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Article

Dendritically Encapsulated, Water-Soluble Fe_4S_4: Synthesis and Electrochemical Properties

Anil K. Sharma, Namjin Kim, Christopher S. Cameron, Matthew Lyndon, and Christopher B. Gorman*

Department of Chemistry, North Carolina State University, Box 8204, Raleigh, North Carolina 28795-8204

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Amphiphilic, Fe_4S_4 cluster core dendrimers can be prepared via ligand exchange with dendrons containing carboxylic acid peripheral groups and a thiol focal group. These amphiphilic dendrons are more susceptible to oxidative disulfide formation than their non-amphiphilic analogues reported previously. Thus, an *in situ* deprotection of an aromatic thioacetate was necessary to prepare the dendrimers. These molecules showed the expected decrease in rate with increasing generation. A slower rate of heterogeneous electron transfer was found when these molecules were compared with non-amphiphilic analogues. This behavior correlated with their larger size and thus a larger effective distance of electron transfer. Voltammetry in DMSO with added water makes the dendrimers easier to reduce, but the change in redox potential is much smaller for all dendrimers when compared to a non-dendritic analogue. This behavior is consistent with the idea that the dendrimers encapsulate the cluster to some degree, creating a hydrophobic microenvironment around the cluster.

Introduction

Iron−sulfur clusters are ubiquitous units in redox-active proteins, where they serve many different functions.[1−4] Although many of these proteins operate in aqueous solvent, simple model compounds such as $Fe_4S_4(SR)_4^{2-}$ (where R is a small organic ligand) are not stable in water, particularly when these are reduced to the trianionic state corresponding to the reduced state in ferredoxins (Fd_{red}).[5−7] Moreover, these model compounds display redox potentials that are substantially more negative than those found in proteins. The redox potential of these models is most strongly influenced by the type of solvent in which they are found, indicating that an environment that encapsulates these clusters against free exposure to solvent is also important to their behavior. Thus, molecules that appropriately encapsulate these clusters against unrestricted interaction with water may be useful in the development of mimics and models. Dendrimers have been explored as encapsulating agents for several biologically relevant clusters including hemes,[8−16] copper oxo dimers,[17] and, most recently, diiron sites in monooxygenases.[18]

We have reported several types of Fe_4S_4-cluster-containing dendrimers and have shown, for example, how dendrimer generation[19,20] and structure[21,22] attenuate the rate of heterogeneous electron transfer to/from these clusters. In films, we have also shown that the size of the dendrimer is a key parameter in controlling the redox potential of the cluster; by

*To whom correspondence should be addressed. E-mail: cbgorman@ncsu.edu.

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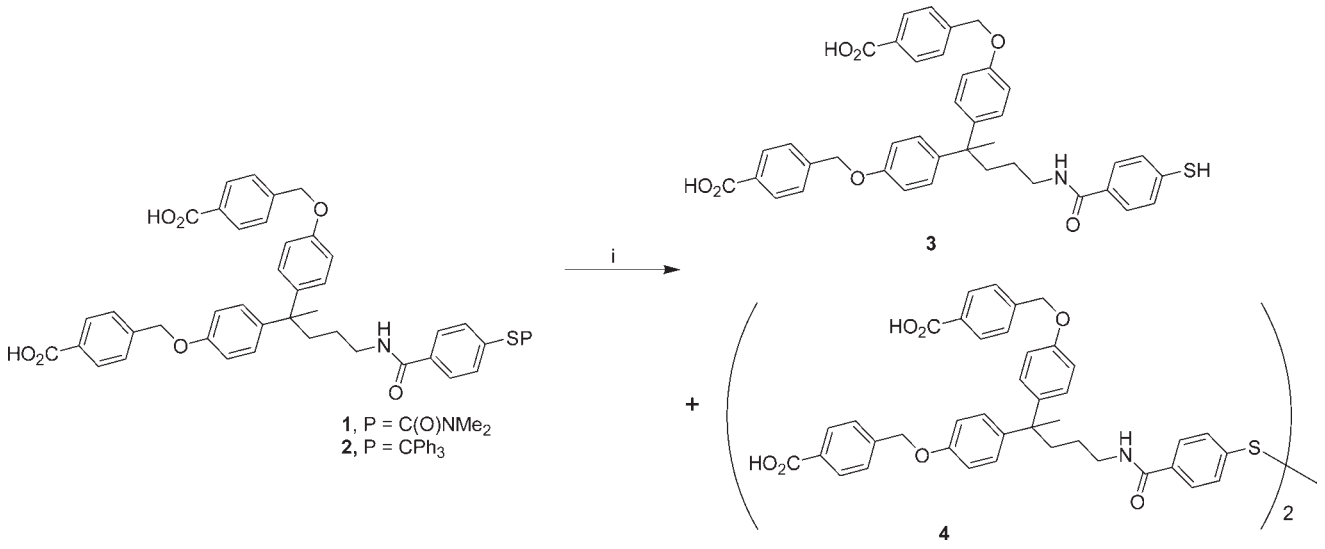
Scheme 1. Deprotection of Amphiphilic Dendritic Thiol Results in Disulfide Formation[a]



[a] For P = $C(O)NMe_2$, (i) NaOH, THF, MeOH; for P = CPh_3, (i) TFA, Et_3SiH.

changing the generation of the dendrimer from two to four, a shift of ca. 500 mV in redox potential was observed.[23]

In this paper, we probe whether a Fe_4S_4 cluster core dendrimer with a carboxylate periphery can render the molecule water-soluble yet encapsulated. In this context, a successfully encapsulated cluster would have a slower rate of heterogeneous electron transfer (e.g., k_o') yet would not be so buried in the molecule that the rate of electron transfer is so slow that it cannot be measured electrochemically. The electrochemically determined redox potential should also reflect the degree of encapsulation. As $Fe_4S_4(SR)_4^{2-}$ is reduced, the potential becomes more positive (e.g., easier to reduce), as the environment around the cluster is more polar.[5]

Results and Discussion

A. Synthesis of Carboxylate-Terminated Dendron Thiols. We have previously reported the synthesis of dendrons focally substituted with a thiol group and subsequent ligand exchange with a preformed iron−sulfur cluster (e.g., $((CH_3)_4N)_2[Fe_4S_4(S\text{-}t\text{Bu})_4]$).[19,20] Our first attempt to synthesize amphiphilic, dendron thiols followed this general procedure. Thiocarbamate-protected dendrons were synthesized (e.g., molecule **1**, Scheme 1) and reacted with base under reflux to deprotect them and form the free thiol (**3**). This process had been found to be efficient for more hydrophobic dendron thiols.[25] However, despite precautions to minimize exposure to oxygen during this reaction and subsequent workup, some disulfide formed (**4**). Clean ligand exchange without side products requires careful control over the dendron ligand to iron−sulfur cluster stoichiometry. Disulfides are insufficiently reactive under ligand exchange conditions. Thus, unsatisfactory and inseparable product mixtures were obtained.

In an attempt to avoid this problem, we sought to reduce the symmetric disulfide back to the thiol. Basu et al. reported good success with somewhat similar, focally substituted dendron disulfides.[26] However, in our hands, reduction of even the first-generation, symmetric disulfide was unsuccessful. A number of reducing agents were surveyed including Zn/acetic acid, dithiothreitol, 2-mercaptoethanol, tris(2-carboxyethyl)phosphine hydrochloride, hypophosphorus acid/diphenyl diselenide, and tributyl phosphine. All were unsuccessful. To avoid basic deprotection conditions (known to accelerate disulfide formation),[27,28] a triphenyl methyl (trityl)-protected dendron was prepared (**2**), and deprotection using refluxing trifluoroacetic acid with a small amount of triethylsilane was attempted. However, some spurious oxidation of thiol to disulfide was again observed.

Thus, it was necessary to devise a dendritic thiol ligand that was protected with a group that could be removed efficiently and in high yield without side reactions. We previously showed that aromatic thioacetate groups were good candidates for *in situ* deprotection prior to ligand exchange.[20] These groups were thus employed and found to be amenable to the requirements. The successful route to these molecules is shown in Scheme 2.

The synthesis was analogous to those previously reported up until the formation of the dendritic methylamines (**13**−**15**). Briefly, triol **6** was reacted with the peripheral moieties **5** to form the first-generation alcohol **7**. The alcohol group of this molecule was then activated as the mesylate **10**, which could then either be converted to the methylamine **13** or again be subjected to molecule **6** to form the second-generation alcohol. The dendritic methylamines were then reacted with *p*-thioacetylbenzoic acid (**16**) using a dicyclohexylcarbodiimide coupling to form **17**−**19** in modest yields. Deprotection, first of the peripheral *tert*-butyl carboxylic acid esters with trifluoroacetic acid and then of the thioacetate group with ammonium hydroxide, produced the desired ligands, as

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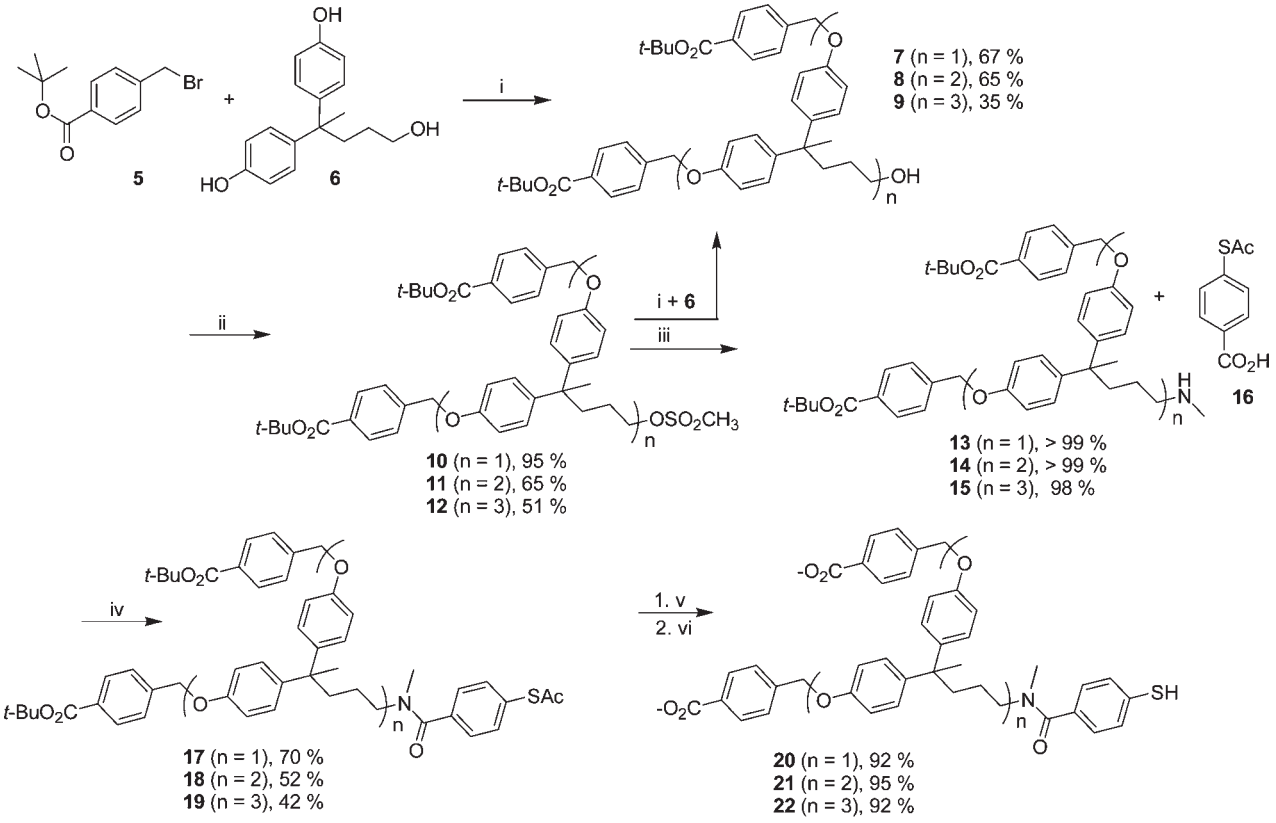
Scheme 2. Synthesis and Deprotection of Thiol Dendrons[a]



[a] (i) K_2CO_3 (5−10 equiv), 18-crown-6 (0.1−1 equiv), acetone, reflux, 12−72 h; (ii) CH_3SO_2Cl, Et_3N, DMAP (cat.), CH_2Cl_2, rt, 12 h; (iii) 40% aq CH_3NH_2, THF, 60 °C, 4 h; (iv) DCC (1 equiv), CH_2Cl_2, 12 h; (v) TFA, rt, 5 min; (vi) NH_4OH, 30 min.

evidenced by NMR and success in the subsequent ligand exchange reactions.

The solvents from these deprotected ligands were then removed under reduced pressure, and the light yellow thiols were each then subjected to ligand exchange reactions (Scheme 3). Introduction of the iron−sulfur cluster in DMF to a solution of thiol in DMF turned the reaction mixture the anticipated red-wine color. The desired dendrimers were obtained in essentially quantitative yield. These dendrimers were characterized by ^{1}H NMR and either MALDI-MS or ESI-MS. ESI-MS spectra of the dendrons corresponded to the masses of the acidified peripheral carboxylic acid groups, as these were acidified after base-catalyzed deprotection of the focal thioacetate group. MALDI-MS spectra of the dendrimers corresponded to the masses of ammonium carboxylate-terminated dendrimers, as these were prepared under basic conditions. By mass spectrometry, all dendrimers were characterized as dianions $[M - 2NMe_4^+]^{2-}$ and thus showed a peak at one-half of the total mass in negative ion mode.

B. Electrochemical Characterization: Generational Dependence of Rate and Potential in DMF. Redox-active cluster core dendrimers generally show a decrease in the rate of heterogeneous electron transfer with increasing generation.[29] In the case of iron sulfur cluster dendrimers where the charge increases upon reduction (from a dianion to trianion), the reduction potential increases in magnitude as the generation increases. This behavior has been attributed to an increasingly hydrophobic environment around the cluster as the generation increases. It was of interest to establish these trends for these amphiphilic molecules and, furthermore, to determine if rate attenuation and/or change in reduction potential with generation was larger or smaller than non-amphiphilic molecules studied previously. These data could provide some insights as to how peripheral units interact with the cluster. Diffusion constants were measured using chronoamperometry, and electrochemical rates were obtained from these values included in a fit of Osteryoung square-wave voltammograms using procedures previously reported.[20,21] Table 1 shows these data.

The rate constant for heterogeneous electron transfer in these dendrimers is smaller than those studied previously

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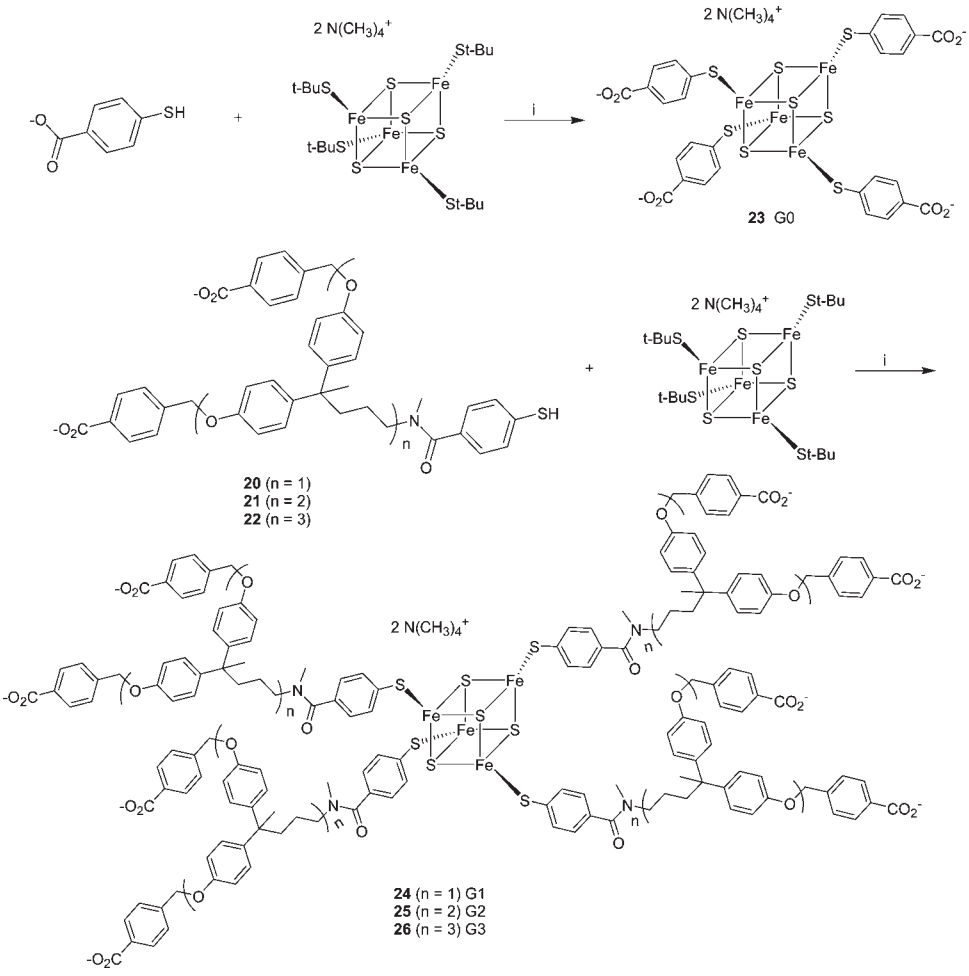
Scheme 3. Ligand Exchange to Form Iron−Sulfur Cluster Core Dendrimers[a]



[a] (i) 4.5 equiv of dendron, DMF, rt 15 min then remove solvent at 40 °C under reduced pressure.

Table 1. Kinetic and Thermodynamic Electrochemical Data Obtained in 100 mM Et_4NBF_4/DMF

compound	$E_{1/2}{}^{a,b}$ (mV)	$\alpha^{a,b}$	$k_o{}^{a,b}$ ($\times 10^3$ cm/s)	$D_o{}^{a,c}$ ($\times 10^6$ cm^2/s)	$R_H{}^{a,d}$ (Å)
23 (G0)	−1322 (1)	0.52 (0.03)	4.90 (0.24)	6.70 (0.65)	4.08 (0.35)
24 (G1)	−1319 (5)	0.66 (0.10)	3.71 (1.29)	4.31 (0.36)	6.33 (0.49)
25 (G2)	−1340 (20)	0.55 (0.11)	0.99 (0.54)	2.37 (0.08)	11.55 (0.04)
26 (G3)	−1311 (5)	0.63 (0.02)	0.26 (0.32)	1.09 (0.21)	25.00 (4.04)

[a] The magnitude of the 90% confidence interval is indicated in parentheses. [b] Obtained from a fit of Osteryoung square -wave voltammetry data. [c] Obtained from chronoamperometry. [d] Calculated using the Stokes−Einstein equation as described previously.[20]

in which the carboxylic acid groups were absent. Specifically, molecule **25** (G2) had a rate constant more than 3 times smaller than its non-carboxylic acid-containing analogue reported previously.[20] Molecule **26** (G3) had a rate constant 1.5 times smaller than its non-carboxylic acid-containing analogue.[20] Molecules **25** and **26** also had larger hydrodynamic radii than their non-carboxylic acid-containing analogues. It appears that the amphiphilic nature of these molecules renders them larger (conformationally more extended) under these conditions (DMF, 100 mM Et_4NBF_4). This would lead to a larger effective distance for electron transfer and a slower rate, as is observed here.

C. Electrochemical Characterization: Generational Dependence of Rate and Potential in Organic/Aqueous Solvent Mixtures. The peripheral carboxylate groups of these molecules rendered them water-soluble. Homogenous, dark-colored solutions of each of the four molecules (**23**−**26**) could be prepared in water. Electrochemistry in water, however, was not successful: no reduction peaks were observed, possibly because the reduction potential of the dendrimers was too close to the water window. This observation was similar to that reported by Holm et al., who studied the effect of water on the reduction potential of $Fe_4S_4(SCH_2CH_2OH)_4{}^{2-}$.[5] This early work, however, provided a nice approach to understand how water affects redox potential albeit at low relative amounts. Specifically, Holm et al. studied the reduction potential of $Fe_4S_4(SCH_2CH_2OH)_4{}^{2-}$ in DMSO/water mixtures. We repeated these experiments on molecules **23** to **26** with a few modifications. A glassy carbon electrode (GCE) was used. Electrode kinetics were not as ideal as on platinum, but the GCE has a wider solvent window in water.

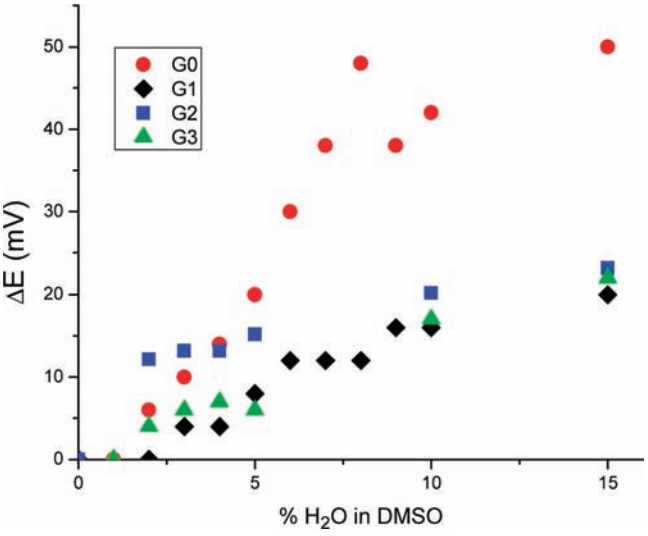


Figure 1. Graph illustrating the shift in the reduction potential determined from DPV (GCE working electrode) as a function of the percentage of water in DMSO.

To minimize background current, differential pulse voltammetry (DPV) was employed. The amount of water was systematically increased and the redox potential measured. Because the reduction potential of $Fe_4S_4(SCH_2CH_2OH)_4^{2-}$ in DMSO is much lower than that of the dendrimers because of the electronic difference between the thiophenol groups on the dendrimers and the β-mercapto ethanol ligands, molecule **23** (G0) was employed for comparison.

Figure 1 illustrates this shift in reduction potential and, most strikingly, compares the change for the dendrimers to that of molecule **23** (G0). Specifically, the shift in redox potential of molecule **23** (G0) increased steadily as the percentage of water increased. The shift in the redox potential of the dendrimers, however, did not. This behavior suggests that the hydrophobic arms of the dendrimers (even the first-generation dendrimer) encapsulated the iron−sulfur cluster as the percentage of water in the DMSO increased.

Conclusions

This work illustrates potential advantages of amphiphilic dendrons as encapsulating agents. Trends in both rate and redox potential with increasing dendrimer generation indicate a greater degree of encapsulation in the amphiphilic dendrimers compared to their non-amphiphilic analogues. These correlations are, to our knowledge, the first time that a amphiphile-based encapsulation strategy has been shown quantitatively to be more efficacious than an a non-amphiphilic strategy, as evidenced by quantitative measurements. Moreover, when water was added, the relatively small change in redox potential indicated that all of the dendritic ligands (including the first-generation ligands) acted to encapsulate the cluster.

Experimental Details

A. Characterization. Electrochemistry was performed on a Bioanalytical Systems CV-50W voltametric analyzer using a three-electrode cell consisting of a Pt working electrode, a Pt counter electrode, and a $Ag/AgNO_3$ reference electrode (an Ag wire contacting a DMF solution of 10 mM $AgNO_3$ and 100 mM tetraethylammonium tetrafluoroborate supporting electrolyte). All electrochemistry was performed in the presence of 100 mM tetraethylammonium tetrafluoroborate supporting electrolyte. MALDI analyses were performed on a Bruker Proflex+TM (Bruker Daltonics, Billerica, MA) linear MALDI-TOF instrument with a 1.2 m flight tube. The system uses a nitrogen laser (337 nm; 3 ns pulse duration), and the laser fluence was adjusted by a variable-beam attenuator. All samples were dissolved in DMF solution to give an approximate concentration of 1 mg/mL. This solution was then mixed with an equal volume of matrix (from 0.2 M solution) in the same solvent, then co-deposited on a 48-spot stainless steel target and allowed to dry and cocrystallize at room temperature for analysis. α-Cyano-4-hydroxycinnamic acid, 2-(4-phenylhydroxyazo)benzoic acid (HABA), and 2,5-dihydroxybenzoic acid (DHB) were used as matrices. The sample preparation was carried out in an inert atmosphere, and the stainless steel target was kept in a bell jar filled with nitrogen prior to analysis. The spectrometer was calibrated with insulin and bombesin. The external calibration provided a mass accuracy of 0.1% of the measured m/z value.

B. Syntheses. All reactions were carried out in flame-dried glassware under a dry nitrogen atmosphere. ^{1}H NMR spectra were referenced to the residual ^{1}H shift in $CDCl_3$ (7.24 ppm). $CDCl_3$ (77.0 ppm) was used as the internal reference for ^{13}C NMR. The following abbreviations were used to denote multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br s = broad singlet. Reactions were monitored by thin-layer chromatography (TLC) on commercial silica precoated plates with a particle size of 60 Å. Developed plates were viewed by UV lamp (254 nm). Flash chromatography was carried out with silica gel 60 Å, 32−63 μm (Sorbent Technologies). Nuclear magnetic resonance characterization was performed at 300 MHz on Varian spectrometers. UV−vis spectra were recorded using a Hewlett-Packard 8452A diode array spectrometer.

Molecules **1** and **2** and unsuccessful attempts to convert them into molecule **4** have been described previously.[24] 4,4-Bis-(4′-hydroxyphenyl)pentanol (**6**) was prepared according to the literature procedure.[25]

4-Bromomethylbenzoic Acid *tert*-Butyl Ester (5). A solution of potassium *tert*-butoxide (3.27 g, 29.14 mmol) in a mixed solvent of THF (35 mL) and *t*ert-butanol (35 mL) was stirred for 30 min. To the solution was added *p*-toluoyl chloride (2.6 mL, 19.40 mmol) dropwise. The reaction mixture was refluxed for 12 h under N_2. After the solution was cooled to room temperature, the solvents were removed under reduced pressure. The crude product was dissolved in ethyl acetate. The solution was washed two times with H_2O then 2 times with 50 mL of saturated Na_2CO_3 aqueous solution. The organic layer was combined and dried with anhydrous magnesium sulfate and then filtered. The filtrates were evaporated to dryness. The resulting product was pure enough to be used in the next step without further purification. Yield: 77% (2.82 g). ^{1}H NMR (CD_3COCD_3): δ (ppm) 1.60 (s, 9H), 2.41 (s, 3H), 7.26 (d, 2H, J = 9.0 Hz), 7.84 (d, 2H, J = 9.0 Hz). To a solution of 4-methylbenzoic acid *tert*-butyl ester (3.94 g, 20.51 mmol) and *N*-bromosuccinimide (3.29 g, 18.37 g) in 50 mL of CH_2Cl_2 was added a catalytic amount of 2,2′-azobisisobutyronitrile to initiate the free radical reaction. The reaction was refluxed for 48 h under N_2. After the solution was cooled to room temperature, the solvent was removed under reduced pressure. The crude product was dissolved in ethyl acetate. The solution was washed two times with 50 mL with H_2O then twice with 50 mL of saturated Na_2CO_3 aqueous solution. The organic layer was combined and dried with anhydrous sodium sulfate and then filtered. The filtrates were evaporated to dryness. The resulting product was pure enough to be used in the next step. Yield: 97% (4.84 g). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.60 (s, 9H), 4.70 (s, 2H), 7.58 (d, 2H, J = 9.0 Hz), 7.95 (d, 2H, J = 9.0 Hz).

General Procedure for the Synthesis of G*n*-OH-Benzoic Acid *tert*-Butyl Ester (7−9, *n* = 1−3). To a suspension of 4,4-bis-(4′-hydroxyphenyl)pentanol (1 equiv), anhydrous potassium

carbonate (5 equiv), and a catalytic amount of 18-crown-6 (0.1 equiv) in 50 mL of dry acetone was added either 4-bromomethylbenzoic acid *tert*-butyl ester (**5**, 2.2 equiv) to prepare **7**, G1-OMs-benzoic acid *tert*-butyl ester (OMs = mesylate) (**10**, 2.4 equiv) to prepare **8**, or G2-OMs-benzoic acid *tert*-butyl ester (**12**, 3 equiv) to prepare **9**. The mixture was refluxed for 12−72 h and stirred vigorously under N_2. At the end of reaction, the suspension was cooled to room temperature and filtered. The filtrate was then evaporated to remove the solvent under reduced pressure. The crude product was purified by column chromatography, eluting with the solvent system of 30% ethyl acetate in hexane.

G1-OH-Benzoic Acid *tert*-Butyl Ester (7). Yield: 67% (1.69 g). IR: 1292, 1710, 2975, 3409 cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 1.35 (m, 2H), 1.50 (s, 3H), 1.53 (s, 18H), 2.00 (m, 2H), 3.53 (t, 2H, J = 6.5 Hz), 5.12 (s, 4H), 6.79 (d, 4H, J = 8.7 Hz), 7.00 (d, 4H, J = 8.9 Hz), 7.40 (d, 4H, J = 8.0 Hz), 7.93 (d, 4H, J = 6.7 Hz). ^{13}C NMR ($CDCl_3$): δ (ppm) 28.1, 28.4, 38.2, 44.9, 63.6, 69.5, 81.3, 114.4, 127.0, 128.5, 129.9, 131.6, 142.1, 142.5, 156.5, 165.7. HRMS (ESI): calcd for [M + Na^+] $C_{42}H_{50}O_9SNa$ 675.3298, found 675.3293.

G2-OH-Benzoic Acid *tert*-Butyl Ester (8). Yield: 65% (10.95 g). IR: 1291, 1711, 2973, 3515 cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 1.35 (m, 2H), 1.40−1.80 (m, 49H), 2.09 (m, 2H), 2.19 (m, 4H), 3.59 (t, 2H, J = 6.1 Hz), 3.86 (t, 4H, J = 6.1 Hz), 5.15 (s, 8H), 6.73 (d, 4H, J = 8.5 Hz), 6.91 (d, 8H, J = 8.4 Hz), 7.06 (d, 4H, J = 8.4 Hz), 7.11 (d, 8H, J = 8.6 Hz), 7.42 (d, 8H, J = 8.2 Hz), 7.95 (d, 8H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$): δ (ppm) 25.2, 28.2, 28.4, 38.5, 44.9, 45.0, 63.6, 68.4, 69.5, 81.3, 113.9, 114.4, 127.0, 128.4, 128.5, 129.9, 131.7, 142.0, 142.1, 142.4, 156.6, 157.00, 165.8. MALDI (TOF): calcd for [M + Na^+] $C_{99}H_{112}O_{15}Na$ 1564.9, found 1565.2 (HABA matrix, positive ion mode).

G3-OH-Benzoic Acid *tert*-Butyl Ester (9). Yield: 35% (1.49 g). IR: 1294, 1710, 2973, 3411 cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 1.35−1.80 (m, 107H), 2.14 (m, 14H), 3.53 (t, 2H, J = 6.2 Hz), 3.82 (t, 12H, J = 6.0 Hz), 5.04 (s, 16H), 6.72 (d, 12H, J = 8.8 Hz), 6.82 (d, 16H, J = 8.7 Hz), 7.03 (m, 28H), 7.43 (d, 16H, J = 8.4 Hz), 7.96 (d, 16H, J = 8.1 Hz). ^{13}C NMR ($CDCl_3$): δ (ppm) 25.2, 28.2, 28.4, 38.6, 44.9, 45.0, 63.5, 68.5, 69.5, 81.2, 113.9, 114.4, 127.0, 127.2, 128.4, 128.5, 129.9, 130.0, 130.2, 131.7, 141.9, 142.0, 142.1, 142.4, 156.6, 157.0, 165.7. MALDI (TOF): calcd for [M + Na^+] $C_{215}H_{240}O_{31}Na$ 3343.2, found 3344.8 (HABA matrix, positive ion mode).

General Procedure for the Synthesis of G*n*-OMs-Benzoic Acid *tert*-Butyl Esters (10−12, *n* = 1−3). To a solution of G*n*-OH-benzoic acid *tert*-butyl ester (**7**−**9**, 1 equiv), triethylamine (3 equiv), and a catalytic amount of 4-dimethylaminopyridine (0.02 equiv) in 50 mL of dichloromethane at 0 °C was added dropwise methane sulfonyl chloride (2 equiv). The reaction mixture was allowed to warm to room temperature and stirred for 12 h. Then 50 mL of water was added to quench the reaction. The solution was extracted with 2 × 50 mL of dichloromethane. The combined organic layers were dried over Na_2SO_4, and the solvents were removed under reduced pressure. The crude product was purified by column chromatography using ethyl acetate/hexane (1:6) as eluent.

G1-OMs-Benzoic Acid *tert*-Butyl Ester (10). Yield: 95% (1.95 g). IR: 1294, 1709, 2975 cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 1.35 (m, 2H), 1.50 (m, 21H), 2.06 (m, 2H), 2.89 (s, 3H), 4.10 (t, 2H, J = 6.3 Hz), 5.03 (s, 4H), 6.79 (d, 4H, J = 8.2 Hz), 7.02 (d, 4H, J = 8.4 Hz), 7.40 (d, 4H, J = 8.0 Hz), 7.93 (d, 4H, J = 8.1 Hz). ^{13}C NMR ($CDCl_3$): δ (ppm) 25.1, 28.1, 28.4, 37.5, 37.9, 44.9, 69.5, 70.8, 81.2, 114.5, 127.0, 128.4, 129.9, 131.7, 141.9, 142.0, 156.7, 165.7. HRMS (ESI): calcd for [M + Na^+] $C_{42}H_{50}O_9SNa$ 753.3073, found 753.3062.

G2-OMs-Benzoic Acid *tert*-Butyl Ester (11). Yield: 65% (0.58 g). IR: 1293, 1711, 2973 cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 1.20 −1.82 (m, 51H), 2.15 (m, 6H), 2.88 (s, 3H), 3.83 (t, 4H, J = 5.4 Hz), 4.10 (t, 2H, J = 6.2 Hz), 5.08 (s, 8H), 6.70 (d, 4H, J = 8.5 Hz), 6.86 (d, 8H, J = 8.6 Hz), 7.01 (d, 4H, J = 8.4 Hz), 7.07 (d, 8H, J = 8.6 Hz). 7.40 (d, 8H, J = 8.2 Hz), 7.93 (d, 8H, J = 8.7 Hz). ^{13}C NMR ($CDCl_3$): δ (ppm) 25.2, 28.2, 28.4, 37.5, 38.6, 44.8, 45.0, 68.5, 69.5, 70.9, 81.2, 114.1, 114.4, 127.1, 128.4, 128.6, 129.9, 131.7, 141.3, 142.1, 142.4, 156.6, 157.1, 157.2, 165.7. MALDI (TOF): calcd for [M + Na^+] $C_{100}H_{114}O_{17}SNa$ 1643.0, found 1644.6 (HABA matrix, positive ion mode).

G3-OMs-Benzoic Acid *tert*-Butyl Ester (12). Yield: 51% (1.12 g). IR: cm^{-1} 1292, 1710, 2773. ^1H NMR ($CDCl_3$): δ (ppm) 1.20−1.82 (m, 107H), 2.15 (m, 14H), 2.9 (s, 3H), 3.85 (m, 12H), 4.1 (t, 2H, J = 5.5 Hz), 5.04 (s, 16H), 6.76 (d, 12H, J = 8.6 Hz), 6.85 (d, 16H, J = 8.6 Hz), 7.03 (m, 28H), 7.45 (d, 16H, J = 8.1 Hz), 8.00 (d, 16H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$): δ (ppm) 25.2, 28.2, 28.4, 37.5, 38.6, 44.8, 45.1, 68.5, 69.5, 81.2, 114.1, 114.5, 127.1, 128.5, 128.6, 129.9, 131.7, 141.3, 142.2, 142.5, 156.7, 157.2, 165.7. MALDI (TOF): calcd for [M + Na^+] $C_{216}H_{242}O_{33}SNa$ 3421.3, found 3424.1 (HABA matrix, positive ion mode).

General Procedure for Synthesis of G*n*-N(CH_3)$COC_6H_4SCO-CH_3$-Benzoic Acid *tert*-Butyl Esters (17−19, *n* = 1−3). Into a sealed tube with a solution of G*n*-OMs-benzoic acid *tert*-butyl ester (**10**−**12**), ca. 0.5−1.0 g in 6 mL of THF, was added methyl amine (40 wt % solution in H_2O) (6 mL). The reaction mixture was then heated to 60−70 °C for 5 h. At the end of the reaction as shown by TLC the mixture was cooled to room temperature, and 20 mL of water was added to quench the reaction. The solution was extracted with 2 × 20 mL of dichloromethane. The combined organic layers were dried over Na_2SO_4. Dichloromethane was removed under reduced pressure to furnish the amines (**13**−**15**), which were pure enough to be used in the next step without further purification, with the exception of the third-generation amine (**19**); see below. To a solution of amine (1 equiv) in dichloromethane (7 mL) was added the activated ester prepared by mixing dicyclohexyl carbodiimide (1 equiv) with carboxylic acid (1 equiv) in dichloromethane (5 mL). The reaction mixture was then stirred at room temperature for 12 h. At the end of the reaction the solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate (5 mL) in which the solubility of cyclohexyl urea byproduct was found to be less than in dichloromethane. The suspension was then filtered, and the filtrate, on concentration under reduced pressure and further on column purification using 20% ethyl acetate as eluent, furnished the desired amides.

G1-N(CH_3)$COC_6H_4SCOCH_3$-Benzoic Acid *tert*-Butyl Ester (17). Yield: 70% (0.372 g). IR: 1295, 1631, 1710, 2976, 3400, 3583 cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 1.35 (m, 2H), 1.50 (m, 21H), 1.87 (m, 1H), 2.06 (m, 1H), 2.35 (s, 3H), 2.65 (s, 1.5H), 2.87 (s, 1.5H), 3.03 (m, 1H), 3.44 (m, 1H), 5.15 (s, 4H), 6.8 (d, 4H, J = 8.1 Hz), 6.9 (d, 2H, J = 8.1 Hz), 7.05 (d, 2H, J = 7.9 Hz) 7.36 (d, 4H, J = 8 Hz), 7.40 (d, 4H, J = 8.3 Hz), 7.93 (d, 4H, J = 8.1 Hz). ^{13}C NMR ($CDCl_3$): δ (ppm) 22.5, 24.0, 28.0, 28.4, 30.5, 32.9, 37.4, 38.5, 38.9, 45.0, 47.7, 51.8, 69.5, 81.2, 114.5, 127.0, 128.4, 128.5, 129.6, 129.9, 131.7, 134.4, 137.9, 142.0, 142.4, 156.6, 165.7, 170.6, 171.2, 193.3. HRMS (ESI): calcd for [M + H^+] $C_{51}H_{58}NO_8S$ 844.3805, found 844.3869.

G2-N(CH_3)$COC_6H_4SCOCH_3$-Benzoic Acid *tert*-Butyl Ester (18). Yield: 52% (0.248 g). IR: 1295, 1710, 2933, 2973, 3402, 3582 cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 1.20−2.0 (m, 53H), 2.15 (m, 4H), 2.37 (s, 3H), 2.65 (s, 1.5H), 2.87 (s, 1.5H), 3.03 (m, 1H), 3.44 (m, 1H), 3.82 (t, 4H, J = 5.7 Hz), 5.03 (s, 8H), 6.70 (d, 4H, J = 8.4 Hz), 6.86 (d, 10H, J = 8.6 Hz), 6.95 (d, 2H, J = 8.4 Hz), 7.02 (d, 8H, J = 8.6 Hz), 7.40 (d, 12H, J = 8.2 Hz), 7.93 (d, 8H, J = 8.5 Hz). ^{13}C NMR ($CDCl_3$): δ (ppm) 24.5, 28.4, 28.4, 30.5, 38.9, 45.0, 68.5, 69.5, 81.2, 114.0, 114.4, 127.0, 128.5, 129.9, 131.7, 134.6, 138.1, 142.1, 142.4, 156.6, 165.7, 193.3. MALDI (TOF): calcd for [M + Na^+] $C_{109}H_{121}NO_{16}SNa$ 1754.8, found 1755.6 (DHB matrix, positive ion mode)

G3-N(CH_3)$COC_6H_4SCOCH_3$-Benzoic Acid *tert*-Butyl Ester (19). After cooling the reaction mixture of the amine, the solution was extracted with 2 × 10 mL of dichloromethane. The combined organic layers were dried over Na_2SO_4. Dichloromethane was removed under reduced pressure to furnish crude amine, which on column purification using a 10% MeOH/EtOAc system provided

amine in 42% yield. The process was then carried out as per the general procedure above. Yield: 42% (0.248 g). IR: 1248, 1295, 1710, 2934, 2973, 3325 cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 1.20−1.82 (m, 107H), 2.16 (m, 14H), 2.35 (s, 3H), 2.65 (s, 1.5H), 2.87 (s, 1.5H), 3.03 (m, 1H), 3.44 (m, 1H), 3.82 (m, 12H), 5.03 (s, 16H), 6.72 (d, 12H, J = 8.0 Hz), 6.82 (d, 16H, J = 8.6 Hz), 7.10 (m, 30H), 7.41 (m, 18H), 7.96 (d, 16H, J = 7.9 Hz). ^{13}C NMR ($CDCl_3$): δ (ppm) 25.2, 28.2, 28.4, 30.5, 30.9, 32.4, 38.6, 45.0, 45.1, 50.0, 57.3, 68.5, 69.6, 81.2, 113.9, 114.4, 127.0, 128.4, 128.5, 129.9, 131.7, 141.9, 142.1, 142.4, 156.6, 157.1, 165.7, 192.6. MALDI (TOF): calcd for [M + K^+] $C_{224}H_{247}NO_{32}SK$ 3536.5, found 3536.7 (HABA matrix, positive ion mode).

General Procedure for the Synthesis of G*n*-N(CH_3)$COC_6H_4SCOCH_3$-Benzoic Acid (20−22, *n* = 1−3). A solution of G*n*-N(CH_3)$COC_6H_4SCOCH_3$-benzoic acid *tert*-butyl ester (**17**−**19**) in trifluoroacetic acid (1 mL per 100 mg of material) was stirred at room temperature for 5 min. The solution was then concentrated under reduced pressure, and the residue was washed twice with diethyl ether (2 × 2 mL). A white solid was obtained by vacuum filtration. This solid was then lyophilized from water to give a white powder. Compounds were then chromatographed on silica gel using 5% $CH_3OH/CHCl_3$.

G1-N(CH_3)$COC_6H_4SCOCH_3$-Benzoic Acid (20). Yield: 92% (82 mg). IR: 1240, 1693, 1776, 2937 (br) cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 1.35 (m, 2H), 1.48 (s, 1H), 1.52 (s, 1H), 1.87 (m, 1H), 2.06 (m, 1H), 2.37 (s, 3H), 2.70 (s, 1.5H), 2.91 (s, 1.5H), 3.12 (m, 1H), 3.46 (m, 1H), 5.06 (s, 4H), 6.80 (d, 4H, J = 8.1 Hz), 6.96 (d, 2H, J = 8.1 Hz), 7.06 (m, 2H), 7.40 (d, 4H, J = 8.4 Hz), 7.46 (d, 4H, J = 8.3 Hz), 8.04 (d, 4H, J = 8.2 Hz), 10.38 (br s, 1H). ^{13}C NMR (DMSO-d_6): δ (ppm) 22.01, 27.8, 30.9, 32.9, 37.4, 38.4, 44.8, 69.2, 114.8, 127.9, 128.2, 128.5, 130.1, 130.7, 134.8, 142.2, 142.5, 142.9, 156.5, 167.8, 169.8, 170.3, 172.7, 193.6. HRMS (EI): calcd for [M + H^+] $C_{43}H_{41}NNaO_8S$ 732.26, found 732.2709.

G2-N(CH_3)$COC_6H_4SCOCH_3$-Benzoic Acid (21). Yield: 95% (174 mg). IR: 1243, 1693, 1772, 2954 (br) cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 1.20−1.82 (m, 15H), 2.15 (m, 6H), 2.37 (s, 3H), 2.64 (s, 1.5H), 2.75 (s, 1.5H), 3.03 (m, 1H), 3.38 (m, 1H), 3.78 (t, 4H), 5.06 (s, 8H), 6.67 (m, 4H,), 6.83 (d, 10H, J = 8.7 Hz), 7.01 (d, 8H, J = 8.4 Hz), 7.2 (br, 2H), 7.36 (m, 4H). 7.47 (d, 8H, J = 8.6 Hz), 7.88 (d, 8H, J = 8.6 Hz). ^{13}C NMR (DMSO-d_6): δ (ppm) 25.1, 25.3, 28.0, 30.8, 34.0, 38.2, 44.7, 44.9, 68.3, 69.2, 114.4, 114.7, 127.9, 128.4, 128.6, 129.0, 130.1, 130.7, 134.7, 138.3, 142.4, 142.9, 156.6, 156.9, 167.8, 169.8, 170.3, 172.7, 193.3. MALDI (TOF): calcd for [M + Na^+] $C_{93}H_{89}NO_{16}SNa$ 1531.8, found 1533.5 (HABA matrix, positive ion mode).

G3-N(CH_3)$COC_6H_4SCOCH_3$-Benzoic Acid (22). Yield: 92% (64 mg). IR: 1698, 1770, 2362 cm^{-1}. ^1H NMR (DMSO d_6): δ (ppm) 1.20−1.82 (m, 30H), 2.16 (m, 4H), 2.35 (s, 3H), 2.65 (s, 1.5H), 2.87 (s, 1.5H), 3.03 (m, 1H), 3.44 (m, 1H), 3.82 (m, 12H), 5.03 (s, 16H), 6.72 (d, 12H), 6.82 (d, 16H), 7.10 (m, 28H), 7.41 (d, 16H), 7.96 (d, 16H). ^{13}C NMR (THF-d_8): δ (ppm) 25.2, 27.5, 29.3, 30.6, 32.1, 38.4, 44.7, 44.8, 56.2, 65.5, 68.1, 69.1, 113.6, 114.1, 126.8, 128.1, 128.3, 129.8, 130.4, 133.9, 141.7, 142.3, 142.7, 156.9, 157.3, 166.6, 191.5. MALDI (TOF): calcd for [M + K^+] $C_{192}H_{183}NO_{32}SK$ 3085.2, found 3085.2 (HABA matrix, positive ion mode).

General Procedure for the Synthesis of [Fe_4S_4(S-G*n*-$COONH_4$)$_4$][N(CH_3)$_4$]$_2$ (23−26, *n* = 0−3). Into a Schlenk flask containing a solution of *p*-$HO_2CC_6H_4SH$ or G*n*-N(CH_3)$COC_6H_4SCOCH_3$-benzoic acid (**20**−**21**, 4.5 equiv; **22**, 5.0 equiv; ca. 50 mg) in 5 mL of dried THF was added 1 mL of degassed ammonium hydroxide solution (30% in water). The flask was covered with aluminum foil, and the solution was stirred for 30 min at room temperature. The solvent was then gradually removed under reduced pressure, and after 5 h, the flask was transferred into a drybox. A solution of [Fe_4S_4(S-*t*-Bu)$_4$][N(CH_3)$_4$]$_2$ (1 equiv) in 10 mL of dried DMF was added into the flask. Upon addition, a red-wine color developed rapidly. After the reaction mixture was stirred for 15 min, the flask was sealed and removed from the drybox and transferred to a Schlenk line. The solvent was then removed *in vacuo* at 40 °C for 12 h. The crude dendrimer (50 mg) was dissolved in 1 mL of DMF in the drybox. A clear but colored solution of dendrimer was obtained. Then, 1 mL of THF was added to remove dendron impurities. To this was added excess toluene until precipitation of the dendrimer commenced. The solid was allowed to settle for at least 15 min. Then, the top, light brown layer of liquid (mother liquor) was slowly decanted into another vial, and the precipitate was further washed with 2 × 1 mL of THF. After removing the THF, the residue of the dendrimer was redissolved in 2 mL of DMF and transferred into a Schlenk flask through a syringe filter (Gelman Acroseal, pore size 0.2 μm). The Schlenk flask was closed and removed from the drybox. The DMF was removed under reduced pressure at 30 °C for 2 h. The flask was further kept at room temperature overnight under the same reduced pressure. The residue in the flask was directly used for NMR and electrochemical analysis.

[Fe_4S_4(S-C_6H_4-COOH)$_4$][N(CH_3)$_4$]$_2$ (23). Yield: 91% (62 mg). ^1H NMR (DMF-d_7): δ 3.5 (br s, 12H), 6.2 (br s, 2H), 8.9 (br s, 2H). HRMS (ESI): calcd for [M − 2NMe_4^+]$^{2-}$ $C_{28}H_{32}Fe_4N_4O_8S_8$ m/z = 481.8168, found 481.8175.

[Fe_4S_4(S-G1-COOH)$_4$][N(CH_3)$_4$]$_2$ (24). Yield: 92% (59 mg). ^1H NMR (DMF-d_7): δ 1.4 (m, 8H), 1.6 (s, 12H), 1.95 (m, 8H), 2.98−3.11 (m, 20H), 3.99−4.18 (m, 24H), 5.09 (s, 16H), 5.80 (br s, 8H) 6.78−7.15 (m, 16H), 7.15−7.38 (br s, 16H), 7.39−7.81 (m, 16H), 8.02−8.19 (s, 16H), 8.20−8.29 (br s, 8H). HRMS (ESI): calcd for [M − 2NMe_4^+]$^{2-}$ $C_{164}H_{152}Fe_4N_4O_{28}S_8$ m/z = 1553.43, found 1553.30.

[Fe_4S_4(S-G2-COOH)$_4$][N(CH_3)$_4$]$_2$ (25). Yield: 95% (55 mg). ^1H NMR (DMF-d_7): δ 1.4 (m, 20H), 1.6 (s, 40H), 2.2 (m, 24H), 2.98−3.11 (m, 5H), 3.4 (br s, 24H), 3.9 (br s, 16H), 5.09 (s, 32H), 5.80 (br s, 8H) 6.67 (m, 16H), 6.83 (br s, 32H), 7.01 (br s, 32H), 7.2 (m, 16H). 7.6 (br s, 32H), 7.88 (br s, 32H), 8.20−8.29 (br s, 8H). HRMS (ESI): calcd for [M − 2NMe_4^+]$^{2-}$ $C_{365}H_{346}Fe_4N_4O_{59}S_8$ m/z = 3106.964, found 3107.027.

[Fe_4S_4(S-G3-$COONH_4$)$_4$][N(CH_3)$_4$]$_2$ (26). Yield: 92% (49 mg). ^1H NMR (DMF-d_7): δ 1.4 (m, 56H), 1.6−1.80 (m, 84H), 2.4 (br s, 56H), 2.98−3.11 (m, 84H), 3.4 (br s, 24H), 3.99 (m, 48H), 5.09 (s, 64H), 5.80 (br s, 8H) 6.72 (br s, 48H), 6.82 (br s, 64H), 7.10 (m, 112H), 7.41 (br s, 64H), 7.96 (br s, 64H), 8.20−8.29 (br s, 8H). MALDI (TOF): calcd for [M − 2NMe_4^+]$^{2-}$ $C_{763}H_{827}Fe_4N_{37}O_{124}S_8$ m/z = 6213.2, found 6211.7 (HABA matrix, negative ion mode).

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