A Tailored Approach to the Syntheses of Electroactive Dendrimers Based on Diaminoanthraquinones[1]

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Received February 2, 1999; Revised Manuscript Received June 16, 1999

ABSTRACT: A variety of extended building blocks, based on isomeric diaminoanthraquinones, has been synthesized and used to construct a series of electroactive dendrimers. The resulting macromolecules are characterized by chromophoric moieties embedded at a specific distance from both the core and the periphery of the dendritic constructs. These anthraquinone-based dendrimers show different electrochemical, spectroscopic, and solubility properties as a function of the nature of the dendritic core and of the isomeric monomer employed.

Introduction

Methods to incorporate utilitarian functionality within the confines of dendritic superstructures[2−11] are gaining increasing attention. Of the many such functional units that could be employed, electroactive moieties[12−16] play a prominent role for a variety of reasons. For instance, dendritic macromolecules possessing units capable of reversibly exchanging electrons and absorbing and emitting light have been used as molecular light harvesters,[17] molecular antennas,[18,19] solvatochromic probes,[20] potential molecular electronic devices,[21] and electrically conducting systems.[22] The majority of these reports involves the incorporation of functionality at specific positions in the macromolecule, of which the easiest synthetically realized are at either the core (focal point) or the periphery. The application of an extended building block approach has permitted the tailored incorporation of specific functionality at a predetermined locus within the molecular construct.[23−25] As we explore this tailored approach, the incorporation of redox centers permits a better understanding of utilizing such internal positions as catalytic sites and electron repositories.[26]

To evaluate the redox character of such specific internal loci, substituted anthraquinone derivatives, well-known as important industrial dye intermediates,[27] were considered. Fuhrhop et al.[28] have investigated the construction of redox-active membranes using diaminoanthraquinone-based bolaamphiphiles[29−31] and noted their potential for use as pool quinones. The reversible reduction of quinonoid moieties has been exploited by Echegoyen and co-workers[32−34] to develop anthraquinone-based metal binding systems, which have implications in studies related to metal ion transport across membranes. The construction of molecular and supramolecular devices requires structural components whose physical behavior (optical, electrical, spectral, etc.) could be modulated by external stimulation and would, thus, constitute molecular switches. Recently, quinonoid-[35] and anthraquinonoid[36−39]-based systems, which undergo reversible electrochemical and photochemical changes, have also been reported; however, incorporation of such electroactive units within the superstructure of dendritic systems has not been investigated.

We herein report the syntheses and properties of dendritic constructs possessing chromophoric diaminoanthraquinonoid moieties specifically pinned within the macromolecular infrastructure.

Experimental Part

All reagents were obtained from Aldrich Chemical Co. and used without further purification. All reactions were conducted under a nitrogen atmosphere, unless otherwise stated. THF was distilled under nitrogen with $LiAlH_4$ as the drying agent and triphenylmethane as indicator.

Melting points were determined with an Electrothermal 9100 and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX250 spectrometer using $CDCl_3$, except where noted. Infrared spectra (IR) were recorded (KBr pellet, unless otherwise noted) on a Bruker Vector 22 infrared spectrometer. UV spectra were recorded on a HP-8452A diode array spectrophotometer, using THF as solvent. Mass spectra were obtained on either a Bruker Esquire electrospray ion trap mass spectrometer or a Bruker Reflex II MALDI-TOF mass spectrometer.

Chemical reductions were achieved by addition of $NaBH_4$ (0.5−1.0 mg) to the corresponding THF solution (10 μmol, quartz cell with 1 cm path length), followed by vigorous agitation. Reduction of the anthraquinonoid moieties was observed (1−30 s) by changes in the UV absorption spectra, when the solutions become colorless. The aerobic oxidation of these reduced solutions occurred at a much slower rate (30−40 min) as observed from the peaks in the UV spectra; a representative example of this reversible process has been reported.[15] Electrochemical studies were preformed using a Princeton Applied Research (PAR) model 173 potentiostat coupled to a model 175 programmer and a Houston Instruments model 2000 X−Y recorder. Resistance compensation was performed using a PAR digital coulometer module (model 179) integrated to the potentiostat. The cyclic voltammetry (CV) experiments were conducted in a 2 mL cell in which a glassy carbon disk electrode (1 mm diameter), a platinum wire, and a Ag wire were properly fitted as the working, counter, and pseudoreference electrodes, respectively. The silver wire (99.99%) was obtained from Aldrich, whereas the cell and electrodes were purchased from Cypress Systems (Lawrance, KS).

Before recording the voltammetric data, the surface of the working electrode was polished in three different steps using

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§ http://www.dendrimers.com.

10.1021/ma990143+ CCC: $18.00
Published on Web 09/08/1999

diamond polishing compound (1 and 0.25 μM) and slurry alumina (0.05 μM) on a felt surface. To avoid oxygen interference, careful deoxygenation was realized by bubbling dry nitrogen gas through the electroactive solution for ca. 10 min. Further dissolution of oxygen from air was prevented by keeping a flow of nitrogen above the solution throughout the duration of the CV experiments.

In a typical run, 1 mL of a 1.0 mM solution of the electroactive material was prepared using as supporting electrolyte a 0.1 M solution of tetraethylammonium tetrafluoroborate (Et_4NTFB, 99% Acros Organics) in dry, distilled *N*,*N*-dimethylformamide (DMF).[40] The electrochemical data were then recorded at 298 K in the −1.6, 1.0 V potential window at a scan rate of 200 mV s^{-1}. Since the potential was followed by means of the pseudoreference silver electrode, a second set of voltammograms was obtained after adding a small amount of ferrocene to the solution. The reversible electrochemical signal of the ferrocene/ferrocenium couple did not interfere with the electrochemistry of any of the materials under investigation and therefore allowed the use of its half-wave potential as a reference against which all the potentials reported herein were measured.

3-Cascade:1-Aminoanthraquinone[1,4]:(3,7-Dioxo-2,8-diazaoctylidyne):*tert*-Butyl Propionate (1). Procedure A. To a stirred ice-cold solution of THF (300 mL) containing glutaroyl chloride (1.63 g, 9.63 mmol) in a three-neck round-bottom flask was added Behera's amine[41−43] (**3**; 4.0 g, 9.64 mmol) and Et(*i*-pr)$_2$N (1.7 mL, 9.64 mmol) in dry THF (50 mL) over a period of 1 h. The mixture was then allowed to warm to 25 °C and stirred for an additional 3 h. A mixture of recrystallized 1,4-diaminoanthraquinone (1,4-DAAQ; 2.52 g, 10.6 mmol) and Et(*i*-pr)$_2$N (1.7 mL, 9.64 mmol) in THF (50 mL) was added at once. After 12 h of stirring, 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 solution (20%, 150 mL), followed by filtration. The filtrate was sequentially washed with aqueous $NaHCO_3$ (10%, 100 mL, 2×), followed by deionized water (100 mL ea. 3×), and finally with a saturated brine solution (100 mL). The organic layer was dried ($MgSO_4$) and the solvent removed in vacuo to give a solid, which was chromatographed (SiO_2) eluting with an EtOAc and CH_2Cl_2 (1:1) mixture. The crude product was rechromatographed on a short silica gel column eluting with EtOAc and cyclohexane (1:3) in order to remove traces of hexaester **2**. Concentration in vacuo afforded (35−40%) the pure monoamine **1**, as a purple-red solid: 2.60 g, 3.47 mmol, mp 78−79 °C. ^{1}H NMR: δ 1.45 (s, CH_3, 27H), 2.00 [br d, (CH_2-CH_2CO_2), 6H], 2.15 (m, $CH_2CH_2CH_2$, 2H), 2.3 (br d, CH_2CH_2-CO_2, 6H), 2.5 (t, C$H_2CH_2CH_2$, J = 5.6 Hz, 4H), 6.05 (s, ^{4}°CN*H*, 1H), 7.05, 7.70, 8.25, 8.90 (Ar*H*, 6H), 7.20 (br s, NH_2, 2H), 12.35 (s, CON*H*-$C_{14}H_6O_2$−NH_2, 1H). ^{13}C NMR: δ 21.6 ($CH_2CH_2CH_2$), 27.9 (*C*H_3), 29.9, 30.2 ($CH_2CH_2CO_2$), 36.3, 37.7 ($CH_2CH_2CH_2$), 57.4 (^{4}°*C*NH), 80.5 (*C*Me$_3$), 110.4, 116.1, 126.3, 126.6, 126.7, 126.8, 132.8, 133.2, 133.8, 133.9, 134.6, 148.3 (C_{Ar}), 171.8, 172.2, 172.8 (*C*ONH), 183.6, 187.1 (CO_{quin}). IR: 3434, 3385 (NH_2), 1718 (ester C═O), 1664 (amide C═O), 1257, 1160 (ester C−O) cm^{-1}. UV: λ_{max} 524 ($\epsilon = 4.13 \times 10^6$), 255 ($3.38 \times 10^7$) nm. MALDI-TOF-MS m/z 749 (M − H). Calcd. mass 750 amu. Anal. Calcd for $C_{41}H_{55}N_3O_{10}$: C, 65.70; H, 7.40; N, 5.60. Found: C, 65.55; H, 7.19; N, 5.44.

12-Cascade:Methane[4]:(2-Oxo-5-oxa-1-azahexylidyne):anthraquinone[1,4]:(3,7-Dioxo-2,8-diazaoctylidyne):*tert*-Butyl Propionate (4). Procedure B. To a stirred THF solution (20 mL) of monoamine **1** (5.39 g, 7.2 mmol) with Et(*i*-pr)$_2$N (1.3 mL, 7.20 mmol) under a nitrogen atmosphere was added 6,6-bis(chlorocarbonyl-2-oxabutyl)-4,8-dioxaundecane-1,11-dicarboxyl chloride (freshly prepared[44,45] from the corresponding tetraacid,[46] mp 107−109 °C; 750 mg, 1.50 mmol). The reaction was stirred at 50 °C for 4 h. The solvent was evaporated in vacuo to give a residue, which was dissolved in CH_2Cl_2. The organic layer was washed sequentially with dilute aqueous HCl (2×, 10%, 50 mL each), dilute aqueous $NaHCO_3$ solution (2×, 10%, 50 mL each), deionized water (2×, 50 mL each), and finally with a saturated brine solution (50 mL). 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 give (60%) the first generation dendrimer **4**, as a deep orange microcrystalline powder: 3.02 g (900 μmol), mp 96−98 °C. ^{1}H NMR: δ 1.4 (br s, CH_3, 108H), 1.95, 2.25 (CH_2CH_2-CO_2, 48H), 2.15 ($CH_2CH_2CH_2$, 8H), 2.60 (CH_2CONH, 24H), 3.60 (CH_2OCH_2, 16H), 6.1 (^{4}°CN*H*, 4H), 7.7 (m), 8.1 (m), 8.85 (s, Ar*H*, 24H), 12.3 (ArN*H*, 8H). ^{13}C NMR: δ 21.4 (CH_2CH_2-CH_2), 28.0 (*C*H_3), 29.8, 29.9 ($CH_2CH_2CO_2$), 36.3, 37.7 (CH_2-CH_2CH_2), 39.5 (OCH_2CH_2), 46.0 (C_{Core}), 57.4 (^{4}°*C*NH), 67.2, 69.9 (CH_2OCH_2), 80.6 (*C*Me$_3$), 116.3, 126.9, 128.8, 132.8, 134.4, 138.1 (C_{Ar}), 170.9, 171.6, 172.2 (*C*ONH), 172.8 (CO_2), 186.3, 186.4 (CO_{quin}). IR: 3340 (NH), 3020, 2975, 2933 (C−H), 1729 (ester C═O), 1639 (amide C═O), 1254, 1157 (ester C−O) cm^{-1}. UV: λ_{max} 484 ($\epsilon = 1.98 \times 10^8$), 255 ($1.36 \times 10^9$) nm. MALDI-TOF-MS: m/z 3373 (M^+ + Na). Calcd mass 3349.9 amu. Anal. Calcd for $C_{181}H_{240}N_{12}O_{48}$: C, 64.86; H, 7.22; N, 5.01. Found: C, 64.63; H, 7.38; N, 4.89.

12-Cascade:Methane[4]:(2-Oxo-5-oxa-1-azahexylidyne):Anthraquinone[1,4]:-(3,7-dioxo-2,8-diazaoctylidyne):Propanoic Acid (5). Procedure C. Ester **4** (1.04 g, 320 μmol) was treated with formic acid (10.0 mL) at 25 °C and stirred for 12 h. The formic acid was removed in vacuo to give a residue, which was dissolved in a 1:1 mixture of acetone−deionized water and concentrated in a similar manner; this procedure was repeated three times. The residue was dried in vacuo for 24 h to afford (80%) the dodecaacid **5**, as a deep orange powder, which was used without further purification: 670 mg (250 μmol), mp 140−142 °C. ^{1}H NMR (DMSO-d_6): δ 2.30, 2.55 ($CH_2CH_2CO_2$, 48H), 2.7−3.0 (m, $CH_2CH_2CH_2$, OCH_2CH_2, 32H), 3.6−4.2 (CH_2OCH_2, CON*H*, 20H), 7.7, 8.1−8.35, 9.1 (CH_{Ar}, 24H), 12.0 (CO_2H, 12H), 12.3 (NH_{Ar}, 8H). ^{13}C NMR (DMSO-d_6): δ 21.2 ($CH_2CH_2CH_2$), 29.2, 30.7 (CH_2CH_2-CO_2), 35.1, 37.2 ($CH_2CH_2CH_2$), 45.5 (C_{core}), 56.4 (^{4}°CNH), 68.0, 69.9 (CH_2OCH_2), 116.0, 127.7, 132.1, 134.5, 137.1, 137.3 (C_{Ar}), 170.3, 171.5, 171.7 (*C*ONH), 174.7 (CO_2H), 185.5 (CO_{quin}). IR: 3677−3000 (acid OH, br), 1700 (acid C═O) cm^{-1}. MALDI-TOF-MS: m/z 2704 (M^+ + Na). Calcd mass 2679 amu.

36-Cascade:Methane[4]:(2-Oxo-5-oxa-1-azahexyylidyne):Anthraquinone[1,4]:(3,7-Dioxo-2,8-diazaoctylidyne):(3-Oxo-2-azapentylidyne):*tert*-Butyl Propionate (6). Procedure D. A mixture of **5** (270 mg, 100 μmol), DCC (350 mg, 1.69 mmol), and 1-HBT (230 mg, 1.69 mmol) in dry DMF (5 mL) was stirred for 1 h at 25 °C. Amine **3** (700 mg, 1.69 mmol) was added, and the reaction was stirred at 25 °C for 48 h. After filtration, DMF was removed in vacuo to give a residue, which was dissolved in CH_2Cl_2. The organic layer was washed with aqueous HCl (10%, 20 mL), followed by water, and brine solution. The solvent was evaporated in vacuo to give a residue, which was column chromatographed (SiO_2) eluting with an EtAc/CH_2Cl_2 (1:1) mixture affording (50%) **6**, as a bright orange solid: mp 92−94 °C; 360 mg (48 μmol). ^{1}H NMR: δ 1.43 (br s, CH_3, 324H), 1.95−2.25 ($CH_2CH_2CO_2$, 144H), 2.15 (CH_2CH_2-CH_2, 8H), 2.6 (CH_2CONH, 72H), 3.6 (CH_2OCH_2, 16H), 6.1 (^{4}°-CN*H* 16H), 7.7 (m), 8.1 (m), 8.85 (s, CH_{Ar}, 24H), 12.3 (NH_{Ar}, 8H). ^{13}C NMR: δ 21.4 ($CH_2CH_2CH_2$), 28.0 (*C*H_3), 29.8, 29.9 ($CH_2CH_2CO_2$), 36.3, 37.7 ($CH_2CH_2CH_2$), 39.5 (OCH_2CH_2), 46.0 (C_{Core}), 57.4, 57.8 (^{4}°CNH), 67.2, 69.9 (CH_2OCH_2), 80.6 (*C*Me$_3$), 116.3, 126.9, 128.8, 132.8, 134.4, 138.1 (C_{Ar}), 170.9, 171.6, 171.9, 172.2 (*C*ONH), 172.8 (CO_2), 186.3, 186.4 (CO_{quin}). IR: 3341 (NH), 1722 (ester C═O), 1653 (amide C═O), 1254, 1151 (ester C−O) cm^{-1}. UV: λ_{max} 484 ($\epsilon = 1.54 \times 10^6$), 255 ($1.01 \times 10^7$) nm. MALDI-TOF-MS: 7449. Calcd mass: 7449 amu. Anal. Calcd for $C_{397}H_{612}N_{24}O_{108}$: C, 63.99; H, 8.28; N, 4.52. Found: C, 63.81; H, 8.13; N, 4.40.

108-Cascade:(2-Oxo-5-oxa-1-azahexylidyne):Anthraquinone[1,4]:(3,7-Dioxo-2,8-diazaoctylidyne):(3-Oxo-2-azapentylidyne)^2:*tert*-Butyl Propionate (8). A mixture of ester **6** (360 mg, 48 μmol) and formic acid (2 mL) was stirred at 25 °C for 12 h. The formic acid was removed in vacuo, followed by addition of a 2:1 acetone−deionized water solution (2:1, 20 mL); this procedure was repeated three times. The resultant residue was dried in vacuo for 24 h to remove traces of residual formic acid. The deep orange residue (80%) of polyacid **7** was characterized and used in the next step: 670

mg (250 μmol), mp 160−164 °C. ^{1}H NMR (DMSO-d_6): δ 2.30, 2.55 (CH_2CH_2CO$_2$, 144H), 2.60−3.00 (CH_2CONH, 72H), 3.6−4.2 (CH_2OCH_2, CONH, 32H), 7.7, 8.1−8.35, 9.1 (CH_{Ar}, 24H), 11.9 (CO$_2H$, 36H), 12.3 (NH_{Ar}, 8H). ^{13}C NMR (DMSO-d_6): δ 21.2 (CH$_2$CH_2CH$_2$), 29.2, 30.7 (CH_2CH$_2$CO$_2$), 35.1, 37.2 (CH_2-CH$_2$CH_2), 45.5 (C_{core}), 56.4 ($^{4°}$CNH), 68.0, 69.9 (CH$_2$OCH$_2$), 116.0, 127.7, 132.1, 134.5, 137.1, 137.3 (C_{Ar}), 170.3, 171.5, 171.7 (CONH), 174.7 (CO$_2$H), 185.5 (CO_{quin}). IR: 3660−3010 (acid OH, br), 1715 (acid C=O) cm^{-1}. MALDI-TOF-MS: m/z 5418. Calcd 5421.4. Anal. Calcd for $C_{253}H_{316}N_{24}O_{108}$: C, 56.05; H, 5.87; N, 6.20. Found: C, 56.19; H, 5.78; N, 6.09.

A mixture of **7** (45 mg, 8.29 μmol), DCC (75 mg, 365 μmol), and 1-HBT (49 mg, 364 μmol) in dry DMF (3.5 mL) was stirred at 25 °C for 1 h. Amine **3** (151 mg, 364 μmol) was added, and the reaction was stirred at 25 °C for 48 h. After filtration, DMF was removed in vacuo to give a residue, which was dissolved in CH_2Cl_2. The organic layer was sequentially washed with aqueous HCl (10%, 20 mL), followed by water, and then a saturated brine solution. The solvent was evaporated in vacuo, and the resultant solid was column chromatographed (SiO_2) eluting with an EtAc/CH_2Cl_2 mixture affording (50%) **8**, as a bright orange solid: mp 65−69 °C; 108 mg (5.5 μmol). ^{1}H NMR: δ 1.43 (br s, CH_3, 972H), 1.95−2.25 (CH_2CH_2CO$_2$, 432H), 2.15 (CH$_2$CH_2CH$_2$, 8H), 2.60 (CH_2CONH, 216H), 3.60 (CH_2OCH_2, 16H), 6.1 ($^{4°}$CNH, 4H), 7.7 (m), 8.1 (m), 8.85 (s, CH_{Ar}, 24H), 12.3 (NH_{Ar}, 52H). ^{13}C NMR: δ 21.4 (CH$_2$CH_2CH$_2$), 28.0 (CH_3), 29.8, 29.9 (CH_2CH_2CO$_2$), 36.3, 37.7 (CH_2CH$_2$CH_2), 39.5 (OCH$_2$CH_2), 46.0 (C_{Core}), 57.4 ($^{4°}$CNH), 67.2, 69.9 (CH$_2$-OCH_2), 80.6 (C(CH$_3$)$_3$), 116.3, 126.9, 128.8, 132.8, 134.4, 138.1 (C_{Ar}), 170.9, 171.6, 172.2 (CONH), 172.8 (CO$_2$), 186.3, 186.4 (CO_{quin}). IR: 1733 (ester C=O), 1656 (amide C=O), 1251, 1153 (ester C−O) cm^{-1}. UV (THF): λ_{max} 484 ($\epsilon = 2.17 \times 10^6$), 255 ($1.48 \times 10^7$) nm. MALDI-TOF-MS: m/z 19766 (M + 1 + Na). Calcd 19742. Anal. Calcd for $C_{1045}H_{1728}N_{60}O_{288}$: C, 63.58; H, 8.82; N, 4.26. Found: C, 63.33; H, 8.62; N, 4.33.

12-Cascade:Tricyclo[3.3.1.1^{3,7}]decane[4−1,3,5,7]:(2-Oxo-1-azaethylidyne):-anthraquinone[1,4]:(3,7-Dioxo-2,8-diazaoctylidyne):*tert*-Butyl Propionate (10). A mixture of 1,3,5,7-adamantanetetracarboxylic acid[45,47] (**9**; 160 mg, 5.0×10^{-4} mol) and $SOCl_2$ (5 mL) was refluxed for 3 h. The $SOCl_2$ was removed in vacuo, and THF (10 mL) was added to give 1,3,5,7-tetra(chlorocarbonyl)adamantane. A solution of monoamine **1** (1.65 g, 2.2×10^{-3} mol) and Et(i-pr)$_2$N (590 mg, 2.2×10^{-3} mol) in dry THF (10 mL) was subsequently added and then maintained at 45 °C. After the mixture was stirred for 15 min, it was refluxed under nitrogen for 30 min and allowed to stir at 25 °C for an additional hour. The solvent was evaporated in vacuo to give a residue, which was dissolved in CH_2Cl_2 (20 mL). The organic solution was sequentially washed with aqueous $NaHCO_3$ (10%, 20 mL), deionized water (2 × 20 mL), and saturated brine (20 mL). After concentration in vacuo, the residue was chromatographed on a short SiO_2 column eluting with EtOAc/CH_2Cl_2 to afford (62%) the dodecaester **10**: 990 mg; mp 110−112 °C. ^{1}H NMR: δ 1.0−3.0 (m, CH$_2$, CH$_3$, 192H), 5.99 (s, $^{4°}$CNH, 4H), 7.26−9.20 (m, H_{ar}, 24H), 12.56, 13.10 (NH_{ar}, 8H). ^{13}C NMR: δ 21.64 (CH$_2$CH_2CH$_2$), 28.24 (CH_3), 30.02, 30.18 (CH_2CH_2CO$_2$), 36.5, 37.9 (COCH$_2$-CH$_2$CH_2CO), 39.95 ($^{4°}C_{ada}$), 44.96 ($^{4°}$CC$H_2^{4°}$C), 57.64 ($^{4°}$CNH), 80.81 (C(CH$_3$)$_3$), 117.0, 117.4, 127.7, 127.8, 129.3, 129.5, 133.2, 133.4, 134.5, 134.7, 138.7, 138.8 (C_{ar}), 171.7, 172.5, 173.0, 175.4 (CO's), 187.1, 187.2 ($CO's_{quin}$). IR: 3348 (NH), 1715 (ester C=O), 1642 (amide C=O), 1290, 1120 (ester C−O) cm^{-1}. UV: λ_{max} 484 ($\epsilon = 8.13 \times 10^7$), 255 ($4.33 \times 10^8$) nm. MALDI-TOF-MS: m/z 3242. Calcd mass 3240 amu. Anal. Calcd for $C_{178}H_{228}N_{12}O_{44}$: C, 65.99; H, 7.09; N, 5.19. Found: C, 65.90; H, 7.15; N, 5.24.

3-Cascade:1-Aminoanthraquinone[1,5]:(3,7-Dioxo-2,8-diazaoctylidyne):*tert*-Butyl Propionate (11) was prepared (35%) as a bright red solid, from glutaroyl chloride (1.63 g, 9.64 mmol), Behera's amine (**3**; 4.0 g, 9.64 mmol), Et(i-pr)$_2$N (3.4 mL, 19 mmol), and 1,5-diaminoanthraquinone (5-DAAQ; 5.74 g, 24 mmol) by procedure A: 2.53 g (3.37 mmol); mp 78−79 °C. ^{1}H NMR: δ 1.36−1.44 (m, CH_3, 27H), 1.92−1.98, 2.16−2.25 (m, CH_2CH_2CO$_2$, 12H), 2.47−2.53 (m, CH_2CH_2CH_2, 6H), 6.61−8.87 (m, ArH, CNH, NH_2, 10H), 12.23 (s, ArNH, 1H). ^{13}C NMR: δ 21.59 (CH$_2$CH_2CH$_2$), 28.15 (CMe$_3$), 29.95, 30.12 (CH_2CH$_2$CO$_2$), 36.41, 37.75 (CH$_2$CH$_2$CH_2), 57.57 ($^{4°}$CNH), 80.68 (CMe$_3$), 112.55, 117.30, 117.45, 121.82, 123.33, 124.61, 134.63, 134.68, 135.29, 135.33, 141.52, 151.18 (ArC's), 171.83, 172.28 (COCH$_2$CH$_2$CH$_2$CO), 172.91 (CO$_2$), 183.90, 187.28 (quinCO's). IR: 3430, 3381 (NH$_2$), 1719 (ester C=O), 1660 (amide C=O), 1251, 1159 (ester C−O) cm^{-1}. UV: λ_{max} 478 (ϵ = 6564), 265 (2.63×10^6), 230 (5.63×10^6) nm. MALDI-TOF-MS: m/z 750. Calcd mass 749.9 amu. Anal. Calcd for $C_{41}H_{55}N_3O_{10}$: C, 65.70; H, 7.40; N, 5.60. Found: C, 65.55; H, 7.19; N, 5.44.

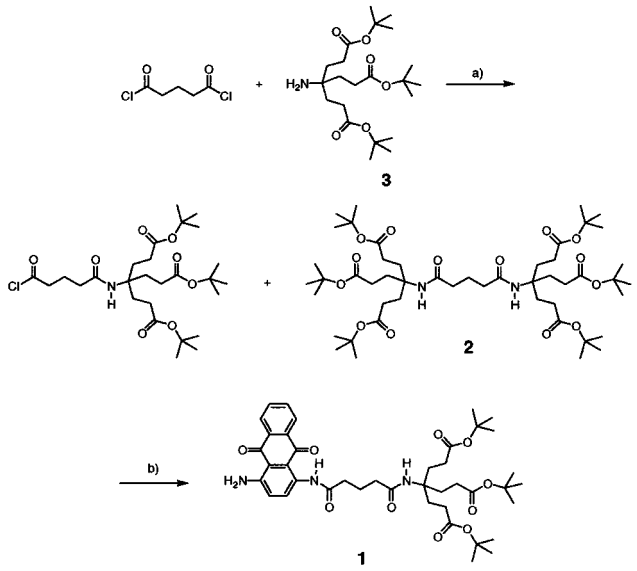
12-Cascade:Methane[4]:(2-Oxo-5-oxa-1-azahexylidyne):Anthraquinone[1,5]:-(3,7-dioxo-2,8-diazaoctylidyne):*tert*-Butyl Propionate (12) was prepared (55%), as a greenish yellow solid, from 6,6-bis(chlorocarbonyl-2-oxabutyl)-4,8-dioxaundecane-1,11-dicarboxyl chloride (140 mg, 281 μmol), monoamine **11** (927 mg, 1.23 mmol), and Et(i-pr)$_2$N (159 mg, 1.23 mmol) by procedure B: 518 mg (155 μmol); mp 133−135 °C. ^{1}H NMR: δ 1.40 (br, s, CH_3, 108H), 1.95, 2.30 (CH_2CH_2-CO$_2$), 48H, 2.45−2.83 (CH_2CH_2CH_2, 24H), 2.60 (CH_2CONH, 8H), 3.45−3.75 (CH_2OCH_2, 16H), 6.15 ($^{4°}$CNH, 4H), 7.40−7.93 (m), 8.85 (m, CH_{Ar}, 24H), 12.05 (N$H_{Ar,}$ 8H) ppm. ^{13}C NMR: δ 21.38 (CH$_2$CH_2CH$_2$), 28.08 (CH_3), 29.83, 29.85 (CH_2CH_2CO$_2$), 36.23, 37.71 (CH_2CH$_2$CH_2), 39.39 (OCH$_2$CH_2), 46.5 (C_{Core}), 57.46 ($^{4°}$CNH), 67.13, 69.87 (CH$_2$OCH$_2$), 80.56 (CMe$_3$), 116.43, 122.23, 125.86, 134.03, 135.85, 141.58 (C_{Ar}), 171.0, 171.77, 172.35 (CONH), 172.83 (CO$_2$), 185.88 (CO_{quin}) ppm. IR: 3357 (NH), 1726 (ester C=O), 1642 (NH), 1258, 1090 (ester C−O) cm^{-1}. UV: λ_{max} 436 (ϵ = 50 251), 265 (1.31×10^5), 230 (1.84×10^5) nm. MALDI-TOF-MS: m/z 3376 (M + Na). Calcd mass 3352 amu. Anal. Calcd for $C_{181}H_{240}N_{12}O_{48}$: C, 64.86; H, 7.22; N, 5.01. Found: C, 64.65; H, 7.19; N, 5.04.

12-Cascade:Methane[4]:(2-Oxo-5-oxa-1-azahexylidyne):Anthraquinone[1,5]:-(3,7-dioxo-2,8-diazaoctylidyne):Propanoic Acid (13) was prepared (80%), as a bright orange solid, from dodecaester (**12**; 500 mg, 149 μmol) by procedure C: 320 mg (119 μmol), mp 146−148 °C. ^{1}H NMR (DMSO-d_6): δ 2.30, 2.55 (CH_2CH_2CO$_2$, 48H), 2.7−3.0 (m, CH_2CH_2CH_2, OCH$_2$CH_2, 32H), 3.6−4.2 (CH_2OCH_2, CONH, 20H), 7.7, 8.1−8.35, 9.1 (CH_{Ar}, 24H), 12.0 (CO$_2H$, 12H), 12.3 (NH_{Ar}, 8H). ^{13}C NMR (DMSO-d_6): δ 21.2 (CH$_2$CH_2CH$_2$), 29.2, 30.7 (CH_2CH$_2$-CO$_2$), 35.1, 37.2 (CH_2CH$_2$CH_2), 45.5 (C_{core}), 56.4 ($^{4°}$CNH), 68.0, 69.9 (CH_2OCH_2), 116.0, 127.7, 132.1, 134.5, 137.1, 137.3 (C_{Ar}), 170.3, 171.5, 171.7 (CONH), 174.7 (CO$_2$H), 185.5 (CO_{quin}). IR: 3675−3010 (acid OH), 1701 (acid C=O), 1639 (amide C=O), 1254 (C−N) cm^{-1}. MALDI-TOF-MS: m/z 2677 (M$^+$ − H). Calcd. mass 2678 amu.

36-Cascade:Methane[4]:(2-Oxo-5-oxa-1-aza-hexylidyne):Anthraquinone[1,5]:-(3,7-dioxo-2,8-diazaoctylidyne):(3-Oxo-2-azapentylidyne):*tert*-Butyl Propionate (14) was prepared (50%) from dodecaacid **13** (270 mg, 100 μmol), DCC (350 mg, 1.69 mmol), 1-HBT (230 mg, 1.69 mmol), and a slight excess of Behera's amine by procedure D: 360 mg (48 μmol), mp 92−94 °C. ^{1}H NMR: δ 1.43 (br s, CH_3, 324H), 1.95−2.25 (CH_2CH_2CO$_2$, 144H), 2.15 (CH$_2$CH_2CH$_2$, 8H), 2.60 (CH_2CONH, 72H), 3.60 (CH_2OCH_2, 16H), 6.1 (CNH, 16H), 7.7 (m), 8.1 (m), 8.85 (s, CH_{Ar}, 24H), 12.3 (NH_{Ar}, 8H). ^{13}C NMR: δ 21.4 (CH$_2$CH_2CH$_2$), 28.0 (CH_3), 29.8, 29.9, 31.76, 33.52 (CH_2CH_2-CO$_2$), 36.3, 37.7 (CH_2CH$_2$CH_2), 39.5 (OCH$_2$CH_2), 46.0 (C_{Core}), 57.4, 57.7 (CNH), 67.2, 69.9 (CH$_2$OCH$_2$), 80.6 (CMe$_3$), 116.3, 126.9, 128.8, 132.8, 134.4, 138.1 (C_{Ar}), 170.9, 171.6, 172.2, 172.4 (CONH), 172.8 (CO$_2$), 186.3, 186.4 (CO_{quin}). IR: 3315 (NH), 1733 (ester C=O), 1635 (amide C=O), 1153 (ester C−O) cm^{-1}. UV 436 (ϵ = 83 800), 265 (2.05×10^5), 230 (2.79×10^5) nm. MALDI-TOF-MS: m/z 7444. Calcd mass 7449 amu. Anal. Calcd for $C_{397}H_{612}N_{24}O_{108}$: C, 63.99; H, 8.28; N, 4.52. Found: C, 63.79; H, 8.19; N, 4.44.

3-Cascade:2-Aminoanthraquinone[1,6]:(3,7-Dioxo-2,8-diazaoctylidyne):*tert*-Butyl Propionate (15) was prepared (10%) as a bright yellow solid, from glutaroyl chloride (1.63 g, 9.64 mmol), Behera's amine (**3**; 4.0 g, 9.64 mmol), Et(i-pr)$_2$N (3.4 mL, 19 mmol), and 2,6-diaminoanthraquinone (2,6-DAAQ; 11.48 g, 48 mmol) by procedure A: 723 mg (964 μmol), mp 178.6−180.0 °C. ^{1}H NMR: δ 1.45 (s, CH_3, 27H), 2.00 [br, d, (CH_2CH$_2$CO$_2$), 6H], 2.15 (m, CH$_2$CH_2CH$_2$, 2H), 2.3 (br, d, CH$_2$CH_2CO$_2$, 6H), 2.5 (t, CH_2CH$_2$CH_2, 4H), 6.05 (s, $^{4°}$CNH, 1H),

Scheme 1. Schematic Synthesis of the Extended Building Block 1[a]



(a) THF, Et(*i*-pr)$_2$N, 0−25 °C, 4 h; then (b) 1,4-DAAQ, THF, Et(*i*-pr)$_2$N, 12 h. Structures of side-product **2** and monomer **3**.

7.05, 7.70, 8.25, 8.90 (Ar*H*, 6H), 7.20 (br, s, NH_2, 2H), 12.35 (s, CON*H*-$C_{14}H_6O_2$−NH_2, 1H). ^{13}C NMR: δ 21.55 (CH_2CH_2-CH_2), 28.34 (CH_3), 29.7, 29.9 ($CH_2CH_2CO_2$), 35.66, 35.78 (CH_2-CH_2CH_2), 57.54 (NH$C^{4°}$), 80.54 (CMe$_3$), 116.65, 124.21, 127.04, 128.63, 128.85, 133.56, 133.62, 133.69, 134.0, 134.48, 144.38 (C_{Ar}), 171.99, 172.13, 172.36 (CONH), 181.96, 182.78 (CO_{quin}). IR: 3434, 3385 (NH_2), 1719 (ester C═O), 1663 (amide C═O), 1257, 1160 (ester C−O) cm^{-1}. UV: λ_{max} 294 (ϵ = 375), 330 (13 500) nm. MALDI-TOF-MS: *m*/*z* 749 (M^+ − H). Calcd mass 750 amu. Anal. Calcd for $C_{41}H_{55}N_3O_{10}$: C, 65.70; H, 7.40; N, 5.60. Found: C, 65.58; H, 7.29; N, 5.24.

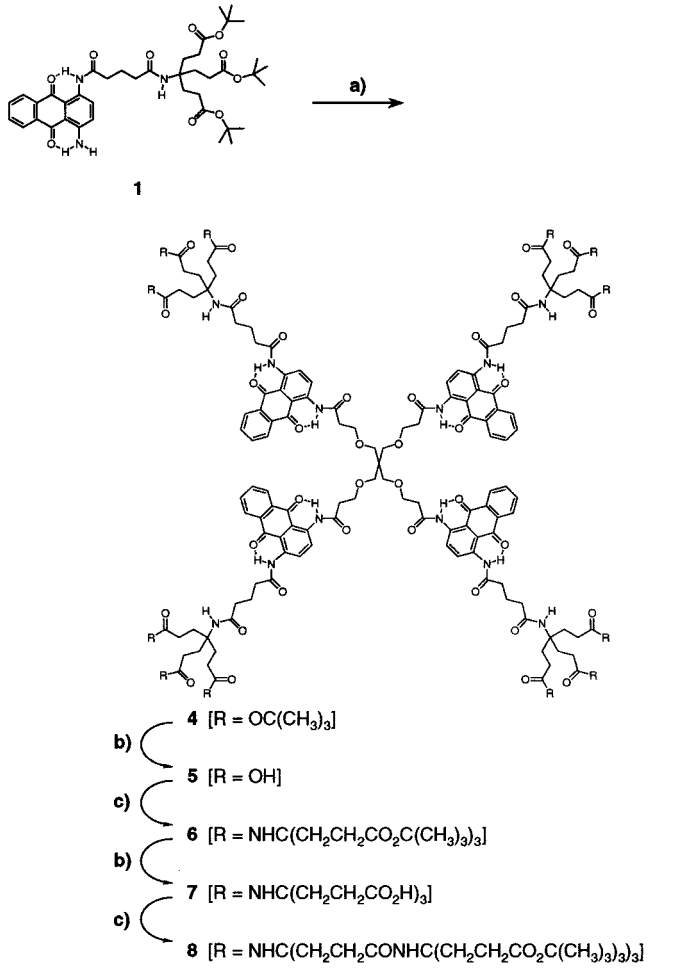
6-Cascade:Anthraquinone[2,6]:(3,7-Dioxo-2,8-diazaoctylidyne):*tert*-Butyl Propionate (**16**) was also obtained as a side product (30%): 1.82 g (1.45 mmol), mp 212−213 °C. ^{1}H NMR: δ 2.80−3.80 (m, CH_2, CH_3, NH$C^{4°}$, 92H), 6.07 (s, N*H*, 2H), 7.20 (s, H_{Ar}, 6H), 8.12 (s, NH_{Ar}, 2H) ppm. ^{13}C NMR: δ 21.68 ($CH_2CH_2CH_2$), 28.22 (CH_3), 30.19, 30.20 ($CH_2CH_2CO_2$), 35.84, 36.26 ($CH_2CH_2CH_2$), 57.97 ($^{4°}$CNH), 81.16 (CMe$_3$), 118.0, 124.0, 128.9, 135.0, 144.3 (C_{Ar}), 172.1, 172.5 (NHCO), 173.3 (COO), 183.0 (CO_{Quin}) ppm. IR: 3346 (amide NH), 1729 (ester C═O), 1639 (amide C═O), 1254, 1151 (ester C−O) cm^{-1}. UV: λ_{max} 294 (ϵ = 5000), 322 (18 770) nm. Anal. Calcd for $C_{68}H_{90}N_4O_{18}$: C, 65.26; H, 7.25; N, 4.48. Found: C, 65.47; H, 7.14; N, 4.42.

Discussion

1. 1,4-Diaminoanthraquinone-Based Dendrimers. A high dilution technique,[48] using a simple three-component system,[49] was used to synthesize the desired extended monomer **1** (Scheme 1). Thus, 1 equiv of di-*tert*-butyl 4-amino-4-[2-(*tert*-butoxycarbonyl)ethyl]-1,7-heptanedioate[43] (**3**) was treated with glutaroyl dichloride, followed by the monoacylation of 1,4-DAAQ, to afford a facile route to the "extended" monomer **1** that could subsequently be used to integrate anthraquinone functionality within the cascade framework.

This two-step, general reaction sequence afforded (35−40%) **1**, which was supported (^{13}C NMR) by absorptions at 36.3, 21.6, 37.7 ($CH_2CH_2CH_2$), 57.4 ($^{4°}$CNH), 27.9 (CH_3), and 80.5 CMe$_3$ ppm. The aromatic region (^{13}C NMR) displayed 12 distinct signals specifically corresponding to the unsymmetrically substituted anthraquinone as well as five different carbonyl absorptions, in contrast to the parent 1,4-DAAQ, which

Scheme 2. Structures of Dendrimers 4−8[a]



[a] (a) $C(CH_2OCH_2CH_2COCl)_4$, Et(*i*-pr)$_2$N, THF, 50 °C, 4 h; (b) HCO_2H, 25 °C, 12 h; (c) **3**, DCC, 1-HBT, DMF, 25 °C, 48 h.

displayed the expected six signals for the 12 aromatic carbons and one signal for both quinone carbonyl carbon atoms based on symmetry. The two quinone carbonyl carbon signals for **1** are well separated (Δ = 2.7 ppm), indicative of the amine/amide substitution pattern. Monomer **1** has a deep red color (λ_{max} 524 nm), which is in stark contrast to the intense purple coloration (λ_{max} 544 nm) exhibited by the parent 1,4-DAAQ. Further, its MALDI-TOF MS showed a sharp peak at *m*/*z* = 749 (calcd mass 749.9 amu) providing evidence for the proposed structure.

A side product obtained in ca. 15% yield was the hexaester **2**, which could be used as a two-directional core for the generation of simple bolaamphiphiles,[29−31] structurally similar to the previously reported arborols.[50,51] Treatment of the four-directional tetrakis(acyl halide) core[44] with the extended monomer **1** in the presence of anhydrous Et(*i*-pr)$_2$N using a minimum volume of dry THF afforded the corresponding four-directional, first-tier dendrimer **4**. The desired complete transformation at each of the four sites is directly related to (a) the purity of the starting materials, (b) moisture content of solvent used (THF), and (c) a stoichiometric excess, generally 20%, of monomer **1**. Formation of **4** can be easily monitored visually by the dramatic color change observed during the course of the amidation (Scheme 2). The intense red color for monomer **1** changed to a bright orange (λ_{max} 484 nm), indicative of 1,4-DAAQ diacylation. Evidence for the

formation of the tetrakisquinonoid dendrimer **4** includes the previously described building block alkyl resonances (^{13}C NMR) and a visually (six absorptions) simplified set of aromatic absorptions indicating the amidation. However, closer examination of the aromatic region revealed a second set of six peaks possessing very slight differences in the chemical shifts for the juxtaposed and similar, but yet dissymmetric, aryl carbons. The ^{13}C NMR spectrum ($CDCl_3$) further displayed the expected four C═O signals at 172.8, 172.1, 171.6, and 170.9 ppm as well as the two distinct peaks at 186.4 and 186.3 ppm for the similar but again slightly different (inward vs outward) quinonoid carbonyl groups, thus supporting the structure of the desired assembly. The ^{1}H NMR spectra of both **1** and **4** displayed the expected first-order analyses; as well, far downfield absorptions (12.1 and 12.2 ppm) attributed to the amide N*H* moieties adjacent to the quinones suggested *H*-bonded, cyclic conformations. The first-tier dodecaester **4** has exceptional solubility in CH_2Cl_2, $CHCl_3$, and solvents of higher polarity. Elemental analysis and MALDI-TOF mass spectra (*m*/*z* 3349, calcd 3350 amu) of **4** further support the assigned structure and molecular weight.

Deprotection of the 12 peripheral *tert*-butyl ester groups of **4** was smoothly achieved (80%) by the treatment with formic acid at 25 °C for 12 h. Formation of the dodecacarboxylic acid dendrimer **5** was established by the absence of the typical ester signals. The MALDI-TOF mass spectrum of **5** showed a single (M^+ + Na) peak at 2704 (calcd mass 2679 amu), while the IR spectrum revealed the expected broad stretch for O−H stretching (3677−3000 cm^{-1}) and C═O absorption (1701 cm^{-1} for carboxylic acid vs 1726 cm^{-1} for the ester peak of **4**). Confirmation of structure was also provided (^{13}C NMR) by the retention of the signals for the intact amide carbonyl groups; cleavage of the amide bonds on related dendrimers has not been observed[49] under these mild conditions.

Dodecaacid **5** was further treated with excess Behera's amine (**3**) in the presence of DCC and 1-HBT[52] to yield (50%) the second-generation dendrimer **6** (Scheme 2), possessing 36 ester moieties at its periphery and a molecular weight of ca. 7449 amu (MALDI-TOF-MS: *m*/*z* 7449). Evidence for the formation of **6** was further supported by the ^{13}C NMR spectrum, which is similar, for the most part, to that of the first tier dodecaester **4** except for the presence of two new peaks at 57.8 and 171.9 ppm corresponding to $^{4°}$*C*NH and *C*ONH signals from the additional generation. The R_f value (silica TLC plate eluting with 1:1 EtOAc/CH_2Cl_2) for the second-tier macromolecule **6** is greater than the first-tier relative **4**, as expected due to its decreased internal, polar characteristics caused by the increased spherical, alkyl surface.

Hydrolysis of **6** with formic acid generated (78%) polyacid **7** possessing 36 peripheral carboxylic acid groups, which was supported by its MALDI-TOF-MS *m*/*z* = 5418 amu (calcd formula weight: *m*/*z* = 5421 amu). The ^{13}C NMR spectrum of **7** in DMSO-d_6 confirmed the complete removal of the *tert*-butyl moieties and the presence of a new signal at 174.3 ppm supporting the ester (172.6 ppm) to acid conversion. The broad peak in the IR spectrum of **7** for the O−H stretching band (3660−2930 cm^{-1}) and the intense absorption (1700 cm^{-1}) for the C═O absorption further support this conversion.

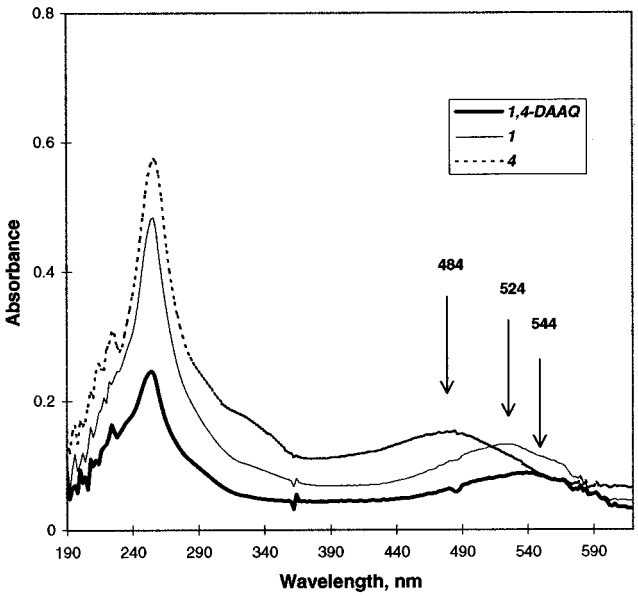


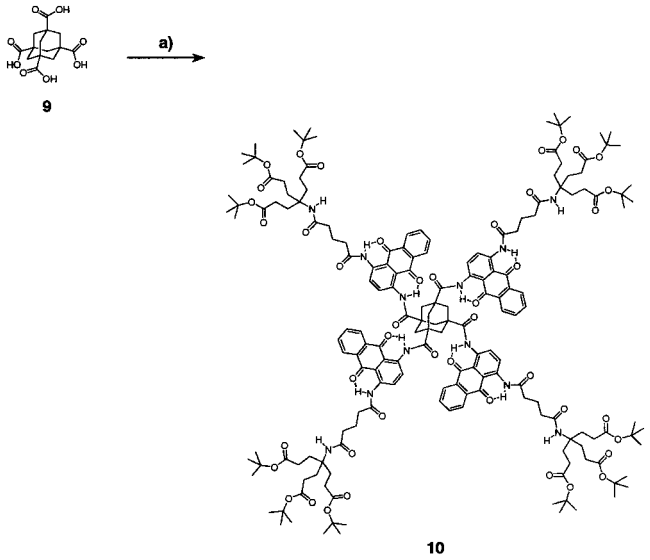
Figure 1. UV−vis spectra of 1,4-DAAQ, **1**, and **4** in CH_2Cl_2.

Polyacid **7** was then treated with excess Behera's amine (**3**) under the above amidation conditions (DCC and 1-HBT in DMF) to afford (50%) **8**, which ideally would have 108 *tert*-butyl ester groups. The carbons from the anthraquinonoid moieties (^{13}C NMR) located deep in the dendritic interior appeared as small signals compared with the intense peaks observed for those of the peripheral *tert*-butyl ester moieties. Three peaks at 58.27, 57.91, and 57.46 ppm corresponding to the three unique set of quaternary carbons ($^{4°}$*C*NH) which are the branching points for each generation provided the key evidence for the formation of **8**. The ^{1}H NMR spectrum was not very helpful due to the imbalanced aliphatic to aromatic proton ratio, thus making assignments by this technique difficult.

This series of cascade molecules going from the first to third generation (**4** → **6** → **8**) afforded interesting physicochemical information. Thin-layer chromatography indicates R_f of 0.24, 0.76, and 0.87, respectively, for the series on a silica gel plate using a C_6H_{12}/EtOAc (1:3) mixture, as the eluent system. This can be attributed to the increasing aliphatic surface character and the decreasing availability of the internal polar functional moieties. A decreasing trend in the melting points was also noted for the ester series (**4**, 96−98 °C; **6**, 92−94 °C; **8**, 65−69 °C) indicative of decreasing polar character. The intense colors of the parent 1,4-DAAQ and its dendritic derivatives prompted an UV correlation. For the UV study, micromolar solutions of the ester-terminated dendrimers were made in CH_2Cl_2, and the results are summarized in Figure 1. The absorption maximum at the longest wavelength shifts (Δ = 20 nm) going from 1,4-DAAQ to monoamide **1** and a further shift (Δ = 40 nm) upon diamidation. There is no observable shift in the absorption maxima for the large generation dendrimers (**6** and **8**), since the growth of these macromolecules does not involve further modification of the chromophore.

2. 1,4-Diaminoanthraquinone-Based Dendrimer with a Rigid Adamantane Core. The effect of changing the core from a flexible, tetradirectional *C*-based core to one possessing a related but more rigid one was investigated to evaluate mobile vs restricted anthraquinone environments. 1,3,5,7-Adamantanetetracarboxylic

Scheme 3. Synthesis of an Electroactive Dodecaester 10 with a Rigid Adamantane-Base Core[a]



[a] (a) $SOCl_2$, THF, 3 h; then $Et(i\text{-}pr)_2N$, **1**, THF, 45 °C.

acid[45,47] was an accessible and previously used central core for dendritic construction and possessed the necessary directivity and rigidity to isolate the quinone units. The reaction of 4 equiv of monomer **1** with 1,3,5,7-tetrakis(chlorocarbonyl)adamantane, prepared from the corresponding tetraacid with $SOCl_2$, was conducted in a matter similar to that previously described for dendrimer **4** (Scheme 3). The MALDI-TOF mass spectrum of **10** showed a single sharp peak at 3242 amu (calcd MW 3240 amu) which supports its composition. The visual decrease in the number of signals (^{13}C NMR) in the aromatic region of the product (**10**) was expected and observed. But as noted above, a simplified set of aromatic absorptions indicated the desired amidation; however, expansion of the aromatic region revealed the second set of slightly different chemical shifts for the similarly juxtaposed but yet dissymmetric carbons. Dendrimer **10** demonstrated similar spectral properties to those of **4**, except that it possessed a higher melting point (10 °C).

The electrochemical response of the 1,4-DAAQ-based dendrimers was studied by cyclic voltammetry experiments in MeCN solutions (Bu_4NPF_6 0.1 M) at 298 K.[15] As can be seen in Figure 3, all the voltammograms are characterized by two quasi-reversible waves that reflect the sequential uptake of one electron by each of the anthraquinone moieties.[34,53,54] For the extended monomer **1**, the two $E_{1/2}$ potential values are shifted to more positive potential values as compared to those of the parent 1,4-DAAQ (Table 1). This effect was expected since monoamidation not only decreases the electron release character of the diamine but also improves its intramolecular H-bonding characteristics with the quinone oxygen, thus making it more prone to reduction.[55−58] Consistent with this trend, CV experiments of the first-tier dendrimer **4** (Figure 2c) reflect a further positive potential shift due to bisamidation of the electroactive anthraquinone moieties. The voltammograms of the two higher generation dendrimers **6** and **8** (Figure 2d for **6** and voltammogram not shown for dendrimer **8**) do not reveal important changes in the half-wave potentials, since no further chemical modification of the amine groups in the chromophoric units is involved in their preparation.

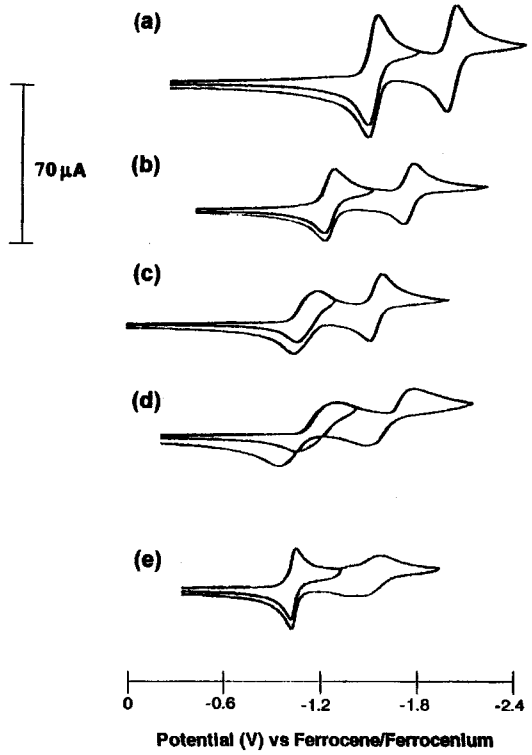


Figure 2. CV response of 1.0 mM solutions of (a) 1,4-DAAQ, (b) **1**, (c) **4**, (d) **6**, and (e) **10** in 0.1 M of Bu_4PF_6 in MeCN at 298 K; scan rate 100 mV s^{-1}.

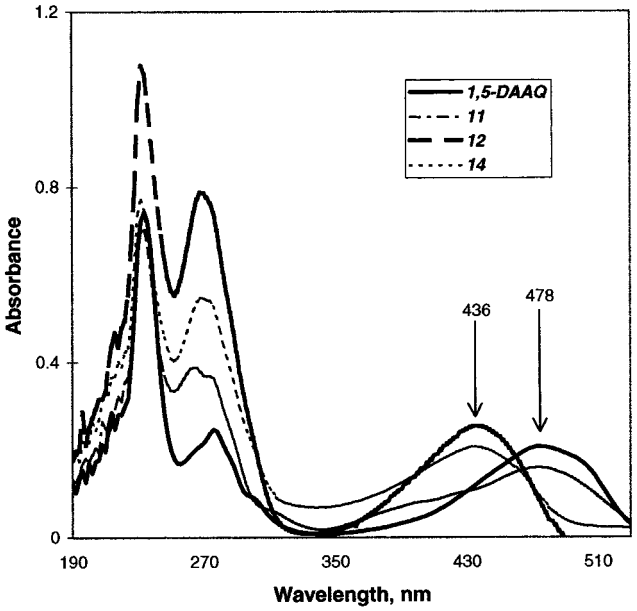


Figure 3. UV−vis spectra of 1,5-DAAQ, **11**, **12**, and **14** in CH_2Cl_2.

An important observation, however, is an increase in the irreversibility of the electrochemical waves as the dendritic structure grows around the electroactive centers, i.e., from **1** → **4** → **6** → **8**. Not surprisingly, this trend has been observed by us[59] and by others[12,21,60,61] and is believed to be a direct consequence of the slow kinetics that characterizes the electron transfer process between an increasingly "buried" electroactive site within a dendritic structure and the electrode surface.

CV experiments of **10** were expected to show the effect that a rigid core would exert on the electrochemical behavior of these dendrimers. Comparison of parts c and

Table 1. Half-Wave Potentials, $E_{1/2}$ [mV], for 1,4-DAAQ, 1,5-DAAQ, and 2,6-DAAQ Based Dendrimers at 298 K[a]

compd	$E_{1/2}$ (1)	ΔE_p (1)	$E_{1/2}$ (2)	ΔE_p (2)
1,4-DAAQ	−1577	74	−2063	74
1	−1293	71	−1785	75
4	−1123	145	−1564	88
6	−1122	157	−1620	272
8				
10	−1037	32		
1,5-DAAQ	−1471	76	−2012	78
11	−1211	78	−1696	78
12				
2,6-DAAQ[b]	−1683	65	−2050	63
15[b]	−1350	70	−1863	67
16[b]	−1378	70	−1845	75

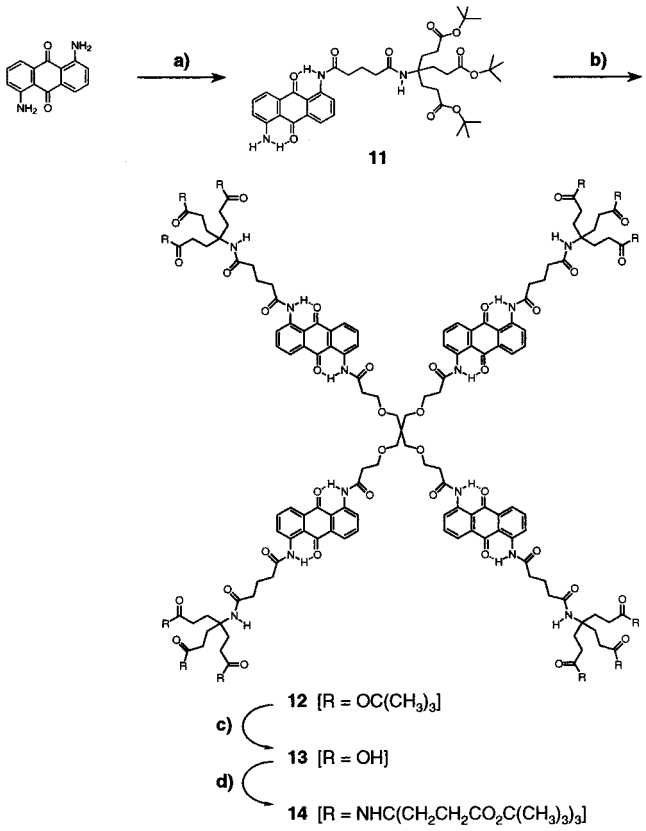
[a] Fc/Fc^+ as internal standard. No values could be reported for $E_{1/2}$ (1) and (2) for dendrimers **8** and **12** and $E_{1/2}$ (2) for **10** since they exhibited irreversible behavior. [b] CV experiments were carried out in DMF solutions using 0.1 M Et_4NTFB as supporting electrolyte.

e of Figure 2, for instance, reveals that the adamantane core in **10** does affect both the half-wave potentials and the shape of the redox waves. As can be seen by inspection of Table 1, the reduction of dendrimer **10** occurs at more positive potentials than that of **4**. This clearly indicates that the degree of packing around the anthraquinone units does result in a different chemical environment that translates into different redox potentials. A more interesting characteristic of the electrochemical response of **10**, however, is that the most negative wave splits into two separate waves. On the basis of previous reports,[62] it is possible to speculate that the splitting observed in Figure 2e is a consequence of intramolecular electronic coupling between the monoreduced anthraquinone sites in the densely packed structure that characterizes dendrimer **10**.

1,5-Diaminoanthraquinone-Based Dendrimers. Switching the position of the amino functionalities on the diaminoanthraquinone structure should also change the properties of these isomeric, extended monomers and dendrimers. Hence, since 1,5-DAAQ is commercially available and is unique in that it can also H-bond with the quinone moieties, monomer **11** was synthesized from 1,5-DAAQ, glutaroyl chloride, and Behera's amine (**3**) under high dilution conditions, as previously described. Key ^{13}C NMR signals at 57.57 ($4°CNH$), 171.83 (*C*ONH), 172.28 (*C*ONH), 172.91 (*C*OO), 183.9, 187.3 (CO_{quin}) ppm provided evidence for the formation of **11**. Additionally, a sharp peak at *m*/*z* 750 (calcd mass 749.9 amu) in the MALDI-TOF MS of **11** added further proof of the structure. The UV spectrum of extended monomer **11** appeared to be almost identical to that of the starting diamine (λ_{max} 474 nm, Figure 3).

This extended building block **11** on treatment with the *C*-based tetraacid chloride core afforded (55%) the first-tier macromolecule **12** (Scheme 4). The ^{13}C NMR spectrum for **12** showed appropriate peaks at 57.46 ($4°CNH$), 67.13, 69.87 (CH_2OCH_2), 80.56 (CMe_3), 171.0, 171.77, 172.35 (*C*ONH), and 172.83 (*C*OO) ppm in support of the assigned structure. In addition, the MALDI-TOF mass spectrum of **12** possessed a (M^+ + Na) peak at *m*/*z* = 3376 (calcd mass 3352 amu) and the hypsochromic shift of 42 nm in the UV spectrum compared to that of monomer **11** (Figure 3) supplied supplementary data supporting its proposed structure. The ^1H and ^{13}C NMR spectra for **11** and **12** demonstrated numerous similarities with spectra with those for the related 1,4-DAAQ counterparts. Dendrimer **12**

Scheme 4. Structures of Monomer 11 and Dendrimers 12−14 Based on 1,5-DAAQ[a]



[a] (a) $CH_2(CH_2COCl)_2$, **3**, Et(*i*-pr)$_2$N, THF, 0−25 °C, 16 h; (b) $C(CH_2OCH_2CH_2COCl)_4$, Et(*i*-pr)$_2$N, THF, 50 °C, 4 h; (c) HCO_2H, 25 °C, 12 h; (d) **3**, DCC, 1-BHT, DMF, 48 h.

on treatment with formic acid (procedure B) afforded the desired dodecaacid **13**, which gave a single (M^+ − H) peak in the mass spectrum at *m*/*z* = 2677 (calcd mass = 2678 amu). The conversion of **12** to **13** was further confirmed from the loss of the intense peak (IR) at 1723 cm^{-1} (ester C═O), the appearance of a broad peak between 3675 and 3010 cm^{-1} (O−H stretch), and an intense acid C═O absorption at 1700 cm^{-1}. DCC coupling reaction (procedure C) of (excess) amine **3** with dodecaacid **13** in DMF as the solvent yielded dendrimer **14**. Key signals in the ^{13}C NMR spectrum at 57.66, 57.80 ($4°CNH$), 170.9, 171.6, 172.75 (*C*ONH), and 172.95 (*C*OO) ppm and in its MALDI-TOF mass spectrum a sharp peak at *m*/*z* = 7444 (calcd mass 7449 amu) supported the assigned structure of **14**.

Cyclic voltammetry experiments conducted on this 1,5-DAAQ series showed, in general terms, similar electrochemical responses to that of the 1,4-quinone series. As can be noted by inspection of Figure 4a,b, monoamidation of 1,5-DAAQ results in a positive shift of the half-wave potentials. The CV response of the first-tier dendrimer **12**, however, seems to be more complicated than that of its analogue **4**. As can be seen in Figure 6c, the electrochemical response of **12** is characterized by a clearly irreversible electron-transfer process. The observed irreversibility is due to the structural position of the amine groups in the anthraquinone moiety; however, the effects of a more hindered electroactive site or to other factors, such as dendritic packing or solvent exposure of the anthraquinone groups, remains to be investigated.

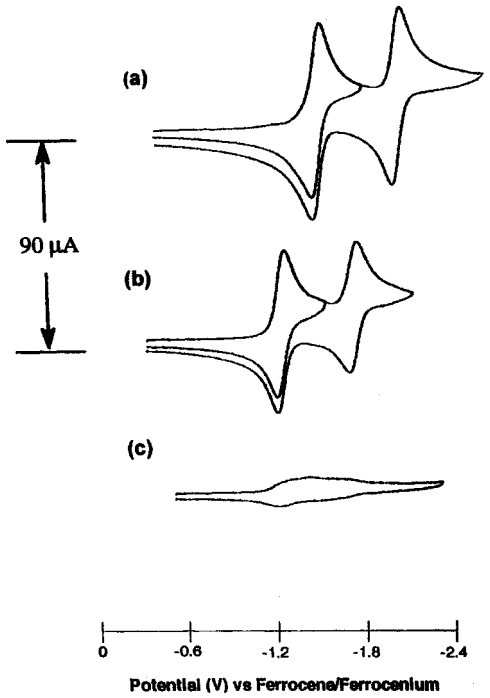


Figure 4. CV response of 1.0 mM solutions of (a) 1,5-DAAQ, (b) **11**, and (c) **12** in 0.1 M of Bu_4PF_6 in MeCN at 298 K; scan rate mV s^{-1}.

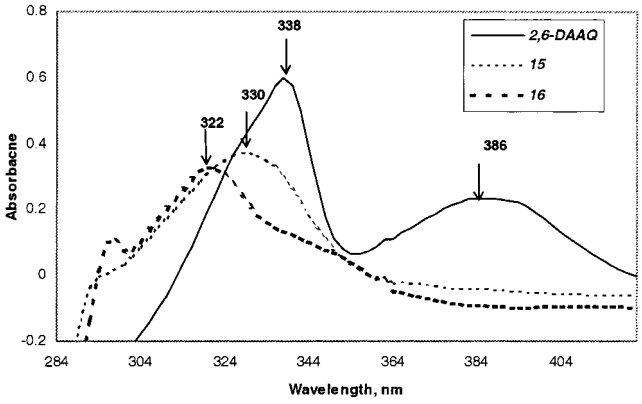


Figure 5. UV−vis spectra of 2,6-DAAQ, **15**, and **16** in CH_2Cl_2.

4. 2,6-Diaminoanthraquinone-Based Dendrimers. Amine groups in the 2 and 6 positions of the 9,10-anthraquinone system constitute a very interesting isomer for dendrimerization since they are removed from the quinone oxygen atoms, and thus intramolecular H-bonding is not possible. Unfortunately, the high dilution reaction conditions used to synthesize the above monomeric building blocks led to a meager 10% of the desired product **15** and about 30% of the hexaester **16** (Scheme 5). Signals at 57.54 ($NHC^{4°}$), 80.54 (CMe_3), 171.99, 172.13, 172.36 (*C*ONH), 181.96, and 182.78 (CO_{quin}) ppm for monomer **15** and a distinct set of 12 peaks in the aromatic region of the ^{13}C NMR spectrum revealed the desired dissymmetry associated with the monoamidation of 2,6-DAAQ.

Evidence for the formation of **15** was obtained from a sharp peak in the mass spectrum (m/z = 750, calcd mass = 749.9 amu), and the ^{13}C NMR spectrum showed a simplified set of six peaks [118.0, 124.0, 128.9, 135.0, 144.3 (C_{Ar}), and 183.0 (CO_{Quin})] for the anthraquinonoid moiety, indicating its symmetric character. It was also noted that the solubility of the 2,6-diamino isomer in THF was very poor, which may explain why the formation of dendrimer **16** is the major product. The low solubility of 2,6-DAAQ in most solvents including THF suggests inter- rather than intramolecularly H-bonded amines inherent with both the 1,4- and 1,5-series. No positive effects were observed in the proportion or amounts of products formed when the reaction was conducted in either DMF or a 1:1 mixture of DMF and THF. The UV−vis spectrum (Figure 5) of the 2,6-series was distinct in comparison with those of 1,4- and 1,5-DAAQs with the longest wavelength of absorption being ca. 350 nm (as compared to 544 nm for 1,4- and 478 nm for 1,5-DAAQ isomers). This could be attributed to the fact that when the amines are situated at any of the 1, 4, 5, or 8 positions of the 9,10-anthraquinone system, the free pair of electrons on nitrogen are available for direct conjugation with the adjacent carbonyl groups unlike the case when situated at the 2, 4, 6, or 7 positions, thus allowing longer wavelength (or low energy) absorption bands possible.

Hexaester **16** could be described as a two-directional dendrimer with 2,6-DAAQ as the core unit. It is,

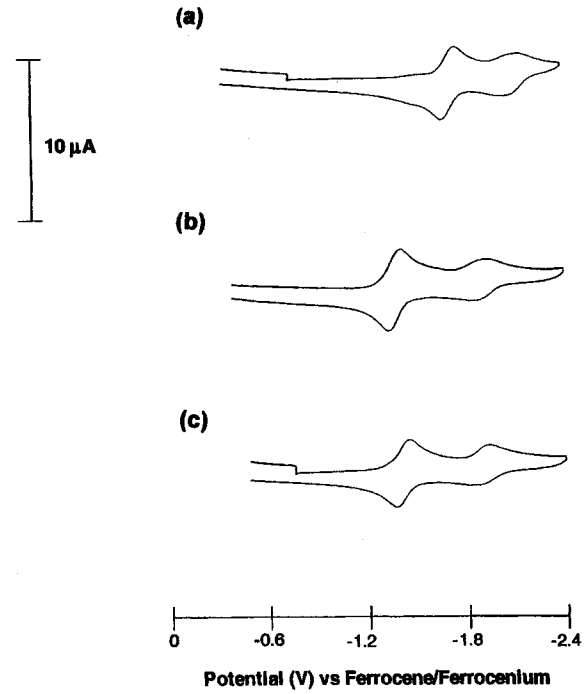
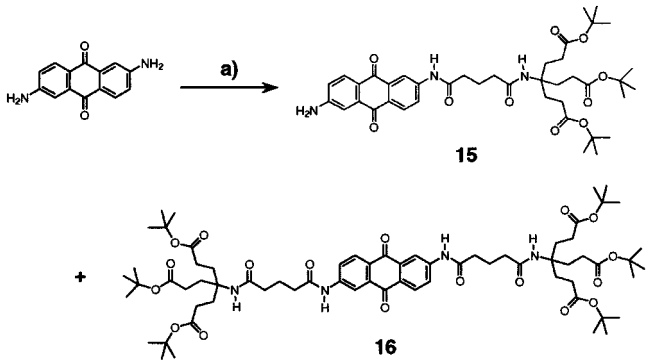


Figure 6. CV response of 1.0 mM solutions of (a) 2,6-DAAQ, (b) **15**, and (c) **16** in 0.1 M of Et_4TFB in DMF at 298 K; scan rate 200 mV s^{-1}.

Scheme 5. Structures of Building Block 15 and Hexaester 16 Based on 2,6-DAAQ[a]



[a] (a) $CH_2(CH_2COCl)_2$, **3**, $Et(i\text{-}pr)_2N$, THF, 0−25 °C, 16 h.

however, interesting to note that formation of isomers of **16** was not noticed in either of the corresponding building block reactions of the related 1,4- (i.e., **1**) and 1,5-counterparts (i.e., **11**).

Due to solubility problems, the electrochemical experiments on the 2,6-DAAQ series were conducted in DMF solutions. As opposed to the previous anthraquinone isomers, 2,6-derivatives do not form intramolecular H-bonds between the amine groups and quinone oxygens; therefore, the effect of amidation should correspond to the decrease in electron release character only. On the basis of previous electrochemical studies on substituted anthraquinones,[55−58] it is possible to suggest that such an effect in the CV response should be relatively small. This seems to be the case when comparing the mono- and bisamidated derivatives (Figure 6) but is difficult to reconcile with the large positive potential shift observed when going from the 2,6-DAAQ to any one of the two-dendrimerized derivatives. The reason for such a large change in the redox potential is not clear at this point and could be due to some interaction between the dendritic arm and the anthraquinone anion species formed upon reduction. In view of these results, further studies on the electrochemical reduction mechanism of these substituted anthraquinones are needed.

Thus, simple variation of the different units that constitute the extended monomeric building blocks and dendrimers has afforded a variety of chromophoric dendrimers based on covalently linked electroactive anthraquinonoid moieties at specific loci within the superstructure. All new building blocks and dendrimers were characterized by UV−vis, ^{1}H and ^{13}C NMR, MALDI-TOF MS, IR, and cyclic voltammetry. These chromophoric cascade molecules also underwent reversible chemical reduction with $NaBH_4$, as the reducing agent, which was monitored by UV−vis spectroscopy.

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

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