Review

Synthesis of Neutral Metallodendrimers Possessing Adamantane Termini: Supramolecular Assembly with β-Cyclodextrin

George R. Newkome,*,†,‡ Hyung Jin Kim,§ Kyung Ho Choi,§ and Charles N. Moorefield‡

Departments of Polymer Science and Chemistry and Maurice Morton Institute of Polymer Science, The University of Akron, Akron, Ohio 44325-4717, and Department of Applied Chemistry, Chonnam National University, Kwangju 500-757, Korea

Received May 20, 2004; Revised Manuscript Received June 15, 2004

ABSTRACT: First and second generations of 1 → (2 + 1) C-branched metallodendrimers were prepared employing terpyridine−Ru^{II}−terpyridine connectivity. Each surface dendron is comprised of a terpyridinyl (focal group), a diester (capable of easy hydrolysis), and a terminal adamantyl moiety (for encapsulation). Internal incorporation of counterbalancing carboxylate moieties derived by ester cleavage with formic acid and subsequent treatment of the intermediate diacid with base gave access to overall charge−neutral dendritic macromolecules. Aqueous solubility was effected by the supramolecular encapsulation of the terminal adamantane moieties with β-cyclodextrin, causing dissolution of the water-insoluble dendrimers (**11** and **15**) into an aqueous environment.

Introduction

In recent years, metallodendritic chemistry[1−11] has emerged as one of the most interesting topics within suprasupermolecular chemistry[12−15] due to the inherent novel physical properties. This has facilitated studies in sensor arrays,[16] optical,[17] redox,[18] electrochemical,[19−24] and photochemical characteristics[20,25−31] as well as biological diagnostic[32,33] and catalytic attributes.[34−42] Such metallodendrimers generally incorporate metal ions into their infrastructure via use as cores, branching centers, arm connectors, and termini or by metal incorporation at specific loci within the preassembled dendritic framework. In our previous work,[43−50] the bis(2,2′;6′,2″-terpyridine)ruthenium(II) complex (i.e., [−<Ru>−]) has been employed as a building block connector and has afforded entrance to numerous metallodendritic assemblies, all utilizing external counterions, such as Cl^-, BF_4^-, and PF_6^-. Recently, Schubert and co-workers[51−65] have utilized this [−<Ru>−] mode of connectivity for the assembly of related stable metallostars as well as linear polymers.

Later, we reported overall charge−neutral metallodendrimers,[45,47,49] incorporating [−<Ru>−] connectivity and covalently connected, internal carboxylate moieties as the neutralizing counterions. This change from external to internal counterions in these zwitterionic metallodendrimers yielded a marginal effect on their spectra, stability, and most of the physical properties; however, the solubility of these neutral species decreased in polar solvents, such as MeOH and H_2O when compared to those constructs possessing external Cl^- counterions, which were quite soluble in the same solvents.

To circumvent this limited solubility, the covalent and noncovalent incorporation of water-soluble units onto the dendritic framework was necessary. Toward this goal, the use of β-cyclodextrin (β-CD), one of the cyclic oligosaccharides, presented an attractive option due to its demonstrated potential to form stable inclusion complexes with molecular guests in aqueous solution.[66,67] For example, β-CD strongly binds to adamantane by forming a 1:1 inclusion complex with a stability constant[68] on the order of 10^4 M^{-1}. The use of CDs, as cores, for dendritic construction has been reported,[69] and they have subsequently been shown to readily host adamantane units that serve as polymer caps. Among the many reports using β-CD as the molecular host are the elegant works of Kaifer et al.,[70] in which the CDs readily encapsulate cobaltocenes attached to a dendritic surface, Lui et al.,[71] where bis(pseudopolyrotaxane)s are encircled with β-CDs creating a threaded polymer chain, and Michels, Huskens, and Reinhoudt,[72] who employed the phenomenon for gold and platinum nanoparticle construction.

Thus, as an extension of our previous work, we designed a series of new 1 → (2 + 1) branching monomers[73] (e.g., **6**) possessing in this case covalently attached: (1) an adamantyl guest for encapsulation of a β-CD host and (2) a focal terpyridinyl moiety, for metal connectivity, with neighboring dicarboxylate groups. Herein, we describe the formation of metallodendrimers possessing either 4 or 12 [−<Ru>−] linkages initially employing external counterions and subsequent conversion to internal counterions; then finally we probed the host−guest character of the terminal adamantane units with β-CD.

* Corresponding author. E-mail newkome@uakron.edu.
† Departments of Polymer Science and Chemistry, The University of Akron.
‡ Maurice Morton Institute of Polymer Science, The University of Akron.
§ Chonnam National University.

10.1021/ma048996b CCC: $27.50
Published on Web 07/29/2004

Experimental Section

General Section. The melting points were determined in capillary tubes with an Electrothermal 9100 apparatus and are uncorrected. All commercially available solvents were used without further purification, except for THF, which was dried by refluxing with benzophenone/Na under N_2. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, on a Bruker Gemini 300 spectrometer and were obtained in $CDCl_3$, unless otherwise stated. Mass spectral data were obtained on either a Bruker Esquire-LC ion trap mass spectrometer (ESI-MS) or an ABI Voyager-DE STR mass spectrometer (MALDI−TOF).

Di-*tert*-butyl 4-[3-(2-Cyanoethoxy)propyl]-4-[4-(2,2′;6′,2″-terpyridin-4′-yloxy)butyrylamino]heptanedioate (3). To a stirred solution of 4-[4′-oxa-(2,2′;6′,2″-terpyridinyl]butanoic acid[44] (**2**; 2.415 g, 7.202 mmol) in DMF (20 mL) was added DCC (1.486 g, 7.202 mmol) and 1-HOBT (973 mg, 7.202 mmol) at 25 °C. After 30 min, amine[74] **1** (2.87 g, 7.202 mmol) was added. After stirring for 24 h at 25 °C, the mixture was filtered. The filtrate was concentrated in vacuo to give a crude product, which was column chromatographed (basic Al_2O_3) eluting with a 1:1 mixture of *n*-hexane/EtOAc to afford (67%) nitrile **3** as a white solid: 3.47 g; mp 129−130 °C. ^1H NMR δ: 1.41 [s, 18H, C(C*H*$_3$)$_3$], 1.48 (m, 2H, C*H*$_2$CH$_2$O), 1.78 (m, 2H, C*H*$_2$CH$_2$CH$_2$O), 1.95 (t, J = 8.0 Hz, 4H, C*H*$_2$CH$_2$CO$_2$), 2.16 (m, 2H, C*H*$_2$CH$_2$CONH), 2.22 (t, J = 8.0 Hz, 4H, C*H*$_2$CO$_2$), 2.37 (t, J = 7.2 Hz, 2H, C*H*$_2$CONH), 2.53 (t, J = 6.4 Hz, 2H, C*H*$_2$CN), 3.40 (t, J = 6.3 Hz, 2H, C*H*$_2$O), 3.56 (t, J = 6.4 Hz, 2H, OC*H*$_2$CH$_2$CN), 4.26 (t, J = 6.0 Hz, 2H, tpyOC*H*$_2$), 5.79 (s, 1H, N*H*), 7.32 (did, J = 7.5, 4.8, 0.9 Hz, 2H, 5,5″-tpy*H*), 7.84 (td, J = 7.8, 1.5 Hz, 2H, 4,4″-tpy*H*), 8.01 (s, 2H, 3′,5′-tpy*H*), 8.61 (d, J = 7.8 Hz, 2H, 3,3″-tpy*H*), 8.68 (d, J = 4.5 Hz, 2H, 6,6″-tpy*H*). ^{13}C NMR δ: 18.9 (*C*H$_2$CN), 23.8 (*C*H$_2$CH$_2$O), 25.2 (*C*H$_2$CH$_2$CONH), 28.2 (*C*H$_3$), 30.0 (*C*H$_2$CO$_2$), 30.3 (*C*H$_2$CH$_2$CO$_2$), 31.6 (*C*H$_2$CONH), 33.5 (*C*H$_2$CH$_2$CH$_2$O), 57.9 (CONH*C*), 65.4 (O*C*H$_2$CH$_2$CN), 67.3 (*C*H$_2$O), 71.4 (tpyO*C*H$_2$), 80.8 (*C*Me$_3$), 107.5 (3′,5′-tpy*C*), 118.0 (*C*N), 121.5 (3,3″-tpy*C*), 124.0 (5,5″-tpy*C*), 137.0 (4,4″-tpy*C*), 149.2 (6,6″-tpy*C*), 156.2 (2,2″-tpy*C*), 157.3 (2′,6′-tpy*C*), 167.2 (4′-tpy*C*), 171.6 (*C*ONH), 173.1 (*C*O$_2$^{t}Bu). ESI-MS for $C_{40}H_{53}N_5O_7$: calcd 715.4, found 737.9 $(M + Na)^+$.

Di-*tert*-butyl 4-[3-(3-Aminopropoxy)propyl]-4-[4-(2,2′;6′,2″-terpyridin-4′-yloxy)butyrylamino]heptanedioate (4). To a solution of nitrile **3** (2.20 g, 3.073 mmol) in MeOH (120 mL) was added Raney cobalt[75] (2.0 g, slurry in water); the mixture was stirred under 40 atm of H_2 for 6 h at 40 °C. After cooling to 25 °C, the mixture was filtered and the filtrate was concentrated in vacuo to afford (98%) amine **4** as a liquid: 2.17 g. ^1H NMR δ: 1.41 [s, 18H, C(C*H*$_3$)$_3$], 1.48 (m, 2H, C*H*$_2$CH$_2$O), 1.66 (m, 2H, C*H*$_2$CH$_2$NH$_2$), 1.75 (m, 2H, C*H*$_2$CH$_2$CH$_2$O), 1.98 (t, J = 8.1 Hz, 4H, C*H*$_2$CH$_2$CO$_2$), 2.16 (m, 2H, C*H*$_2$CH$_2$CONH), 2.21 (t, J = 8.1 Hz, 4H, CH$_2$C*H*$_2$CO$_2$), 2.37 (t, J = 7.3 Hz, 2H, C*H*$_2$CONH), 2.76 (br t, 2H, C*H*$_2$NH$_2$), 3.34 (t, J = 6.3 Hz, 2H, OC*H*$_2$CH$_2$CH$_2$NH$_2$), 3.42 (t, J = 6.0 Hz, 2H, C*H*$_2$O), 4.26 (t, J = 6.0 Hz, 2H, tpyOC*H*$_2$), 5.85 (s, 1H, NH), 7.32 (ddd, J = 6.9, 5.4, 0.9 Hz, 2H, 5,5″-tpy*H*), 7.84 (td, J = 7.8, 1.5 Hz, 2H, 4,4″-tpy*H*), 8.00 (s, 2H, 3′,5′-tpy*H*), 8.61 (d, J = 8.1 Hz, 2H, 3,3″-tpy*H*), 8.67 (d, J = 4.8 Hz, 2H, 6,6″-tpy*H*). ^{13}C NMR δ: 23.5 (*C*H$_2$CH$_2$O), 25.0 (*C*H$_2$CH$_2$CONH), 27.9 (*C*H$_3$), 29.8 (*C*H$_2$CO$_2$), 30.0 (*C*H$_2$CH$_2$CO$_2$), 30.4 (C*H*$_2$CH$_2$NH$_2$), 31.4 (*C*H$_2$CONH), 33.3 (*C*H$_2$CH$_2$CH$_2$O), 37.3 (*C*H$_2$NH$_2$), 57.5 (CONH*C*), 67.1 (*C*H$_2$O), 69.0 (O*C*H$_2$CH$_2$CH$_2$NH$_2$), 70.7 (tpyO*C*H$_2$), 80.4 (*C*Me$_3$), 107.2 (3,3′-tpy*C*), 121.2 (3,3″-tpy*C*), 123.8 (5,5″-tpy*C*), 136.7 (4,4″-tpy*C*), 148.9 (6,6″-tpy*C*), 155.9 (2,2″-tpy*C*), 157.0 (2′,6′-tpy*C*), 166.9 (4′-tpy*C*), 171.4 (*C*ONH), 172.8 (*C*O$_2$^{t}Bu). ESI-MS for $C_{40}H_{57}N_5O_7$: calcd 719.4, found 720.0 $(M + H)^+$.

Di-*tert*-butyl 4-(3-[3-[(Adamantane-1-carbonyl)amino]-propoxy]propyl)-4-[4-(2,2′;6′,2″-terpyridin-4′-yloxy)butyrylamino]heptanedioate (6). To a stirred mixture of amine **4** (1.26 g, 1.75 mmol) and Et_3N (212 mg, 2.10 mmol) dissolved in dry THF (15 mL) was slowly added a solution of 1-(chlorocarbonyl)adamantane[76] (**5**; 417 mg, 2.10 mmol) in dry THF (5 mL) at 0 °C. After addition, the mixture was slowly warmed to 25 °C and stirred for a further 6 h. The mixture was then filtered and concentrated in vacuo to give a crude product, which was column chromatographed (Al_2O_3) eluting with an equal mixture of *n*-hexane/EtOAc to afford (84%) the pure bisamide **6** as a colorless liquid: 1.30 g. ^1H NMR δ: 1.42 [s, 18H, C(C*H*$_3$)$_3$], 1.50 (m, 2H, C*H*$_2$CH$_2$O), 1.70−2.01 (m, 15H, adamantane),1.73 (m, 2H, C*H*$_2$CH$_2$NHCO), 1.75 (m, 2H, C*H*$_2$-CH$_2$CH$_2$O), 1.97 (t, J = 8.4 Hz, 4H, C*H*$_2$CH$_2$CO$_2$), 2.17 (m, 2H, C*H*$_2$CH$_2$CONH), 2.22 (t, J = 8.4 Hz, 4H, CH$_2$C*H*$_2$CO$_2$), 2.38 (t, J = 7.4 Hz, 2H, C*H*$_2$CONH), 3.31 (t, J = 6.0 Hz, 2H, C*H*$_2$-NHCO), 3.37 (t, J = 6.6 Hz, 2H, OC*H*$_2$CH$_2$CH$_2$NHCO), 3.45 (t, J = 6.0, 5.7 Hz, 2H, CH$_2$CH$_2$C*H*$_2$O), 4.27 (t, J = 6.0 Hz, 2H, tpyOC*H*$_2$), 5.92 (s, 1H, NH), 7.32 (ddd, J = 6.0, 4.5, 1.2 Hz, 2H, 5,5″-tpy*H*), 7.84 (td, J = 7.8, 1.5 Hz, 2H, 4,4″-tpy*H*), 8.01 (s, 2H, 3′,5′-tpy*H*), 8.61 (d, J = 8.1 Hz, 2H, 3,3″-tpy*H*), 8.69 (d, J = 4.5 Hz, 2H, 6,6″-tpy*H*). ^{13}C NMR δ: 23.8 (*C*H$_2$-CH$_2$O), 25.1 (*C*H$_2$CH$_2$CONH), 28.1 (CH$_3$), 28.2 (*C*H of adamantane), 29.1 (C*H*$_2$CH$_2$NHCO), 29.9 (*C*H$_2$CO$_2$), 30.2 (*C*H$_2$-CH$_2$CO$_2$), 31.5 (*C*H$_2$CONH), 33.4 (*C*H$_2$CH$_2$CH$_2$O), 36.6 and 39.3 (*C*H$_2$ of adamantane), 37.8 (*C*$^{4°}$ of adamantane), 40.5 (*C*H$_2$-NHCO), 57.7 (CONH*C*), 67.3 (*C*H$_2$O), 69.8 (O*C*H$_2$CH$_2$CH$_2$-NHCO), 70.7 (tpyO*C*H$_2$), 80.4 (*C*Me$_3$), 107.2 (3,3′-tpy*C*), 121.4 (3,3″-tpy*C*), 123.9 (5,5″-tpy*C*), 136.9 (4,4″-tpy*C*), 149.1 (6,6″-tpy*C*), 156.1 (2,2″-tpy*C*), 157.2 (2′,6′-tpy*C*), 167.2 (4′-tpy*C*), 171.6 (*C*ONH), 173.l (*C*O$_2$^{t}Bu), 178.0 (*C*O-adamantane). ESI-MS for $C_{51}H_{71}N_5O_8$: calcd 881.5, found 904.5 $(M + Na)^+$.

Di-*tert*-butylruthenium(III) Complex of 4-(3-[3-[(Adamantyl-1-carbonyl)amino]propoxy]propyl)-4-[4-(2,2′;6′,2″-terpyridin-4′-yloxy)butyrylamino]heptanedioate (7). To a solution of bisamide **6** (1.10 g, 1.247 mmol) in MeOH (50 mL) was added $RuCl_3 \cdot H_2O$ (326 mg, 1.247 mmol), and then the mixture was refluxed for 2 h. Upon cooling to 25 °C, the resultant solid was filtered and washed successively with MeOH (5 mL), water (10 mL), and MeOH (5 mL) and then dried in vacuo to afford (76%) the Ru(III) complex **7** as a red solid (1.03 g), which was used without further purification.

Tetrakisruthenium(II) Metallodendrimer (9). To a suspension of complex **7** (192 mg, 176 μmol) in MeOH (15 mL) was added a solution of tetrakisterpyridine core[44] (**8**; 52 mg, 40 μmol) and *N*-ethylmorpholine (25 mg) in $CHCl_3$ (5 mL) at 25 °C, and then the mixture was refluxed for 2 h. After cooling to 25 °C, the mixture was filtered and the filtrate was sealed into a membrane (cutoff mass = 1000) to dialyze for 24 h. The solution inside the membrane was concentrated in vacuo to give (91%) the Ru(II) complex **9** as a red solid: 200 mg; mp >210 °C. ^1H NMR (CD_3OD) δ: 1.38 [s, 72H, C(C*H*$_3$)$_3$], 1.53−2.58 (br m, 140H, C*H*, C*H*$_2$), 3.22 (br t, 8H, C*H*$_2$NH), 3.42 (m, 16H, OC*H*$_2$), 3.56 (s, 4H, NH), 3.78 (br s, 8H, C$^{4°}$C*H*$_2$O), 3.89 (br t, 8H, OC*H*$_2$), 4.61 and 4.77 (br t, 16H, tpyOC*H*$_2$), 7.22 (br m, 16H, 5,5″-tpy*H*), 7.50 (br m, 16H, 6,6″-tpy*H*), 7.92 (m, 16H, 4,4″-tpy*H*), 8.64 (br s, 16H, 3′,5′-tpy*H*), 8.73−8.78 (br m, 16H, 3,3″-tpy*H*). ^{13}C NMR (CD_3OD) δ: 24.8 (*C*H$_2$CH$_2$O), 26.1 (*C*H$_2$-CH$_2$CONH), 28.5 [C(*C*H$_3$)$_3$], 29.7 (*C*H of adamantane), 30.6 (*C*H$_2$CH$_2$O), 30.8 (C*H*$_2$CH$_2$NHCO), 30.9 (*C*H$_2$CO$_2$), 31.0 (*C*H$_2$-CH$_2$CO$_2$), 32.1 (*C*H$_2$CONH), 33.6 (*C*H$_2$CH$_2$CH$_2$O), 37.7 and 40.3 (*C*H$_2$ of adamantane), 38.2 (*C*$^{4°}$ of adamantane), 41.8 (*C*H$_2$-NHCO), 47.1 (*C*$^{4°}$), 59.1 (CONH*C*), 68.8, 69.3, 70.1, 70.6, 71.7, 72.1 (all *C*H$_2$O), 81.6 (*C*Me$_3$), 112.6 (3,3′-tpy*C*), 126.0 (3,3″-tpy*C*), 129.0 (5,5″-tpy*C*), 139.2 (4,4″-tpy*C*), 153.5 (6,6″-tpy*C*), 157.9 (2,2″-tpy*C*), 160.0 (2′,6′-tpy*C*), 167.6 and 167.8 (4′-tpy*C*), 174.7 (*C*ONH, *C*O$_2$), 180.7 (*C*O-adamantane). MALDI−TOF MS for $C_{281}H_{356}Cl_8N_{32}O_{40}Ru_4$: calcd 5506.05 (M^+), found 5506 (broad signal; 2,5-dihydroxybenzoic acid (DHB) matrix).

Octaacid Metallodendrimer (10). Octaester (**9**; 150 mg, 28.7 μmol) was dissolved in HCO_2H (10 mL) and stirred for 6 h at 25 °C. After removal of HCO_2H in vacuo, the residue was dissolved in MeOH to dialyze for 24 h, and then the solution was concentrated in vacuo to afford (97%) octaacid **10** as a red solid: 134 mg; mp >275 °C. ^1H NMR (CD_3OD) δ: 1.48−2.49 (br m, 140H, C*H*, C*H*$_2$), 3.15 (br t, 8H, C*H*$_2$NH), 3.33 (m, 16H, OC*H*$_2$), 3.76 (br s, 8H, C$^{4°}$C*H*$_2$O), 3.86 (br t, 8H, OC*H*$_2$CH$_2$-CH$_2$O), 4.55 and 4.72 (br t, 16H, tpyOC*H*$_2$), 7.19 (br m, 16H, 5,5″-tpy*H*), 7.45 (br m, 16H, 6,6″-tpy*H*), 7.88 (m, 16H, 4,4″-tpy*H*), 8.62 (br s, 16H, 3′,5′-tpy*H*), 8.69 (br m, 16H, 3,3″-tpy*H*). ^{13}C NMR (CD_3OD) δ: 25.0 (*C*H$_2$CH$_2$O), 26.0 (*C*H$_2$CH$_2$CONH), 29.7 (*C*H of adamantane), 30.6 (OCH$_2$*C*H$_2$CH$_2$O), 30.9 (C*H*$_2$-CH$_2$NHCO), 32.2 (*C*H$_2$CONH), 32.4 (*C*H$_2$CO$_2$), 33.7 (*C*H$_2$CH$_2$-

CO_2), 37.7 and 40.4 (CH_2 of adamantane), 38.4 ($CH_2CH_2CH_2O$), 38.5 (C^{4° of adamantane), 41.9 (CH_2NHCO), 47.1 (C^{4°), 59.4 (CONH*C*), 68.7, 69.4, 70.1, 70.5, 71.8, 72.4 (all CH_2O), 112.5, 112.7 (3,3′-tpy*C*), 126.0 (3,3″-tpy*C*), 128.9, 129.1 (5,5″-tpy*C*), 139.2 (4,4″-tpy*C*), 153.4, 153.6 (6,6″-tpy*C*), 157.9, 158.0 (2,2″-tpy*C*), 160.0, 160.1 (2′,6′-tpy*C*), 167.7 (4′-tpy*C*), 174.2 (*C*ONH), 180.4 (CO_2H), 180.7 (*C*O-adamantane). MALDI−TOF MS for $C_{249}H_{292}Cl_8N_{32}O_{40}Ru_4$: calcd 5057.548 ($M^+$), found 4807.97 $(M - 7Cl)^+$, 4771.74 $(M - 8Cl)^+$, 3-indoleacrylic acid (IAA) as matrix.

Neutral Tetrakisruthenium Metallodendrimer (11). Octaacid **10** (120 mg, 23.7 μmol) was dissolved in a mixture of MeOH (10 mL) and aqueous KOH solution (10 mL, 1 N) and then rapidly stirred at 25 °C. After 30 min, the solution was sealed into a membrane (cutoff mass = 1000) and dialyzed for 24 h. The solution inside the membrane was concentrated in vacuo to dryness to afford (98%) the neutral metallodendrimer **11** as a red solid: 111 mg; mp >260 °C (dec). ^{1}H NMR (CD_3OD) δ: 1.58−2.58 (br m, 140H, C*H*, CH_2, CH_3), 3.21 (br t, 8H, CH_2NH), 3.44 (m, 16H, OCH_2), 3.84 (br s, 8H, $C^{4^\circ}CH_2O$), 3.96 (br t, 8H, OC$H_2CH_2CH_2O$), 4.39 (s, 4H, N*H*), 4.63 and 4.78 (br t, 16H, tpyOCH_2), 7.25−7.35 (br m, 16H 5,5″-tpy*H*), 7.46−7.53 (br m, 16H, 6,6″-tpy*H*), 8.00 (m, 16H, 4,4″-tpy*H*), 8.61 (br s, 16H, 3′,5′-tpy*H*), 8.71−8.74 (br m, 16H, 3,3″-tpy*H*). ^{13}C NMR (CD_3OD) δ: 24.8 (CH_2CH_2O), 26.0 (CH_2CH_2CONH), 29.5 (*C*H of adamantane), 30.3 (CH_2CH_2NHCO), 30.6 (CH_2CH_2O), 32.5 (CH_2CONH), 32.9 (CH_2CO_2), 33.5 ($CH_2CH_2CO_2$), 34.0 ($CH_2CH_2CH_2O$), 37.6 and 40.2 (CH_2 of adamantane), 38.2 (C^{4° of adamantane), 41.8 (CH_2NHCO), 47.0 (C^{4°), 59.7 (CONH*C*), 68.6, 69.6, 69.9, 70.5, 71.7, 72.5 (all CH_2O), 112.1 and 112.5 (5,5″-tpy*C*), 125.9, 126.1 (4,4″-tpy*C*), 128.9, 129.2 (3,3″-tpy*C*), 139.3, 139.5 (3′,5′-tpy*C*), 153.0, 153.4 (6,6″-tpy*C*), 157.7, 157.9 (2,2″-tpy*C*), 159.7, 159.9 (2′,6′-tpy*C*), 167.5, 167.6 (4′-tpy*C*), 174.7 (*C*ONH), 181.1 (*C*O-adamantane), 182.6 (CO_2^-). MALDI−TOF MS for $C_{249}H_{284}N_{32}O_{40}Ru_4$: calcd 4770.74 $(M + H)^+$, found 4771.97 with an IAA matrix.

Dodecaruthenium(II) Metallodendrimer (13). To a solution of metalloappendage (**7**; 140 mg, 128.5 μmol) in MeOH (10 mL) was added a solution of the dodecaterpyridine core[43] (**12**; 34 mg, 8.6 μmol) in $CHCl_3$ (10 mL) and *N*-ethylmorpholine (20 mg) at 25 °C, and then the mixture was refluxed for 3 h. After cooling, the mixture was filtered and the filtrate was sealed into a membrane (mass cutoff = 3500) to dialyze for 24 h. The solution inside the membrane was concentrated in vacuo to afford (98%) dodecaruthenium(II) complex **13** as a red solid:140 mg; mp >240 °C. ^{1}H NMR (CD_3OD) δ: 1.44 [s, 216H, C(CH_3)$_3$], 1.58−2.62 (br m, 452H, C*H*, CH_2), 3.28 (br t, 24H, CH_2NH), 3.47 (m, 48H, OCH_2), 3.78−3.99 (br m, 16H, $C^{4^\circ}CH_2O$, OC$H_2CH_2CH_2O$), 4.66 and 4.87 (br t, 48H, tpyOCH_2), 7.25 (br m, 48H, 5,5″-tpy*H*), 7.54 (br m, 48H, 6,6″-tpy*H*), 7.94 (m, 48H, 4,4″-tpy*H*), 8.69−8.92 (br m, 96H, 3′,5′-tpy*H*, 3,3″-tpy*H*). ^{13}C NMR (CD_3OD) δ: 23.5 (CH_2CH_2O), 24.9 (CH_2CH_2CONH), 27.3 [C(*C*H$_3$)$_3$], 28.5 (*C*H of adamantane), 29.4 (CH_2CH_2NHCO), 29.7 (CH_2CO_2), 29.8 ($CH_2CH_2CO_2$), 30.9 ($C^{4^\circ}CH_2CH_2CH_2O$), 32.4 ($CH_2CH_2CH_2O$), 36.5 and 39.2 (CH_2 of adamantane), 37.0 (OCH_2CH_2CONH, $C^{4^\circ}$of adamantane), 40.6 (CH_2NHCO), 45.8 (C^{4°), 57.9 (CONH*C*), 68.9, 69.5, 70.9 (all CH_2O), 80.4 (CMe_3), 111.4 (3,3′-tpy*C*), 124.8 (3,3″-tpy*C*), 127.8 (5,5″-tpy*C*), 138.0 (4,4″-tpy*C*), 152.3 (6,6″-tpy*C*), 156.6, 156.7 (2,2″-tpy*C*), 158.8, 158.9 (2′,6′-tpy*C*), 166.4 and 166.8 (4′-tpy*C*), 173.5 (*C*ONH, CO_2), 179.5 (*C*O-adamantane). MALDI−TOF MS for $C_{849}H_{1072}Cl_{24}N_{100}O_{116}Ru_{12}$: calcd 16 586.211 ($M^+$), found 16 609 $(M + Na)^+$ as a broad signal with DHB matrix.

Tetracosaacid Metallodendrimer (14). Tetracosaester (**13**; 130 mg, 7.83 μmol) was dissolved in HCO_2H (10 mL) and stirred for 12 h at 25 °C. After removal of HCO_2H in vacuo, the residue was dissolved in MeOH to dialyze for 24 h, and then the solution was concentrated in vacuo to afford (99%) tetracosaacid **14** as a red solid: 119 mg; mp >275 °C. ^{1}H NMR (CD_3OD) δ: 1.59−2.52 (br m, 452H, C*H*, CH_2), 3.27 (br t, 24H, CH_2NH), 3.47 (m, 48H, OCH_2), 3.78−3.99 (br m, 16H, $C^{4^\circ}CH_2O$, OC$H_2CH_2CH_2O$), 4.66 and 4.87 (br t, 48H, tpyOCH_2), 7.22 (br m, 48H, 5,5″-tpy*H*), 7.42 (br m, 48H, 6,6″-tpy*H*), 7.95 (m, 48H, 4,4″-tpy*H*), 8.65−8.88 (br m, 96H, 3′,5′-tpy*H*, 3,3″-tpy*H*). ^{13}C NMR (CD_3OD) δ: 24.0 (CH_2CH_2O), 24.7 (CH_2CH_2CONH), 28.4 (*C*H of adamantane), 29.2 (CH_2CH_2NHCO), 30.5 ($C^{4^\circ}CH_2CH_2CH_2O$), 31.3 (CH_2CO_2), 32.7 ($CH_2CH_2CO_2$), 37.8 ($CH_2CH_2CH_2O$), 36.6 and 39.2 (CH_2 of adamantane), 37.6 (OCH_2CH_2CONH, C^{4° of adamantane), 40.7 (CH_2NHCO), 45.8 (C^{4°), 58.3 (CONH*C*), 69.4, 71.5 (all CH_2O), 111.7 (3,3′-tpy*C*), 125.2 (3,3″-tpy*C*), 128.1 (5,5″-tpy*C*), 138.3 (4,4″-tpy*C*), 152.0 (6,6″-tpy*C*), 156.5, 156.6 (2,2″-tpy*C*), 158.5, 158.8 (2′,6′-tpy*C*), 166.5, 166.7 (4′-tpy*C*), 172.7 (CONH), 179.0 (CO_2H), 179.5 (*C*O-adamantane). MALDI−TOF MS for $C_{753}H_{880}Cl_{24}N_{100}O_{116}Ru_{12}$: calcd 15 240.71 ($M^+$), found 15 263 $(M + Na)^+$ as a broad signal with DHB matrix.

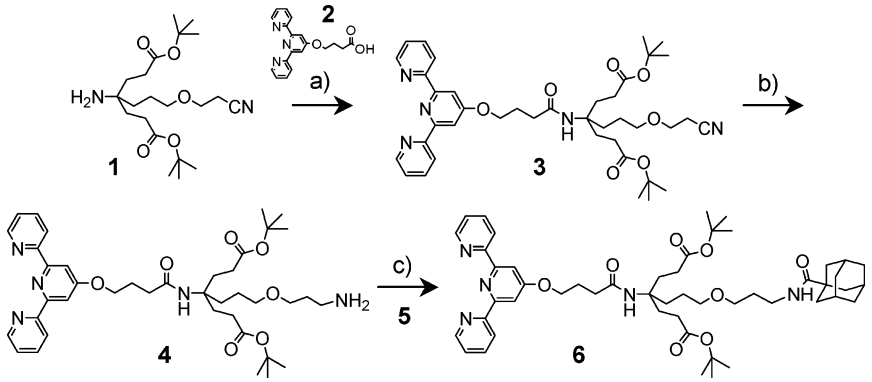
Neutral Dodecaruthenium(II) Metallodendrimer (15). Tetracosaacid **14** (100 mg, 6.6 μmol) was dissolved in a mixture of MeOH (10 mL) and aqueous KOH solution (10 mL, 1 N) and then stirred for 30 min at 25 °C. The solution was sealed into a membrane (cutoff mass = 3500) to dialyze for 24 h. The solution inside the membrane was concentrated in vacuo to dryness to afford (94%) the neutral metallodendrimer **15** as a red solid: 89 mg; mp >270 °C. ^{1}H NMR (CD_3OD) δ: 1.57−2.56 (br m, 452H, C*H*, CH_2), 3.25 (br t, 24H, CH_2NH), 3.45 (m, 48H, OCH_2), 3.62−3.98 (br m, 16H, $C^{4^\circ}CH_2O$, OC$H_2CH_2CH_2O$), 4.62 and 4.95 (br t, 48H, tpyOCH_2), 7.28 (br m, 48H, 5,5″-tpy*H*), 7.45 (br m, 48H, 6,6″-tpy*H*), 8.00 (m, 48H, 4,4″-tpy*H*), 8.69−8.89 (br m, 96H, 3′,5′-tpy*H*, 3,3″-tpy*H*). ^{13}C NMR (CD_3OD) δ: 24.6 (CH_2CH_2O), 25.4 (CH_2CH_2CONH), 28.9 (*C*H of adamantane), 29.0 (CH_2CH_2NHCO), 29.9 ($C^{4^\circ}CH_2CH_2CH_2O$), 32.7 (CH_2CO_2), 33.1 ($CH_2CH_2CO_2$), 37.2 ($CH_2CH_2CH_2O$, CH_2 of adamantane), 38.0 (C^{4° of adamantane), 39.7 (CH_2 of adamantane), 41.2 (CH_2NHCO), 45.8 (C^{4°), 59.0 (CONH*C*), 69.7, 72.2 (all CH_2O), 112.1 (3,3′-tpy*C*), 125.9 (3,3″-tpy*C*), 128.7 (5,5″-tpy*C*), 138.9 (4,4″-tpy*C*), 152.7 (6,6″-tpy*C*), 157.1, 157.3 (2,2″-tpy*C*), 159.1, 159.4 (2′,6′-tpy*C*), 167.2 (4′-tpy*C*), 173.1 (*C*ONH), 180.0 (*C*O-adamantane), 181.5 (CO_2^-). MALDI−TOF MS for $C_{753}H_{856}Cl_{24}N_{100}O_{116}Ru_{12}$: calcd 14 377.27 ($M^+$), found 14 400 $(M + Na)^+$ using DHB as the matrix.

Preparation of Dendrimer·β-Cyclodextrin Complexes. To a solution of β-CD (1 mL of 4 mM D_2O solution, 4 μmol) was added the dendrimer **11** (4.77 mg, 1 μmol), and then the mixture was ultrasonicated for 30 min, affording a clear red solution of the **11**·(β-CD)$_4$ complex. The complex **11**·(β-CD)$_8$ was prepared in a similar manner. Attempted preparation of **15**·(β-CD)$_{24}$ and **15**·(β-CD)$_{48}$ following the same stoichiometric route failed to give complete dissolution, but when excess of β-CD was added, a clear aqueous red solution was obtained.

Results and Discussion

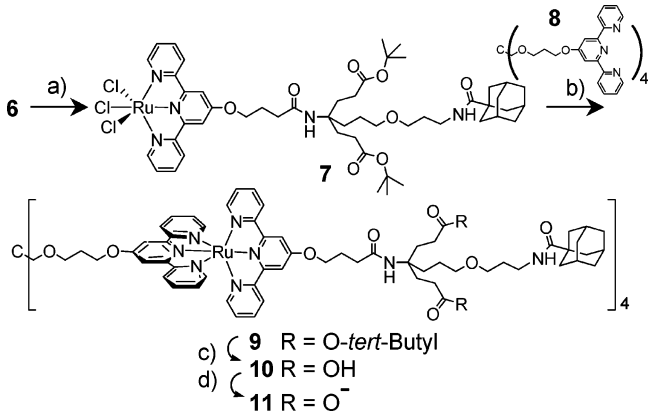
A. Syntheses of Metallodendrimers. An ideal starting material to prepare the appendage **7** would be a 1 → (2 + 1) branching monomer (**1**; Scheme 1) having both amino and nitrile functionalities, each of which can be selectively manipulated. Thus, amine **1** was reacted with 4-[4′-oxa-(2,2′;6′,2″-terpyridinyl)]butanoic acid (**2**) under a standard peptide coupling condition[77,78] to afford (67%) terpyridinyl derivative **3**. Amidation was confirmed by a chemical shift (^{13}C NMR) from 52.2 ($H_2N^{3^\circ}C$) to 57.9 ppm ($CONH^{3^\circ}C$) and appearance of two carbonyl peaks possessing an approximate 2:1 ratio as well as an ESI MS peak at 737.9 $(M + Na)^+$. Reduction of the nitrile group in **3** was accomplished (98%) by means of the Raney cobalt catalyst[75] under 40 atm of H_2 at 40 °C to afford the corresponding amine **4**, whose structure was confirmed by the chemical shift (^{13}C NMR) from 118.0 (*C*N) to 37.3 ppm (CH_2NH_2) and the ESI-MS peak at 720 $(M + H)^+$. The resulting amine **4** was capped by treatment with 1-(chlorocarbonyl)adamantane[76] (**5**) in the presence of Et_3N to give (84%) the desired terpyridine **6** possessing an adamantyl terminus. Structural confirmation of **6** was supported by a downfield shift (Δ = 3.2 ppm) for CH_2NH_2 to CH_2NHCO and a new peak at 178.0 ppm for the NH*C*O-adamantane connection as well as the mass peak (ESI-MS) at

Scheme 1[a]



[a] (a) **2**, DCC, HOBT, DMF, 25 °C, 24 h; (b) Raney Co, MeOH, 40 atm of H_2, 40 °C, ca. 6 h; (c) 1-(chlorocarbonyl)adamantane (**5**), dry THF, Et_3N, 25 °C, 6 h.

Scheme 2[a]



[a] (a) $RuCl_3 \cdot H_2O$, reflux 2 h; (b) tetraligand **8**, *N*-ethylmorpholine, MeOH, reflux, 2 h; (c) formic acid, 25 °C, 6 h, dialysis; (d) KOH, MeOH, 25 °C, 30 min, dialysis.

m/*z* 904.5 $(M + Na)^+$. This appendage **6** was activated by treatment with $RuCl_3 \cdot 3H_2O$ in boiling MeOH (Scheme 2) to furnish (76%) the paramagnetic ruthenium(III) complex **7**, which was used without further purification.

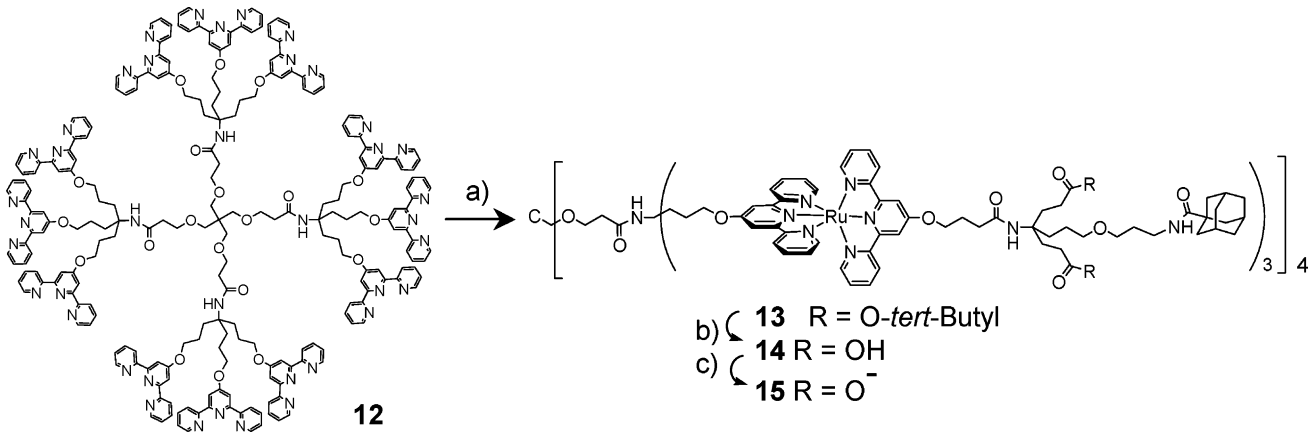
Assembly of two different metallodendrimers (**9** and **13**; Schemes 2 and 3, respectively) was realized via a reductive complexation of this metalloappendage **7** with two different cores **8** and **12**, respectively. Thus, treatment of the simplest core **8** with 4 equiv of metalloappendage **7** in the presence of 4-ethylmorpholine, as reducing agent, in boiling MeOH gave the tetrakis[−<Ru>−]-linked metallodendrimer **9**. Although initially appendage **7** possessed limited solubility in MeOH, it readily dissolved upon the addition of the reducing agent to afford the expected deep red [−<Ru>−] complex. After dialysis, pure metallodendrimer **9** was isolated, and its structure was confirmed by the molecular peak (MALDI−TOF) at *m*/*z* 5057.55. The significant downfield shift (^{13}C NMR) of all terpyridine carbons except 4′-tpy*C* and the appearance of two equal sets of peaks for the terpyridine carbons support the presence of inner and outer complexed terpyridines in the construct.

The *tert*-butyl groups were quantitatively removed by subjecting **9** with formic acid at 25 °C to afford acid metallodendrimer **10**, which was characterized by downfield shift (^{13}C NMR) of the carbonyl carbon ($\Delta = 5.7$ ppm), clearly indicative of the transformation to the acid. Formation of its neutral counterpart **11** was accomplished by treatment with a slight excess of KOH in a H_2O/MeOH solution, followed by dialysis for 24 h. The desired neutral complex **11** was characterized by a downfield shift (^{13}C NMR) of the carboxylate carbon ($\Delta = 2.2$ ppm), and the mass peak (MALDI−TOF) at *m*/*z* 4771.97 $[(M + H)^+]$ further confirmed its composition.

In the similar manner, core **12**[43] was reacted with 15 equiv of **7** in boiling MeOH in the presence of 4-ethylmorpholine as reducing agent to give after dialysis (98%) the red, crystalline dodecaruthenium metallodendrimer **13** (Scheme 3), whose structure was confirmed by the MALDI−TOF MS peak at 16 609 for $(M + Na)^+$ as well as the significant downfield shift (^{13}C NMR) of all terpyridine carbons except 4′-tpy*C*, which, however, demonstrated the in−out (166.4 and 166.8 ppm) orientation of the terpyridine moieties. Removal of *tert*-butyl groups from **13** by treatment with formic acid at 25 °C readily afforded (99%) the metallodendritic acid **14**, which showed a typical downfield shift (^{13}C NMR) of the carbonyl carbon ($\Delta = 5.5$ ppm), strongly indicating the transformation into the acid. Treatment of **14** with KOH in H_2O/MeOH solution afforded a hygroscopic red solid, which after dialysis gave (94%) the desired neutral complex **15**. Although peak broadening was observed for the terpyridine carbon signals in the ^{13}C NMR spectrum, there was only one downfield shift for the carbonyl carbon ($\Delta = 2.5$ ppm); this coupled with the observed mass peak (MALDI−TOF) at *m*/*z* 14 387.38 $[(M + Na)^+]$ supports the formation of the carboxylate anions.

B. Complexation of Terminal Adamantane Moieties with *β*-Cyclodextrin in an Aqueous Medium. The series of adamantyl-terminated dendrimers **9**−**11** was completely insoluble in water, but in the presence of a slight excess of *β*-cyclodextrin relative to the end groups, they were readily soluble in the aqueous environment, affording clear red solutions. These observations support the host−guest interactions of the hydrophobic termini within the *β*-cyclodextrin cavity. To verify this complexation, NMR spectroscopy studies were conducted with neutral dendrimer **11** and *β*-cyclodextrin (i.e., **16**; Scheme 4) in D_2O. The chemical shift of the H-3 proton (3.84 ppm, uncomplexed) located at the inner surface of the cyclodextrin cavity was monitored relative to the anomeric H-1 proton signal (4.94 ppm). The H-1 peak is insensitive to guest inclusion due to its remote location on the outer cavity surface.[79,80] As illustrated in Figure 1, prominent upfield shifts of H-3 ($\Delta\delta = -0.034$ and -0.067) were observed for the mixtures of **11**·$(\beta\text{-CD})_8$ and **11**·$(\beta\text{-CD})_4$, while the chemical shifts of the H-2 and H-4, positioned outside the

Scheme 3[a]



[a] (a) 12 equiv of **7**, *N*-ethylmorpholine, MeOH, reflux, 3 h; (b) formic acid, 25 °C, 12 h, dialysis; (c) KOH, MeOH, 25 °C, 30 min, dialysis.

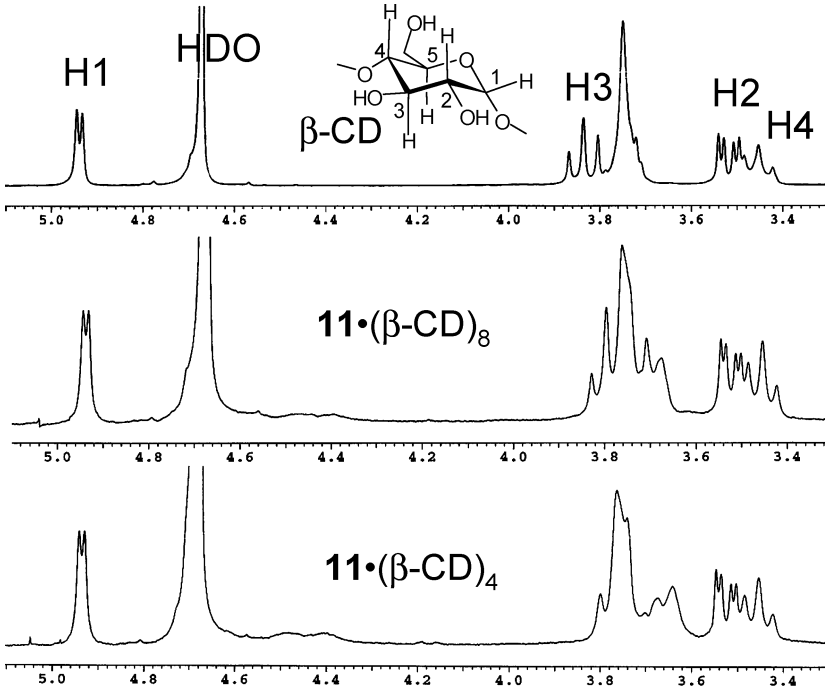
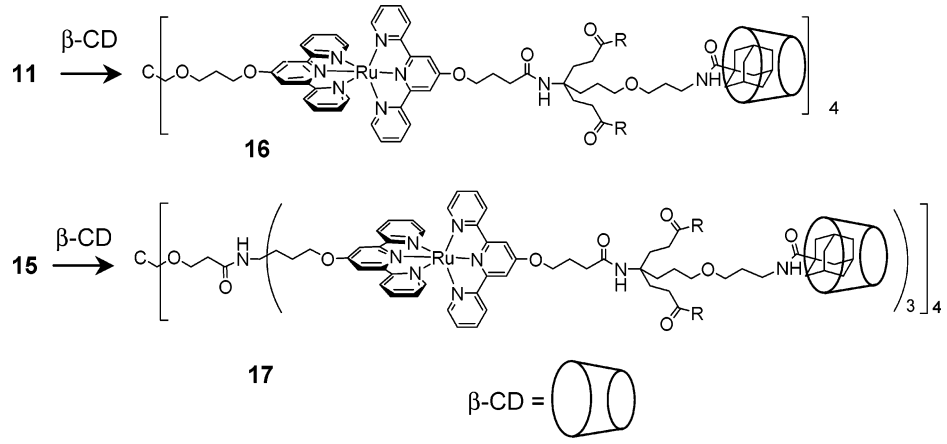


Figure 1. ^{1}H NMR spectra of (a) the uncomplexed *β*-CD, (b) *β*-CD in the **11**·(*β*-CD)$_8$ complex, and (c) *β*-CD in the **11**·(*β*-CD)$_4$ complex in D_2O at 25 °C.

Scheme 4. Formation of the Supramolecular *β*-Cyclodextrin−Dendrimer Complexes



β-CD cavity, were negligible ($\Delta\delta$ < 0.002). This observation implies that the terminal adamantane moieties have been encapsulated within the *β*-cyclodextrin cavity. A similar observation was shown for the **15**·(*β*-CD) complexes (i.e., **17**), but compared to **11**, dendrimer **15** was not completely soluble in the presence of a stoichio-

metric amount of β-CD; however, when the molar ratio of β-CD to **15** was increased to a 2−4 times excess, complete dissolution occurred.

Conclusions

Low generation metallodendrimers, assembled via terpyridine−Ru(II)−terpyridine connectivity, were prepared, characterized, and shown to be water insoluble. The branching motif used in their construction conveniently permitted the internal incorporation of counterbalancing carboxylate moieties; thus, in a quantitative two-step process, overall charge−neutral species were created. The terminal adamantane "guests" were subsequently encapsulated by β-cyclodextrin, resulting in the complete solubilization of these metallodendrimers in aqueous media.

Acknowledgment. We gratefully acknowledge financial support from the Office of Naval Research (N00014-01-1-0856), the Air Force Office of Scientific Research (F49620-02-1-0428), the National Science Foundation (DMR-0196231 and INT-0405242), the Korean Research Foundation (KRF-2003-042-C0006), and the Ohio Board of Reagents.

References and Notes

(1) Cuadrado, I.; Morán, M.; Losada, J.; Casado, C. M.; Pascual, C.; Alonso, B.; Lobete, F. In *Advances in Dendritic Macromolecules*; Newkome, G. R., Ed.; JAI: Greenwich, CT, 1996; pp 151−195.
(2) Gorman, C. *Adv. Mater.* **1998**, *10*, 295−309.
(3) Fischer, M.; Vögtle, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 885−905.
(4) Cuadrado, I.; Morán, M.; Casado, C. M.; Alonso, B.; Losada, J. *Coord. Chem. Rev.* **1999**, *193−195*, 395−445.
(5) Majoral, J.-P.; Caminade, A.-M. *Chem. Rev.* **1999**, *99*, 845−880.
(6) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689−1746.
(7) Stoddart, F. J.; Welton, T. *Polyhedron* **1999**, *18*, 3575−3591.
(8) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. In *Dendrimers and Dendrons: Concepts, Syntheses, Applications*; Wiley-VCH: Weinheim, Germany, 2001.
(9) Schubert, U. S.; Eschbaumer, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2892−2926.
(10) Tor, Y. *C. R. Chimie* **2003**, *6*, 755−766.
(11) Rossell, O.; Seco, M.; Angurell, I. *C. R. Chimie* **2003**, *6*, 803−817.
(12) Newkome, G. R.; Güther, R.; Cardullo, F. *Macromol. Symp.* **1995**, *98*, 467−474.
(13) Newkome, G. R. *Pure Appl. Chem.* **1998**, *70*, 2337−2343.
(14) Narayanan, V. V.; Newkome, G. R. *Top. Curr. Chem.* **1998**, *197*, 19−77.
(15) Lehn, J.-M. *Polym. Int.* **2002**, *51*, 825−839.
(16) Crooks, R. M.; Ricco, A. J. *Acc. Chem. Res.* **1998**, *31*, 219−227.
(17) Goodson, T., III In *Dendrimers and Other Dendritic Polymers*; Fréchet, J. M. J., Tomalia, D. A., Eds.; John Wiley & Sons, Ltd.: West Sussex, UK, 2001; pp 515−545.
(18) Gorman, C. B. *C. R. Chimie* **2003**, *6*, 911−918.
(19) Denti, G.; Campagna, S.; Sabatino, L.; Serroni, S.; Ciano, M.; Balzani, V. In *Photochemistry, Conversion and Storage of Solar Energy*; Pelizzetti, E., Schiavello, M., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991; pp 27−45.
(20) Venturi, M.; Serroni, S.; Juris, A.; Campagna, S.; Balzani, V. *Top. Curr. Chem.* **1998**, *197*, 193−228.
(21) Casado, C. M.; Cuadrado, I.; Morán, M.; Alonso, B.; Garcia, B.; González, B.; Losada, J. *Coord. Chem. Rev.* **1999**, *185−186*, 53−79.
(22) Venturi, M.; Credi, A.; Balzani, V. *Coord. Chem. Rev.* **1999**, *185−186*, 233−256.
(23) Cardona, C. M.; Mendoza, S.; Kaifer, A. E. *Chem. Soc. Rev.* **2000**, *29*, 37−42.
(24) Devadoss, C. In *Supramolecular Photosensitive and Electroactive Materials*; Nalwa, H. S., Ed.; Academic Press: New York, 2001; pp 793−858.
(25) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26−34.
(26) Balzani, V.; Ceroni, P.; Juris, A.; Venturi, M.; Campagna, S.; Puntoriero, F.; Serroni, S. *Coord. Chem. Rev.* **2001**, *219−221*, 545−572.
(27) Serroni, S.; Campagna, S.; Puntoriero, F.; Di Pietro, C.; McClenaghan, N. D.; Loiseau, F. *Chem. Soc. Rev.* **2001**, *30*, 367−375.
(28) Campagna, S.; Di Pietro, C.; Loiseau, F.; Maubert, B.; McClenaghan, N.; Passalacqua, R.; Puntoriero, F.; Ricevuto, V.; Serroni, S. *Coord. Chem. Rev.* **2002**, *229*, 67−74.
(29) Dirksen, A.; De Cola, L. *C. R. Chimie* **2003**, *6*, 873−882.
(30) Serroni, S.; Campagna, S.; Puntoriero, F.; Loiseau, F.; Ricevuto, V.; Passalacqua, R.; Galletta, M. *C. R. Chimie* **2003**, *6*, 883−893.
(31) Balzani, V.; Vögtle, F. *C. R. Chimie* **2003**, *6*, 867−872.
(32) Krause, W.; Hackmann-Schlichter, N.; Maier, F. K.; Müller, R. *Top. Curr. Chem.* **2000**, 261−308.
(33) Wiener, E. C.; Narayanan, V. V. In *Advances in Dendritic Macromolecules*; Newkome, G. R., Ed.; Elsevier Science Ltd.: Kidlington, Oxford, UK, 2002; pp 129−247.
(34) Reetz, M. T. *J. Heterocycl. Chem.* **1998**, *35*, 1065−1073.
(35) Hearshaw, M. A.; Hutton, A. T.; Moss, J. R.; Naidoo, K. J. In *Advances in Dendritic Macromolecules*; Newkome, G. R., Ed.; JAI Press: Stamford, CT, 1999; pp 1−60.
(36) Astruc, D.; Blais, J.-C.; Cloutet, E.; Djakovitch, L.; Rigaut, S.; Ruiz, J.; Sartor, V.; Valério, C. *Top. Curr. Chem.* **2000**, *210*, 229−259.
(37) Crooks, R. M.; Zhao, M.; Sun, L.; Chechik, V.; Yeung, L. K. *Acc. Chem. Res.* **2001**, *34*, 181−190.
(38) Kleij, A. W.; Ford, A.; Jastrzebski, J. T. B. H.; van Koten, G. In *Dendrimers and Other Dendritic Polymers*; Fréchet, J. M. J., Tomalia, D. A., Eds.; John Wiley & Sons, Ltd.: West Sussex, UK, 2001; pp 485−514.
(39) Oosterom, G. E.; Reek, J. N. H.; Kamer, P. C. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1828−1849.
(40) Astruc, D.; Chardac, F. *Chem. Rev.* **2001**, *101*, 2991−3023.
(41) Reek, J. N. H.; de Groot, D.; Oosterom, G. E.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Rev. Mol. Biotech.* **2002**, *90*, 159−180.
(42) Rodrígues, G.; Lutz, M.; Spek, A. L.; van Koten, G. *Chem.−Eur. J.* **2002**, *8*, 46−57.
(43) Newkome, G. R.; Cardullo, F.; Constable, E. C.; Moorefield, C. N.; Thompson, A. M. W. C. *J. Chem. Soc., Chem. Commun.* **1993**, 925−927.
(44) Newkome, G. R.; He, E. *J. Mater. Chem.* **1997**, *7*, 1237−1244.
(45) Newkome, G. R.; He, E.; Godínez, L. A.; Baker, G. R. *Chem. Commun.* **1999**, 27−28.
(46) Newkome, G. R.; Patri, A. K.; Godínez, L. A. *Chem.−Eur. J.* **1999**, *5*, 1445−1451.
(47) Newkome, G. R.; He, E.; Godínez, L. A.; Baker, G. R. *J. Am. Chem. Soc.* **2000**, *122*, 9993−10006.
(48) Newkome, G. R.; Yoo, K. S.; Moorefield, C. N. *Chem. Commun.* **2002**, 2164−2165.
(49) Newkome, G. R.; Yoo, K. S.; Kim, H. J.; Moorefield, C. N. *Chem.−Eur. J.* **2003**, *9*, 3367−3374.
(50) Newkome, G. R.; Yoo, K. S.; Moorefield, C. N. *Tetrahedron* **2003**, *59*, 3955−3964.
(51) Gohy, J.-F.; Lohmeijer, B. G. G.; Varshney, S. K.; Schubert, U. S. *Macromolecules* **2002**, *35*, 7427−7435.
(52) Gohy, J.-F.; Lohmeijer, B. G. G.; Schubert, U. S. *Macromolecules* **2002**, *35*, 4560−4563.
(53) Gohy, J.-F.; Lohmeijer, B. G. G.; Schubert, U. S. *Macromol. Rapid Commun.* **2002**, *23*, 555−560.
(54) Gohy, J.-F.; Lohmeijer, B. G. G.; Varshney, S. K.; Déchamps, B.; Leroy, E.; Boileau, S.; Schubert, U. S. *Macromolecules* **2002**, *35*, 9748−9755.
(55) Heller, M.; Schubert, U. S. *Macromol. Rapid Commun.* **2001**, *22*, 1358−1363.
(56) Heller, M.; Schubert, U. S. *Macromol. Rapid Commun.* **2002**, *23*, 411−415.
(57) Hofmeier, H.; Schubert, U. S. *Macromol. Chem. Phys.* **2003**, *204*, 1391−1397.
(58) Holder, E.; Meier, M. A. R.; Marin, V.; Schubert, U. S. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3954−3964.
(59) Lohmeijer, B. G. G.; Schubert, U. S. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 1413−1427.
(60) Lohmeijer, B. G. G.; Schubert, U. S. *Angew. Chem., Int. Ed.* **2002**, *41*, 3825−3829.

(61) Lohmeijer, B. G. G.; Schubert, U. S. *Macromol. Chem. Phys.* **2003**, *204*, 1072−1078.
(62) Meier, M. A. R.; Lohmeijer, B. G. G.; Schubert, U. S. *Macromol. Rapid Commun.* **2003**, *24*, 852−857.
(63) Schmatloch, S.; González, M. F.; Schubert, U. S. *Macromol. Rapid Commun.* **2002**, *23*, 957−961.
(64) Schubert, U. S.; Hien, O.; Eschbaumer, C. *Macromol. Rapid Commun.* **2000**, *21*, 1156−1161.
(65) Schubert, U. S.; Hofmeier, H. *Macromol. Rapid Commun.* **2002**, *23*, 561−566.
(66) Fulton, D. A.; Stoddart, J. F. *Bioconjug. Chem.* **2001**, *12*, 655−672.
(67) Harada, A. *Acc. Chem. Res.* **2001**, *34*, 456−464.
(68) Godínez, L. A.; Schwartz, L.; Criss, C. M.; Kaifer, A. E. *J. Phys. Chem. B* **1997**, *101*, 3376−3380.
(69) Newkome, G. R.; Godínez, L. A.; Moorefield, C. N. *Chem. Commun.* **1998**, 1821−1822.
(70) González, B.; Casado, C. M.; Alonso, B.; Cuadrado, I.; Morán, M.; Wang, Y.; Kaifer, A. E. *Chem. Commun.* **1998**, 2569−2570.
(71) Liu, Y.; Zhang, H.-Y.; Zhao, Y.-L.; Wu, X. *Macromolecules* **2002**, *35*, 9934−9938.
(72) Michels, J. J.; Huskens, J.; Reinhoudt, D. N. *J. Chem. Soc., Perkin Trans. 2* **2002**, 102−105.
(73) Newkome, G. R.; Kim, H. J.; Moorefield, C. N.; Maddi, H.; Yoo, K.-S. *Macromolecules* **2003**, *36*, 4345−4354.
(74) Newkome, G. R.; Lin, X. *Macromolecules* **1991**, *24*, 1443−1444.
(75) de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1308−1311.
(76) Purchased from Aldrich (11,772−2; mp 51−54 °C; corrosive and lachrymator).
(77) Klausner, Y. S.; Bodansky, M. *Synthesis* **1972**, 453−463.
(78) Han, S.-Y.; Kim, Y.-A. *Tetrahedron* **2004**, *60*, 2447−2467.
(79) Schneider, H.-J.; Hacket, F.; Rüdiger, V. *Chem. Rev.* **1998**, *98*, 1755−1785.
(80) Rekharsky, M. V.; Goldberg, R. N.; Schwarz, F. P.; Tewari, Y. B.; Ross, P. D.; Yamashoji, Y.; Inoue, Y. *J. Am. Chem. Soc.* **1995**, *117*, 8830−8840.

MA048996B