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Dendrimers Based on Thermally Reversible Furan−Maleimide Diels−Alder Adducts

Michael L. Szalai,[†] Dominic V. McGrath,*,[†] David R. Wheeler,[§] Thomas Zifer,[‡] and James R. McElhanon*,[‡]

Department of Chemistry, University of Arizona, Tucson, Arizona 85721; Materials Chemistry Department, Sandia National Laboratories, Livermore, California 94551; and the Micro-Total-Analytical Systems Department, Sandia National Laboratories, Albuquerque, New Mexico 87185

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ABSTRACT: Thermally labile dendrimers based on the reversible furan−maleimide Diels−Alder reaction are described. First through fourth generation benzyl aryl ether based dendrons **3a**−**d** that contained furan moieties at their focal point were allowed to react with bismaleimide central linker **4** to provide the corresponding dendrimers **5**−**8**. Thermal degradation and reassembly of these dendrimers were studied under a variety of conditions and monitored by GPC and NMR.

Introduction

Dendrimers[1] are established components of the nanoscopic toolbox,[2] and their utility is tempered by our ability to alter their structure in a precise fashion.[3] Responsive dendrimers allow the tailoring of dendrimer properties through covalent,[4,5] ligational,[6] configurational,[7,8] and conformational[9] structural changes mediated by physical and chemical stimuli. The Diels−Alder reaction has been used in dendrimer chemistry for assembly[10] or periphery modification[11] and represents a facile example of covalent structural modification. Its reliability, particularly of certain variants such as the furan−maleimide DA reaction, has included it in the pantheon of "click chemistry" reactions.[12] The reversibility of the furan−maleimide DA reaction[13] is responsible for its extensive use in thermally responsive systems.[14] In addition to being used for cross-linking linear polymers[15−17] and in the synthesis of alternating,[18] block,[19] and graft[20] copolymers, it has been utilized for making thermally responsive self-healing,[21] nonlinear optical,[22] hydrogel,[23] and interpenetrating network (IPN)[24] materials as well as for nanoscale lithography.[25] We have previously reported the integration of furan−maleimide DA adducts into thermally cleavable encapsulants, foams, and surfactants.[26,27] Herein we report the synthesis of dendrimers up to the fourth generation based on furan−maleimide DA adducts.[28] These materials represent a covalent macromolecular (self)assembly system with thermal reponsiveness.

Results and Discussion

Synthesis of Dendrons and Dendrimers. Our convergent approach toward developing covalently reassembling DA dendrimers was based on reacting appropriately functionalized furan dendrons with a multifunctional maleimide. First through third generation furan dendrons **3a**−**3c** were prepared as described previously by alkylation of diol **2** with 2 equiv of the appropriate benzyl bromide in anhydrous DMF/NaH (Scheme 1).[28] Fourth generation substituted furan dendron **3d** was prepared in a similar fashion.

Commercially available 1,1′-(methylenedi-4,1-phenylene)-bismaleimide (**4**) served as both a reactive dienophile and a bisfunctional central linker in this DA directed dendrimer assembly. DA reaction of furan dendrons **3a**−**d** with **4** in EtOAc solution between 50 and 60 °C yielded first through fourth generation dendrimers **5**−**8** (Scheme 2). We noted that the rates of reaction and predominate conversion to the thermodynamically stable exo−exo isomer[29] for **5**−**8** could be significantly accelerated through a series of solvent evaporation steps at elevated temperature. Dendrimers **5**−**8** were isolated as pure exo−exo isomers through precipitation, column chromatography, and preparative GPC techniques. The ^{1}H NMR spectra of dendrimers **5**−**8** contain diagnostic peaks that provide conclusive evidence of the endo/exo ratio for the two DA adducts in the macromolecules. All dendrimers were characterized as pure exo−exo isomers as evidenced by a singlet appearing ca. 5.35 ppm. The singlet arises from the bridgehead protons of the conformationally rigid 7-oxabicyclo[2.2.1]heptene DA adduct. A large dihedral angle between the bridgehead protons on C-1/C-4 and exo protons on C-5/C-6 of the bicyclic ring system results in a negligible coupling constant between the two sets of protons. Absence of a multiplet at ca. 5.1 ppm confirms that endo DA adducts are not present in prepared samples of dendrimers **5**−**8**.[29] All new compounds were fully characterized by ^{1}H and ^{13}C NMR and combustion analysis. Dendrimers **6**−**8** were also characterized by MALDI MS.

GPC Analysis of Dendrimer Degradation and Assembly. GPC proved to be an excellent method to qualitatively evaluate the extent of dendrimer degradation and reassembly for first through fourth generation dendrimers **5**−**8**. Initially, elution volumes of pure samples of furan dendrons **3a**−**d** and dendrimers **5**−**8** were determined (Figure 1). For dendrimers **5**−**8** and dendrons **3a**−**d**, higher generation compounds eluted at lower elution volumes in generational order as expected.

The retro-DA reaction of furan−maleimide adducts is known to occur in solution at temperatures >60 °C.[13] Accordingly, dendrimer solutions (1 mM) in toluene were heated to 95 °C, and aliquots were taken out at various times and analyzed by

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* Corresponding authors. E-mail: jrmcelh@sandia.gov, phone 925-294-2514, fax 925-294-3410. E-mail: mcgrath@u.arizona.edu, phone 520-626-4690, fax 520-621-8407.

[†] University of Arizona.

[‡] Materials Chemistry Department, Sandia National Laboratories.

[§] Micro-Total-Analytical Systems Department, Sandia National Laboratories.

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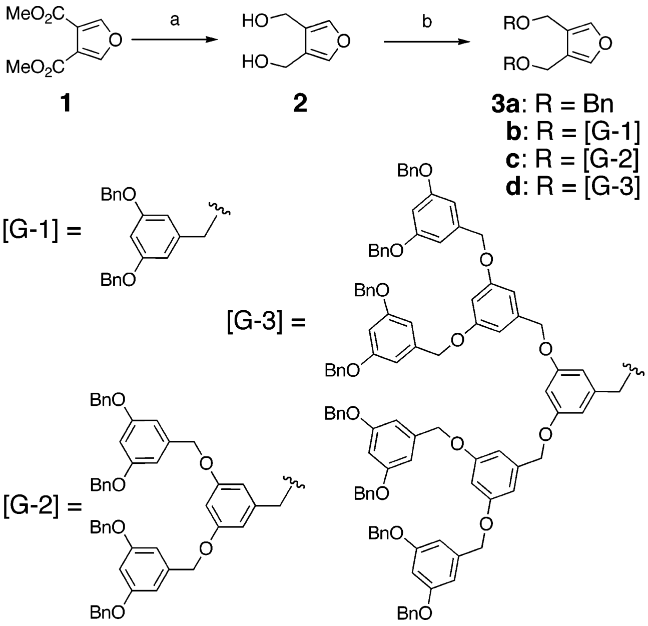
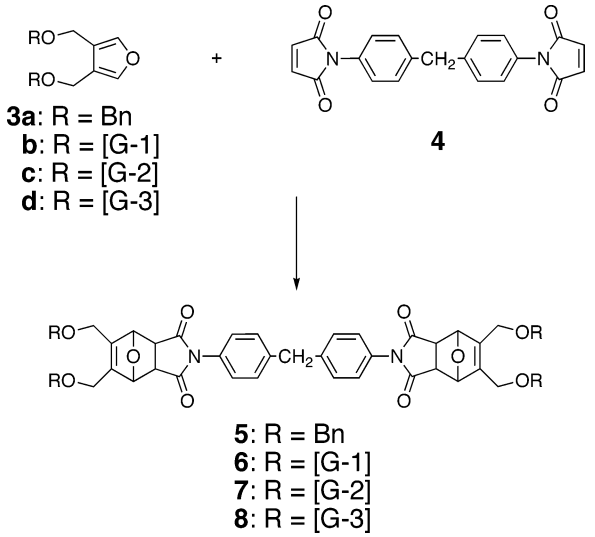
Scheme 1[a]



[a] a = $LiAlH_4/Et_2O$; b = RBr/NaH or KH/DMF.

Scheme 2



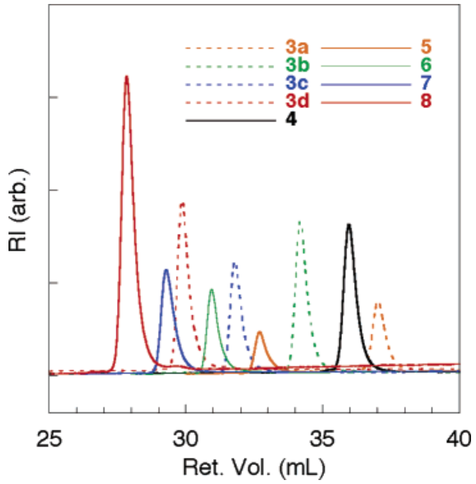


Figure 1. GPC chromatograms of dendrons **3a**−**d** (dotted), dendrimers **5**−**8** (solid), and core **4** (black).

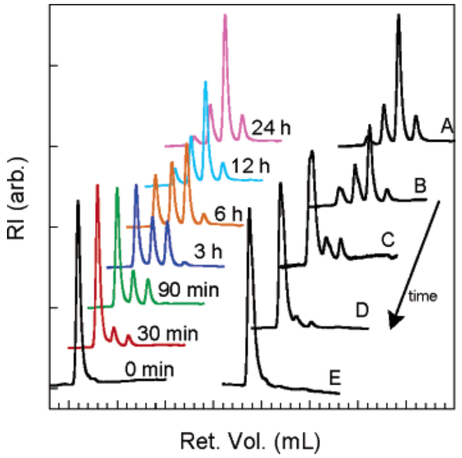


Figure 2. GPC degradation and reassembly of second generation dendrimer **6**. (left) Heated to 95 °C in toluene (1 mM) for indicated time. (right) Conditions: (A) 95 °C for 24 h; (B) solvent removed in vacuo at RT and immediately redissolved; (C) 60 °C for 5 h (neat); (D) 60 °C for 24 h (neat); (E) 45 °C for 72 h (neat). For data on dendrimers **5**, **7**, and **8**, see the Supporting Information.

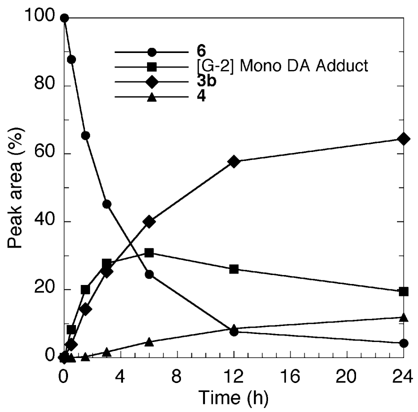


Figure 3. Degradation of second generation dendrimer **6** heated to 95 °C in toluene (1 mM) for indicated time as monitored by GPC. Differential refractive indices were not determined. For data on dendrimers **5**, **7**, and **8**, see the Supporting Information.

GPC. As each parent dendrimer cleaved during the retro-DA reaction, three new species were observed by GPC during thermal treatment for first through third generation dendrimers **5**−**7** (Figure 2). Comparison with GPC elution volumes of authentic samples of dendrons **3a**−**d** and bismaleimide **4** identified two of the three species generated during degradation of **5**−**7** as the corresponding [G-*n*] furan dendrons **3a**−**c** and bismaleimide **4**. While not definitive, the third species that appeared during degradation of **5**−**7** was identified as the [G-*n*] mono-DA adduct. Not surprisingly, the peak assigned to this adduct initially increased in relative area, reached a maximum, and then slowly decreased as it further disassembled into furan dendron **3a**, **b**, or **c** and bismaleimide **4**, concomitant with an increase in the peak areas assigned to those species (Figure 3). The mono-DA adduct was an expected transient species as the parent dendrimer cleaved, and its presence indicated that the retro-DA reaction was sufficiently slow to easily monitor. Indeed, the half-life for disappearance of **5**−**7** was between 1.5 and 3 h under these conditions. Degradation of fourth generation dendrimer **8** proceeded in a similar fashion to **5**−**7**. However, only two smaller fragments were observed by GPC; furan

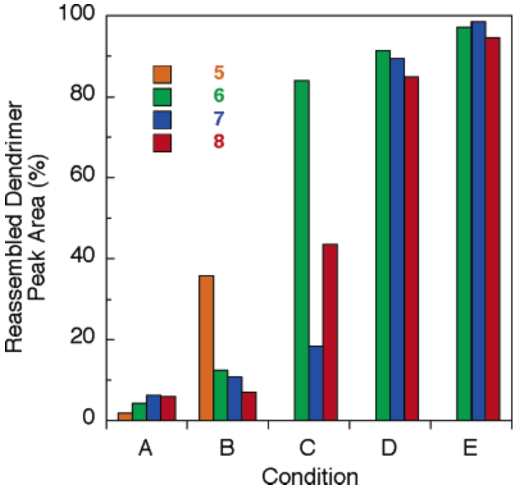


Figure 4. GPC reassembly of **5**−**8**. Conditions: (A) 95 °C for 24 h; (B) solvent removed in vacuo at RT and immediately redissolved; (C) 60 °C for 5 h (conc.); (D) 60 °C for 24 h (conc.); (E) 45 °C for 72 h (conc.).

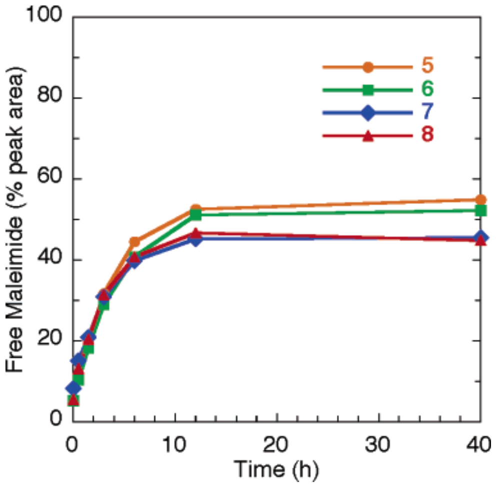


Figure 5. Degradation of **5**−**8** followed by the appearance of free maleimide protons in the ^{1}H NMR (toluene-d_7) at 95 °C.

dendron **3d** and the mono DA adduct likely eluted with identical retention times, and this was followed by elution of bismaleimide **4**. In all cases, heating dendrimer solutions to 95 °C for 24 h resulted in <5% parent dendrimer remaining as determined by total peak area ratios (Figure 3). No decomposition products were observed under these conditions.

Reassembly of dendrimers **5**−**8** was investigated using the samples heated for 24 h from the degradation experiments discussed above. The rate of reassembly of dendrimers **5**−**8** was expected to be concentration dependent as evidenced by our initial preparation. Consequently, we focused on the reassembly of **5**−**8** in minimal solvent. Each sample was first concentrated in vacuo and allowed to reassemble at mild temperatures. Aliquots were diluted in toluene, and GPC analysis was performed at various time intervals to obtain the normalized percent dendrimer reassembly of the samples of degraded **5**−**8** (Figure 4). After heating at 60 °C for 24 h, greater than 84% complete reassembly occurred for second through fourth generation dendrimers **6**−**8**. Further treatment of the concentrated samples at 45 °C for 72 h resulted in 97, 98, and 94% complete reassembly back to **6**−**8**, respectively. First generation **5** also underwent reassembly. However, parent dendrimer peak comparison and integration was not possible due to the appearance of a new shoulder, likely due to formation of endo−exo and endo−endo isomers of slightly different hydrodynamic volume (see Supporting Information).

^{1}H NMR Analysis of Dendrimer Degradation and Reassembly. Degradation of **5**−**8** upon heating toluene solutions of the dendrimers (7 mM) at 95 °C was monitored by ^{1}H NMR at time intervals. Specifically, degradation of **5**−**8** was indicated by the appearance of a singlet at 5.7 ppm that arose due to the formation of free maleimide protons. As dendrimers **5**−**8** undergo the retro-DA reaction, free maleimide protons arise from two different species: the bismaleimide core molecule **4** and the [G-*n*] mono-DA adduct. As indicated by the GPC results above, the degradation reaction is sufficiently slow to allow significant amounts of [G-*n*] mono-DA adduct to form upon cleavage of dendrimers **5**−**8**. NMR studies revealed that the chemical shift for the free maleimide protons of **4** and the [G-*n*] mono-DA adducts were identical, as observation of a single maleimide singlet was observed, despite confirmation of the presence of both species by GPC (vide supra). Therefore, any signal appearing at 5.7 ppm must be attributed to formation of both **4** and the [G-*n*] mono-DA adduct. Similarly, the bridgehead protons for dendrimers **5**−**8** and the corresponding [G-*n*] mono-DA adducts that form during the retro-DA reaction have identical chemical shifts at ca. 5.3 ppm.

The free maleimide proton signal at 5.7 ppm was monitored during degradation and plotted as a percentage of the sum of the maleimide and bridgehead proton signal at ca. 5.35 ppm (Figure 5). At time zero, 100% intact dendrimer, no free maleimide peak was observed at 5.7 ppm. As dendrimer solutions of **5**−**8** were heated over time, free maleimide generation occurred as evidenced by the growth of the peak at 5.7 ppm concomitant with a decrease in the exo proton peak at 5.3 ppm. After ∼15 h of heating at 95 °C, only 50% of the parent dendrimer had disassembled, and an apparent equilibrium state was established in which little or no additional free maleimide was generated upon further heating of the samples. This is in stark contrast to the GPC experiments where more than 50% of the parent dendrimer had disassembled in only 3 h, suggesting that a true equilibrium has not been reached. It should be noted that the NMR samples were 7 times more concentrated than those used for the GPC experiments.

Thermal reassembly of samples of **5**−**8** was investigated by NMR using the thermally treated samples and chemical shifts discussed above. The fragmented samples were concentrated in vacuo and allowed to reassemble at mild temperatures in minimal solvent. After 24 h of heating at 60 °C, the percent free maleimide decreased from approximately 50% to 23, 26, 12, and 14% for **5**−**8**, respectively (Figure 6). Continued heating at 45 °C for 3 days resulted in further decrease in free maleimide to 11, 6, 9, and 11%, respectively. This data indicates that approximately 90% of each dendrimer had reassembled. During reassembly of **5**−**8**, endo DA adduct formation was observed as evidenced by the appearance of multiplets at 5.1 and 3.0 ppm. After 96 h of heating, 12, 11, 8.6, and 6.0% of the DA adducts formed for **5**−**8**, respectively, were endo isomers.

Summary

In summary, a covalent macromolecular (self)assembly system has been described using thermally reversible furan−maleimide DA adducts. Benzyl aryl ether based dendrons **3a**−**d** containing furan moieties at their focal point were allowed to react with commercial bismaleimide central linker **4** to provide

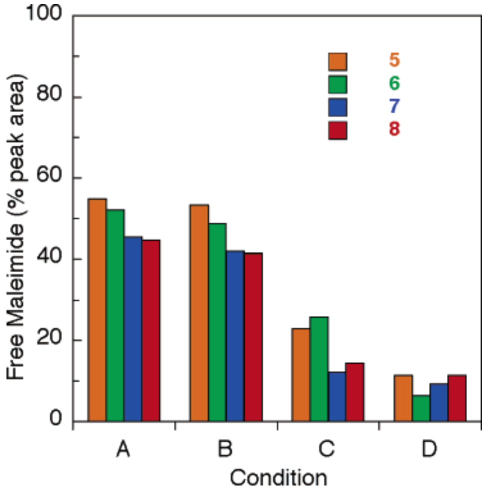


Figure 6. Reassembly of dendrimers **5**−**8** under different conditions followed by disappearance of free maleimide protons in the ^{1}H NMR. Conditions: (A) 95 °C for 40 h (toluene-d_7); (B) solvent removed in vacuo at RT and immediately redissolved; (C) 60 °C for 24 h (neat); (D) 45 °C for 72 h (neat).

first through fourth generation DA dendrimers **5**−**8**. GPC and NMR studies revealed that dendrimers **5**−**8** efficiently undergo cleavage and reassembly at relatively mild temperature conditions. In accord with our previous work,[28] we anticipate many other thermally reversible DA directed dendrimer assemblies. Selection of appropriately functionalized dienes, dienophiles, and dendrons will likely lead to a suite of new nanoscopic materials which can be activated through a noninvasive thermal trigger.

Experimental Section

Materials and Methods. NMR data were collected on a Varian 300 MHz spectrometer. Chemical shifts were referenced to TMS for ^{1}H NMR and the deuterated solvent resonance for ^{13}C NMR. GPC studies were run using a Waters Alliance 2695 Separations Module with Jordi DVB columns (500, 1000, 10 000 Å columns in series) with CH_2Cl_2 as the mobile phase at a flow rate of 1 mL/min. Data were collected with a Wyatt Technology Optilab DSP RI detector. Compound **1** was obtained from commercial sources and used without purification. Commercially available 1,1′-(methylenedi-4,1-phenylene)bismaleimide was purchased from Aldrich (95%) and recrystallized from CH_2Cl_2/hexanes before use. Benzyl aryl ether dendrons [G-1]-Br, [G-2]-Br, and [G-3]-Br were prepared according to literature procedures.[30]

3,4-Bis(hydroxymethyl)furan (2). To a cold (0 °C) suspension of $LiAlH_4$ (1.26 g, 33.2 mmol) in anhydrous ether (100 mL) was added with stirring dimethyl 3,4-furandicarboxylate (**1**) (2.70 g, 12.7 mmol). The reaction was warmed to RT while stirring (0.5 h) and then quenched sequentially by slow addition of water (1.25 mL), 2 N NaOH (1.25 mL), and water (3.75 mL). The reaction mixture was stirred for 45 min and subsequently gravity filtered, dried ($MgSO_4$), and filtered, and the filtrate was concentrated in vacuo to yield **2** (1.33 g, 82%) as a colorless oil. ^{1}H NMR (400 MHz, acetone-d_6): δ 7.42 (s, 2H), 4.51 (d, $J = 5.6$ Hz, 4H), 4.17 (t, $J = 5.6$ Hz, 2H).

3,4-Bis(benzyloxymethyl)furan (3a). To a cold solution (0 °C) of 3,4-bis(hydroxymethyl)furan (**2**) (1.32 g, 10.3 mmol) in anhydrous DMF was added NaH (600 mg, 25.0 mmol) in three portions over 10 min. After 15 min, benzyl bromide (2.45 mL, 20.6 mmol) was added dropwise over 15 min. The reaction was warmed to RT while stirring under N_2 and monitored by TLC (SiO_2, 9:1 petroleum ether−EtOAc) until complete (15 h). The reaction mixture was quenched with water (100 mL) and diluted with ethyl ether (100 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl ether (2 × 50 mL). The organic layers were combined, dried ($MgSO_4$), filtered, and concentrated in vacuo to yield a crude yellow oil. Purification by flash chromatography (SiO_2, 9:1 petroleum ether−EtOAc) yielded **3a** (2.65 g, 84%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (s, 2H), 7.38−7.29 (m, 10 H), 4.53 (s, 4H), 4.48 (s, 4H).

[G-2] Furan Dendron (3b). Following the procedure for **3a**, a solution of 3,4-bis(hydroxymethyl)furan (**2**) (246 mg, 1.92 mmol), [G-1]-Br (1.53 g, 3.83 mmol), anhydrous DMF (15 mL), and NaH (130 mg, 5.42 mmol) yielded, after purification by flash chromatography (SiO_2, 4:1 petroleum ether−EtOAc), **3b** (934 mg, 66%) as a colorless solid; mp 89−91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.27 (m, 22H), 6.57 (d, $J = 2.4$ Hz, 4H), 6.52 (t, $J = 2.4$ Hz, 2H), 4.98 (s, 8H), 4.43 (s, 4H), 4.42 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 141.8, 140.6, 136.8, 128.5, 127.9, 127.5, 121.7, 106.6, 101.3, 71.7, 70.0, 62.4. Anal. Calcd for $C_{48}H_{44}O_7$: C, 78.67; H, 6.05. Found: C, 78.87; H, 6.21.

[G-3] Furan Dendron (3c). Following the procedure for **3a**, a solution of 3,4-bis(hydroxymethyl)furan (**2**) (150 mg, 1.17 mmol), [G-2]-Br (1.87 g, 2.32 mmol), KH (122 mg, 3.05 mmol), and anhydrous THF (30 mL) yielded, after purification by flash chromatography (SiO_2, 4:1 CH_2Cl_2−petroleum ether), **3c** (1.36 g, 74%) as a colorless glass. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38−7.26 (m, 40 H), 6.63 (d, $J = 2.4$ Hz, 8H), 6.55 (d, $J = 2.0$ Hz, 4H), 6.53 (t, $J = 2.4$ Hz, 4H), 6.48 (t, $J = 2.0$ Hz, 2H), 4.96 (s, 16 H), 4.89 (s, 8H), 4.43 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 159.9, 141.9, 140.6, 139.3, 136.7, 128.5, 127.9, 127.5, 121.7, 106.5, 106.3, 101.5, 101.3, 71.8, 70.0, 69.8, 62.4. Anal. Calcd for $C_{104}H_{92}O_{15}$: C, 78.97; H, 5.86; Found: C, 79.37; H, 5.76.

[G-4] Furan Dendron (3d). To a cold solution (0 °C) of 3,4-bis(hydroxymethyl)furan (**2**) (84 mg, 0.65 mmol) and dry DMF (10 mL) was added NaH (63 mg, 2.61 mmol) over 5 min, and the mixture was stirred for 20 min under Ar. Solid [G-3]-Br (2.21 g, 1.33 mmol) was then added to the reaction mixture over a 10 min period, after which time the reaction mixture was allowed to warm to RT over 15 h with stirring. The reaction was quenched with water, and the resulting mixture was extracted with CH_2Cl_2 (2 × 50 mL). The organic layer was washed with brine, dried over $MgSO_4$, and filtered, and the filtrate was concentrated to an oil. Flash chromatography (SiO_2, CH_2Cl_2) of the oil gave **3d** as a colorless glassy foam (1.99 g, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24−7.39 (m, 82H), 6.62 (d, $J = 2.1$ Hz, 16H), 6.60 (d, $J = 2.1$ Hz, 8H), 6.55 (d, $J = 1.8$ Hz, 4H), 6.52 (t, 8H), 6.48 (t, 6H), 4.94 (s, 32H), 4.85 (s, 16H), 4.83 (s, 8H), 4.40 (s, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.1, 160.0, 159.9, 141.9, 140.7, 139.3, 139.2, 136.7, 128.5, 127.9, 127.5, 121.7, 106.3, 101.5, 71.9, 70.0, 69.9, 62.5, 48.5. MS (MALDI in dithranol) 3303.25 $[M + Na]^+$. Anal. Calcd for $C_{216}H_{188}O_{31}$: C, 79.10; H, 5.78. Found: C, 79.07; H, 5.95.

[G-1] DA Dendrimer (5). A solution of 3,4-bis(benzyloxymethyl)furan (**3a**) (955 mg, 3.10 mmol), 1,1′-(methylenedi-4,1-phenylene)bismaleimide (**4**) (508 mg, 1.42 mmol), and EtOAc (15 mL) was stirred at 50 °C until TLC indicated consumption of starting materials. The crude reaction mixture was allowed to stand at RT for 24 h, which resulted in formation of a white precipitate which was gravity filtered and washed with cold EtOAc to yield exo isomer **5** (389 mg, 28%) as a colorless solid. The filtrate was concentrated in vacuo and purified by flash chromatography (SiO_2, 1:1 EtOAc−petroleum ether) to yield a mixture of exo/endo isomers of [G-1] dendrimer **5** as a light yellow solid (653 mg, 47%). Repeated concentration of the endo/exo mixture in 50 °C EtOAc resulted in conversion to exo isomer **5**. ^{1}H NMR (300 MHz, $CDCl_3$) (exo isomer): δ 7.24−7.40 (m, 24H), 7.20 (d, $J = 8.1$ Hz, 4H), 5.38 (s, 4H), 4.56 and 4.52 (AB pattern, $J = 12.3$ Hz, 4H), 4.49 and 4.45 (AB pattern, $J = 11.7$ Hz, 4H), 4.19 (s, 8H), 4.02 (s, 2H), 3.13 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.3, 142.5, 141.0, 137.5, 129.9, 129.7, 128.5, 127.9, 127.7, 126.6, 83.6, 72.7, 63.0, 48.3, 41.1. Anal. Calcd for $C_{61}H_{54}N_2O_{10}$: C, 75.14; H, 5.58; N, 2.87. Found: C, 74.92; H, 5.81; N, 3.03.

[G-2] DA Dendrimer (6). Following the procedure for **5**, [G-1] furan dendron **3b** (953 mg, 0.60 mmol), 1,1′-(methylenedi-4,1-

phenylene)bismaleimide (**4**) (107 mg, 0.30 mmol), and EtOAc (20 mL) yielded, after purification by flash chromatography (SiO_2, Et_2O (500 mL), then 1:1 $CH_2Cl_2-Et_2O$), exo **6** (505 mg, 93%) as a glassy solid. ^1H NMR (300 MHz, $CDCl_3$): δ 7.25−7.43 (m, 44H), 7.20 (d, $J = 8.4$ Hz, 4H), 6.55 (m, 12H), 5.37 (s, 4H), 4.49 and 4.45 (AB pattern, $J = 12.0$ Hz, 4H), 4.42 and 4.38 (AB pattern, $J = 12.3$ Hz, 4H), 4.17 (s, 8H), 4.03 (s, 2H), 3.10 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.3, 160.1, 142.5, 141.0, 139.9, 136.8, 129.9, 129.7, 128.5, 127.9, 127.5, 126.6, 106.5, 101.5, 83.6, 72.6, 70.0, 63.0, 48.3, 41.1. MS (MALDI in dithranol) *m*/*z* 755.25 ([G-2] furan dendron + Na)$^+$. Anal. Calcd for $C_{117}H_{102}N_2O_{18}$: C, 77.04; H, 5.64; N, 1.54. Found: C, 76.68; H, 6.00; N, 1.78.

[G-3] DA Dendrimer (7). A solution of [G-3] furan dendron **3c** (1.22 g, 0.77 mmol), 1,1′-(methylenedi-4,1-phenylene)bismaleimide (**4**) (0.134 g, 0.38 mmol), and EtOAc (10 mL) was heated to 60 °C for 2 days. The solution was concentrated, and unreacted starting materials were separated from the resulting oil by flash chromatography (SiO_2, 95:5 $CH_2Cl_2-Et_2O$) to give a mixture of bis- and mono-DA products (95:5) as a colorless glass (1.13 g, 86%). Isolation of exo dendrimer **7** was achieved by preparative GPC as needed. ^1H NMR (300 MHz, $CDCl_3$): δ 7.25−7.40 (m, 80H), 7.13 (m, 8H), 6.65 (d, $J = 2.4$ Hz, 16H), 6.53 (m, 20H), 5.36 (s, 4H), 4.96 (s, 32H), 4.92 (s, 16H), 4.48 and 4.44 (AB pattern, $J = 12.3$ Hz, 4H), 4.41 and 4.37 (AB pattern, $J = 12.3$ Hz, 4H), 4.17 (s, 8H), 3.83 (s, 2H), 3.10 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.3, 160.1, 160.0, 142.4, 140.8, 140.0, 139.2, 136.7, 129.9, 129.6, 128.5, 127.9, 127.5, 126.5, 106.3, 101.6, 101.5, 83.7, 72.6, 70.0, 69.9, 63.0, 48.3. MS (MALDI in dithranol) *m*/*z* 1604.59 ([G-3] furan dendron + Na)$^+$. Anal. Calcd for $C_{229}H_{198}N_2O_{34}$: C, 78.09; H, 5.67; N, 0.80. Found: C, 77.81; H, 5.88; N, 0.96.

[G-4] DA Dendrimer (8). [G-4]-furan dendron **3d** (1.26 g, 0.38 mmol) and 1,1′-(methylenedi-4,1-phenylene)bismaleimide (**4**) (0.067 g, 0.188 mmol) were dissolved in 10 mL of EtOAc and heated to 60 °C for 4 days. The solution was concentrated, and unreacted starting materials were separated from the resulting oil by flash chromatography (SiO_2, 95:5 $CH_2Cl_2-Et_2O$) gave a mixture of bis- and mono-DA products (95:5) as a colorless glass (1.15 g, 84%). Isolation of exo dendrimer **8** was achieved by preparative GPC as needed. ^1H NMR (300 MHz, $CDCl_3$): δ 7.22−7.39 (m, 160H), 7.10 (m, 8H), 6.61 (d, $J = 1.8$ Hz, 48H), 6.50 (m, 36H), 5.33 (s, 4H), 4.92 (s, 64H), 4.85 (s, 16H), 4.83 (s, 32H), 4.44 and 4.39 (AB pattern, $J = 12.6$ Hz, 4H), 4.36 and 4.32 (AB pattern, $J = 12.9$ Hz, 4H), 4.12 (s, 8H), 3.78 (s, 2H), 3.04 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.6, 160.5, 160.4, 142.8, 141.3, 140.4, 139.61, 139.57, 137.1, 130.3, 130.0, 128.9, 128.3, 127.9, 126.9, 106.8, 101.9, 84.0, 72.9, 70.4, 70.2, 63.4, 48.7. MS (MALDI in dithranol) 3304.15 ([G-4] furan dendron + Na)$^+$, 3320.11 ([G-4] furan dendron + K)$^+$. Anal. Calcd for $C_{453}H_{390}N_2O_{66}$: C, 78.65; H, 5.68; N, 0.40. Found: C, 78.57; H, 5.87; N, 0.62.

GPC Studies. Solutions of each dendrimer in toluene (1 mM) were heated at 95 °C, and aliquots were taken out at time intervals. The toluene aliquots were directly injected into the GPC instrument with no further workup. To monitor the reassembly process, the same disassembled samples that had been heated for the longest period of time were concentrated in vacuo, heated for various times, diluted, and analyzed by GPC. Peak areas were measured with commercial software.

NMR Studies. Solutions of each dendrimer in toluene-d_7 (7 mM) were heated at 95 °C. At time intervals the samples were removed from the heating bath, and ^1H NMR spectra were collected at ambient temperature.

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Supporting Information Available: Additional data on the degradation and reassembly of dendrimers **5**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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