Electroactive, Internal Anthraquinonoid Dendritic Cores[1]

George R. Newkome,*,† Venkatraj V. Narayanan,†,‡ and Luis A. Godínez†,§

Center for Molecular Design and Recognition, Department of Chemistry, University of South Florida, Tampa, Florida 33620

Received August 11, 1999

The modification of the extended 1 → 3 anthraquinonoid monomer **1** by substitution of the central aliphatic moiety with a more rigid, aromatic moiety has allowed the syntheses of the new branched building block **6** possessing multiple, internal redox sites. This monomer was used to generate the first tier, dendritic macromolecules **8** and **9**, which incorporate different internal redox centers within the infrastructure as well as the traditional peripheral multifunctionality. Using cyclic voltammetry experiments, the electrochemical response and electronic interactions between the two electroactive sites (the anthraquinonoid and nitroaromatic moieties) of these dendritic constructs were explored.

Introduction

Since the experimental work of Friedrich Wöhler in 1828 in which ammonium cyanate was transformed to an obvious organic material, urea, one of the most significant aspirations of chemists has been to invent novel organic materials with unusual, yet predetermined, properties. Dendrimers, a relatively precise series of oligomeric macromolecules, constitute an important example of materials that can be synthetically tailored to address specific chemicophysical needs.[2−13] Thus, the molecular incorporation, either by entrapment or inclusion, of chromophoric substrates into their internal regime offers an avenue to novel polymeric materials.

The high sensitivity even in dilute concentrations of dye molecules to optical parameters, such as absorption and fluorescence, has made them important tools in the study and development of utilitarian dendrimers.[14,15] Toward this goal Meijer and co-workers have demonstrated[16−18] the encapsulation and selective release of dye molecules (e.g., Bengal Rose) from a "dendritic box". Fréchet's group has reported[19−21] the synthesis of polyaryl-ether dendrimers wherein the terminally attached chromophores (coumarin-based dyes) acted as antennas absorbing incident light and subsequently transferring energy to the central dye moiety, which in turn acted as the fluorescent probe. Diederich's research group[22−27] and others[28−40] have used porphyrin-based dendrimers in

* E-mail: http://www.dendrimers.com.

† University of South Florida.

‡ Current address: Biomedical Magnetic Resonance Laboratory, University of Illinois at Urbana−Champaign, 2100 South Goodwin Avenue, Urbana, Illinois 61801.

§ Current address: Departamento de Electroquímía, Centro de Investigación y Desarrollo Tecnológico en Electroquímía S.C., Parque Tecnológico Querétaro Sanfandila, Apdo Postal 064, C.P. 76700, Pedro Escobedo, Querétaro, México.

(1) Narayanan, V. V.; Newkome, G. R. Supramolecular Chemistry within Dendritic Structures. In *Topics in Current Chemistry*; Vögtle, F., Ed.; Springer-Verlag: Berlin/Heidelberg, 1998; Chapter 2, pp 19−77.

(2) Tomalia, D. A.; Durst, H. D. *Top. Curr. Chem.* **1993**, *165*, 193−313.

(3) Fréchet, J. M. J. *Science* **1994**, *263*, 1710−1715.

(4) Issberner, J.; Moors, R.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2413−2420.

(5) Voit, B. I. *Acta Polym.* **1995**, *46*, 87−99.

(6) Newkome, G. R.; Moorefield, C. N. Dendrimers. In *Comprehensive Supramolecular Chemistry*; Reinhoudt, D. N., Ed.; Pergamon: Elmsford, NY, 1996; Chapter 25, pp 777−832.

(7) Newkome, G. R. *J. Heterocycl. Chem.* **1996**, *33*, 1445−1460.

(8) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules: Concepts, Syntheses, Perspective*; VCH: Weinheim, Germany, 1996.

(9) Astruc, D. *C. R. Acad. Sci. Ser. II: Mec. Phys. Chim. Sci. Terre Univers.* **1996**, *322*, 757−766.

(10) Chow, H.-F.; Mong, T. K. K.; Nongrum, M. F.; Wan, C.-W. *Tetrahedron* **1998**, *54*, 8543−8660.

(11) Majoral, J.-P.; Caminade, A.-M. Divergent Approaches to Phosphorus-Containing Dendrimers and their Functionalization. In *Topics in Current Chemistry*; Vögtle, F., Ed.; Springer-Verlag: Berlin, 1998; Chapter 3, pp 79−124.

(12) Matthews, O. A.; Shipway, A. N.; Stoddart, J. F. *Prog. Polym. Sci.* **1998**, *23*, 1−56.

(13) Kaifer, A. E. *Acc. Chem. Res.* **1999**, *32*, 62−71.

(14) Newkome, G. R.; Narayanan, V. V.; Godínez, L. A.; Pérez-Cordero, E.; Echegoyen, L. *Macromolecules* **1999**, *32*, 6782−6791.

(15) Newkome, G. R. *Pure Appl. Chem.* **1999**, *70*, 2337−2343.

(16) Jansen, J. F. G. A.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Science* **1994**, *266*, 1226−1229.

(17) Jansen, J. F. G. A.; Meijer, E. W.; de Brabander-van den Berg, E. M. M. *J. Am. Chem. Soc.* **1995**, *117*, 4417−4418.

(18) Jansen, J. F. G. A.; Meijer, E. W.; de Brabander-van den Berg, E. M. M. *Macromol. Symp.* **1996**, *102*, 27−33.

(19) Gilat, S. L.; Adronov, A.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 1422−1426.

(20) Hawker, C. J.; Wooley, K. L.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1993**, *115*, 4375−4376.

(21) Kawa, M.; Fréchet, J. M. J. *Chem. Mater.* **1998**, *10*, 286−296.

(22) Mattei, S.; Seiler, P.; Diederich, F.; Gramlich, V. *Helv. Chim. Acta* **1995**, *78*, 1904−1912.

(23) Mattei, S.; Wallimann, P.; Kenda, B.; Amrein, W.; Diederich, F. *Helv. Chim. Acta* **1997**, *80*, 2391−2417.

(24) Collman, J. P.; Fu, L.; Zingg, A.; Diederich, F. *Chem. Commun.* **1997**, 193−194.

(25) Dandliker, P. J.; Diederich, F.; Gross, M.; Knobler, C. B.; Louati, A.; Sanford, E. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1739−1742.

(26) Dandliker, P. J.; Diederich, F.; Gisselbrecht, J.-P.; Louati, A.; Gross, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2725−2728.

(27) Dandliker, P. J.; Diederich, F.; Zingg, A.; Gisselbrecht, J.-P.; Gross, M.; Louati, A.; Sanford, E. *Helv. Chim. Acta* **1997**, *80*, 1773−1801.

(28) Bhyrappa, P.; Young, J. K.; Moore, J. S.; Suslick, K. S. *J. Am. Chem. Soc.* **1996**, *118*, 5708−5711.

(29) Bhyrappa, P.; Vaijayanthimala, G.; Suslick, K. S. *J. Am. Chem. Soc.* **1999**, *121*, 262−263.

(30) Jiang, D.-L.; Aida, T. *Chem. Commun.* **1996**, 1523−1524.

(31) Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **1998**, *120*, 10895−10901.

(32) Mak, C. C.; Bampos, N.; Sanders, J. K. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 3020−3023.

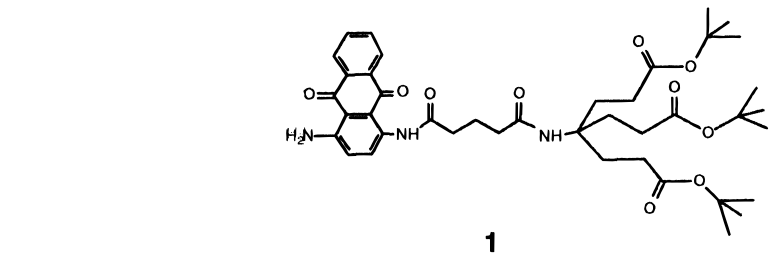
(33) Norsten, T.; Branda, N. *Chem. Commun.* **1998**, 1257−1258.

(34) Pollak, K. W.; Leon, J. W.; Fréchet, J. M. J.; Maskus, M.; Abruña, H. D. *Chem. Mater.* **1998**, *10*, 30−38.

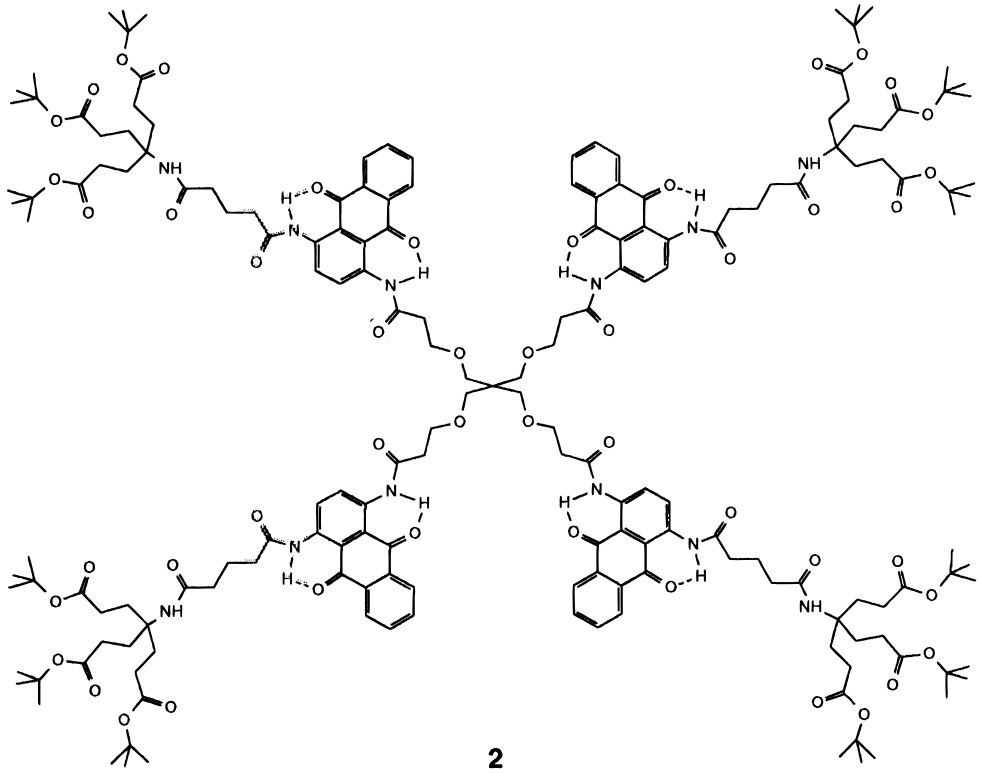
(35) Sadamoto, R.; Tomioka, N.; Aida, T. *J. Am. Chem. Soc.* **1996**, *118*, 3978−3979.

(36) Suslick, K. S.; Bhyrappa, P. *J. Inorg. Biochem.* **1997**, 234.

10.1021/jo991278g CCC: $19.00
Published on Web 02/25/2000



1



2

Figure 1. Structures of the building block **1** and the first tier dendrimer **2**.

designing synthetic models for globular proteins. Toward their efforts in studying dendritic host−guest systems, Watkins et al.[41] have used the fluorescence emission properties of the dye nile-red.

In this context, we reported[6,14,42−46] the construction of electroactive dendrimers based on diaminoanthraquinone molecules covalently incorporated within the dendritic infrastructure. The synthetic strategy to obtain these macromolecules consisted of preparing the extended building block **1**, treating it with a four-directional core to obtain the electroactive dodecaester **2**, and then divergently building subsequent tiers (Figure 1).

We herein report our efforts toward replacing the five-carbon alkyl spacer unit in monomer **1** with a more versatile aryl moiety for future internal attachments. The spacer selected, apart from affecting the properties of the resultant building block and the dendrimers subsequently constructed from it, must also be able to introduce a useful synthon for future infrastructure modifications. 5-Nitroisophthaloyl chloride (**3**) was chosen, because the nitro moiety could be subsequently reduced to an amino functionality when desired, thus allowing the incorporation of a new chemically active functional group *within* the electroactive dendritic superstructure.

Initially, monomer **6** was synthesized, using a high-dilution technique[47] similar to that for the preparation

(37) Takasu, D.; Tomioka, N.; Jiang, D.-L.; Aida, T.; Kamachi, T.; Okura, I. *J. Inorg. Biochem.* **1997**, *67*, 242.

(38) Tomioka, N.; Takasu, D.; Takahashi, T.; Aida, T. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1531−1534.

(39) Tomoyose, Y.; Jiang, D.-L.; Jin, R.-H.; Aida, T.; Yamashita, T.; Horie, K.; Yashima, E.; Okamoto, Y. *Macromolecules* **1996**, *29*, 5236−5238.

(40) Pollak, K. W.; Sanford, E. M.; Fréchet, J. M. J. *J. Mater. Chem.* **1998**, *8*, 519−527.

(41) Watkins, D. M.; Sayed-Sweet, Y.; Klimash, J. W.; Turro, N. J.; Tomalia, D. A. *Langmuir* **1997**, *13*, 3136−3141.

(42) Newkome, G. R.; Narayanan, V. V.; Patri, A.; Gross, J.; Moorefield, C. N.; Baker, G. R. *Polym. Mater. Sci. Eng.* **1995**, *73*, 222−223.

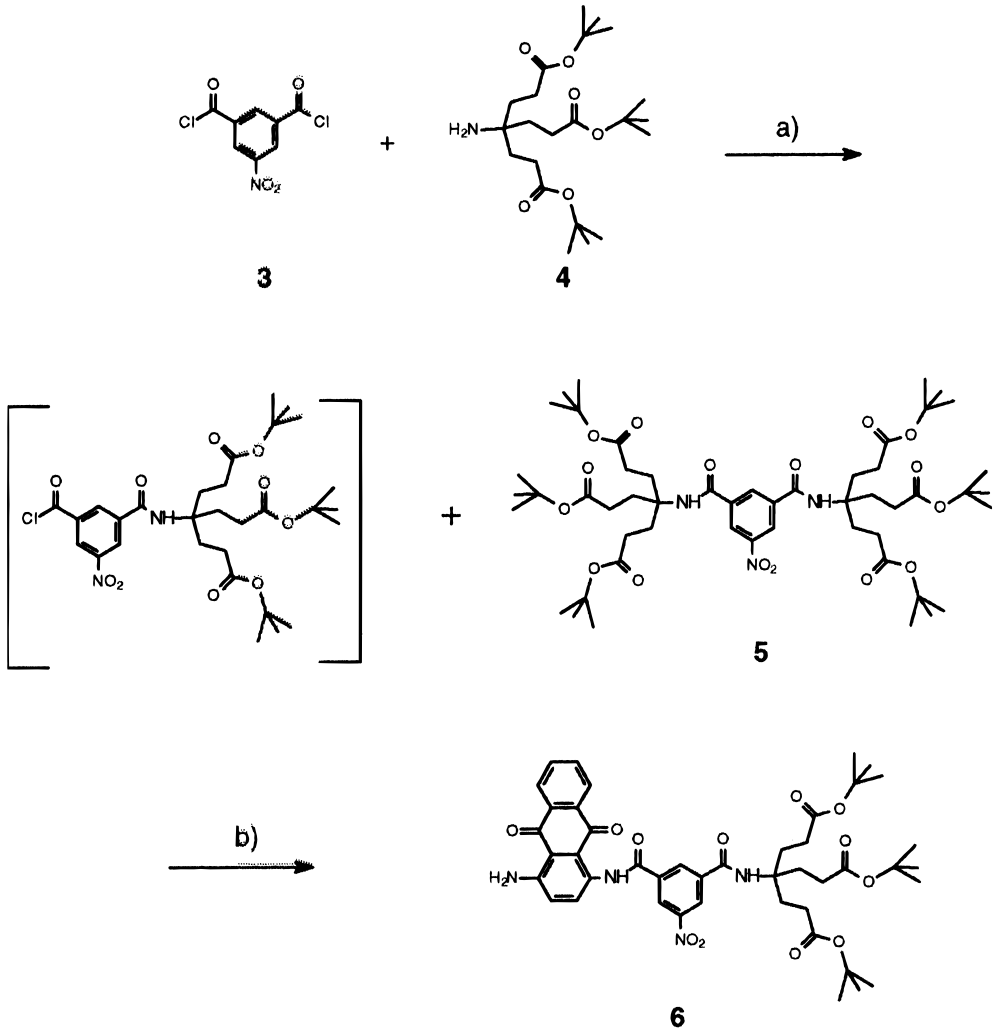
(43) Newkome, G. R.; Baker, G. R.; Moorefield, C. N.; Woosley, B. D.; Shade, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1996**, *37*, 415−416.

(44) Newkome, G. R.; Narayanan, V. V.; Echegoyen, L.; Pèrez-Cordero, E.; Luftmann, H. *Macromolecules* **1997**, *30*, 5187−5191.

(45) Newkome, G. R.; Baker, G. R.; Moorefield, C. N.; He, E.; Epperson, J.; Weis, C. D. *Polym. Mater. Sci. Eng.* **1997**, *77*, 65−66.

(46) Newkome, G. R.; Moorefield, C. N.; Baker, G. R.. U.S. Patent 5,650,101, 1997.

Scheme 1. Construction of a 1 → 3 Extended Building Block (6) with an Aromatic Spacer[a]



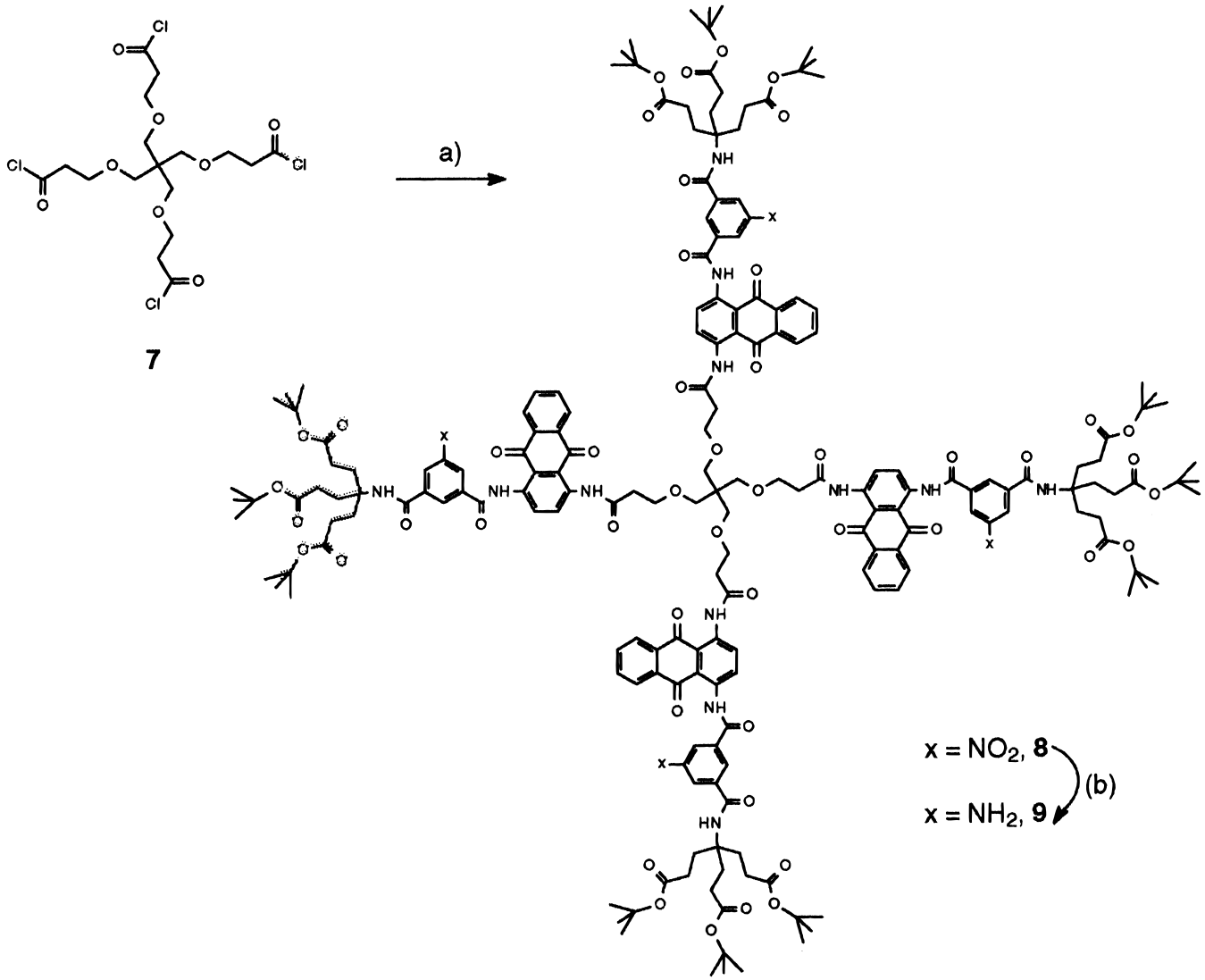
[a] (a) Et(*i*-Pr)$_2$N, benzene, 0−25 °C, 8 h; (b) 1,4-DAAQ, Et(*i*-Pr)$_2$N, THF, 40 °C, 12 h

of **1**, from 1 equiv each of **3**, **4** (Behera's amine),[48,49] and 1,4-diaminoanthraquinone (1,4-DAAQ). Unfortunately, under these conditions, **5** (40%) was isolated as the major product and the desired **6** was formed in lower (ca. 18−20%) yields. The ^{13}C NMR spectrum of purified **5** exhibited a simplified set of eleven peaks, especially the symmetrical four-peak pattern [124.1, 133.2, 136.5, 148.5 ppm] shown for the aryl carbons. It was then hypothesized that Behera's amine, although a hindered primary amine, was more nucleophilic than 1,4-DAAQ when reacted with bis-acid chloride **3**, thus giving rise to **5** as the major component. To address this problem, the reaction was conducted in a (1:1) benzene/THF mixture with the initial slow addition of 1 equiv of **4** in benzene to the bis-acid chloride **3** in benzene with subsequent addition of 1,4-DAAQ, which increased yields of **6** at the expense of **5**. Key signals (^{13}C NMR) for **6** that appeared at 57.4 (4° *C*NH), 171.8, 172.2, 172.8 (*C*ONH) ppm, as well as a spike at 829 amu (calcd 830 amu) in the MALDI-TOF MS, provided evidence for its formation.

It is interesting to note that monoamine **6** has a deep-purple color in the solid state, similar to the color of 1,4-DAAQ, but in a solution of CH_2Cl_2 it exhibits a deep red coloration. In contrast, the building block **1** exhibits similar but lighter shades of red.[14] This could be attributed to the extended conjugation (λ_{max} at 530 nm for **6** vs λ_{max} at 524 nm for **1**) in **6** as compared to that of **1**. Another unique feature to be noted for monoamine **6**, as compared to **1**, is in its solubility characteristics. While monoamine **1** is highly soluble in benzene or CH_2Cl_2 and all organic solvents of higher polarity, monomer **6** is not very soluble in either MeOH or MeCN; however, it is very soluble in CH_2Cl_2 and $CHCl_3$. This behavior may be attributed, in part, to the rigidity introduced by the aromatic spacer.The purified building block **6** was then treated with the four-directional core (tetraacid chloride **7**),[50] prepared from the corresponding acid,[51] in dry THF to afford (60%) the desired dodecaester **8** (Scheme 2). The ^{13}C NMR spectrum of **8** exhibited several novel features in contrast to that of **2**. As can be seen (Figure 1), the anthraquinone moieties in dendrimer **2** are flanked by

(47) Knops, P.; Sendhoff, N.; Mekelburger, H.-B.; Vögtle, F. *Top. Curr. Chem.* **1991**, *161*, 1−36.
(48) Newkome, G. R.; Behera, R. K.; Moorefield, C. N.; Baker, G. R. *J. Org. Chem.* **1991**, *56*, 7162−7167.
(49) Newkome, G. R.; Weis, C. D. *Org. Prep. Proced. Int.* **1996**, *28*, 485−488.
(50) Newkome, G. R.; Young, J. K.; Baker, G. R.; Potter, R. L.; Audoly, L.; Cooper, D.; Weis, C. D.; Morris, K. F.; Johnson, C. S., Jr. *Macromolecules* **1993**, *26*, 2394−2396.
(51) Newkome, G. R.; Weis, C. D. *Org. Prep. Proced. Int.* **1996**, *28*, 242−246.

Scheme 2. Synthesis of Electroactive Dodecaester 8 and 9[a]



[a] (a) monomer **6**, Et(*i*-Pr)$_2$N, THF, 60 °C, 30 min; (b) anhydrous HCO_2NH_4, 10% Pd−C, EtOH, reflux, 2 h

different but similar alkyl chains that give rise to two very similar sets of seven peaks (including two signals for the quinone carbonyl carbon atoms 186.2/3 ppm) in the ^{13}C NMR spectrum. In contrast, the aromatic region of the ^{13}C NMR spectrum of **8** exhibited 20 different signals, 18 due to each of the electronically different aromatic carbons (including those from the spacer nitro-aromatic unit) and two well-separated signals (186.3 and 187.2 ppm) for the quinone carbonyl carbon atoms (Figure 2). A peak at 3687 amu (M^+ + Na peak, calcd 3663.9 amu) in the MALDI-TOF MS provided further proof-of-structure for its formation.

One interesting feature of **8** is that chemical as well as electrochemical reactions can be conducted within the dendritic superstructure to generate specific and chemical characteristics. For example, the reduction of the internal nitro groups of dendrimer **8** to the corresponding amines, which can be used for subsequent internal attachments. Toward this end, we decided to prepare the dendritic amino-derivative **9** by treating **8** with ammonium formate[52] and 10% Pd−C in ethanol as solvent under reflux conditions. The reaction afforded a good (72%) yield of **9** as a dark-green lustrous powder after purification (Scheme 2). Evidence for the formation of **9** was obtained, in part, from a broad new peak (^{1}H NMR) at 4.2 (br, NH_2, 8H) ppm. Key signals at 149.38 (NH_2C_{Ar}), 162.55, 163.07 ($COC_6H_5NO_2CO$), 171.17 (*C*ONH), 173.45 (CO_2), and 186.24, 187.28 (CO_{quin}) ppm also provided evidence supporting its proposed structure. Additionally, the UV spectrum showed a new absorption maximum at 436 nm that was absent in the nitro-precursor (Figure 3).

The electrochemical properties of these compounds were also explored using cyclic voltammetry (CV) experiments in *N*,*N*-dimethylformamide at 298 K. It is well know that anthraquinones exhibit two reversible, one-electron reduction processes during the negative scan and the two associated reversible oxidations during the positive potential scan.[53−55] As can be seen in Figure 4a, the monosubstituted 1,4-DAAQ (**1**) showed the expected

(52) Ram, S.; Ehrenkaufer, R. E. *Tetrahedron Lett.* **1984**, *25*, 3415−3418.

(53) Chambers, J. Q. Electrochemistry of Quinones. In *The Chemistry of Quinonoid Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: London, 1988; Chapter 12, pp 719−757.

(54) Echegoyen, L.; Gustowski, D. A.; Gatto, V. J.; Gokel, G. W. *J. Chem. Soc., Chem. Commun.* **1986**, 220−223.

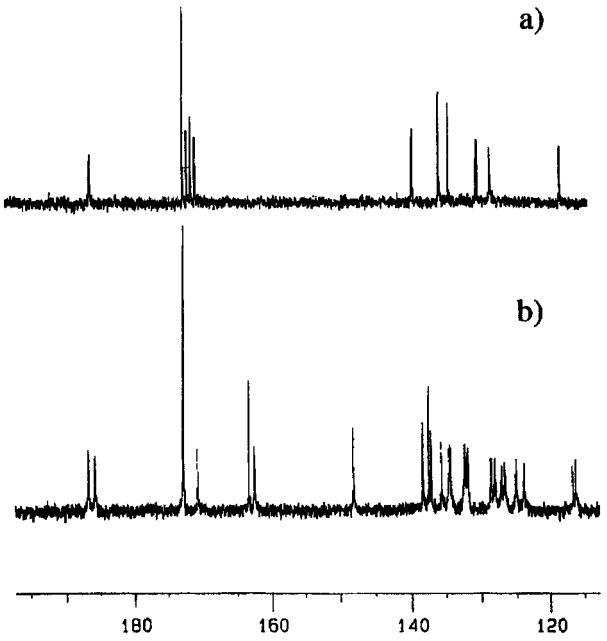


Figure 2. Comparison of the aromatic region of the ^{13}C NMR spectra of (a) dendrimer **2** and (b) dendrimer **8**.

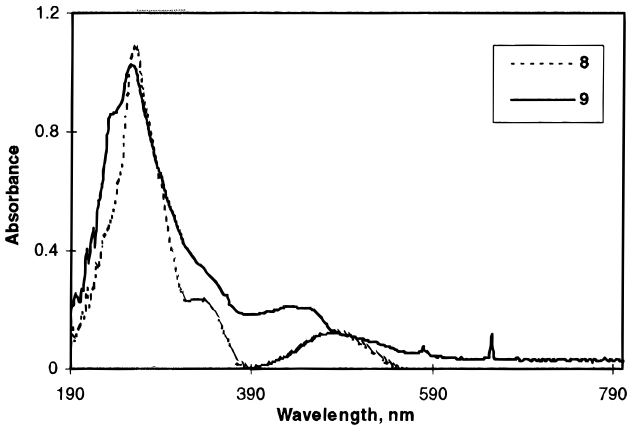


Figure 3. UV−vis spectra of dendrimers **8** and **9**.

two-wave electrochemical behavior in DMF; this will be the reference for comparisons.

The other moiety that needs to be considered is that of the widely studied aromatic nitro compounds.[56] Depending on the solvent and other factors, the electrochemical reduction of the nitro functional group can be coupled to specific chemical reactions to give anion radicals, hydroxylamines, and even fully reduced amines. According to Fry and co-workers,[57] the reduction of aromatic nitro-species in organic solvents can in fact be represented by a two-wave voltammogram. The first wave corresponds to a one-electron-transfer process, in which an anion radical is formed in solution. At more negative potentials, a second electron is transferred to form a 2-anion radical that is a strong nucleophile. Abstraction of a proton from the medium by this species and further release of a hydroxyl group yields a nitroso

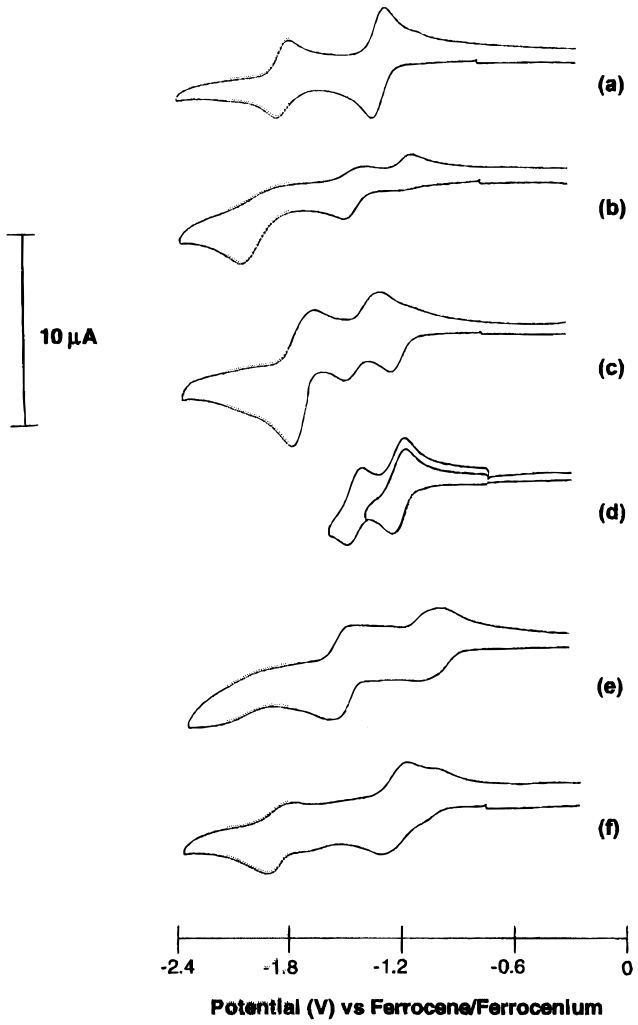


Figure 4. CV response of 1.0 mM solutions of compounds (a) **1**, (b) **5**, (c) **6**, (d) **6** (see Table 1), (e) **8**, and (f) **9** in 0.1 M of Et_4NTFB in DMF at 298 K. Scan rate 0.2 V s^{-1}.

derivative that in turn is easier to reduce than the singly charged anion radical. As a consequence, a two-electron reduction of the nitroso derivative to yield the hydroxylamine takes place at the same potential of that corresponding to the second wave. As a result of these coupled chemical and electrochemical reactions, the second reduction wave is larger than the first one and the anodic part of the voltammogram does not reveal the oxidation of the anion radical formed during the negative scan.[58]

In Figure 4b, the CV of compound **5** in DMF showed two cathodic waves of different sizes and two unsymmetrical anodic peaks. Since this compound only bears an electroactive aromatic nitro group[a], it is possible to suggest that the electrochemical−chemical reduction mechanism, noted above, may indeed be operable. (Controlled experiments with a compound similar to **5**, in which the nitro group has been chemically reduced to the amine, further showed that its hyperbranched structure is electrochemically inert in the potential range under study.) This being the case, the cathodic peak at −1455 mV would correspond to the formation of a radical anion, and the large peak at −2000 mV would represent the further electrochemical reduction that triggers the chemi-

(55) Gustowski, D. A.; Delgado, M.; Gatto, V. J.; Echegoyen, L.; Gokel, G. W. *J. Am. Chem. Soc.* **1986**, *108*, 7553−7360.
(56) Ketti, K. V.; Gali, H.; Smith, C. J.; Berning, D. E. *Acc. Chem. Res.* **1999**, *32*, 9−17.
(57) Fry, A. J. *Synthetic Organic Electrochemistry*; John Wiley & Sons: New York, 1989.
(58) Schubert, U. S.; Newkome, G. R.; Göldel, A.; Pemp, A.; Kersten, J. L.; Eisenbach, C. D. *Heterocycles* **1998**, *48*, 2141−2148.

Table 1. Reduction Potentials, *E* Values (mV) for Compounds 1, 5, 6, 8, and 9, Studied in 0.1 M Et_4NBF_4/DMF[a]

Figure 4	compd	E_{pa1}	E_{pc1}	E_{pa2}	E_{pc2}	E_{pa3}	E_{pc3}
a	**1**	−1240	−1307	−1748	−1808		
b	**5**	−1095	−1455	−1350	−2000		
c	**6**	−1230	−1200	−1298	−1450	−1602	−1715
d	**6**	−1230	−1200	−1298	−1450		
e	**8**	−940		−998	−1517	−1425	
f	**9**	−1173	−1279	−1760	−1869		

[a] Fc/Fc^+ as internal standard. Compd = a−f refer to Figure 4. E_{pan} = Potential at anodic peak number *n*, and E_{pcn} = potential at cathodic peak number *n* (*n* = 1, 2, or 3).

cally coupled transformations previously discussed. In this way, the anodic peak at −1350 mV would represent the oxidation of the chemically unreacted anion, and the peak at −1095 mV would correspond to the irreversible signal due to the oxidation of the electrochemical−chemically formed species at the large cathodic peak positioned at −2000 mM (see Table 1).

The unsymmetrical extended monomer **6** is an interesting electroactive species since it incorporates both anthraquinone and nitro functionalities in close juxtaposition. The CV response of **6**, however, does not show the overlapped signals of the two analogues **1** and **5** (Figure 4c). This clearly suggests that both electroactive groups in **6** influence the electrochemical behavior of each other. Comparison of Figures 4a−c shows for instance that during the cathodic scan the first reduction wave for **6** appears at more positive potentials than that corresponding to monomer **1**. The roughly 100 mV peak potential shift is in fact consistent with the electron-withdrawing effect that the presence of the aromatic nitro group should impose on the anthraquinone part of the molecule.[44] The second reduction peak, however, appears at the same potential as that of the first reduction of the nitro model **5**. This suggests that the second reduction peak corresponds to the one-electron reduction of the nitro group in **6** and that the delocalized electron in the anthraquinone moiety does not influence this process. In this way, the first two one-electron reduction processes in Figure 4c correspond to the formation of a *stable* 2^- anion, in which one electron is localized into each of the electroactive moieties of **6**.

Incorporation of an additional electron to **6** at more negative potential results in the third cathodic wave observed in Figure 4c. According to the reduction potentials of the models **1** and **5**, this electron-transfer process should correspond to the formation of a 2^- anion in the anthraquinone moiety of **6**. This is further supported by the cathodic peak potential that is again about 100 mV more positive than that of the second reduction peak of **1**. The size of the peak corresponding to the third reduction process and the virtual disappearance of the second reduction wave for the nitro functional group of **6** suggests that the one-electron reduction of the anthraquinone radical anion is not the only process taking place at this potential. On the basis of the mechanism described for the reduction of model **5**, it is possible to *speculate* that once the 2^- anthraquinone anion is formed, an *intramolecular* electron transfer from the anthraquinone to the nitro group occurs to generate the 2^- nitro anion. As was previously discussed for **5**, this doubly charged nitro anion is a very strong nucleophile that readily undergoes chemical and electrochemical coupled reactions. In this way, the third large reduction peak of **6** may indeed correspond to the simultaneous incorporation of a total of four electrons in a process that involves intramolecular electron transfer and associated chemical reactions.

This explanation is further supported by CV experiments of **6** in which the potential was switched before the reduction process defined by the third wave (Figure 4c) could take place. As can be seen in Figure 4d, the two electrochemical waves in this potential window are fully reversible. Since the two anodic peaks in Figure 4d appear at potentials different from those presented in the voltammogram of Figure 4c, it is possible to suggest that the first two reduction waves correspond to stable anion species and that the third reduction during the negative scan is the event that triggers a series of associated chemical and electrochemical coupled reactions that ultimately result in the electrochemical irreversibility observed in Figure 4c.

On the basis of the results discussed so far, the CV response of the first tier dendrimer **8** was expected to be similar to that of the extended monomer **6**. As can be observed by comparing Figures 4c and 4e, the shapes of the voltammograms for **6** and **8** are in general terms similar, but there are also important differences. The reduction peaks of the anthraquinone moiety in **8** are shifted to more positive potentials. This is expected because of the electron-withdrawing effect that the amidation of **6** to obtain **8** exerts on the electroactive anthraquinone group and is also consistent with previous electrochemical studies of similar compounds.

There is also a substantial broadening of the peaks when the voltammograms of **6** and the corresponding first tier dendrimer **8** are compared. This effect has also been previously observed by us and by others and has been attributed to a slow electron-transfer process due to the confinement of the electroactive groups within the dendritic structure.[25,26,59−61] Moreover, the peak broadening effect that characterizes the electrochemistry of dendrimers can also be observed (Figure 4f) where the CV response of the first tier dendrimer **9** is presented. As can be observed by inspecting its chemical structure, this compound is the reduced form of dendrimer **8**, and therefore its electrochemical response should correspond to that of the anthraquinone groups only. Comparison of Figures 4a, **4**c, and 4f for instance show that this is the case, since the electrochemical response of **9** is much closer to that of **1** than to that of the extended monomer **6**. Once again, the main differences between the voltammograms of **1** and **9** are a positive shift on the redox potentials and a peak broadening due to confinement effects. In any case, comparison of the CV responses of the first tier dendrimers **8** and **9** and their corresponding building blocks clearly show the influence that the nitro group exerts on their electrochemical behavior.

The preparation and study of dendrimers bearing internal moieties that can undergo intramolecular or intermolecular chemical reactions as a consequence of an induced excitation signal are relevant for the design and synthesis of molecular devices and catalysts. This par-

(59) Gorman, C. B.; Parkhurst, B. L.; Su, W. Y.; Chen, K.-Y. *J. Am. Chem. Soc.* **1997**, *119*, 1141−1142.
(60) Gorman, C. B.; Hager, M. W.; Parkhurst, B. L.; Smith, J. C. *Macromolecules* **1998**, *31*, 815−822.
(61) Newkome, G. R.; Güther, R.; Moorefield, C. N.; Cardullo, F.; Echegoyen, L.; Pérez-Cordero, E.; Luftmann, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2023−2026.

ticular line of research is under intense investigation in our laboratory.

Experimental Section

All starting reagents were obtained from Aldrich Chemical Co. THF was dried from $LiAH_4$ before use. All melting points were taken in capillary tubes and are uncorrected. ^1H and ^{13}C NMR spectra were determined on a Bruker 250 MHz spectrometer, using $CDCl_3$ as solvent except when noted, with Me_4Si, as the internal standard. Cyclic voltammograms at 20 °C were obtained using a PAR (Princeton Applied Research) model 175 universal programmer, a model 173 potentiostat, and a Houston Instruments X−Y recorder. IR compensation was performed in all experiments by means of a PAR model 179 module. A conventional three-electrode configuration 2 cm^3 cell (Cypress Systems, Lawrence, Kansas) was used with a 1 mm diameter glassy-carbon working electrode, a platinum wire as the counter electrode, and a silver wire as a pseudo-reference electrode. The working electrode was polished before the experiments in sequential stages using diamond polishing compound of 0.25 μm particle size and a 0.05 μm alumina−water mixture on a felt surface. All of the solutions were carefully deoxygenated by bubbling dry N_2 for at least 10 min before obtaining the CV data. The solvent used in all CV experiments was a 0.1 M electrochemical grade Et_4NBF_4 solution in HPLC grade DMF. The electrochemical response of the internal ferrocene/ferrocenium couple was used as a reference against which the potentials reported in this work were measured.

The extended monomer **1** and the corresponding dendrimer **2** [^{13}C NMR (see peaks in Figure 2a) δ 116.3−138.1 (C_{Ar}), 170.9, 171.6, 172.2 (*C*ONH), 172.8 (CO_2), 186.3, 186.4 (CO_{Quin})] were reported[14] elsewhere and utilized herein for comparative purposes.

Synthesis of 3-Cascade:1-aminoanthraquinone[1,4]:(1-oxo-2-azaethylidyne):5-nitrophenylene[2-1,3]:(3-oxo-2-azapropylidyne):*tert*-butyl Propanoate (6). To a stirred, ice-cold solution of benzene (300 mL) containing freshly prepared bis-acid chloride[62] **3** (2.39 g, 9.63 mmol) were added amine[49] **4** (2.0 g, 4.82 mmol) and di(isopropyl)ethylamine (DIEA; 1.7 mL, 9.64 mmol) in dry benzene (50 mL) over a period of 1 h. The mixture was warmed to 25 °C and then stirred for an additional 7 h. A solution of excess 1,4-DAAQ (**1**; 5.04 g, 21.2 mmol) and DIEA (1.7 mL, 9.64 mmol) in THF (50 mL) was added at once to the mixture and stirred for 12 h at 40 °C.

The solvent was evaporated in vacuo to give a residue, which was dissolved in CH_2Cl_2. The organic layer was washed with aqueous HCl (20%) and then filtered. The filtrate was sequentially washed with aqueous $NaHCO_3$ (10%, 2×), deionized water (3×), and brine solution. The organic layer was dried ($MgSO_4$), and the solvent was removed in vacuo to afford a residue, which was chromatographed (SiO_2) eluting with an EtOAc/CH_2Cl_2 (1:1) mixture. The crude product was rechromatographed on a short silica column eluting with an EtOAc/cyclohexane (1:3) mixture to remove traces of hexaester **5** [^{13}C NMR δ 28.1 (CH_3), 29.3, 29.4 (CH_2CH_2), 58.1 (4° *C*NH), 80.91 (*C*Me_3), 124.1, 133.2, 136.5, 148.2 (C_{Ar}), 164.9 (*C*ONH), 174.2 (CO_2). Anal. Calcd for $C_{52}H_{83}N_3O_{16}$: C, 62.07; H, 8,32; N, 4.18. Found: C, 62.11; H, 8.19; N, 4.19.] Concentration of the eluent in vacuo afforded (30%) the pure **6**, as a purple solid: 2.39 g, mp 232.0−232.6 °C; ^1H NMR δ 1.45 (s, 27H), 2.00 (br d, 6H), 2.15 (m, 2H), 2.3 (br d, 6H), 2.5 (t, J = 7.2 Hz, 4H), 6.05 (s, 1H), 7.05, 7.70, 8.25, 8.90 (Ar*H*, 6H), 7.20 (br s, 2H), 12.35 (s, 1H); ^{13}C NMR δ 21.6, 27.9, 29.9, 30.2, 36.3, 37.7, 57.4, 80.5, 110.4, 116.1, 126.3, 126.6, 126.7, 126.8, 132.8, 133.2, 133.8, 133.9, 134.6, 148.3, 171.8, 172.2, 172.8, 183.6, 187.1; IR 3348, 3295 (NH_2), 1719 (ester C═O), 1640 (amide C═O), 1310 (CN), 1290 (ester C−O) cm^{-1}; UV λ_{max} 530 (ϵ = 8292), 255 (ϵ = 23217) nm; MALDI-TOF MS *m*/*z* 829, calcd mass 828.9 amu. Anal. Calcd for $C_{44}H_{52}N_4O_{12}$: C, 63.75; H, 6.32; N, 6.75. Found: C, 63.50; H, 6.48; N, 6.41.

Synthesis of 12-Cascade:methane[4]:(2-oxo-5-oxa-1-azahexylidyne):anthraquinone[2-1,4]:(1-oxo-2-azaethylidyne):5-nitrophenylene[2-1,3]:(3-oxo-2-azapropylidyne):*tert*-butyl Propanoate (8). To a stirred THF solution (20 mL) of the extended amine **6** (5.97 g, 7.2 mmol) with DIEA (1.3 mL, 7.20 mmol) under nitrogen was added tetraacid chloride **7** (750 mg, 1.50 mmol), freshly prepared[63,64] from the corresponding tetraacid.[51] After 30 min of stirring at 60 °C, the THF was evaporated in vacuo, and the residue was dissolved in CH_2Cl_2. The organic layer was sequentially washed with aqueous HCl (10%, 2×), aqueous $NaHCO_3$ solution (10%, 2×), deionized water (2×), and saturated brine. The organic layer was dried ($MgSO_4$), followed by concentration in vacuo to afford a dark orange residue, which was chromatographed (SiO_2) eluting with an EtOAc/CH_2Cl_2 (1:1) mixture to afford (60%) dendrimer **8**, as a deep-orange, microcrystalline powder: 3.29 g, 900 μmol; mp 168.0−169.6 °C; ^1H NMR δ 1.42 (br s, 108H), 2.21, 2.39 (48H), 2.64 (8H), 3.56, 3.74 (16H), 7.71 (4H), 8.05−9.02 (m, 24H), 12.85, 13.49 (8H); ^{13}C NMR δ 28.23, 30.14, 30.38, 39.68, 45.83, 58.71, 67.33, 70.07, 81.07, 116.58, 117.09, 124.39, 125.30, 127.08, 127.68, 128.62, 129.15, 132.23, 132.80, 132.97, 134.77, 134.92, 136.26, 137.80, 137.97, 138.90, 148.68, 162.95, 163.47, 171.07, 173.33, 186.27, 187.18; IR 3295 (NH), 1712 (ester C═O), 1640 (amide C═O), 1500 (N−O), 1310 (CN), 1290 (ester C−O) cm^{-1}; UV λ_{max} 484 (ϵ = 25650), 265 (ϵ = 1.92 × 10^5) nm; MALDI-TOF MS *m*/*z* 3687.15 (M^+ + Na), calcd mass 3663.9. Anal. Calcd for $C_{193}H_{224}N_{16}O_{56}$: C, 63.27; H, 6.16; N, 6.12. Found: C, 63.10; H, 6.35; N, 5.99.

Synthesis of 12-Cascade:methane[4]:(2-oxo-5-oxa-1-azahexylidyne):anthraquinone[2-1,4]:(1-oxo-2-azaethylidyne):5-aminophenylene[2-1,3]:(3-oxo-2-azapropylidyne):*tert*-butyl Propanoate (9). To a solution of the dodecaester **8** (1.00 g, 2.73 × 10^{-4} mol) in EtOH was added 10% Pd−C (150 mg), and then the mixture was stirred for 5 min at 35 °C. Ammonium formate (500 mg, 7.94 × 10^{-3} mol) was added, and then the mixture was refluxed for 2 h. After cooling to 25 °C, the solution was filtered through Celite. The filtrate was concentrated in vacuo to afford a residue, which was dissolved in CH_2Cl_2, washed with deionized water, and dried ($MgSO_4$). Concentration in vacuo, followed by flash chromatography on a short SiO_2 column eluting with an EtOAc/CH_2Cl_2 (1:1) mixture afforded (72%) **9**, as a dark-green lustrous powder: 690 mg, 193 μmol; mp 140−145 °C; ^1H NMR δ 1.44 (br s, 108H), 2.21, 2.25 (48H), 2.74 (8H), 3.46, 3.54 (16H), 4.2 (br, 8H), 7.71 (4H), 8.05−9.02 (m, 24H), 12.80, 13.39 (8H); ^{13}C NMR δ 28.21, 30.0, 30.28, 39.48, 45.33, 57.71, 67.33, 69.57, 80.87, 116.58, 116.63, 124.39, 124.45, 127.08, 127.21, 128.52, 129.61, 132.13, 132.23, 132.97, 134.77, 134.92, 136.26, 137.80, 137.97, 138.90, 149.38, 162.55, 163.07, 171.17, 173.45, 186.24, 187.28; IR 3310, 3295 (NH_2), 1717 (ester C═O), 1645 (amide C═O), 1290, 1120 (ester C−O) cm^{-1}; UV λ_{max} 436 (ϵ = 35442), 265 (ϵ = 1.95 × 10^5) nm. Anal. Calcd for $C_{193}H_{232}N_{16}O_{48}$: C, 65.41; H, 6.60; N, 6.32. Found: C, 65.26; H, 6.75; N, 6.15.

Acknowledgment. Support for this work was provided in part from the National Science Foundation (DMR-96-22609), the Army Research Office (DAAH04-95-1-0373; DAAH04-96-1-0306), and the Office of Naval Research (N00014-99-1-0082).

JO991278G

(62) Newkome, G. R.; Lin, X.; Young, J. K. *Synlett* **1992**, 53−54.

(63) Bruson, H. A. U.S. Patent 2,401,607, 1946.

(64) Newkome, G. R.; Nayak, A.; Behera, R. K.; Moorefield, C. N.; Baker, G. R. *J. Org. Chem.* **1992**, *57*, 358−362.