrich and used without further purification unless otherwise noted. Compounds **1**[39] and **2**[40] were prepared as previously described.

S-Tetrahydropyranyl-4-hydroxy thiophenol into an oven dried flask were weighed *p*-hydroxythiophenol (1 equiv., 25.67 g) and pyridinum-*p*-toluenesulfonate (0.05 equiv., 2.5 g), dissolved in dry dichloromethane. The solution was cooled in an ice bath and to the cold solution was added dihydropyran (2.74 equiv., 50 mL) dropwise with stirring over a period of 30 min. After the addition, the mixture was allowed to warm to room temperature and stirring continued overnight. The mixture was then washed with 10% aq. NaOH, water, saturated NaCl, and dried over anhydrous sodium sulfate. The salts were filtered off and the filtrate rotary evaporated to dryness. Yield: 62.2% (36.9 g). The crude bis-THP substituted *p*-hydroxythiophenol (1 equiv., 36.9 g) was dissolved in methanol and the solution cooled in an ice bath. To the cold solution, was added 6 M HCl (1.3 equiv., 29 mL). The reaction mixture was stirred for 4 h while monitoring using TLC. Methanol was removed in vacuo and the residue taken with water and the organics extracted into dichloromethane. Removal of solvent gave a sticky product, which was subsequently heated with hexane, and the supernatant solution was decanted hot. A white precipitate was obtained on cooling the hexane solution. The process was repeated several times and the white, crystalline, solid collected. Yield: 40% (10.5 g). HRFAB (*m*/*z*): 210.1888. Calcd for $C_{11}H_{14}SO_2$: 210.2964, mp 87–89°C, ^{1}H NMR ($CDCl_3$) δ (ppm): 1.50–2.10 (m, 6H), 3.50–3.60 (m, 1H), 4.15–4.25 (m, 1H), 5.04 (t, 1H, J=4.5 Hz), 6.60–6.75 (m, 2H), 7.30–7.40 (m, 2H).

4.1.1. General method for nucleophilic coupling reaction. To a solution of the phenol derivative (1 equiv.), dry acetone (50–60 equiv.), potassium carbonate (1.1 equiv. per OH in phenol), and 18-crown-6 (0.01–0.02 equiv.), was added a benzyl halide derivative (1.1–1.2 equiv. per OH in phenol). The mixture was then refluxed for 2–3 days under nitrogen with vigorous stirring. The mixture was then cooled and concentrated to half the volume. Water was added to dissolve the salts and the organics extracted into ethyl acetate, DCM, or ether. The organic extract was washed with brine or $NaHCO_3$ and dried over anhydrous Na_2SO_4 or $MgSO_4$. Filtration and concentration of the filtrate under reduced pressure gave the product, which was purified as described below.

Compound **3** Purified by column filtration using silica gel and hexanes/ethyl acetate/DCM 80:15:5 as eluent. The product was a yellow-white, sticky solid. Yield: 86% (16.9 g). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.93 (s, 3H), 4.77 (s, 4H), 4.93 (s, 8H), 5.12 (s, 6H), 6.45 (t, 1H, J=2.2 Hz), 6.54 (t, 2H, J=2.2 Hz), 6.74 (d, 4H, J=2.2 Hz), 6.77 (d, 2H, J=2.2 Hz), 7.25 – 7.45 (m, 32H). ^{13}C NMR ($CDCl_3$) δ (ppm): 166.59, 160.20, 159.94, 152.58, 139.94, 139.13, 136.99, 136.85, 128.58, 128.49, 128.31, 127.99, 127.88, 127.59, 127.42, 125.49, 109.49, 106.74, 106.23, 101.94, 76.67, 74.95, 71.32, 70.08, 69.84, 52.30. HRFAB (*m*/*z*): 1090.4266 Calcd for $C_{71}H_{62}O_{11}$: 1090.4292. Anal. Calcd for $C_{71}H_{62}O_{11}$: C, 78.16; H, 5.69; Found: C, 78.17; H, 5.77.

Compound **4** Purified by column filtration through silica gel with an eluent of 70% hexanes/30% ethyl acetate. The product was a yellow-white, sticky solid. Yield: 92.5% (3.95 g). ^{1}H NMR (CD_3CN) δ (ppm): 3.70 (s, 3H), 4.57 (s, 4H), 4.97 (s, 8H), 5.12 (s, 4H), 5.37 (s, 2H), 6.31 (d, 2H, J=8.8 Hz), 6.58 (d, 4H, J=8.1 Hz), 7.00 (t, 1H, J=8.8 Hz), 7.02–7.21 (m, 24H), 7.28–7.35 (m, 6H), 7.36 (s, 2H). ^{13}C NMR (CD_3COCD_3) δ (ppm): 52.09, 61.16, 64.31, 70.67, 70.90, 106.26, 106.52, 109.67, 115.08, 116.89, 124.97, 127.71, 128.01, 128.23, 128.49, 128.93, 129.14, 130.46, 130.92, 138.38, 138.75, 144.78, 154.36, 159.48, 159.76, 167.32. Anal. Calcd for $C_{71}H_{62}O_{11}$: C, 78.16; H, 5.69; Found: C, 78.25; H, 5.75.

Compound **9** Purified by column filtration through silica gel with an eluent of 70% hexanes/25% ethyl acetate/5% DCM. The product was a white, sticky solid. Yield: 75% (1.33 g). ^{1}H NMR (CD_3COCD_3) δ (ppm): 1.50–2.05 (m, 6H), 3.45 (m, 1H), 4.05 (m, 1H), 4.82 (s, 4H), 4.95 (s, 8H), 4.99 (s, 2H), 5.00 (m, 1H), 5.05 (s, 2H), 5.11 (s, 4H), 6.45 (t, 1H, J=2.2 Hz), 6.53 (t, 2H, J=2.2 Hz), 6.78 (d, 4H, J=2.2 Hz), 6.81 (d, 2H, J=2.2 Hz), 6.91 (t, 4H, J=8.8 Hz), 7.25–7.45 (m, 32H). ^{13}C NMR ($CDCl_3$) δ (ppm): 160.19, 159.95, 158.45, 153.04, 140.36, 139.57, 137.05, 136.88, 134.27, 132.65, 128.57, 128.49, 127.98, 127.87, 127.60, 125.94, 115.44, 107.55, 106.75, 106.11, 101.80, 86.28, 75.06, 71.36, 70.25, 70.06, 69.86, 64.73, 31.61, 25.62, 21.78. Anal. Calcd for $C_{81}H_{74}O_{11}S$: C, 77.49; H, 5.95; Found: C, 77.45; H, 6.04.

Compound **10** Purified by column filtration through silica gel using hexane 80%/ethyl acetate 15%/DCM 5% as eluent. Product was a white, crystalline solid. Yield: 84% (1.68 g). ^{1}H NMR (CD_3CN) δ (ppm): 1.5–1.87 (m, 6H), 3.49 (m, 1H), 4.08 (m, 1H), 4.63 (s, 4H), 4.75 (s, 2H), 4.98 (s, 8H), 5.02 (m, 1H), 5.08 (s, 4H), 5.19 (s, 2H), 6.38 (d, 2H, J=8.1 Hz), 6.63 (d, 4H, J=8.1 Hz), 6.76 (s, 2H), 6.85 (d, 2H, J=8.8 Hz), 7.02 (t, 1H, J=8.1 Hz), 7.11–7.25 (m, 26H), 7.28–7.39 (m, 8H). ^{13}C NMR ($CDCl_3$) δ (ppm): 22.49, 26.17, 32.22, 61.17, 63.72, 65.56, 70.89, 70.99, 71.28, 86.99, 106.28, 106.52, 106.54, 108.31, 115.58, 115.94, 117.33, 127.57, 127.67, 127.80, 128.02, 128.15, 128.73, 129.02, 129.70, 130.32, 131.29, 134.97, 137.88, 138.62, 139.88, 154.65, 159.33, 159.48, 159.53, 159.62. Anal. Calcd for $C_{81}H_{74}O_{11}S$; C, 77.49; H, 5.95; S, 2.55; Found: C, 77.74; H, 6.14; S, 2.24.

4.1.2. General method for reduction. The ester (1 equiv.) was cannulated into a solution of $LiAlH_4$ (1.3 equiv.) in dry THF (20.8 equiv.) cooled in an ice-water bath stirring continuously for 2 hours. The reaction was quenched with H_2O, 15% NaOH, or aqueous NH_4Cl. This was followed by addition of 6 M HCl to dissolve the salts. After the reaction was complete (a few hours for **5** and overnight for **6**) the reaction was carefully worked up with water and the solids filtered by passing through a bed of Celite. The organics were extracted into ethyl acetate or dichloromethane. The organic layer was dried over anhydrous Na_2SO_4, filtered, rotary evaporated, and placed under vacuum overnight. The crude alcohol was purified as described below.

Compound **5** Purified by column filtration through silica gel using hexane 75%/ethyl acetate 20%/DCM 5% as eluent and resulted in a white solid. Yield: 90% (11.38 g). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.75 (t, OH, J=5.9 Hz), 4.58 (d, 2H, J=5.9 Hz), 4.77 (s, 4H), 4.91 (s, 8H), 5.06 (s, 2H), 5.09 (s, 4H), 6.44 (t, 1H, J=2.2 Hz), 6.53 (t, 2H, J=2.2 Hz), 6.70 (s, 2H), 6.72 (d, 4H, J=2.2 Hz), 6.80 (d, 2H, J=2.2 Hz), 7.25–7.41 (m, 30H). ^{13}C NMR ($CDCl_3$) δ (ppm): 65.39, 69.82, 70.04, 71.27, 75.03, 101.77, 103.39, 106.07, 106.73, 127.58, 127.84, 127.95, 128.46, 128.55, 136.86, 139.60, 152.93, 159.92, 160.15. Anal. Calcd for $C_{70}H_{62}O_{10}$: C, 79.08; H, 5.89; Found: C, 79.31; H, 6.12.

Compound **6** Purified by silica gel column chromatography using 25% ethyl acetate/5% DCM/hexanes as eluent and resulted in a white, crystalline solid. Yield: 87% (1.28 g). ^{1}H NMR (CD_3COCD_3) δ (ppm): 3.87 (t, OH, J=5.9 Hz), 4.44 (d, 2H, J=5.9 Hz), 4.58 (s, 4H), 4.98 (s, 8H), 5.15 (s, 4H), 5.35 (s, 2H), 6.31 (d, 2H, J=8.8 Hz), 6.61 (d, 4H, J=8.1 Hz), 6.78 (s, 2H), 6.92 (t, 1H, J=8.8 Hz), 7.11–7.24 (m, 26H), 7.37 (d, 6H, J=6.6 Hz). ^{13}C NMR (CD_3COCD_3) δ (ppm): 60.46, 63.50, 64.76, 70.51, 105.99, 106.21, 106.47, 115.29, 117.26, 127.47, 127.67, 127.86, 128.51, 128.77, 129.67, 130.28, 137.10, 138.07, 138.65, 154.29, 159.14, 159.43. Anal. Calcd for $C_{70}H_{62}O_{10}$: C, 79.08; H, 5.89; Found: C, 78.96; H, 5.81.

Compound **7** To a solution of the alcohol **5** (1 equiv., 2.94 g) and proton sponge (1.37 equiv., 0.81 g) dissolved in methylene chloride and cooled in an ice bath, was added thionyl chloride (1.48 equiv., 0.3 mL) dropwise while stirring. The mixture was then allowed to warm to room temperature and stirring continued. After 2 h, a color change was observed and the mixture was quenched with water. The organics were extracted with methylene chloride three times. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated. The chloride product resulted in a yellow-white solid and was carried on without further purification. Yield: 70% (2.09 g). ^{1}H NMR ($CDCl_3$) δ (ppm): 4.50 (s, 2H), 4.77 (s, 4H), 4.92 (s, 8H), 5.04 (s, 2H), 5.07 (s, 4H), 6.44 (t, 1H, J=2.2 Hz), 6.53 (t, 2H, J=2.2 Hz), 6.68 – 7.73 (m, 6H), 6.77 (d, 2H, J=2.2 Hz), 7.25–7.4 (m, 30H). ^{13}C NMR ($CDCl_3$) δ (ppm): 70.4, 70.6, 71.9, 75.6, 102.3, 102.4, 106.7, 107.3, 109.1, 128.2, 128.5, 128.6, 129.0, 129.1, 133.7, 137.4, 137.6, 139.1, 140.0, 140.1, 153.5, 160.5, 160.7. HRFAB (m/z): 1080.3959; Calcd for $C_{70}H_{61}O_9Cl$: 1080.4004. Anal. Calcd for $C_{70}H_{61}O_9Cl$: C, 77.73; H, 5.68; Found: C, 77.92; H, 5.84.

Compound **8** To a solution of the alcohol **6** (1.1 equiv., 2.80 g) in THF or DCM cooled in an ice bath, was added, by cannulating, a solution of carbon tetrabromide (2.5 equiv., 2.19 g) and tri-phenyl phosphine (2.5 equiv., 1.73 g) in THF or DCM, dropwise while stirring. The temperature was allowed to rise to ambient over 2 h. The reaction was quenched with water and stirred for an additional 2 h. The organics were extracted with dichloromethane and washed with saturated NaCl and dried using Na_2SO_4 or $MgSO_4$. The mixture was filtered and concentrated. The compound was a yellow-white solid and was used without further purification. Yield: 63% (1.85 g). ^{1}H NMR (CD_3COCD_3) δ (ppm): 4.35 (s, 2H), 4.57 (s, 4H), 4.99 (s, 8H), 5.13 (s, 4H), 5.34 (s, 2H), 6.31 (d, 2H, J=8.8 Hz), 6.66 (d, 4H, J=8.8 Hz), 6.83 (s, 2H), 6.94 (t, 1H, J=8.1 Hz), 7.08–7.28 (m, 26H), 7.38 (d, 6H, J=7.3 Hz). ^{13}C NMR (CD_3COCD_3) δ (ppm): 60.78, 63.69, 70.67, 70.73, 106.31, 106.57, 109.12, 115.10, 117.04, 127.70, 127.83, 127.06, 128.18, 128.67, 128.80, 128.93, 129.99, 130.58, 138.17, 138.72, 154.39, 159.27, 159.59. Anal. Calcd for $C_{70}H_{61}O_9Br$: C, 74.66; H, 5.46; Found: C, 74.70; H, 5.66.

4.1.3. Deprotection of tetrahydropyranyl protected thiols. Tetrahydropyranyl (THP) protected thiol **9** or **10** (1 equiv.) was dissolved in tetrahydrofuran. Excess of silver nitrate was added. Water was then added to the mixture until a bright yellow precipitate formed. The mixture was then stirred for 20 min and diluted ten-fold with methylene chloride. NaSH (solid, 10 equiv.) was added and stirred vigorously for thirty minutes. The result was a black precipitate, which was removed by filtration. The precipitate was washed twice with methylene chloride. The aqueous and the organic phases were separated and the organic phase washed three times with aq. ammonium chloride solution. The product was dried over magnesium sulfate. Remaining methylene chloride was evacuated under vacuum. A singlet around 3.4 ppm in the ^{1}H NMR spectrum identified the resulting thiol.

Compound **11** The product was a white solid. Yield: 88% (0.17 g). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.31 (s, SH), 4.73 (s, 4H), 4.86 (2×s, 10H), 5.03 (2×s, 6H), 6.41 (t, 1H, J=2.2 Hz), 6.49 (t, 2H, J=2.2 Hz), 6.68 (m, 6H), 6.76 (d, 2H, J=2.2 Hz), 6.79 (d, 2H, J=8.8 Hz), 7.18 (t, 2H, J=8.8 Hz), 7.25–7.48 (m, 28H).

Compound **12** The product was a white solid. Yield: 91% (0.09 g). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.84 (s, SH), 4.49 (s, 4H), 4.57 (s, 2H), 4.90 (s, 8H), 5.16 (s, 4H), 5.38 (s, 2H), 6.20 (d, 2H, J=8.8 Hz), 6.58 (d, 4H, J=8.8 Hz), 6.71–6.92 (m, 9H), 7.03–7.33 (m, 30H).

4.1.4. General method for ligand exchange. To a Schlenk flask, 1 equiv. of $(n\text{Bu}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{S-}t\text{Bu})_4]$[41] was added under inert atmosphere in a dry box. The flask was sealed with a rubber septum and parafilm and transferred to a double manifold vacuum line and purged with argon. To a second Schlenk flask sealed with a rubber septum and parafilm, the thiol **11** or **12** (4.8 equiv.) was added and dissolved in anhydrous dimethylformamide under inert atmosphere to a concentration of 0.1 M. The thiol solution was then transferred to the flask containing the iron–sulfur cluster via a canula needle. The flask containing the two

components was sealed with a glass stopper and stirred for 30 min. The flask was placed under vacuum slowly to avoid bumping, while stirring continuously at 40° C overnight. The flask was then transferred into a dry box for further use.

Compound **13** The product was a glossy, black solid. Yield 90% (0.16 g). ^{1}H NMR (DMSO-d_6) δ (ppm): 0.93 (t, 24H, J=7.3 Hz), 1.32 (m, 16H), 1.56 (m, 16H), 3.13 (m, 16H), 4.73 (m, 16H), 4.81–5.05 (m, 56H), 5.06 (s, 8H), 5.75 (br, 8H), 6.41 (s, 4H), 6.49 (s, 8H), 6.69 (m, 24H), 6.86 (s, 8H), 7.15 – 7.35 (m, 120H), 7.82 (s, 8H). Anal. Calcd for $C_{336}H_{332}O_{40}Fe_4N_2S_8$: C, 73.13; H, 6.28; Found: C, 74.04; H, 6.06.

Compound **14** The product was a glossy, black solid. Yield 86%. ^{1}H NMR (DMF-d_6) δ (ppm): 0.93 (t, 24H, J=7.3 Hz), 1.39 (m, 16H), 1.76 (m, 16H), 3.38 (m, 16H), 4.71 (m, 16H), 4.88 (m, 16H), 5.04–5.19 (m, 32H), 5.36 (m, 16H), 5.82 (br, 8H), 6.44 (m, 8H), 6.69 (m, 16H), 6.93 (m, 8H), 7.04 (m, 12H), 7.19–7.40 (m, 120H), 7.76 (br, 8H). MALDI-TOF (m/z): 5025.90; Calcd for $C_{336}H_{332}O_{40}Fe_4N_2S_8$: 5027.36. Anal. Calcd for $C_{336}H_{332}O_{40}Fe_4N_2S_8$: C, 73.13; H, 6.28; S, 4.65; Found: C, 74.51; H, 6.27; S, 4.37.

4.1.5. Rhenium selenide cluster core dendrimers. *General considerations*. All reagents were used as received except hydriodic acid, which was purchased as either 55–57% or 47% and then diluted according to the certificate of analysis concentration. The compounds $[Re_6Se_8(CH_3CN)_6](SbF_6)_2$,[42] G1-OMs (**15**)[43] and G2-OMs (**16**)[43] were prepared according to literature procedures.

Compound **17** G1-OMs (**15**) (0.5345 g, 1.007 mmol), 4-cyanophenol (0.1268 g, 1.064 mmol), K_2CO_3 (1.7019 g, 4.028 mmol), and 0.05 equiv. (0.53 g, 2 mmol) of 18-crown-6 was added to a round bottom flask. Acetone (40 mL) was added and the solution was refluxed overnight under N_2. The solution was cooled to room temperature and the solvent was removed under reduced pressure. The remaining solid was dissolved in dichloromethane (20 mL). Deionized H_2O (20 mL) was added and the organic layer was collected. Extraction with dichloromethane was repeated three times on the aqueous layer. The organic layer was dried with $MgSO_4$ and the crude product was purified by flash chromatography (CH_2Cl_2). Yield: 5.0 g, 90%. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.62 (m, 5H), 2.20 (m, 2H), 3.94 (t, 2H, J=6.6 Hz), 5.03 (s, 4H), 6.89 (d, 6H, J=8.7 Hz), 7.13 (d, 4H, J=8.7 Hz), 7.30–7.44 (m, 10H), 7.56 (d, 2H, J=8.7 Hz). ^{13}C NMR (CD_2Cl_2) δ (ppm): 25.38, 25.44, 28.28, 38.69, 45.46, 56.55, 70.23, 70.71, 70.88, 99.27, 114.94, 116.69, 128.33, 128.69, 128.83, 128.98, 129.28, 136.61, 137.39, 138.12, 142.65, 157.59, 165.89. Anal. Calcd for $C_{38}H_{35}NO_3$: C, 82.47; H, 6.37; N, 2.53; Found: C, 82.26; H, 6.46; N, 2.58.

Compound **18** was prepared using a procedure analogous to that for compound **17**. Yield: 3.0 g, 59%. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.60 (m, 15H), 2.19 (m, 6H), 3.85 (t, 3H, J=6.4 Hz), 3.90 (t, 3H, J=6.0 Hz), 5.02 (s, 8H), 6.74 (d, 4H, J=8.8 Hz), 6.87 (m, 10H), 7.11 (m, 12H), 7.30–7.43 (m, 20H), 7.54 (d, 2H, J=8.8 Hz). ^{13}C NMR ($CDCl_3$) δ (ppm): 25.46, 25.79, 28.33, 38.77, 38.95, 45.40, 45.49, 69.11, 69.61, 70.71, 104.43, 111.20, 114.53, 114.86, 115.91, 119.96, 128.34, 128.66, 128.90, 129.02, 129.26, 134.70, 138.16, 142.32, 142.92, 157.52, 157.80, 163.16. Anal. Calcd for $C_{85}H_{81}NO_7$: C, 83.13; H, 6.73; N, 1.13; Found: C, 82.87; H, 6.73; N, 1.24.

4.1.6. General procedure for synthesis of rhenium selenide cluster core molecules. $[Re_6Se_8(CH_3CN)_6](SbF_6)_2$ (0.1353 g, 0.0562 mmol) was combined with 4-methoxybenzonitrile (0.0582 g, 0.437 mmol, 7.78 equiv.) and dissolved in dry 1,2-dichlorobenzene (6 mL). The mixture was heated under N_2 at 110°C overnight. The solvent was removed by vacuum at 60°C. The residue was then dissolved in dichloromethane. This residue was precipitated with diethyl ether and the solid was collected. This precipitation was repeated until only one spot on TLC (ether) was observed on the baseline. The solution was then filtered through a celite plug. The solvent was allowed to evaporate off yielding a red/orange solid.

$[Re_6Se_8(p\text{-}CH_3OC_6H_4CN)_6](SbF_6)_2$, Compound **19**. Yield: 89.5 mg, 71%. ^{1}H NMR (CD_2Cl_2) δ (ppm): 3.92 (s, 18H), 7.12 (d, 12H, J=8.8 Hz), 7.76 (m, 12H). ESI-MS (m/z): Calculated for $[Re_6Se_8(p\text{-}CH_3OC_6H_4CN)_6]^{2+}$1273.46; Found: 1273.83.

$[Re_6Se_8(p\text{-}G1OC_6H_4CN)_6](SbF_6)_2$, Compound **20**. Yield: 59.2 mg, 40.5%. ^{1}H NMR (CD_2Cl_2) δ (ppm): 1.54 (m, 12H), 1.62 (s, 18H), 2.12 (br, 12H), 2.21 (m, 12H), 4.01 (t, 12H, J=6.0 Hz), 5.03 (s, 24H), 6.89 (d, 24H, J=8.8 Hz), 7.04 (d, 12H, J=9.2 Hz), 7.14 (d, 24H, J=8.8 Hz), 7.30–7.43 (m, 60H), 7.70 (d, 12H, J=8.8 Hz). ESI-MS (m/z): Calculated for $[Re_6Se_8(p\text{-}G1OC_6H_4CN)_6]^{2+}$ 2535.53; Found: 2538.83. Anal. Calcd for $C_{228}H_{210}N_6O_{18}F_{12}Re_6Se_8Sb_2$: C, 49.36; H, 3.79; N, 1.52; Found: C, 49.49; H, 3.95; N, 1.64.

$[Re_6Se_8(p\text{-}G2OC_6H_4CN)_6](SbF_6)_2$, Compound **21**. Yield: 310 mg, 46%. ^{1}H NMR (CD_2Cl_2) δ (ppm): 1.59 (br, 90H), 2.17 (br, 36H), 3.85 (br, 24H), 3.96 (br, 12H), 5.00 (s, 48H), 6.75 (d, 24H, J=7.6 Hz), 6.86 (m, 48H), 6.98–7.12 (m, 24H), 7.29–7.41 (m, 120H), 7.66 (d, 12H, J=8.8 Hz). ESI-MS (m/z): Calculated for $[Re_6Se_8(p\text{-}G2OC_6H_4CN)_6]^{2+}$ 4602.20; Found: 4603.40.

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