Electroactive Metallomacromolecules via Tetrabis(2,2′:6′,2″-terpyridine)ruthenium(II) Complexes: Dendritic Nanonetworks toward Constitutional Isomers and Neutral Species without External Counterions

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Abstract: The concept of dendritic networks via four bis(2,2′:6′,2″-terpyridine)ruthenium(II) connectivities was utilized to create "dendritic methane"-type metallomacromolecules. In addition, two structurally isomeric metallodendrimers (**16** and **17**) were designed, synthesized, and characterized. These two isomers were spectrally alike and displayed very similar physical and chemical properties; however, the internal density and void regions of these molecules were differentiated by cyclic voltammetry. The effects of the bulkiness of internal and external dendritic branches on the terpyridine−ruthenium complexes are described. A similar synthetic strategy allowed the preparation of two generations of neutral metallomacromolecules (**33** and **36**) possessing no external counterions. The benefits of these internally charge-balanced, neutral species are described, and the effects of increasing dendritic branching on their electrochemical behavior are detailed.

Introduction

Various routes for the construction of metallo-macromolecules have been widely investigated[1−11] due to their purported or envisioned magnetic, electronic, photooptical, or catalytic properties. An important feature of many of the synthetic strategies is the use of branched monomers[12] for the construction of dendritic architectures,[13,14] which provide the inherent synthetic control to afford predetermined structures, incorporating the desired utilitarian subunits into the superstructure. The assembly of diverse dendritic subunits led to the creation of a series of "dendritic networks",[15−20] which can, at least structurally, mimic molecular assemblies but on the nanoscopic scale. This type of modular chemistry, at the same time, provides the possibility of discovering new materials possessing utilitarian applications.

Discrete constitutional (or structural) isomers are common in small molecules, but are not seen in highly branched macromolecules (nanoscopic regime) or polymers, although recently, Stang's metallacycles have been demonstrated[21] to possess diastereomeric properties. The first criterion for being constitutional isomers is that the related molecules need to possess a single molecular weight and composition. Dendrimers, which are constructed via stepwise syntheses, should have a single molecular weight, if no defects are present. In contrast, hyperbranched macromolecules and regular polymers are generally synthesized via a one-pot reaction and are polydisperse, thus displaying a molecular weight distribution. Even if structural isomers may be present in the bulk materials, there are yet no known methods to isolate two isomeric hyperbranched macromolecules or polymers in pure, defect-free form from the reaction mixtures. On the other hand, since dendrimers possess precise molecular weights, access to their pure isomeric forms should be possible.

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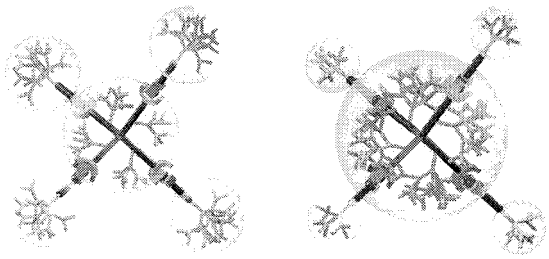
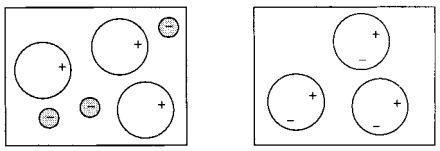


16 **17**

Figure 1. Idealized representation of two isomeric metallodendrimers illustrating the concept of a "dendritic network" based on a "methane" architecture.

The strategy for the construction of isomeric macromolecules is based on simple organic molecular models and supramolecular dendritic networks. The emergence of supramolecular chemistry—"chemistry beyond molecules," as defined by Lehn[22,23]—has led dendrimer chemistry into a new era. Many suprasupermolecular assemblies,[3] such as rosettes of metallodendrimers,[24−26] double-[27] and triple-helical[28] metal complexes, racks, ladders, and grids of metal complex arrays,[29−31] are in fact different types of molecular networks formed by using either metal−ligand coordination bonding or *H*-bonding. Common aspects of various networks include self-assembly, geometric compatibility of components, and the incorporation of redundant atomic motifs. Combining these parameters with related terpyr−Ru−terpyr (depicted as [−⟨*Ru*⟩−])-based chemistries developed in our laboratories, "dendritic methane" topologies (a 1 → 4 nanoscopic dendritic network via metal complexation) can be envisioned (see Figure 1). Essentially, the central dendritic core can be viewed (for descriptive purposes only) as a nanoscale "carbon" atom, and the appendage dendrimers can be considered as nanoscale "hydrogen" atoms. The use of [−⟨*Ru*⟩−] connectivity capitalizes on the formation of four stable complexes connecting the dendritic core with four identical monomeric dendrons, which can be viewed as the bonding between the "C" and "H". The shape of "CH_4" is created through a suprasupermolecular network in nanoscopic scale. In the quest for new procedures toward tailor-made supramolecular dendritic assemblies, the two new isomeric metallomacromolecules **16** and **17** are created (Figure 1).

Additional considerations concerning metallomacromolecules[3] include counterion associations, which traditionally have been limited to the normal series of external counterions, such as Cl^-, BF_4^-, and PF_6^-. Construction of metallodendrimers without external counterions not only provides additional synthetic challenges but also provides a better understanding of these materials. Some interesting questions can be answered by the construction of a series of related neutral metallodendrimers, for example: whether they will have less ionic character because of their zwiterionic behavior than those with typical external counterions (Figure 2); whether the physical, chemical, and electrochemical properties of these materials will be different when compared to our previous metallodendrimers; whether their solubility characteristics would change; whether the counterions would be conveniently interchangeable; whether they would be more volatile, thus aiding in mass spectrometric characterization.



Metallodendrimers in association with their counterion in solutions

Neutral Metallodendrimers Unimolecular behavior in solutions

Figure 2. Neutral metallodendrimers vs metallodendrimers with counterions.

Our approach to the construction of such a neutral metallodendrimer takes advantage of a supramolecular dendritic network concept utilizing four [−⟨*Ru*⟩−] linkages, which generate precise predetermined structures due to the discrete assembly process associated with the complexation sequence. On the basis of the structural analysis of its components, eight internal carboxylate ions are designed to compensate the charges of these four Ru(II) centers; the external counterions can be removed during the final step of the synthesis.

Experimental Section

Apparatus and Materials. Melting points are uncorrected and were measured on a Mel-Temp melting point apparatus. ^{1}H- and ^{13}C NMR spectra were recorded on a Bruker DPX 250 MHz spectrometer using $CDCl_3$ as solvent, unless otherwise indicated, with Me_4Si as the internal standard (0 ppm). Infrared spectra (IR) were recorded on a Mattson Genesis Fourier transform infrared spectrophotometer. UV−vis spectra were recorded on a HP8452A diode array spectrophotometer; molar absorptivities were determined via single-point measurements. M-H-W Laboratories, Phoenix, AZ, and Atlantic Microlab, Inc., Norcross, GA, performed elemental analyses. Electrospray mass spectra were obtained on a Bruker Esquire electrospray-ion trap mass spectrometer; constant microspray of the sample was made by loading the solutions (1.0×10^{-4} to 1.0×10^{-3} M in MeOH or MeCN) into a 250 μL syringe with a delivery rate of 70 μL/h. MALDI-TOF mass spectra were performed on a Bruker Reflex II mass spectrometer using a Nd:YAG laser (355 nm) in linear and reflectron modes. Samples were prepared by mixing 10 μL of a 70% MeOH/H_2O solution of sample (1.0×10^{-4} to 1.0×10^{-3} M) with 10 μL of a saturated solution of the indicated matrix; 1 μL of this solution was loaded onto the stainless steel sample plate and allowed to evaporate to dryness.

Cyclic voltammetry (CV) experiments on 1.0 mM solutions of the desired compound were conducted in dried and deoxygenated MeCN or DMF. CV experiments utilized 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 electrochemical experiments were conducted using a three electrode standard setup (Cypress Systems, Lawrence, Kansas), in which a glassy carbon disk electrode (1 mm diameter), a platinum wire, and a silver wire were properly fitted as the working, counter and pseudoreference electrodes, respectively. All

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the solutions [1.0 mM of the electroactive dendrimer in 0.1 M of Et_4NBF_4 in anhydrous MeCN or DMF] were carefully deoxygenated by bubbling dry nitrogen for at least 10 min. Since the potential was followed through a 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 compounds under study and therefore allowed its use as a reference against which the potentials reported in this work were measured.

All reagents where purchased from Aldrich Chemical Co. Column chromatography was performed using activated basic aluminum oxide (~150 mesh, Brockmann I; Aldrich Chemical Co.). All reactions were conducted under nitrogen atmosphere, unless obviously unnecessary or otherwise specified.

General Procedures. Method 1 (DCC coupling).[32] The reaction mixture was stirred for 24−48 h, after which the white precipitate was filtered. The filtrate was concentrated in vacuo affording a crude oil, which was dissolved in Et_2O (100 mL), washed sequentially with 10% aqueous Na_2CO_3 (2 × 80 mL) and brine (2 × 80 mL), dried ($MgSO_4$), and concentrated in vacuo to afford the crude product.

Method 2 (Pd/C Reduction). The slurry was heated to 50 °C with stirring, and then HCO_2NH_4 (2.0 g, excess) was added; after 30 min, the mixture was cooled to 25 °C and then filtered through Celite. The filtrate was concentrated in vacuo to give a solid, which was extracted by Et_2O or CH_2Cl_2 (2 × 100 mL). Solvent was evaporated in vacuo to give the crude solid.

Method 3 (Acyl Chloride Coupling). The solution was stirred for 12−24 h, and then the white precipitate was filtered and washed well with dry THF. The filtrate was collected, and the THF was removed to give a light yellow solid that was dissolved in $CHCl_3$ (200 mL). The solution was washed with 10% aqueous Na_2CO_3 (2 × 100 mL) and brine (3 × 100 mL). (It could take considerable time before the two layers separated.) The organic layer was dried ($MgSO_4$) and concentrated in vacuo to give a crude product.

Method 4 (Metal Complexation). The mixture was refluxed for 4−6 h until turning into a clear red solution. After cooling to 25 °C, excess saturated NH_4PF_6 in MeOH (10 mL) was added, and then the MeOH was removed. The solid was dissolved in a small amount of $CHCl_3$ and precipitated with Et_2O (120 mL). H_2O (100 mL) was added into the solid that was ground into powder form. The slurry was stirred for 1 h; the solid was collected and then dried in vacuo to afford the product.

Method 5 (Metal Complexation). The mixture was refluxed for 6 h during which the solution turned clear red. After cooling to 25 °C, the solution was filtered to remove any insoluble materials, the EtOH was removed from the filtrate to afford a red solid, which was dissolved in MeOH (4 mL), and then H_2O (50 mL) was added. The solution was sealed into a membrane (cutoff mass = 1000) to dialyze for 24 h. The solution was concentrated and dried in vacuo to afford the product.

Method 6 (Deprotection). After the reaction, the formic acid was removed in vacuo; a mixture of MeOH (5 mL) and H_2O (50 mL) was added to dissolve the resultant material. The solution was sealed into a membrane (cutoff mass = 3500) to dialyze for 24 h, and then the solution was concentrated and dried in vacuo to afford the product.

***N*-{Tris[(2-*tert*-butoxycarbonyl)ethyl]methyl-1-nitroisophthalamide Monocarboxylic Acid (3).** To a stirred solution of Behera's amine[33−35] **2** (2.72 g, 6.54 mmol) and Et_3N (1.65 g, 2.5 equiv) in dry THF (100 mL) at −5 °C, was added dropwise a solution of nitroisophthalic monoacyl chloride[36] (**1**, 1.50 g, 6.53 mmol) in THF (20 mL). After 12 h of agitation, the white precipitate was filtered and washed well with dry THF. The filtrate was collected, and the THF was removed in vacuo to give a white solid, which was dissolved in CH_2Cl_2 (150 mL). The solution was washed sequentially with 10% cold aqueous HCl (2 × 80 mL) and brine (2 × 80 mL), dried ($MgSO_4$), and concentrated in vacuo to give a crude product, which was dissolved in $CHCl_3$ (20 mL) and then slowly added into Et_2O (200 mL) to yield a white solid. When left overnight, half of the solvent evaporated; the resulting solid was collected and then dried in vacuo to afford (54%) **3**, as a white solid: 2.14 g; mp 168−170 °C ($CHCl_3$); ^{1}H NMR δ 1.43 (s, C*H*$_3$, 27H), 2.18 (t, J = 7.0 Hz, C*H*$_2$CO$_2$, 6H), 2.37 (t, J = 7.1 Hz, C*H*$_2$CH$_2$CO$_2$, 6H), 8.30 (s, N*H*, 1H), 8.93−9.00 (m, Ar*H*, 3H); ^{13}C NMR δ 28.2 (*C*H$_3$), 30.3, 30.6 (*C*H$_2$*C*H$_2$), 58.7 (4°*C*), 81.6 (*C*Me$_3$), 126.8, 127.3 (2, 6-Ar*C*), 132.0 (Ar*C*CO$_2$H), 134.3 (Ar*C*CONH), 137.5 (4-Ar*C*), 148.7 (Ar*C*NO$_2$), 163.5 (*C*ON), 167.6 (*C*O$_2$H), 173.9 (*C*O$_2$C); IR (KBr) 3381, 3090, 2981, 2937, 1726, 1600, 1540, 1463, 1342, 1156, 849, 723 cm^{-1}; ESI-MS *m*/*z* 631.7 (M + Na)$^+$. Anal. Calcd for $C_{30}H_{44}N_2O_{11}$: C, 59.20; H, 7.29; N, 4.60. Found: C, 59.17; H, 7.35; N, 4.40.

***N*-{Tris[(2-*tert*-butoxycarbonyl)ethyl]methyl}-*N*′-[4′-oxa-(2,2′:6′,2″-terpyridinyl)]nitroisophthalamide (5).** To a solution of acid **3** (307 mg, 504 μmol) in dry DMF (10 mL) were added dicyclohexylcarbodiimide (DCC; 104 mg, 504 μmol) and 1-hydroxybenzotriazole (1-HOBT; 68 mg, 504 μmol) at 25 °C. The mixture was stirred for 1 h, then 5-aminopentyl 4′-(2,2′: 6′,2″-terpyridinyl) ether[37] (**4**, 169 mg, 504 μmol) was added. Following Method 1, the crude product was column chromatographed eluting with 20% of EtOAc in CH_2Cl_2 to afford (84%) **5**, as a white solid: 392 mg [In larger-scale reactions, when the crude product was greater than 1.0 g, it was dissolved in Et_2O (20 mL), and pure **5** generally precipitated within 1 h.]; mp 133−136 °C (Et_2O); ^{1}H NMR δ 1.33 (s, C*H*$_3$, 27H), 1.38−1.84 (br m, C*H*$_2$C*H*$_2$C*H*$_2$, 6H), 2.05 (t, J = 7.1 Hz, C*H*$_2$CO$_2$, 6H), 2.23 (t, J = 7.2 Hz, C*H*$_2$CH$_2$CO$_2$, 6H), 3.42 (t, J = 6.0 Hz, C*H*$_2$NH, 2H), 4.12 (t, J = 6.1 Hz, OC*H*$_2$, 2H), 7.21 (m, 5,5″-tpy*H*, 2H), 7.75 (td, J = 7.2, 1.6 Hz, 4,4″-tpy*H*, 2H), 7.85 (s, 3′,5′-tpy*H*, 2H), 7.89 (s, N*H*, 1H), 7.92 (s, N*H*, 1H), 8.48 (d, J = 8.0 Hz, 3,3″-tpy*H*, 2H), 8.55 (d, J = 4.9 Hz, 6,6″-tpy*H*, 2H), 8.71 (m, Ar*H*, 3H); ^{13}C NMR δ 23.6 (*C*H$_2$CH$_2$CH$_2$-NH), 28.2 (*C*H$_3$), 28.7, 29.3 (*C*H$_2$CH$_2$*C*H$_2$CH$_2$NH), 30.1 (*C*H$_2$CO$_2$), 30.5 (*C*H$_2$CH$_2$CO$_2$), 40.5 (*C*H$_2$NH), 58.5 (4°*C*), 67.9 (OCH$_2$), 81.2 (*C*Me$_3$), 107.5 (5,5″-tpy*C*), 121.5 (4,4″-tpy*C*), 123.9 (3,″-tpy*C*), 124.3, 125.0, 131.1, 136.8, 136.9 (2,6,4,3,5-Ar*C*), 137.1 (3′,5′-tpy*C*), 148.6 (Ar*C*NO$_2$), 149.1 (6,6″-tpy*C*), 156.2 (2,2″-tpy*C*), 157.2 (2′,6′-tpy*C*), 163.5 (*C*ONHC), 164.6 (CH$_2$NH*C*O), 167.2 (4′-tpy*C*), 173.4 (*C*O$_2$); IR (KBr) 3339, 3081, 2982, 2938, 1727, 1672, 1655, 1600, 1583, 1556, 1462, 1363, 1154, 851, 791, 741 cm^{-1}; ESI-MS *m*/*z* 947.8 (M + Na)$^+$. Anal. Calcd for $C_{50}H_{64}N_6O_{11}$: C, 64.92; H, 6.97; N, 9.08. Found: C, 64.88; H, 6.87; N, 8.86.

First Tier Key Building Block (6). To a solution of **5** (1.50 g. 1.62 mmol) in MeOH (80 mL), was added 10% Pd/C (1.0 g). Following Method 2, the crude material was column chromatographed eluting with 20% CH_2Cl_2 in EtOAc to give (87%) **6**, as a white solid: 1.26 g; ^{1}H NMR δ 1.31 (s, C*H*$_3$, 27H), 1.38−1.74 (br m, C*H*$_2$C*H*$_2$C*H*$_2$, 6H), 1.99 (t, J = 7.4 Hz, C*H*$_2$CO$_2$, 6H), 2.17 (t, J = 7.4 Hz, C*H*$_2$CH$_2$CO$_2$, 6H), 3.31 (t, J = 5.9 Hz, C*H*$_2$NH, 2H), 4.06 (t, J = 6.1 Hz, OC*H*$_2$, 2H), 6.75 (s, NH, 1H), 6.97 (s, NH, 1H), 7.08−7.37 (m, 5,5″-tpy*H*, Ar*H*, 5H), 7.72 (td, J = 7.9, 1.6 Hz, 4,4″-tpy*H*, 2H), 7.87 (s, 3′,5′-tpy*H*, 2H), 8.48 (d, J = 8.0 Hz, 3,3″-tpy*H*, 2H), 8.56 (d, J = 4.9 Hz, 6,6″-tpy*H*, 2H); ^{13}C NMR δ 23.4 (*C*H$_2$CH$_2$CH$_2$NH), 28.0 (*C*H$_3$), 28.6, 29.3 (*C*H$_2$CH$_2$*C*H$_2$CH$_2$NH), 29.8, 30.0 (*C*H$_2$*C*H$_2$COO), 39.9 (*C*H$_2$NH), 57.9 (4°*C*), 67.9 (O*C*H$_2$), 80.7 (*C*Me$_3$), 107.3 (5,5″-tpy*C*), 114.0, 116.1, 116.4 (4,3,5-Ar*C*), 121.3 (4,4″-tpy*C*), 123.8 (3,3″-tpy*C*), 136.0, 136.2 (2,6-Ar*C*), 136.8 (3′,5′-tpy*C*), 147.5 (Ar*C*NH$_2$), 148.9 (6,6″-tpy*C*), 156.0 (2,2″-tpy*C*), 157.0 (2′,6′-tpy*C*), 166.5, 167.1, 167.3 (*C*ONHC, CH$_2$-NH*C*O, 4′-tpy*C*), 172.9 (*C*O$_2$); IR (KBr) 3443, 3361, 3251, 3060, 2976, 2938, 1727, 1644, 1594, 1567, 1528, 1363, 1149, 846, 791, 741 cm^{-1}; ESI-MS *m*/*z* 918.5 (M + Na)$^+$. Anal. Calcd for $C_{50}H_{66}N_6O_9$: C, 67.09; H, 7.42; N, 9.39. Found: C, 67.08; H, 7.62; N, 9.27.

Triacid (7). A solution of **5** (1.60 g, 1.73 mmol) in formic acid (50 mL) was stirred for 12 h at 25 °C, then most of the formic acid was removed in vacuo; H_2O (20 mL) and acetone (100 mL) were subsequently added to dissolve the residual oil. All the solvents were

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again removed in vacuo to ensure the removal of excess formic acid; this was repeated twice. The residue was dissolved in hot acetone (3 mL), and then the solution was carefully added into Et_2O (200 mL) with stirring to afford a white precipitate, which was filtered and dried in vacuo to give (95%) **7**, as a white solid: 1.25 g; mp 166−168 °C; ^{1}H NMR (DMSO-d_6) δ 1.40−1.60 [br m, (CH_2)$_3$, 6H], 2.05−2.20 (br m, CH_2CH_2CO$_2$H, 12H), 3.34 (t, J = 6.4 Hz, CH_2NH, 2H), 4.17 (t, J = 6.1 Hz, OCH_2, 2H), 7.44 (m, 5,5″-tpy*H*, 2H), 7.89−8.06 (br m, N*H*, 4,4″,3′,5′-tpy*H*, 6H), 8.54 (d, J = 7.8 Hz, 3,3″-tpy*H*, 2H), 8.65 (d, J = 5.0 Hz, 6,6″-tpy*H*, 2H), 8.76−8.98 (m, Ar*H*, 3H); ^{13}C NMR (DMSO-d_6) δ 23.1 (*C*H$_2$CH$_2$CH$_2$NH), 28.3, 28.4, (*C*H$_2$*C*H$_2$COOH), 28.8, 29.1 (*C*H$_2$CH$_2$*C*H$_2$CH$_2$NH), 40.5 (*C*H$_2$NH), 58.1 (4°*C*), 67.9 (O*C*H$_2$), 106.8 (5,5″-tpy*C*), 121.0 (4,4″-tpy*C*), 124.2 (d, 2,6-Ar*C*), 124.5 (3,3″-tpy*C*), 132.6, 136.1, 137.1 (4,3,5-Ar*C*), 137.3 (3′,5′-tpy*C*), 147.7 (Ar*C*NO$_2$), 149.2 (6,6″-tpy*C*), 155.0 (2,2″-tpy*C*), 156.7 (2′,6′-tpy*C*), 163.8 (*C*ONHC), 164.1 (CH$_2$NH*C*O), 166.8 (4′-tpy*C*), 174.6 (*C*O$_2$); IR (KBr) 3355, 3085, 2942, 1734, 1718, 1652, 1552, 1462, 1205, 792 cm^{-1}; ESI-MS m/z 757.8 (M + H)$^+$. Anal. Calcd for $C_{38}H_{40}N_6O_{11}$: C, 60.31; H, 5.33; N, 11.11. Found: C, 60.47; H, 5.37; N, 11.25.

Nitro Nonaester (8). To a solution of triacid **7** (800 mg, 1.06 mmol) in dry DMF (10 mL) were added DCC (654 mg, 3.17 mmol) and 1-HOBT (428 mg, 3.17 mmol) at 25 °C. The mixture was stirred for 1 h, and then amine **2** (1.318 g, 3.17 mmol) was added. Following Method 1, the crude product was column chromatographed eluting with a solution of EtOAc (70%) in hexane to afford (90%) **8**, as a white solid: 1.86 g; ^{1}H NMR δ 1.33 (br s, CH_3, 81H), 1.38−2.15 (br m, CH_2CH_2CONH, CH_2CH_2CO$_2$, CH_2CH_2CH_2, 54H), 3.46 (br s, CH_2NH, 2H), 4.16 (t, J = 6.0 Hz, OCH_2, 2H), 7.21 (m, 5,5″-tpy*H*, 2H), 7.75 (td, J = 7.2, 1.6 Hz, 4,4″-tpy*H*, 2H), 7.91 (br m, N*H*, 3′,5′-tpy*H*, 4H), 8.51 (d, J = 8.2 Hz, 3,3″-tpy*H*, 2H), 8.58 (d, J = 4.7 Hz, 6,6″-tpy*H*, 2H), 8.83−8.98 (m, Ar*H*, 3H); ^{13}C NMR δ 23.4 (*C*H$_2$CH$_2$CH$_2$NH), 28.0 (*C*H$_3$), 28.3, 28.7 (*C*H$_2$CH$_2$*C*H$_2$CH$_2$NH), 29.5,29.8 (*C*H$_2$*C*H$_2$CO$_2$), 31.8, 32.0 (*C*H$_2$*C*H$_2$CONH), 40.3 (*C*H$_2$NH), 57.5 (3 $^{4^{\circ}}$*C*), 58.6 (4°*C*), 67.9 (O*C*H$_2$), 80.5 (*C*Me$_3$), 107.3 (5,5″-tpy*C*), 121.2 (4,4″-tpy*C*), 123.7 (3,3″-tpy*C*), 124.4, 125.7, 130.3, 136.5, 136.6 (2,6,4,3,5-Ar*C*), 136.7 (3′,5′-tpy*C*), 148.7 (Ar*C*NO$_2$), 148.9 (6,6″-tpy*C*), 156.0 (2,2″-tpy*C*), 157.0 (2′,6′-tpy*C*), 163.6 (*C*ONHC), 164.5 (CH$_2$NH*C*O), 167.1 (4′-tpy*C*), 172.7 (*C*O$_2$), 173.0 (CH$_2$*C*ONH); IR (KBr) 3365, 3058, 2976, 2937, 1726, 1655, 1556, 1452, 1370, 1151, 850 cm^{-1}; ESI-MS m/z 1973.6 (M + Na)$^+$. Anal. Calcd for $C_{104}H_{157}N_9O_{26}$: C, 64.07; H, 8.12; N, 6.47. Found: C, 63.88; H, 8.10; N, 6.28.

Second Tier Key Building Block (9). To a solution of **8** (2.45 g. 1.26 mmol) in MeOH (80 mL), was added 10% Pd/C (1.0 g). Following Method 2, the crude material was column chromatographed eluting with a solution of MeOH (5%) and hexane (20%) in EtOAc to give (83%) **9**, as a white solid: 2.01 g; ^{1}H NMR δ 1.33−1.40 (br s, CH_3, 81H), 1.40−2.15 (br m, CH_2CH_2CONH, CH_2CH_2CO$_2$, CH_2CH_2CH_2, 54H), 3.42 (br s, CH_2NH, 2H), 4.16 (t, J = 6.0 Hz, OCH_2, 2H), 6.25 (s, NH_2, 2H), 7.21−7.52 (m, NH, Ar*H*, 5,5″-tpy*H*, 7H), 7.74 (td, J = 7.9, 1.4 Hz, 4,4″-tpy*H*, 2H), 7.91 (s, 3′,5′-tpy*H*, 2H), 8.51 (d, J = 7.9 Hz, 3,3″-tpy*H*, 2H), 8.58 (d, J = 4.0 Hz, 6,6″-tpy*H*, 2H); ^{13}C NMR δ 23.4 (*C*H$_2$CH$_2$CH$_2$NH), 28.0 (*C*H$_3$), 28.6, 29.0 (*C*H$_2$CH$_2$CH$_2$CH$_2$NH), 29.5,29.7 (*C*H$_2$CH$_2$CO$_2$), 31.8, 32.3 (*C*H$_2$*C*H$_2$CONH), 39.9 (*C*H$_2$NH), 57.3 (3 $^{4^{\circ}}$*C*), 58.2 (4°*C*), 67.9 (O*C*H$_2$), 80.5 (*C*Me$_3$), 107.3 (5,5″-tpy*C*), 113.8, 116.1, 117.0 (4,3,5-Ar*C*), 121.2 (4,4″-tpy*C*), 123.7 (3,3″-tpy*C*), 135.5, 135.8 (2,6-Ar*C*), 136.6 (3′,5′-tpy*C*), 147.6 (Ar*C*NH$_2$), 148.9 (6,6″-tpy*C*), 156.0 (2,2″-tpy*C*), 156.9 (2′,6′-tpy*C*), 166.7, 167.1, 167.3 (*C*ONHC, CH$_2$NH*C*O, 4′-tpy*C*), 172.6 (*C*OO), 173.0 (CH$_2$*C*ONH); IR (KBr) 3359, 3063, 2976, 2947, 1732, 1655, 1567, 1452, 1370, 1151, 848, 790 cm^{-1}; ESI-MS m/z 1942.8 (M + Na)$^+$. Anal. Calcd for $C_{104}H_{159}N_9O_{24}$; C, 65.08; H, 8.35; N, 6.57. Found: C, 64.93; H, 8.43; N, 6.40.

First Tier Dendritic Core (11). To a stirred solution of first tier building block **6** (800 mg, 894 μmol) and Et_3N (135 mg, 1.34 mmol) in dry THF (40 mL) at −5 °C, was added dropwise a solution of tetraacid chloride[38] **10** (111 mg, 223 μmol) in THF (10 mL). Following Method 3, crude material was column chromatographed eluting with a solution of $CHCl_3$ (30%) in EtOAc, followed by a mixture of MeOH (5%) in EtOAc to afford (72%) the pure **11**, as a light yellow solid: 631 mg; ^{1}H NMR δ 1.30 (br s, CH_3, 108H), 1.38−1.72 (br m, CH_2CH_2CH_2, 24H), 2.00−2.20 (br m, CH_2CH_2CO$_2$, 48H), 2.43 (br s, CH_2CONH, 8H), 3.32 (br m, CH_2CHCONH, CONHCH_2, 16H), 3.55−4.10 (br m, OCH_2, 16H), 6.84 (s, N*H*, 4H), 7.21 (m, 5,5″py*H*, 8H), 7.30 (s, N*H*, 4H) 7.68−8.06 (br m, Ar*H*, 4,4″,3′,5′-tpy*H*, 28H), 8.45 (d, J = 8.0 Hz, 3,3″-tpy*H*, 8H), 8.55 (d, J = 4.5 Hz, 6,6″-tpy*H*, 8H), 9.16 (s, N*H*, 4H); ^{13}C NMR δ 23.5 (*C*H$_2$CH$_2$CH$_2$NH), 28.0 (*C*H$_3$), 28.6, 29.2 (*C*H$_2$CH$_2$*C*H$_2$CH$_2$NH), 29.7,29.8 (*C*H$_2$*C*H$_2$CO$_2$), 37.9 (*C*H$_2$-CONH), 40.1 (CONH*C*H$_2$), 45.3 (4°*C*), 58.1 (4°*C*), 67.5, 67.9, 70.3 (all O*C*H$_2$), 80.6 (*C*Me$_3$), 107.4 (5,5″-tpy*C*), 120.4 (4-Ar*C*), 121.3 (4,4″-tpy*C*), 123.8 (3,3″-tpy*C*), 135.7, 136.1, (2,3,5,6-Ar*C*), 136.8 (3′,5′-tpy*C*), 139.2 (Ar*C*NHCO), 148.9 (6,6″-tpy*C*), 156.0 (2,2″-tpy*C*), 157.0 (2′,6′-tpy*C*), 166.1, 166.8 (*C*ONH, CH$_2$NH*C*O), 167.1 (4′-tpy*C*), 170.8 (OCH$_2$CH$_2$*C*ONH), 172.8 (*C*O$_2$); IR (KBr) 3328, 3064, 2976, 2938, 2872, 1727, 1661, 1561, 1440, 1367, 1154, 840, 791, 741 cm^{-1}; ESI-MS m/z 1988.7 (M + 2Na)$^{2+}$. Anal. Calcd for $C_{217}H_{284}N_{24}O_{44}$: C, 66.27; H, 7.28; N, 8.54. Found: C, 65.93; H, 7.40; N, 8.40.

Second Tier Dendritic Core (12). To a stirred solution of the second tier building block **9** (1.80 g, 938 μmol) and Et_3N (142 mg, 1.41 mmol, 6 equiv.) in dry THF (40 mL) at −5 °C, was added dropwise a solution of tetraacid chloride **10** (117 mg, 234 μmol) in THF (10 mL). Following Method 3, the crude material was column chromatographed eluting with a solution of hexane (25%) in EtOAc, followed by a solution of MeOH (5%) in EtOAc to afford (24%) the pure **12**, as a light yellow solid: 452 mg; ^{1}H NMR δ 1.30 (br s, CH_3, 324H), 1.38−2.50 (br m, CH_2, 224H), 3.32 (br m, CH_2O, CONHCH_2, 16H), 3.55−4.10 (br m, OCH_2, 16H), 6.94 (s, N*H*, 4H), 7.20 (m, 5,5″-tpy*H*, 8H), 7.30 (s, N*H*, 4H) 7.68−8.06 (br m, Ar*H*, 4,4″,3′,5′-tpy*H*, 28H), 8.45 (d, J = 8.0 Hz, 3,3″-tpy*H*, 8H), 8.60 (d, J = 4.2 Hz, 6,6″-tpy*H*, 8H), 9.16 (s, N*H*, 4H); ^{13}C NMR δ 23.5 (*C*H$_2$CH$_2$CH$_2$NH), 28.0 (*C*H$_3$), 28.3, 28.8 (*C*H$_2$-CH$_2$*C*H$_2$CH$_2$NH), 29.8,29.9 (*C*H$_2$*C*H$_2$CO$_2$), 33.2, 33.2 (*C*H$_2$*C*H$_2$CONH), 38.6 (*C*H$_2$CONH), 40.2 (CONH*C*H$_2$), 45.6 (4°*C*), 57.3 (12 4°*C*), 58.6 (4 4°*C*), 68.0, 68.1, 69.7 (all O*C*H$_2$), 80.3 (*C*Me$_3$), 107.4 (5,5″-tpy*C*), 120.4 (4-Ar*C*), 121.2 (4,4″-tpy*C*), 123.7 (3,3″-tpy*C*), 135.8, 135.9, (2,3,5,6-Ar*C*), 136.6 (3′,5′-tpy*C*), 138.7 (Ar*C*NHCO), 148.9 (6,6″-tpy*C*), 156.1 (2,2″-tpy*C*), 156.9 (2′,6′-tpy*C*), 166.1, 166.5 (*C*ONH, CH$_2$-NH*C*O), 167.2 (4′-tpy*C*), 170.7 (OCH$_2$CH$_2$*C*ONH), 172.7 (*C*O$_2$), 173.0 (CH$_2$*C*ONH); IR (KBr) 3361, 3063, 2976, 2936, 1729, 1652, 1558, 1453, 1370, 1150, 847 cm^{-1}; MALDI-TOF-MS m/z 8075 (M + 2Na −H)$^+$, 2,5-dihyroxybenzoic acid (DHB) matrix. Anal. Calcd for $C_{433}H_{656}N_{36}O_{104}$: C, 64.77; H, 8.23; N, 6.28. Found: C, 64.93; H, 8.43; N, 6.40.

Dendritic Assembly (15). To a suspension of complex **13** (143 mg, 153 μmol) in MeOH (20 mL), were added the first tier dendritic core **11** (150 mg, 38.1 μmol) and 4-ethylmorpholine (4 drops). Following Method 4, complex **15** was isolated (97%) as a red solid: 311 mg; mp > 152 °C (dec); ^{1}H NMR (CD$_3$CN) δ 1.20−1.40 (br d, CH_3, 216H), 1.50−2.50 (br m, CH_2, 128H), 3.00−3.40 (br m, CH_2, 24H), 4.40−4.50 (br m, OCH_2, 32H), 6.39 (br s, N*H*, 4H), 7.00−8.70 (br m, N*H*, Ar*H*, tpy*H*, 104H); ^{13}C NMR (CD$_3$CN) δ 24.4 (*C*H$_2$CH$_2$CH$_2$NH), 25.3 (OCH$_2$*C*H$_2$CH$_2$CONH), 28.4 (*C*H$_3$), 28.6, 29.0 (*C*H$_2$CH$_2$*C*H$_2$CH$_2$NH), 30.8 (d, *C*H$_2$CH$_2$CO$_2$), 33.0 (OCH$_2$CH$_2$*C*H$_2$CONH), 37.9 (OCH$_2$*C*H$_2$-CONH), 40.2 (CONH*C*H$_2$), 45.2 (4°*C*), 58.8 (12 4°*C*), 59.6 (4 4°*C*), 66.0, 68.5, 70.7, 71.7 (all O*C*H$_2$), 81.2, 81.3 (all *C*Me$_3$), 112.6 (d, 5,5″-tpy*C*), 122.8 (4-Ar*C*), 125.8 (d, 4,4″-tpy*C*), 128.8 (d, 3,3″-tpy*C*), 136.7, 137.2 (2,3,5,6-Ar*C*), 139.1 (d, 3′,5′-tpy*C*), 140.9 (Ar*C*NHCO), 153.7 (d, 6,6″-tpy*C*), 157.7 (d, 2,2″-tpy*C*), 159.7 (d, 2′,6′-tpy*C*), 167.2 (d, 4′-tpy*C*), 67.2, 167.6 (*C*ONH, CH$_2$NH*C*O), 171.8 (OCH$_2$CH$_2$*C*ONH), 173.3 (OCH$_2$CH$_2$CH$_2$*C*ONH), 174.0 (d, *C*O$_2$); IR (KBr) 3428, 3081, 2976, 2938, 1721, 1650, 1617, 1540, 1457, 1369, 1154, 846, 791, 758; UV−vis λ_{max} 242 (ϵ = 2.74 × 10^5), 268 (2.37 × 10^5), 306 (2.32 × 10^5), 488 nm (6.67 × 10^4 dm^3 mol^{-1} cm^{-1}); MALDI-TOF-MS m/z 8283 (M − PF$_6$)$^+$, DHB matrix. Anal. Calcd for $C_{381}H_{508}F_{48}N_{40}O_{76}P_8Ru_4$: C, 54.29; H, 6.08; N, 6.65. Found: C, 54.34; H, 6.13; N, 6.79.

Isomeric Metallodendrimer (16). To a solution of complex **14** (200 mg, 102 μmol) in MeOH (30 mL), were added the first tier dendritic core **11** (100 mg, 25.4 μmol) and 4-ethylmorpholine (4 drops). Following Method 4, complex **16** was generated (93%) as a red solid: 296 mg; mp > 152 °C (dec); ^{1}H NMR (CD$_3$CN) due to peaks overlapping and broadening, the spectrum did not afford discernible data; ^{13}C NMR (CD$_3$CN) δ 23.2 (*C*H$_2$CH$_2$CH$_2$NH), 24.8 (OCH$_2$*C*H$_2$-

(38) Newkome, G. R.; Lin, X. *Macromolecules* **1991**, *24*, 1443−1444.

CH_2CONH), 28.1 (d, *C*H_3), 28.6, 29.0 (*C*H_2CH_2*C*H_2CH_2NH), 29.8 (d, 36CH_2*C*H_2CO_2), 31.5 (d, 12*C*$H_2CH_2CO_2$), 33.0 (OCH_2CH_2*C*H_2CONH), 34.7 (d, *C*H_2CH_2CONH), 37.8 (OCH_2CH_2CONH), 40.2 ($CONHCH_2$), 45.0 ($4^{\circ}C$), 57.7 (36 $4^{\circ}C$), 58.3, 58.4 (4 $4^{\circ}C$ and 12 $4^{\circ}C$), 66.0, 68.5, 69.3, 71.1 (all O*C*H_2), 80.6, 81.4 (all *C*Me_3), 111.2 (d, 5,5″-tpy*C*), 121.5 (4-Ar*C*), 124.6 (d, 4,4″-tpy*C*), 127.7 (d, 3,3″-tpy*C*), 136.1, 136.4, (2,3,5,6-Ar*C*), 137.9 (d, 3′,5′-tpy*C*), 138.8 (Ar*C*NHCO), 152.0 (d, 6,6″-tpy*C*), 156.0 (d, 2,2″-tpy*C*), 158.2 (d, 2′,6′-tpy*C*), 166.3 (d, 4′-tpy*C*), 166.4, 166.5 (*C*ONH, CH_2NHCO), 171.8 (OCH_2CH_2CONH), 172.4 (12CH_2CH_2*C*ONH), 172.8 (36 *C*O_2), 173.5 (12 CO_2); IR (KBr) 3411,-3075, 2982, 2938, 1732, 1655, 1611,1534, 1457,1363, 1154, 842 cm^{-1}; UV−vis λ_{max} 242 ($\epsilon = 2.54 \times 10^5$), 268 ($2.15 \times 10^5$), 306 ($2.15 \times 10^5$), 488 nm ($6.54 \times 10^4$ dm^3 mol^{-1} cm^{-1}); MALDI-TOF-MS *m*/*z* 12 369 ($M - PF_6$)$^+$, DHB matrix. Anal. Calcd for $C_{597}H_{880}F_{48}N_{52}O_{136}P_8Ru_4$: C, 57.25; H, 7.08; N, 5.81. Found: C, 56.86; H, 6.93; N, 5.42.

Isomeric Metallodendrimer (17). To a solution of complex **13** (84.3 mg, 89.7 μmol) in MeOH (30 mL), were added the second tier dendritic core **12** (180 mg, 22.4 μmol) and 4-ethylmorpholine (4 drops). Following Method 4, complex **17** was isolated (80%) as a red solid: 223 mg; mp > 152 °C (dec); ^{1}H NMR (CD_3CN) due to peaks overlapping and broadening, the spectrum did not afford discernible data; ^{13}C NMR (CD_3CN) δ 24.6 (*C*$H_2CH_2CH_2NH$), 25.2 (OCH_2*C*H_2-CH_2CONH), 28.7 (d, *C*H_3), 28.8, 29.0 (*C*H_2CH_2*C*H_2CH_2NH), 30.8 (d, all *C*H_2*C*H_2CO_2), 32.5 (d, CH_2CH_2CONH), 32.9 (OCH_2CH_2*C*H_2-CONH), 38.8 (OCH_2*C*H_2CONH), 41.2 ($CONHCH_2$), 45.2 ($4^{\circ}C$), 58.6 (36 $4^{\circ}C$), 58.9, 59.8 (4 $4^{\circ}C$ and 12 $4^{\circ}C$), 66.1, 68.7, 70.7, 71.4 (all O*C*H_2), 81.2, 81.3 (all *C*Me_3), 112.5 (d, 5,5″-tpy*C*), 122.3 (4-Ar*C*), 125.8 (d, 4,4″-tpy*C*), 128.8 (d, 3,3″-tpy*C*), 136.8, 137.6, (2,3,5,6-Ar*C*), 139.1 (d, 3′,5′-tpy*C*), 140.2 (Ar*C*NHCO), 153.8 (d, 6,6″-tpy*C*), 157.8 (d, 2,2″-tpy*C*), 159.7 (d, 2′,6′-tpy*C*), 167.2 (d, 4′-tpy*C*), 167.7, 168.3 (*C*ONH, CH_2NHCO), 172.1 (OCH_2CH_2CONH), 173.3 ($OCH_2CH_2CH_2CONH$), 173.9 (36 *C*O_2), 174.4 (12CO_2); IR (KBr) 3405,3074, 2980, 2936, 1734, 1652, 1558, 1156, 841 cm^{-1}; UV−vis λ_{max} 242 ($\epsilon = 2.82 \times 10^5$), 268 ($2.54 \times 10^5$), 306 ($2.58 \times 10^5$), 488 nm ($6.73 \times 10^4$ dm^3 mol^{-1} cm^{-1}); MALDI-TOF-MS *m*/*z* 12 372 ($M - PF_6$)$^+$, DHB matrix. Anal. Calcd for $C_{597}H_{880}F_{48}N_{52}O_{136}P_8Ru_4$: C, 57.25; H, 7.08; N, 5.81. Found: C, 57.02; H, 6.99; N, 5.75.

Di-*tert*-butyl 4-Nitro-4-methylheptanedicarboxylate (18). To a solution of *tert*-butyl acrylate (128.2 g, 1.00 mol) in liquid NH_3 (300 mL), was added $EtNO_2$ (75.07 g, 1.00 mol) at −78 °C slowly. The mixture was stirred overnight and allowed to warm to 25 °C. The resulting solid was further dried in vacuo to afford (95%) **18**, as a white solid: 314.8 g; mp 46−47 °C; ^{1}H NMR δ 1.36 (s, 18H), 1.51 (s, 3H), 2.00−2.45 (m, 8H); ^{13}C NMR δ 21.8 (*C*H_3), 28.1 (CMe_3), 30.2 (CH_2*C*H_2CO_2), 34.4 (*C*$H_2CH_2CO_2$), 81.1 (*C*Me_3), 89.9 (O_2N*C*), 171.3 (*C*O_2); IR (KBr) 3003, 2979, 2940, 1726, 1537, 1159 cm^{-1}; ESI-MS *m*/*z* 332.6 $(M + H)^+$. Anal. Calcd for $C_{16}H_{29}NO_6$: C, 57.99; H, 8.82; N, 4.23. Found C, 58.16; H, 8.59; N, 4.31.

Di-*tert*-butyl 4-Amino-4-methylheptanedicarboxylate (19). To a solution of **18** (30.0 g, 93.5 mmol) in absolute EtOH (250 mL) was added prepared Raney Nickel (20 g) catalyst. The reaction slurry was shaken in a sealed bottle under H_2 (60 psi) for 12 h at 25 °C, and then the black (pyrophoric) catalyst was filtered *with great caution*. The filtrate was collected, concentrated, and dried in vacuo to afford (96%) **19**, as a white oil: 26.2 g; ^{1}H NMR δ 1.10 (s, N*H*$_2$, 2H), 1.38 (s, C*H*$_3$, 3H), 1.52 (s, C*H*$_3$, 18H), 1.75 (t, $J = 7.1$ Hz, C*H*$_2$CO$_2$, 4H), 2.20 (t, $J = 7.1$ Hz, C*H*$_2$CH$_2$CO$_2$, 4H); ^{13}C NMR δ 27.3 (*C*H_3), 28.1 [C(*C*H_3)$_3$], 30.6 (CH_2*C*H_2CO_2), 37.5 (*C*$H_2CH_2CO_2$), 50.9 (H_2N*C*), 80.3 (*C*Me_3), 173.4 (*C*O_2); IR ($CHCl_3$) 3019, 2979, 2932, 1727, 1214, 1159 cm^{-1}; ESI-MS *m*/*z* 324.7 $(M + Na)^+$. Anal. Calcd for $C_{16}H_{31}NO_4$: C, 63.75; H, 10.37; N, 4.65. Found C, 63.84; H, 10.17; N, 4.77.

Monocarboxylic Acid (20). To a stirred solution of amine **19** (2.63 g, 8.71 mmol) and Et_3N (2.20 g, 21.8 mmol, 2.5 equiv) in dry THF (100 mL) at −5 °C, was added dropwise a solution of nitroisophthalic acid monoacyl chloride **1** (2.00 g, 8.71 mmol) in THF (50 mL). After the solution was stirred for 12 h, the white precipitate was filtered and washed well with dry THF. The filtrate was collected and the THF was removed in vacuo to give a white solid, which was dissolved in CH_2Cl_2 (200 mL). The solution was washed sequentially with 5% cold aq. HCl (2 × 100 mL), brine (2 × 150 mL), dried ($MgSO_4$), and concentrated in vacuo to give a crude product, which was dissolved in $CHCl_3$ (15 mL), then added into Et_2O (200 mL); the solution was allowed to stand for 36 h during which time half of the solvent evaporated. The precipitated solid was collected and then dried in vacuo to give (58%) **20**, as a white solid: 2.50 g; mp 164−166 °C; ^{1}H NMR δ 1.43 (br s, C*H*$_3$, 21H), 2.16 (t, $J = 7.0$ Hz, C*H*$_2$CO$_2$, 4H), 2.38 (t, $J = 7.1$ Hz, C*H*$_2$CH$_2$CO$_2$, 4H), 7.95 (s, N*H*, 1H), 8.80−8.99 (m, Ar*H*, 3H); ^{13}C NMR δ 23.5 (*C*H_3), 28.0 [C(*C*H_3)$_3$], 30.4 (CH_2*C*H_2CO_2), 33.4 (*C*$H_2CH_2CO_2$), 56.4 ($4^{\circ}C$), 81.4 (*C*Me_3), 126.1, 126.9, 132.8, 133.9, 137.3 (2,3,4,5,6-Ar*C*), 148.4 (Ar*C*NO_2), 164.0 (*C*ONH), 165.9 (*C*O_2H), 174.1 (*C*O_2); IR (KBr) 3405, 3090, 2980, 2940, 1734, 1710, 1671, 1545, 1467, 1167, 851, 734 cm^{-1}; ESI-MS *m*/*z* 517.7 $(M + Na)^+$. Anal. Calcd for $C_{24}H_{34}N_2O_9$: C, 58.29; H, 6.93; N, 5.66. Found C, 58.18; H, 6.95; N, 5.68.

Nitro Precursor (21). To a solution of acid **20** (500 mg, 1.01 mmol) in dry DMF (12 mL) were added DCC (209 mg, 1.01 mmol) and 1-HOBT (137 mg, 1.01 mmol) at 25 °C. The mixture was stirred for 1 h, then 5-aminopentyl 4′-(2,2′: 6′,2″-terpyridinyl) ether (**4**, 338 mg, 1.01 mmol) was added. Following Method 1, the crude product was dissolved in ether (20 cm^3), from which an insoluble white solid (urea) was filtered. The filtrate was allowed to stand for 2 days affording a solid, which was flash column chromatographed eluting with a solution of EtOAc (30%) in CH_2Cl_2 to yield (92%) **21**, as a white solid: 753 mg; the recrystallized mother solution was also collected, dried, and column chromatographed eluting with 20% of EtOAc in CH_2Cl_2: ^{1}H NMR δ 1.31 (br m, 35H), 3.34 (br s, C*H*$_2$NHCO, 2H), 4.16 (br s, OC*H*$_2$, 2H), 7.20 (m, 5,5″-tpy*H*, 2H), 7.60−7.90 (br m, N*H*, N*H*, 3′,5′,4,4″-tpy*H*, 6H), 8.30−8.95 (br m, Ar*H*, 3,3″,6,6″-tpy*H*, 7H); ^{13}C NMR δ 23.5 (d, *C*$H_2CH_2CH_2NHCO$, *C*H_3), 28.0 (*C*H_3), 28.6, 29.1 (*C*H_2-CH_2*C*H_2CH_2NHCO), 30.3 (*C*H_2CO_2), 33.3 (*C*$H_2CH_2CO_2$), 40.4 (*C*H_2-NHCO), 56.2 ($4^{\circ}C$), 67.9 (O*C*H_2), 81.0 (*C*Me_3), 107.3 (5,5″-tpy*C*), 121.4 (4,4″-tpy*C*), 123.9 (3,3″-tpy*C*), 124.2, 124.7, 131.2, 136.6, 136.7 (2,3,4,5,6-ar*C*), 136.9 (3′,5′-tpy*C*), 148.2 (Ar*C*NO_2), 148.9 (6,6″-tpy*C*), 155.9 (2,2″-tpy*C*), 156.9 (2′,6′-tpy*C*), 163.8, 164.8 (*C*ONHC, CH_2-NH*C*O), 167.0 (4′-tpy*C*), 173.7 (*C*O_2); IR (KBr) 3342, 3082, 2980, 2940, 1734, 1671, 1537, 1371, 1151, 796, 734 cm^{-1}; ESI-MS *m*/*z* 812.0 $(M + H)^+$. Anal. Calcd for $C_{44}H_{54}N_6O_9$: C, 65.17; H, 6.71; N, 10.36. Found C, 64.92; H, 6.58; N, 10.25.

Amino Terpyridine Monomer (22). To a solution of **21** (4.40 g. 5.43 mmol) in MeOH (80 mL), was added 10% Pd/C (1.5 g). Following Method 2, the crude material was column chromatographed eluting a solution of CH_2Cl_2 (10%) in EtOAc, then with 5% MeOH in CH_2Cl_2 to give (90%) **22**, as a white solid: 3.81 g; ^{1}H NMR δ 1.20−1.80 (br m, 27H), 2.10−2.35 (br m, 8H), 3.32 (br s, C*H*$_2$NHCO, 2H), 4.28 (br s, OC*H*$_2$, 2H), 6.45 (s, 2H), 6.75−7.35 (br m, N*H*, 5,5″-tpy*H*, Ar*H*, 7H), 7.68 (br s, 4,4″-tpy*H*, 2H), 7.88 (s, 3′,5′-tpy*H*, 2H), 8.36−8.60 (br m, 3,3″,6,6″-tpy*H*, 4H); ^{13}C NMR δ 23.1, 23.5 (*C*$H_2CH_2CH_2NHCO$, *C*H_3), 27.8 (*C*H_3), 28.3, 29.0 (*C*H_2CH_2*C*H_2CH_2NHCO), 30.1 (*C*H_2CO_2), 33.1 (*C*$H_2CH_2CO_2$), 39.7 (*C*H_2NHCO), 55.4 ($4^{\circ}C$), 67.6 (O*C*H_2), 80.2 (*C*Me_3), 107.0 (5,5″-tpy*C*), 113.7 (4-Ar*C*), 115.8 (d, 2,6-Ar*C*), 121.1 (4,4″-tpy*C*), 123.6 (3,3″-tpy*C*), 135.7, 136.2 (3,5-Ar*C*), 136.6 (3′,5′-tpy*C*), 147.5 (Ar*C*NH_2), 148.6 (6,6″-tpy*C*), 155.6 (2,2″-tpy*C*), 156.6 (2′,6′-tpy*C*), 166.7, 166.8,167.3 (*C*ONHC, CH_2NH*C*O, 4′-tpy*C*), 172.9 (*C*O_2); IR (KBr) 3445, 3357, 3066, 2980, 2940, 1734, 1655, 1584, 1561, 1537, 1372, 1151, 797, 750 cm^{-1}; ESI-MS *m*/*z* 782.2 $(M + H)^+$. Anal. Calcd for $C_{44}H_{56}N_6O_7$: C, 67.67; H, 7.23; N, 10.76. Found C, 67.52; H, 6.98; N, 10.57.

Tetra*kis*terpyridine Core (23). To a stirred solution of amine **22** (1.00 g, 1.28 mmol) and Et_3N (194 mg, 7.68 mmol) in dry THF (30 mL) at −5 °C, was added a solution of tetraacyl chloride **10** (159.5 mg, 320 μmol) in THF (2 mL). Following Method 3, the crude material was column chromatographed eluting with a solution of MeOH (3%) and hexane (25%) in EtOAc to give (67%) pure **23**, as a light yellow solid: 745 mg; ^{1}H NMR δ 1.15−1.75 (br m, 108H), 2.10−2.40 (br m, 40H), 3.32−3.53 (br m, 24H), 4.05 (br s, OC*H*$_2$, 8H), 6.87 (s, N*H*, 4H), 7.20 (br s, 5,5″-tpy*H*, 8H), 7.51 (s, N*H*, 4H), 7.75 (br m, 4,4″-tpy*H*, Ar*H*, 12H), 7.83 (s, 3′,5′-tpy*H*, 8H), 8.05 (s, Ar*H*, 8H), 8.46−8.60 (br m, 3,3″,6,6″-tpy*H*, 16H); 9.40 (s, N*H*, 4H); ^{13}C NMR δ 23.4, 23.7 (*C*$H_2CH_2CH_2NHCO$, *C*H_3), 28.0 (*C*H_3), 28.6, 29.1 (*C*H_2CH_2*C*H_2-CH_2NHCO), 30.3 (*C*H_2CO_2), 33.1 (*C*$H_2CH_2CO_2$), 37.8 (CH_2*C*H_2-CONH), 40.1 ($CONHCH_2$), 45.1 (*C* - core) 55.9 ($4^{\circ}C$), 67.4 (O*C*H_2-CH_2CONH), 68.6 (*C*H_2Otpy), 70.1 (*C*H_2OCH_2), 80.5 (*C*Me_3), 107.3

(5,5″-tpy*C*), 120.5 (4-Ar*C*), 121.1 (4,4″-tpy*C*), 123.8 (3,3″-tpy*C*), 135.6, 136.2 (2,3,5,6-Ar*C*), 136.8 (3′,5′-tpy*C*), 139.1 (Ar*C*NHCO), 148.9 (6,6″-tpy*C*), 156.0 (2,2″-tpy*C*), 156.9 (2′,6′-tpy*C*), 166.4, 167.0, 167.1 (*C*ONHC, CH_2NHCO, 4′-tpy*C*), 170.9 (OCH_2CH_2CONH), 173.1 (CO_2); IR (KBr) 3326, 3066, 2980, 2940, 1734, 1663, 1569, 1160, 796 cm^{-1}; ESI-MS *m*/*z* 1,740.7 $(M + 2H)^{2+}$. Anal. Calcd for $C_{193}H_{244}N_{24}O_{36}$: C, 66.69; H, 7.08; N, 9.69. Found C, 66.56; H, 7.15; N, 9.23.

Propyl 4′-(2,2′:6′,2″-Terpyridinyl) Ether (25). To a suspension of powdered KOH (2.0 g) in dry DMSO (25 mL), was added propanol (561 mg, excess). The suspension was heated to 60 °C for 30 min, then 4′-chloro-2,2′:6′,2″-terpyridine[39] (4′-Cl-tpy, **24**; 500 mg, 1.87 mmol) was added. After 24 h at 60 °C, the mixture was cooled and poured into cold water (300 mL). The resultant solid was filtered, washed with water, and dried in vacuo to give an off-colored white material, which was flash column chromatographed eluting with a solution of hexanes (50%) in CH_2Cl_2 to afford (93%) **25**, as a white solid: 506 mg; mp 112−114 °C; ^{1}H NMR δ 0.94 (t, J = 7.4 Hz, C*H*$_3$, 3H), 1.76 (m, $CH_2CH_2CH_3$, 2H), 4.04 (t, J = 6.3 Hz, OC*H*$_2$, 2H), 7.16 (br s, 5,5″-tpy*H*, 2H), 7.68 (td, J = 7.2, 1.6 Hz, 4,4″-tpy*H*, 2H), 7.89 (s, 3′,5′-tpy*H*, 2H), 8.47 (d, J = 7.9 Hz, 3′,3″-tpy*H*, 2H), 8.55 (s, 6,6″-tpy*H*, 2H); ^{13}C NMR δ 10.6 ($CH_2CH_2CH_3$), 22.5 ($CH_2CH_2CH_3$), 69.7 (OCH_2), 107.4 (5,5″-tpy*C*), 121.4 (4,4″-tpy*C*), 123.8 (3,3″-tpy*C*), 136.8 (3′,5′-tpy*C*), 149.0 (6,6″-tpy*C*), 156.2 (2,2″-tpy*C*), 157.0 (2′,6′-tpy*C*), 167.4 (4′-tpy*C*); IR (KBr) 3060, 2972, 2941, 2878, 1570, 1469, 1210, 1034, 801 cm^{-1}; ESI-MS *m*/*z* 292.4 $(M + H)^+$. Anal. Calcd for $C_{18}H_{17}N_3O$: C, 74.21; H, 5.88; N, 14.42. Found C, 74.26; H, 6.09; N, 14.45.

Propyl 4′-(2,2′:6′,2″-Terpyridine) Ether $RuCl_3$ Complex (26). A solution of $RuCl_3 \cdot 3H_2O$ (179.5 mg, 686 μmol) and **25** (200 mg, 686 μmol) in EtOH (30 mL) was refluxed for 6 h. After cooling, the precipitate was filtered, washed sequentially with EtOH (10 mL), water (2 × 20 mL), and Et_2O (2 × 10 mL), then dried in vacuo to afford (89%) **26**, as a golden solid: 304 mg; mp > 300 °C; IR (KBr) 3428, 3066, 2966, 2928, 1607, 1556, 1468, 1217, 795 cm^{-1}; UV−vis λ_{max} 206 ($\epsilon = 1.97 \times 10^4$), 238 ($1.73 \times 10^4$), 274 ($1.92 \times 10^4$), 312 ($1.60 \times 10^4$), 370 ($4.18 \times 10^3$), 530 nm ($3.40 \times 10^3$ dm^3 mol^{-1} cm^{-1}). Anal. Calcd for $C_{18}H_{17}Cl_3N_3ORu$: C, 43.35; H, 3.44; N, 8.42; Cl, 21.32. Found C, 43.30; H, 3.69; N, 8.32; Cl, 21.22.

Terpyridine Triethyl Ester Monomer (29). To a solution of acid **28** (500 mg, 1.49 mmol) in dry DMF (30 mL), were added DCC (308 mg, 1.49 mmol) and 1-HOBT (202 mg, 1.49 mmol) at 25 °C. This mixture was stirred for 1 h, and then Lin's amine **27** (629 mg, 1.49 mmol) was added. Following Method 1, the crude material was column chromatographed eluting with a solution of CH_2Cl_2 (40%) in EtOAc to give (86%) pure **29**, as a colorless oil: 947 mg; ^{1}H NMR δ 1.16 (t, J = 7.1 Hz, C*H*$_3$, 9H), 2.09 (m, J = 6.6 Hz, $CH_2CH_2CH_2CONH$, 2H), 2.35 (t, J = 7.2 Hz, CH_2CH_2CONH, 2H), 2.44 (t, J = 6.2 Hz, $OCH_2CH_2CO_2Et$, 6H), 3.60 (t, J = 6.2 Hz, $OCH_2CH_2CO_2Et$, 6H), 3.63 (s, CH_2OCH_2, 6H), 4.04 (q, J = 7.2 Hz, OCH_2CH_3, 6H), 4.21 (t, J = 5.9 Hz, tpyOC*H*$_2$, 2H), 6.09 (s, N*H*, 1H), 7.24 (td, J = 5.3, 2.1 Hz, 5,5″-tpy*H*, 2H), 7.76 (td, J = 7.9, 1.2 Hz, 4,4″-tpy*H*, 2H), 7.94 (s, 3′,5′-tpy*H*, 2H), 8.53 (d, J = 8.0 Hz, 3′,3″-tpy*H*, 2H), 8.60 (d, J = 4.3 Hz, 6,6″-tpy*H*, 2H); ^{13}C NMR δ 14.3 (CH_2CH_3), 25.1 (CH_2CH_2CONH), 33.3 (CH_2CH_2CONH), 35.0 (CH_2CO_2Et), 59.8 ($4^{\circ}C$), 60.5 (OCH_2CH_3), 66.8 ($OCH_2CH_2CO_2Et$), 67.3 (tpyO*C*H$_2$), 69.2 ($CH_2OCH_2CH_2CO_2$), 107.4 (5,5″-tpy*C*), 121.3 (4,4″-tpy*C*), 123.9 (3,3″-tpy*C*), 136.8 (3′,5′-tpy*C*), 149.1 (6,6″-tpy*C*), 156.1 (2,2″-tpy*C*), 157.1 (2′,6′-tpy*C*), 167.2 (4′-tpyC), 171.7 (CO_2Et); IR ($CHCl_3$) 3018, 2987, 1733, 1676, 1581, 1563, 1217 cm^{-1}; ESI-MS *m*/*z* 739.8 $(M + H)^+$. Anal. Calcd for $C_{38}H_{50}N_4O_{11}$: C, 61.77; H, 6.82; N, 7.58. Found C, 61.53; H, 6.59; N, 7.58.

Second Tier Ru(III)−Metalloappendage (30). A solution of $RuCl_3 \cdot 3H_2O$ (361 mg, 1.38 mmol) and **29** (1.02 g, 1.38 mmol) in EtOH (50 mL) was refluxed for 6 h. After cooling, the precipitate was filtered, washed sequentially with EtOH (5 mL), water (2 × 20 mL), and Et_2O (2 × 10 mL), then dried in vacuo yielding (84%) **30**, as a yellow-brown solid: 1.10 g; mp > 250 °C (dec); IR (KBr) 3457, 3350, 3073, 2979, 2878, 1733, 1676, 1607, 1550, 1469, 1216, 1103, 856, 794 cm^{-1}; UV−vis λ_{max} 208 ($\epsilon = 3.05 \times 10^4$), 226 ($2.91 \times 10^4$), 276 ($2.63 \times 10^4$), 302 ($1.34 \times 10^4$), 394 ($5.15 \times 10^3$), 462 nm ($1.25 \times 10^3$ dm^3 mol^{-1} cm^{-1}). Anal. Calcd for $C_{38}H_{50}Cl_3N_4O_{11}Ru$: C, 48.23; H, 5.33; N, 5.92; Cl, 11.24. Found C, 48.06; H, 5.40; N, 6.20; Cl, 11.49.

The First Generation of *Tert*-butyl Ester Metallodendrimer (31). To a suspension of the first generation of metalloappendage **26** (229 mg, 459 μmol) in EtOH (30 mL) were added tetra*kis*terpyridine core **23** (400 mg, 115 μmol) and 4-ethylmorpholine (6 drops). Following Method 5, complex **31** was isolated (93%) as a red solid: 569 mg; mp > 210 °C (dec); ^{1}H NMR (MeOD) δ 1.25−1.49 (C*H*$_3$, 96H), 1.60−2.60 (br m, C*H*$_2$, 80H), 3.20−3.55 (br m, overlap H_2O, OC*H*$_2$, NHC*H*$_2$, 24H), 4.25 (br s, OC*H*$_2$, 8H), 7.20 (br s, 5,5″-tpy*H*, 16H), 7.42 (br s, 6,6″-tpy*H*, 16H), 7.80−8.25 (br m, Ar*H*, 4,4″-tpy*H*, 28H), 8.60 (s, 3′,5′-tpy*H*, 16H), 8.87 (br m, 3,3″-tpy*H*, 16H); ^{13}C NMR (MeOD) δ 10.6 ($CH_2CH_2CH_3$), 23.1 ($CH_2CH_2CH_3$), 23.8, 24.1 (*C*H$_3$, *C*H$_2$CH$_2$CH$_2$Opy), 28.0 (*C*H$_3$), 29.2, 29.7 (*C*H$_2$CH$_2$CH$_2$CH$_2$Opy), 31.0 ($CH_2CH_2CO_2$), 34.0 ($CH_2CH_2CO_2$), 38.2 (OCH_2CH_2CONH), 40.5 (CONHC*H*$_2$), 44.9 ($4^{\circ}C$), 56.7 ($4^{\circ}C$), 68.0, 70.2, 70.9, 72.6 (*C*H$_2$OCH$_2$CH$_2$CONH, *C*H$_2$Otpy, tpyO*C*H$_2$CH$_2$CH$_3$), 81.2 (*C*Me$_3$), 111.9 (5,5″-tpy*C*), 122.3 (4-Ar*C*), 125.4 (4,4″-tpy*C*), 128.4 (3,3″-tpy*C*), 136.4, 137.4 (2,3,5,6-Ar*C*), 138.6 (3′,5′-tpy*C*), 140.0 (Ar*C*NHCO), 152.9 (6,6″-tpy*C*), 157.3 (2,2″-tpy*C*), 159.4 (2′,6′-tpy*C*), 167.3 (d, *C*ONH, *C*ONH), 168.5 (4′-tpy*C*), 172.3 (OCH_2CH_2CONH), 174.4 (CO_2); IR (KBr) 3397, 3255, 3060, 2980, 2940, 1726, 1655, 1616, 1545, 1222, 1159, 796 cm^{-1}; UV−vis λ_{max} 214 ($\epsilon = 2.50 \times 10^5$), 240 ($2.57 \times 10^5$), 266 ($2.18 \times 10^5$), 304 ($2.20 \times 10^5$), 484 nm ($6.03 \times 10^4$ dm^3 mol^{-1} cm^{-1}); MALDI-TOF-MS a broad signal at correct formula mass, IAA matrix. Anal. Calcd for $C_{265}H_{312}Cl_8N_{36}O_{40}Ru_4$: C, 59.72; H, 5.90; N, 9.46; Cl, 5.32. Found C, 59.25; H, 6.00; N, 9.08; Cl, 5.48.

The First Generation of Acid Metallodendrimer (32). A solution of **31** (120 mg, 22.5 μmol) in formic acid (20 mL) was stirred for 6 h at 25 °C. Following Method 6, complex **32** was formed (98%) as a red solid: 107 mg; mp > 220 °C (dec); ^{1}H NMR (MeOD) δ 1.26 (br m, C*H*$_3$, 12H), 1.50 (br s, C*H*$_3$, 12H), 1.70−2.65 (br m, C*H*$_2$, 80H), 3.20−3.55 (br m, overlap H_2O, OC*H*$_2$, NHC*H*$_2$, 24H), 4.50 (br s, OC*H*$_2$, 8H), 7.20−8.90 (br m, Ar*H*, tpy*H*, 92H); ^{13}C NMR (MeOD) δ 11.5 ($CH_2CH_2CH_3$), 23.9 ($CH_2CH_2CH_3$), 24.6, 24.9 (*C*H$_3$, *C*H$_2$CH$_2$CH$_2$Opy), 30.1, 30.2 (*C*H$_2$CH$_2$CH$_2$CH$_2$Opy), 31.7 ($CH_2CH_2CO_2$), 35.0 ($CH_2CH_2CO_2$), 38.3 (OCH_2CH_2CONH), 41.9 (CONHC*H*$_2$), 46.8 ($4^{\circ}C$), 57.4 ($4^{\circ}C$), 68.6, 69.0, 71.9, 73.4 (*C*H$_2$OCH$_2$CH$_2$CONH, *C*H$_2$Opy, pyO*C*H$_2$CH$_2$CH$_3$), 112.7 (5,5″-tpy*C*), 123.2 (4-Ar*C*), 126.2 (4,4″-tpy*C*), 129.2 (3,3″-tpy*C*), 137.3, 138.3 (2,3,5,6-Ar*C*), 139.4 (3′,5′-tpy*C*), 140.9 (Ar*C*NHCO), 153.8 (6,6″-tpy*C*), 158.1 (2,2″-tpy*C*), 160.3 (2′,6′-tpy*C*), 166.8, 168.0, 168.1 (*C*ONH, *C*ONH, 4′-tpy*C*), 173.1 (OCH_2CH_2CONH), 177.9 (CO_2H); IR (KBr) 3405, 3263, 3066, 2971, 2932, 1726, 1655, 1616, 1545, 1222, 796 cm^{-1}; UV−vis λ_{max} 214 ($\epsilon = 2.58 \times 10^5$), 240 ($2.59 \times 10^5$), 266 ($2.18 \times 10^5$), 304 ($2.23 \times 10^5$), 484 nm ($5.63 \times 10^4$ dm^3 mol^{-1} cm^{-1}); MALDI-TOF-MS *m*/*z* 4902 $(M + Na)^+$, DHB matrix; *m*/*z* 4740 $(M - 4Cl)^+$, 4603 $(M - 8Cl)^+$, 4600 $(M - 8Cl)^+$, IAA matrix. Anal. Calcd for $C_{233}H_{248}Cl_8N_{36}O_{40}Ru_4$: C, 57.34; H, 5.12; N, 10.33; Cl, 5.81. Found C, 57.89; H, 5.43; N, 10.68; Cl, 5.76.

The First Generation of Neutral Metallodendrimer (33). To a stirred solution of acid **32** (150 mg, 30.7 μmol) in MeOH (5 mL) and H_2O (50 mL), was added KOH (1.721 mg, 30.7 μmol) in H_2O (30 mL). The solution was sealed into a membrane (cutoff mass = 3500) to dialyze for 24 h, and then the solution was concentrated and dried in vacuo to give (92%) the desired neutral metallodendrimer **33**, as a red solid: 130 mg; mp > 230 °C (dec); ^{1}H NMR (MeOD) δ 1.35−4.00 (br m, overlap H_2O, C*H*$_2$, C*H*$_3$, 128H), 4.70 (br s, OC*H*$_2$, 8H), 7.20−8.90 (br m, Ar*H*, tpy*H*, 92H); ^{13}C NMR (MeOD) δ 10.6 ($CH_2CH_2CH_3$), 23.1 ($CH_2CH_2CH_3$), 23.6, 24.1 (*C*H$_3$, *C*H$_2$CH$_2$CH$_2$Opy), 29.2, 29.6 (*C*H$_2$CH$_2$*C*H$_2$CH$_2$Opy), 32.9 (CH_2CO_2), 35.6 ($CH_2CH_2CO_2$), 37.9 (OCH_2CH_2CONH), 41.5 (CONHC*H*$_2$), 45.8 ($4^{\circ}C$), 57.1 ($4^{\circ}C$), 68.8, 69.0, 71.0, 72.4 (*C*H$_2$OCH$_2$CH$_2$CONH, *C*H$_2$Otpy, tpyO*C*H$_2$CH$_2$CH$_3$), 111.8 (5,5″-tpy*C*), 122.1 (4-Ar*C*), 125.4 (4,4″-tpy*C*), 128.5 (3,3″-tpy*C*), 136.5, 137.8 (2,3,5,6-Ar*C*), 138.7 (3′,5′-tpy*C*), 140.1 (Ar*C*NHCO), 153.1 (6,6″-tpy*C*), 157.3 (2,2″-tpy*C*), 159.4 (2′,6′-tpy*C*), 167.2, 167.7, 168.7 (*C*ONH, *C*ONH, 4′-tpy*C*), 172.0 (OCH_2CH_2CONH), 181.3 (CO_2^-); IR (KBr) 3405, 3263, 3066, 2971, 2932, 1726, 1655, 1616, 1545, 1222, 796 cm^{-1}; UV−vis λ_{max} 212 ($\epsilon = 2.54 \times 10^5$), 242 ($2.50 \times 10^5$), 266 ($2.07 \times 10^5$), 306 ($2.11 \times 10^5$), 486 nm ($5.84 \times 10^4$ dm^3 mol^{-1} cm^{-1});

(39) Constable, E. C.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1990**, 1405−1409.

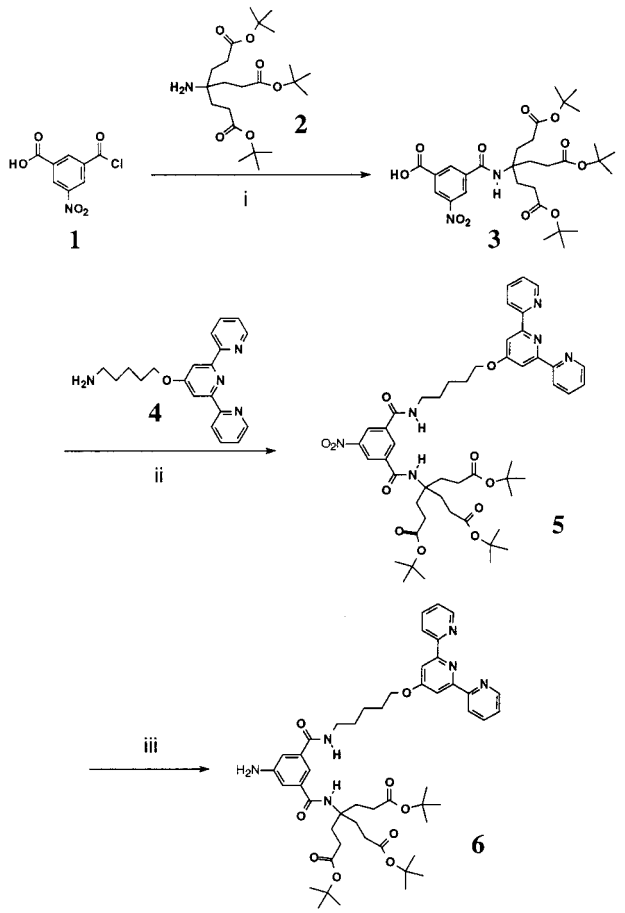
MALDI-TOF-MS *m/z* 4590 $(M + H)^+$, IAA matrix. Anal. Calcd for $C_{233}H_{240}N_{36}O_{40}Ru_4$: C, 60.98; H, 5.27; N, 10.99; Cl, 0.00. Found C, 60.61; H, 5.45; N, 10.23; Cl, 0.00.

The Second Generation of *Tert*-butyl Ester Metallodendrimer (34). To a stirred suspension of the second generation of metalloappendage **30** (109 mg, 115 μmol) in EtOH (20 mL), were added tetra*kis*terpyridine core **23** (100 mg, 28.8 μmol) and 4-ethylmorpholine (6 drops). Following Method 5, complex **34** was isolated (96%) as a red solid: 196 mg; mp > 176 °C (dec); ^{1}H NMR (MeOD) δ 1.31−1.47 (m, C*H*$_3$, 120H), 1.60−2.40 (br m, 40H), 2.2−2.85 (br m, 64H), 3.40−3.90 (br m, overlap H_2O, 72H), 4.20 (br s, 24H), 4.69 (br s, 16H), 7.36 (br s, 5,5′′-tpy*H*, 16H), 7.64 (br s, 6,′′-tpy*H*, 16H), 8.01−8.44 (br m, Ar*H*, 4,4′′-tpy*H*, 28H), 8.60−8.87 (br m, 3,3′′,3′,5′-tpy*H*, 32H); ^{13}C NMR (MeOD) δ 14.6 (CH_2CH_3), 24.1, 24.5, 25.9 ($CH_2CH_2CH_2CONH$, $CH_2CH_2CH_2Otpy$, CH_3), 28.4 (CH_3), 29.6, 30.1 ($CH_2CH_2CH_2CH_2Otpy$), 31.4 ($CH_2CH_2CO_2$), 33.4 ($CH_2CH_2CO_2$), 34.3 ($CH_2CH_2CH_2CONH$), 35.9 ($OCH_2CH_2CO_2$), 37.9 (OCH_2CH_2CONH), 41.4 ($CONHCH_2$), 45.9 ($4^{\circ}C$), 57.1 ($4^{\circ}C$), 61.4 ($4^{\circ}C$), 61.5 (OCH_2CH_3), 68.0 ($OCH_2CH_2CO_2$), 69.8 ($CH_2OCH_2CH_2CO_2$), 70.0, 70.2, 70.4, 70.5 (CH_2Otpy, tpyOCH_2-CH_2CH_2CONH, $CH_2OCH_2CH_2CONH$), 81.4 (CMe_3), 112.3 (5,5′′-tpy*C*), 122.5 (4-Ar*C*), 125.8 (4,4′′-tpy*C*), 128.8 (3, 3′′-tpy*C*), 136.8, 137.9 (2,3,5,6-Ar*C*), 139.0 (3′,5′-tpy*C*), 140.4 (Ar*C*NHCO), 153.4 (6,6′′-tpy*C*), 157.7 (2,2′′-tpy*C*), 159.8 (2′,6′-tpy*C*), 167.3,167.6, 168.9 (*C*ONH, *C*ONH, 4′-tpy*C*), 172.6 (*C*ONHAr), 173.3 (CO_2Et), 174.6 (CO_2t-Bu), 175.0 ($OCH_2CH_2CH_2CONH$); IR (KBr) 3428, 3065, 2979, 2940, 1726, 1651, 1619, 1544, 1468, 1217, 1109 cm^{-1}; UV−vis λ_{max} 214 ($\epsilon = 2.48 \times 10^5$), 242 ($2.57 \times 10^5$), 266 ($2.25 \times 10^5$), 304 ($2.22 \times 10^5$), 484 nm ($6.13 \times 10^4$ dm^3 mol^{-1} cm^{-1}); MALDI-TOF-MS a broad signal at correct formula mass, IAA matrix. Anal. Calcd for $C_{345}H_{444}Cl_8N_{40}O_{80}Ru_4$: C, 58.20; H, 6.29; N, 7.87; Cl, 3.98. Found C, 58.32; H, 6.29; N, 8.02; Cl, 3.62.

The Second Generation of Acid Metallodendrimer (35). A solution of **34** (620 mg, 87.1 μmol) in formic acid (40 mL) was stirred for 6 h at 25 °C. Following Method 6, complex **35** was isolated (97%) as a red solid: 560 mg; mp > 190 °C (dec); ^{1}H NMR (MeOD) δ 1.12 (m, C*H*$_3$, C*H*$_3$, 48H), 1.45−1.95 (br m, 40H), 2.20−2.85 (br m, 64H), 3.15−3.65 (br m, overlap H_2O, 72H), 4.00 (br s, 24H), 4.45 (br s, 16H), 7.12 (br s, 5,5′′-tpy*H*, 16H), 7.45 (br s, 6,6′′-tpy*H*, 16H), 7.70−8.25 (br m, Ar*H*, 4,4′′-tpy*H*, 28H), 8.45−8.80 (br m, 3,3′′,3′,5′-tpy*H*, 32H); ^{13}C NMR (MeOD) δ 14.9 (CH_2CH_3), 24.4, 24.5, 25.9 ($CH_2CH_2CH_2$-CONH, $CH_2CH_2CH_2Otpy$, CH_3), 29.6, 30.2, 30.6 ($CH_2CH_2CH_2CH_2$-Otpy, $CH_2CH_2CO_2$), 33.8 ($CH_2CH_2CO_2$), 34.8 ($CH_2CH_2CH_2CONH$), 36.2 ($OCH_2CH_2CO_2$), 37.8 (OCH_2CH_2CONH), 42.4 ($CONHCH_2$), 46.4 ($4^{\circ}C$), 57.3 ($4^{\circ}C$), 61.8, 61.9 ($4^{\circ}C$, OCH_2CH_3), 68.3 ($OCH_2CH_2CO_2$), 70.1 ($CH_2OCH_2CH_2CO_2$), 70.7−71.3 (m, CH_2Opy, tpy$OCH_2CH_2CH_2$-CONH, $CH_2OCH_2CH_2CONH$), 112.6 (5,5′′-tpy*C*), 122.7 (4-Ar*C*), 125.8 (4,4′′-tpy*C*), 129.1 (3,3′′-tpy*C*), 137.1, 138.1 (2,3,5,6-Ar*C*), 139.3 (3′,5′-tpy*C*), 140.7 (Ar*C*NHCO), 153.7 (6, 6′′-tpy*C*), 157.9 (2,2′′-tpy*C*), 160.0 (2′,6′-tpy*C*), 167.7,167.9, 169.1 (*C*ONH, *C*ONH, 4′-tpy*C*), 172.9 (*C*ONHAr), 173.6 (CO_2Et), 175.4 ($OCH_2CH_2CH_2CONH$), 177.5 (CO_2H); IR (KBr) 3412, 3067, 2934, 1733, 1657, 1613, 1544, 1462, 1210, 1109 cm^{-1}; UV−vis λ_{max} 214 ($\epsilon = 2.56 \times 10^5$), 242 ($2.59 \times 10^5$), 266 ($2.26 \times 10^5$), 304 ($2.28 \times 10^5$), 484 nm ($6.36 \times 10^4$ dm^3 mol^{-1} cm^{-1}); MALDI-TOF-MS *m/z* 6380 $(M - 8HCl)^+$, IAA matrix. Anal. Calcd for $C_{313}H_{380}Cl_8N_{40}O_{80}Ru_4$: C, 56.36; H, 5.74; N, 8.40; Cl, 4.25. Found C, 56.18; H, 5.86; N, 8.46; Cl, 4.62.

The Second Generation of Neutral Metallodendrimer (36). To a stirred solution of acid **35** (420 mg, 63.0 μmol) in MeOH (5 mL) and H_2O (50 mL) was added KOH (3.526 mg, 63.0 μmol) in H_2O (30 mL). The solution was sealed into a membrane (cutoff mass = 3500) to dialyze for 24 h, and the solution was concentrated and dried in vacuo to give (97%) neutral metallodendrimer **36**, as a red solid: 391 mg; mp > 210 °C (dec); ^{1}H NMR (MeOD) δ 1.10−1.30 (m, C*H*$_3$, 48H), 1.55−2.20 (br m, 72H), 2.50−2.65 (br m, 32H), 3.25−3.75 (br m, overlap H_2O, 72H), 4.15 (q, J = 7.0 Hz, CO_2CH_2, 24H), 4.50 (br s, 16H), 7.12 (br s, 5,5′′-tpy*H*, 16H), 7.45 (br d, 6,6′′-tpy*H*, 16H), 7.90−8.15 (br m, Ar*H*, 4,4′′-tpy*H*, 28H), 8.45−8.90 (br m, 3,3′′,3′,5′-tpy*H*, 32H); ^{13}C NMR (MeOD) δ 14.9 (CH_2CH_3), 24.4, 24.5, 26.2 (CH_2CH_2-CH_2CONH, $CH_2CH_2CH_2Otpy$, CH_3), 29.6, 30.2, 30.4 ($CH_2CH_2CH_2$-CH_2Otpy, CH_2CO_2), 33.8, 33.9 ($CH_2CH_2CO_2$, $CH_2CH_2CH_2CONH$), 36.2 ($OCH_2CH_2CO_2$), 38.2 (OCH_2CH_2CONH), 42.2 ($CONHCH_2$), 46.5 ($4^{\circ}C$), 57.6 ($4^{\circ}C$), 61.8, 61.9 ($4^{\circ}C$, OCH_2CH_3), 68.3 ($OCH_2CH_2CO_2$), 70.2 ($CH_2OCH_2CH_2CO_2$), 71.0−71.3 (m, CH_2Otpy, tpy$OCH_2CH_2CH_2$-CONH, $CH_2OCH_2CH_2CONH$), 112.5 (5,5′′-tpy*C*), 122.6 (4-Ar*C*), 126.1 (4,4′′-tpy*C*), 129.3 (3,3′′-tpy*C*), 137.2, 138.5 (2,3,5,6-Ar*C*), 139.3 (3′,5′-tpy*C*), 140.8 (Ar*C*NHCO), 153.6 (6,6′′-tpy*C*), 157.9 (2,2′′-tpy*C*), 160.1 (2′,6′-tpy*C*), 167.6,167.8, 169.2 (*C*ONH, *C*ONH, 4′-tpy*C*), 172.5 (*C*ONHAr), 173.6 (CO_2Et), 175.3 ($OCH_2CH_2CH_2CONH$), 181.7 (CO_2^-); IR (KBr) 3425, 3066, 2934, 1733, 1657, 1619, 1556, 1462, 1216, 1109 cm^{-1}; UV−Vis λ_{max} 212 ($\epsilon = 2.57 \times 10^5$), 242 ($2.58 \times 10^5$), 266 ($2.22 \times 10^5$), 306 ($2.22 \times 10^5$), 486 nm ($5.98 \times 10^4$ dm^3 mol^{-1} cm^{-1}): MALDI-TOF-MS *m/z* 6381 $(M + H)^+$, IAA matrix. Calcd for $C_{313}H_{372}N_{40}O_{80}Ru_4$: C, 58.94; H, 5.88; N, 8.78; Cl, 0.00. Found C, 58.94; H, 5.86; N, 8.71; Cl, 0.00.

Scheme 1. Construction of the First Tier Building Block for the Dendritic Core[a]

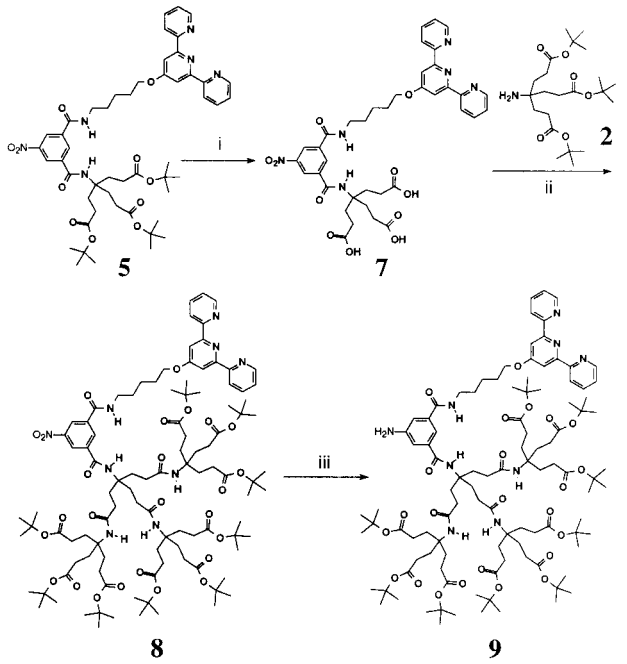


[a] (i) Et_3N, THF, 12 h, −5 °C then 25 °C; (ii) DCC, 1-HOBT, DMF, 24 h, 25 °C; (iii) 10% Pd/C, HCO_2NH_4, MeOH, 0.5 h, 50 °C.

A Tailored Approach to Isomeric Metallomacromolecules

The ideal starting material to construct the dendritic cores **11** or **12** would be an appropriately trisubstituted benzene, such that one site is attached to a branched monomer, which can be further expanded to higher generations; another site possesses a terpyridine unit, which can be used as metal complex ligand for the networks; and the third site is connected to a four-directional core. The candidate chosen was 5-nitroisophthalic acid, which was converted (23%) with 1 equiv of PCl_5 in cold Et_2O into the desired monoacyl chloride[36] **1** by our modified literature procedure (Scheme 1). Its treatment with amine **2**[35] afforded *N*-{tris[(2-*tert*-butoxycarbonyl)ethyl]methylnitroisophthalamide monocarboxylic acid (**3**) in 54% yield. Amidation of **1** was supported (^{13}C NMR) by the shift of the signal assigned to the quaternary carbon moiety (CONH*C*) of amine **2** from

Scheme 2. Construction of the Second Tier Building Block for the Dendritic Core[a]



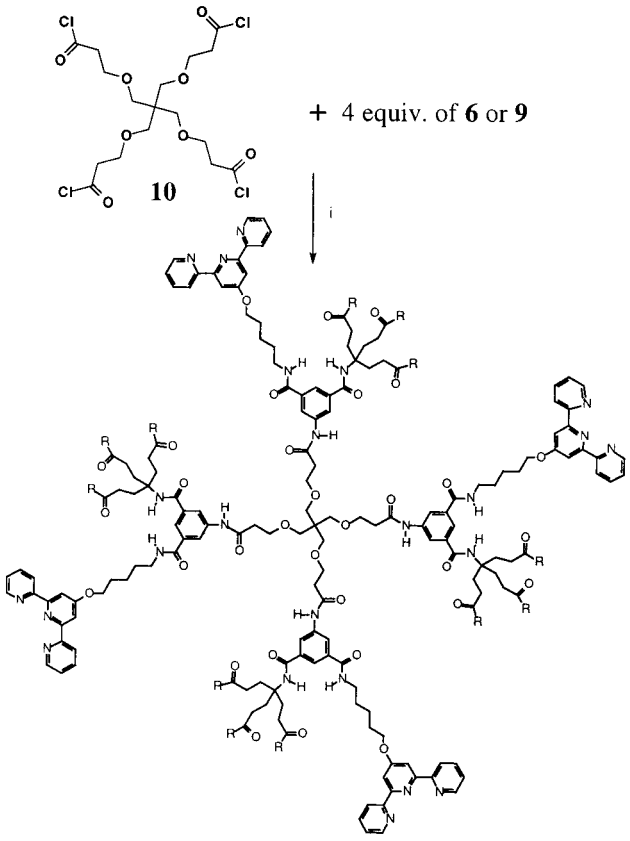
[a] (i) HCOOH, 24 h, 25 °C; (ii) DCC, 1-HOBT, DMF, 48 h, 25 °C; (iii) 10% Pd/C, HCO_2NH_4, MeOH, 0.5 h, 50 °C.

52.8 to 58.7 ppm and the appearance (ESI-IT) of a molecular peak at *m*/*z* 631.7 ($[M + Na]^+$ *m*/*z* 631.7). Monoacid **3** was subsequently treated with 5-aminopentyl 4′-(2,2′: 6′,2″-terpyridinyl) ether[37] (**4**) by the DCC coupling[32] procedure generating (84%) *N*-{tris[(2-*tert*-butoxycarbonyl)ethyl]methyl}-*N*′-[4′-oxa-(2,2′:6′,2″-terpyridinyl)]-nitroisophthalamide (**5**). A downfield shift (^{13}C NMR) for the CONH*C*H_2 observed in the spectrum of nitro-terpyridyl **5** from 42.0 to 40.5 ppm along with a molecular peak at *m*/*z* 947.8 ($[M + Na]^+$ *m*/*z* 948.1) in ESI-MS support its structural assignment. Reduction[40] of the aryl nitro moiety of **5** with 10% Pd/C and a large excess HCO_2NH_4 afforded (87%) the arylamine monomer **6**, which was supported by the chemical shift (^{13}C NMR) for the 1-Ar*C* from 148.6 to 147.5 ppm and the molecular peaks at *m*/*z* 917.5 ($[M + Na^+]$ *m*/*z* 918.1). Alternative reduction conditions using Raney nickel catalyst[35] were also attempted for the conversion of nitro group, but the reaction was not successful.

Hydrolysis of **5** with formic acid gave (95%) the triacid **7** (Scheme 2), whose assignment was confirmed by the signal at 174.6 ppm (*C*O_2H) in the ^{13}C NMR spectrum and the molecular peak at *m*/*z* 757.3 ($[M + H]^+$ *m*/*z* 757.8) in the ESI-MS. Iterative amidation[41] of **7** gave (90%) the desired nonaester **8**, which was structurally established by the new signal for the additional quaternary carbon (CONH*C*) at 57.5 ppm and the molecular peak (ESI-IT) at *m*/*z* 1972.0 ($[M + Na]^+$ *m*/*z* 1972.8). Reduction[40] of the aryl nitro moiety of **8** with 10% Pd/C and a large excess of HCO_2NH_4 afforded (83%) the key arylamine monomer **9**, which was supported by the chemical shift (^{13}C NMR) for the 1-Ar*C* from 148.6 to 147.5 ppm and the molecular peak at *m*/*z* 1,942.8 ($[M + Na]^+$ *m*/*z* 1,942.5).

The first and second tier dendritic cores **11** or **12** were prepared (72 or 24%, respectively) via a coupling reaction of tetraacid chloride[38] **10** (Scheme 3) with 4 equiv of **6** or **9** in

Scheme 3. Construction of the Dendritic Cores[a]



11. R = -$OCMe_3$
12. R = -$NHC[CH_2CH_2CO_2CMe_3]_3$

[a] (i) Et_3N, THF, 24 h, 0 °C then 25 °C.

THF in the presence of Et_3N. In the ^{13}C NMR spectra of **11** or **12**, a significant upfield shift of the signal at 147.5 to 139.2 (138.7 for **12**) ppm corresponding to the Ar*C*NHCO corroborates amidation, as well as the peak at *m*/*z* 1988.7 $[M + 2Na]^{2+}$ (ESI-IT) for **11**, or *m*/*z* 8075 $[M + 2Na - H]^+$ (MALDI-TOF) for **12**, respectively.

The first and second tier metalloappendages **13** and **14** were prepared by a simple divergent process[15] (Figure 3). The complementary metallo-donor and receptor dendritic molecules were readily assembled via four [−⟨*Ru*⟩−] connections to generate a methane-type motif. Reductive assemblage of **11** with 4 equiv of **13** in hot MeOH in the presence of 4-ethylmorpholine afforded (97%) the desired microcrystalline, red dendritic assembly **15** (Scheme 4). Based on its ^{13}C NMR spectra, the absence of any free terpyridine moiety and the presence of two very similar complexed terpyridine moieties (i.e., core vs terminal directed terpyridines) indicated the four, symmetrical attachments. MALDI-TOF mass spectrum gave a molecular peak at *m*/*z* 8283 ($[M - PF_6]^+$ *m*/*z* 8283) for **15**.

Novel isomeric "dendritic methane-type" metallomacromolecules **16** (93%), formed from **11** and 4 equiv of metalloappendages **14**, and **17** (80%), prepared from **12** and **13,** were constructed (Scheme 5) by the same manner as for **15**. MALDI-TOF mass spectrum of each showed a broad molecular peak at *m*/*z* 12 235 ($[M - 2PF_6]^+$ *m*/*z* 12 236) for **16**, and at *m*/*z* 12 234 ($[M - 2PF_6]^+$ *m*/*z* 12 236) for **17**; these results strongly support the isomeric relationship between these two structures. Normal spectroscopic and analytical analyses were indiscernible for these two obviously similar structures; however, electrochemical

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

(41) Young, J. K.; Baker, G. R.; Newkome, G. R.; Morris, K. F.; Johnson, C. S., Jr. *Macromolecules* **1994**, *27*, 3464−3471.

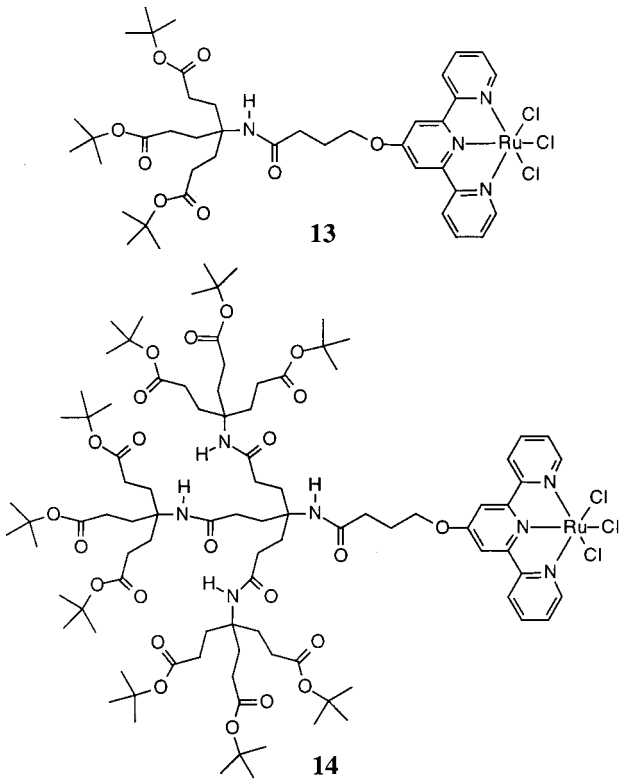
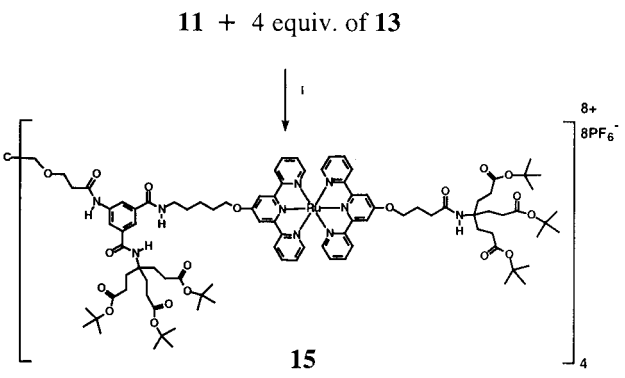


Figure 3. Metallodendritic building blocks.

Scheme 4. Construction of the "Dendritic Methane"[a]



[a] (i) 4-Ethylmorpholine, MeOH, 4 h, reflux.

data (described below) offered insight to the different packing arrays as related to an external electrode surface.

Construction of Neutral Metallodendrimers

To construct neutral metallodendrimers, a dendritic core that has eight covalently attached internal carboxylate groups and four terpyridine ligands was envisioned; thus, the resultant macromolecule will possess the requisite number of internal octacarboxylate counterions. Thematically, the overall procedure is as previously demonstrated, except that there can be only eight internal *tert*-butyl ester moieties and the metalloappendages must possess formic acid-stable substituents. Initially then, $EtNO_2$ was treated with 2 equiv of *tert*-butyl acrylate in liquid NH_3 at −78 °C to give (95%) di-*tert*-butyl 4-nitro-4-methylheptanedicarboxylate (**18**) (Scheme 6). The characteristic carbon signal (^{13}C NMR) for *C*NO_2 at 89.9 ppm strongly supported the desired structure, which is further confirmed by the molecular peak (ESI-IT) at *m*/*z* 332.6 ($[M + H]^+$ *m*/*z* 332.4). Treatment of **18** with Raney Nickel under H_2 at 25 °C afforded di-*tert*-butyl 4-amino-4-methylheptanedicarboxylate (**19**) in 96% yield. The large upfield shift of the carbon peak (^{13}C NMR) of *C*NO_2 to *C*NH_2 ($\Delta = -39$ ppm) clearly indicated the success of reduction and the molecular peak (ESI-IT) at *m*/*z* 324.7 ($[M + Na]^+$ *m*/*z* 324.4) further supported the expected structure. Reaction of **19** with 5-nitroisophthalic acid monoacyl chloride (**1**) in the presence of Et_3N at −5 °C gave (58%) monocarboxylic acid **20**. The downfield shift (^{13}C NMR) of *C*NH_2 to *C*NHC═O ($\Delta = 5.50$ ppm) along with the molecular peak (ESI-IT) at *m*/*z* 517.7 ($[M + Na]^+$ *m*/*z* 517.9) supported the desired the structure. DCC coupling of acid **20** with 1-HOBT and 5-aminopentyl 4′-(2,2′:6′,2″-terpyridinyl) ether (**4**) in DMF at 25 °C afforded nitro precursor **21**, which possessed the correct mass peak (ESI-IT) at *m*/*z* 812.0 ($[M + H]^+$ *m*/*z* 812.0) and was subsequently reduced with 10% Pd/C and ammonium formate in MeOH at 50 °C to afford the desired branched monomer **22**. The clear upfield shift (^{13}C NMR) of 4-Ar*C* ($\Delta = -17.5$ ppm) and Ar*C*NO_2 to Ar*C*NH_2 ($\Delta = -0.7$ ppm) supported the structure of **22**, which was further confirmed by the molecular peak (ESI-IT) at *m*/*z* 782.2 ($[M + H]^+$ *m*/*z* 782.0).

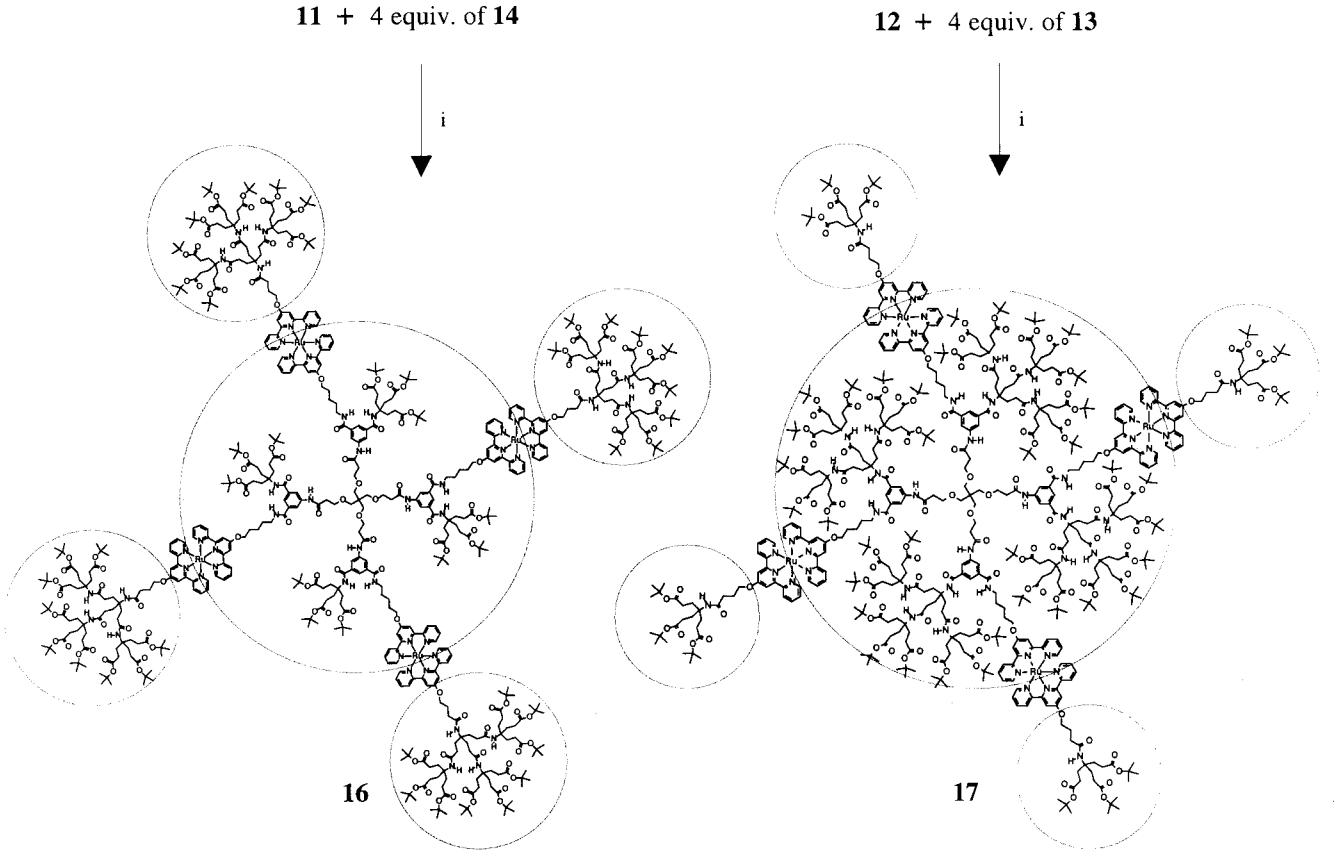
Four equiv of **22** were treated with tetraacyl chloride **10** in the presence of excess of Et_3N at −5 °C to provide (67%) the tetra*kis*terpyridine core **23** (Scheme 7). The downfield shift (^{13}C NMR) of 4-Ar*C* ($\Delta = 6.8$ ppm) and upfield shift of Ar*C*NH_2 to Ar*C*NH(C═O) ($\Delta = -8.4$ ppm) indicated that the tetraamidation had occurred. The desired structure of **23** was further confirmed by the mass peak (ESI-IT) at *m*/*z* 1740.7 ($[M + 2H]^{2+}$ *m*/*z* 1739.1).

A simple capping reagent was prepared from 4′-chloro-2,2′:6′,2″-terpyridine (4′-Cl-tpy, **24**),[39] by heating with 1-propanol and powered KOH in DMSO at 60 °C to give propyl 4′-(2,2′:6′,2″-terpyridinyl) ether (**25**) in 93% yield (Scheme 8). The significant chemical shifts (^{1}H NMR) for 3′,5′-tpy*H* and 5′,5″-tpy*C*, as well as for tpy 4′-tpy*C* (^{13}C NMR) confirmed the formation of 4′-ethereal bond and the molecular peak at *m*/*z* 292.4 ($[M + H]^+$ *m*/*z* 292.4) further supported the structure. Terpyridine ether **25** was then refluxed with $RuCl_3 \cdot 3H_2O$ in EtOH to give (89%) the unbranched building block appendage **26**. Its structure was only supported by combustion analysis; NMR spectra were not measured due to the presence of the paramagnetic Ru(III) metal center.

Branched metalloappendages possessing a formic acid stable functionality were based on the use of Lin's amine.[38] Thus, DCC coupling of 4-[4′-oxa-(2,2′:6′,2″-terpyridinyl)]butanoic acid (**28**)[37] with 1,11-diethyl 6-amino-6-(4-ethoxycarbonyl-2-oxabutyl)-4,8-dioxaundecane-dicarboxylate[38] (**27**) and 1-HOBT in DMF at 25 °C afforded desired terpyridine monomer **29** in 86% yield (Scheme 9). The amidation of **29** was confirmed by the downfield ($\Delta = 3.9$ ppm) shift (^{13}C NMR) of $^{4'}$*C*NH(C═O). The molecular mass (ESI-IT) at *m*/*z* 739.8 ($[M + H]^+$ *m*/*z* 739.8) clearly indicated the correct composition. The branched terpyridine ester **29** was refluxed with $RuCl_3 \cdot 3H_2O$ in EtOH to give (86%) the branched metalloappendage **30**. Both Ru(III) appendage molecules (**26** and **30**) were carried on to the coupling stage without further purification.

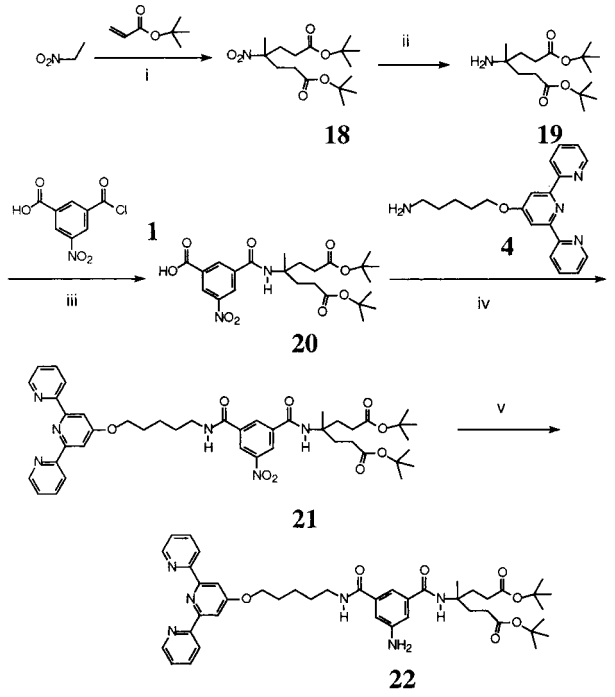
One equiv of core **23** was refluxed with 4 equiv of **26** in EtOH in the presence of 4-ethylmorpholine, as reducing agent, to assemble metallodendrimer **31** in 93% yield (Scheme 10). Although appendage **26** possessed a limited initial solubility, it quickly went into the solution upon addition of the reducing agent, to give the deep-red color of the [−⟨*Ru*⟩−] complex. After dialysis, pure complex **31** was isolated and its structure was supported by the significant downfield shift (^{13}C NMR) of all

Scheme 5. Construction of Two Isomeric Metallodendrimers[a]



[a] (i) 4-Ethylmorpholine, MeOH, 6 h, reflux.

Scheme 6. Construction of the Building Block for the Dendritic Core in Neutral Complexes[a]

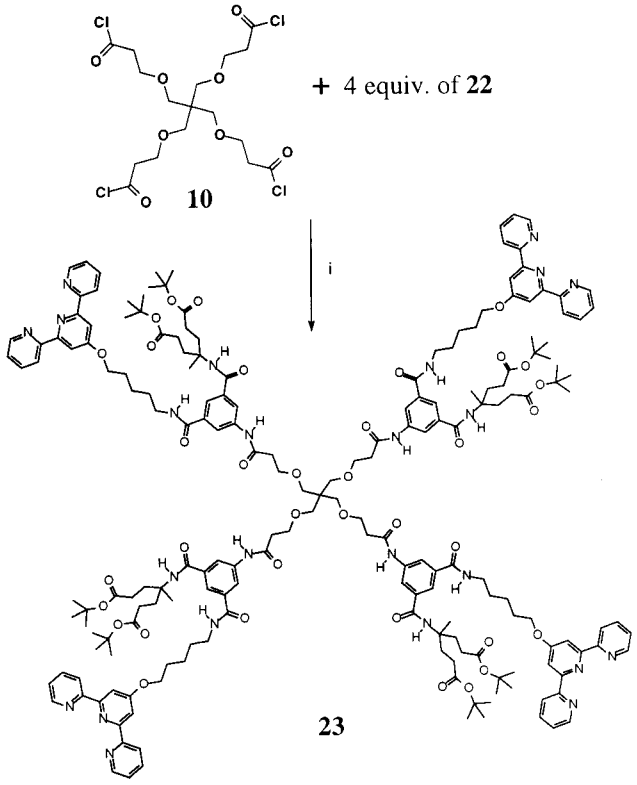


[a] (i) NH_3 (l), 12 h, −78 °C; (ii) Raney Ni, H_2, 4 atm, 12 h, 25 °C; (iii) Et_3N, THF, 12 h, −5 °C then 25 °C; (iv) DCC, 1-HOBT, DMF, 24 h, 25 °C; (v) 10% Pd/C, HCO_2NH_4, MeOH, 0.5 h, 50 °C.

tpy carbons except 4′-tpy*C*. The *tert*-butyl groups were removed from **31** with formic acid at 25 °C affording metallodendrimer **32** in 98% yield. The characteristic downfield shift (^{13}C NMR) of the carbonyl carbon (Δ = 3.5 ppm) clearly indicated the transformation to the acid and the retention of the external alkyl ethyl ester moieties was shown by the presence of the ethyl signals. A sharp mass peak (MALDI-TOF) at *m*/*z* 4902 ([M + Na]$^+$ *m*/*z* 4904) further confirmed the desired conversion. Formation of the neutral metallodendrimer **33** was accomplished by adding a slight excess of KOH into an H_2O/MeOH solution of **32**. After dialysis for 24 h, the desired neutral complex was analyzed (0.00% of Cl), and only one downfield shift (^{13}C NMR) for the internal acid carbonyl carbon (Δ = 3.4 ppm) supported the formation of the carboxylate carbon centers. The mass peak (MALDI-TOF) at *m*/*z* 4590 ([M + H]$^+$ *m*/*z* 4590) confirmed the structure of **33**.

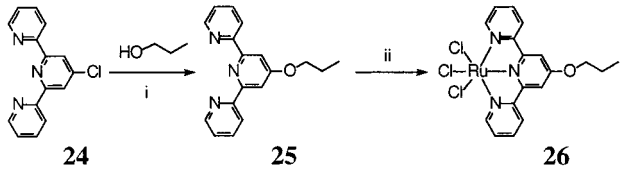
In the same manner, 1 equiv of core **23** was then treated with 4 equiv of **30** in boiling EtOH in the presence of 4-ethylmorpholine as reducing agent to assemble (96%) the second generation of tetra*kis*(−⟨*Ru*⟩−) metallodendrimer **34** (Scheme 10). After purification via dialysis, the structure of **34** was supported by the significant downfield shift (^{13}C NMR) of all tpy carbons except 4′-tpy*C* (similar to the spectrum of **31**). Deprotection of *tert*-butyl groups of **34** by treatment of formic acid at 25 °C afforded the second generation of acid metallodendrimer **35** in 97% yield. The same characteristic downfield shift (^{13}C NMR) of the carbonyl carbon (Δ = 2.9 ppm) clearly indicated the transformation of the acid. A sharp mass peak (MALDI-TOF) at *m*/*z* 6380 ([M − 8HCl]$^+$ *m*/*z* 6379) further confirmed the desired conversion. The neutral metallodendrimer **36** was formed by adding a slight excess of KOH into a H_2O/MeOH solution of **35**. After dialysis for 24 h, the desired neutral complex **36** was isolated and analyzed (0.00% of Cl); there was only one downfield shift (^{13}C NMR) for the internal acid

Scheme 7. Construction of the Dendritic Core in Neutral Complexes[a]



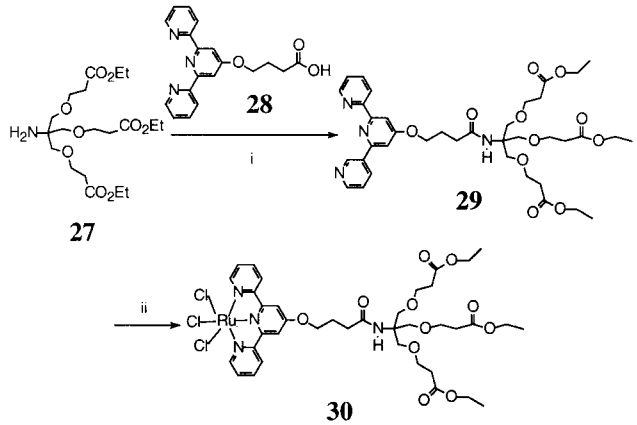
[a] (i) Et_3N, THF, 12 h, −5 °C then 25 °C.

Scheme 8. Synthesis of the first tier metal donor appendage building block[a]



[a] (i) KOH, DMSO, 24 h, 60 °C; (ii) $RuCl_3 \cdot 3H_2O$, EtOH, 6 h, reflux.

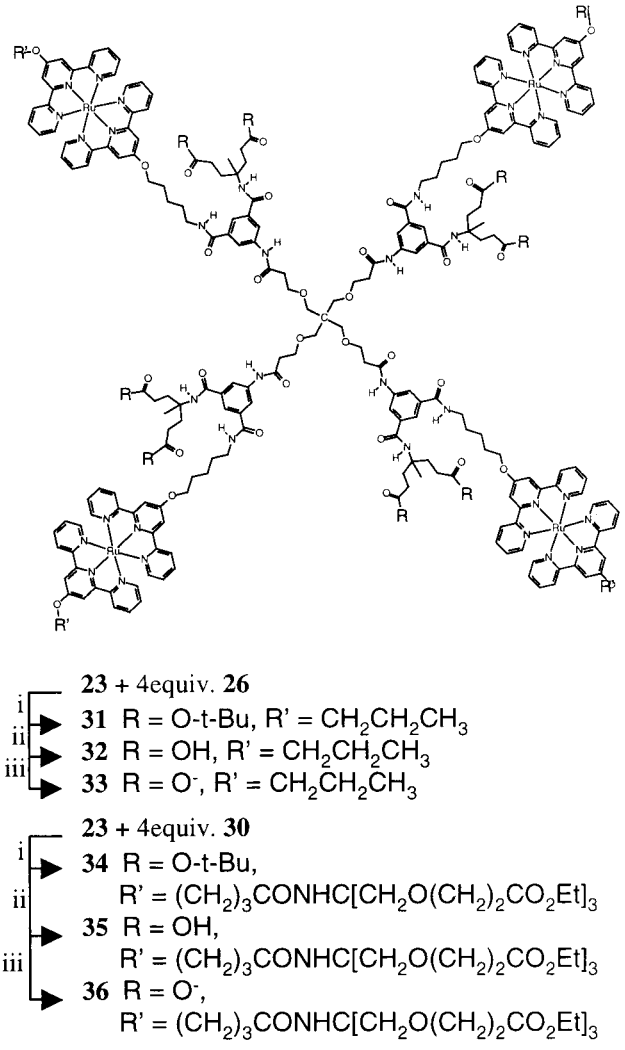
Scheme 9. Synthesis of the Second Tier Metal Donor Appendage Building Block[a]



[a] (i) DCC, 1-HOBT, DMF, 36 h, 25 °C; (ii) $RuCl_3 \cdot 3H_2O$, EtOH, 6 h, reflux.

carbonyl carbon (Δ = 4.2 ppm) supporting the formation of the carboxylate carbon centers. The mass peak (MALDI-TOF) at *m*/*z* 6381 ($[M + H]^+$ *m*/*z* 6380) further confirmed the structure of **36**.

Scheme 10. Syntheses of the Two Generations of Neutral Metallomacromolecules[a]



[a] (i) 4-Ethylmorpholine, EtOH, 6 h, reflux; (ii) HCOOH, 6 h, 25 °C; (iii) KOH, H_2O/MeOH, dialysis, 24 h, 25 °C.

UV−Vis Study of [−⟨*Ru*⟩−] Metallodendrimers

Although correct spectral and analytical analyses of the components leading to the metallodendritic composites and the lack of both paramagnetic Ru(III) loose ends, as well as random mixed [Ru(II)] complexes, were ascertained, it was interesting to utilize UV data in order to relate the extinction coefficient to the number of [−⟨*Ru*⟩−] centers in the structure. These data, if sensitive enough, could be used to ascertain the successful coupling within such assemblies. In UV−vis studies, the molar absorptivity $\epsilon = A/(L \cdot M)$, where A is absorbance, L is the path length, and M is the molar concentration of the solute. Since the molar absorptivity (ϵ) is directly related to the molar concentration (M), it should be proportional to the number of the metal connections, if all the samples only contain single or multiple [−⟨*Ru*⟩−] complexes, which will display intense MLCT (metal ligand charge transfer) signals in visible region.[42] Four major absorption bands (λ_{max} 240−242, 266−268, 304−306, 484−488 nm) were observed for these [−⟨*Ru*⟩−]-connected metallodendrimers. The molar absorptivities (ϵ) of all the complexes have similar values (Table 3), indicative that all nine molecular assemblies have the same number of [−⟨*Ru*⟩−]

(42) Constable, E. C.; Harverson, P. *Inorg. Chim. Acta* **1996**, *252*, 9−11.

Table 1. Electrochemical Parameters for Isomers **16** and **17** in MeCN at 298 K

	terpyridines		Ru(III)/Ru(II)	
compound	$E_{1/2}$ (ΔE_p)[a]	$E_{1/2}$ (ΔE_p)[a]	$E_{1/2}$ (ΔE_p)[a]	$E_{1/2}$ (ΔE_p)[a]
17	−1.923 (0.121)	−1.720 (0.087)	0.719 (0.170)	0.919 (0.092)
16	−1.951 (0.097)	−1.751 (0.093)	0.709 (0.109)	

[a] Potentials against internal ferrocene/ferrocenium. Scan rate: 200 mV/s.

Table 2. Electrochemical Parameters for Metallodendrimers **31**−**36** in DMF at 298 K

	terpyridines		Ru(III)/Ru(II)
compound	$E_{1/2}$ (ΔE_p)[a]	$E_{1/2}$ (ΔE_p)[a]	$E_{1/2}$ (ΔE_p)[a]
31	−1.945 (0.082)	−1.759 (0.068)	0.627 (0.073)
32	I[b]	I[b]	0.629 (0.057)
33	−1.950 (0.072)	−1.788 (0.077)	0.624 (0.059)
34	−1.950 (0.086)	−1.751 (0.088)	0.640 (0.100)
35	I[c]	I[c]	0.627 (0.097)
36	−1.935 (0.102)	−1.767 (0.106)	0.634 (0.089)

[a] Potentials against ferrocene/ferrocenium. Scan rate: 200 mV/s. [b] Irreversible cathodic peak at −1.945 V. [c] Irreversible cathodic peak at −1.968 V.

Table 3. Molar Absorptivities of [−⟨*Ru*⟩−] Metallodendrimers

	$\epsilon \times 10^4$ (dm^3 mol^{-1} cm^{-1}) at λ_{max} (nm)								
compound	240	242	266	268	304	306	484	486	488
15		27.4		23.7		23.2			6.67
16		25.4		21.5		21.5			6.54
17		28.2		25.4		25.8			6.73
31	25.7		21.8		22.0		6.03		
32	25.9		21.8		22.3		5.63		
33	25.0		20.7			21.1		5.84	
34		25.7	22.5		22.2		6.13		
35		25.9	22.6		22.8		6.36		
36		25.8	22.2			22.2		5.98	

connectivities. For the highest absorption of a tetra [−⟨*Ru*⟩−]-containing complex (λ_{max} = 484−488 nm), the average molar absorptivity $\epsilon = 6.21 \times 10^4$ dm^3 mol^{-1} cm^{-1} is about four times as strong as Constable's [−⟨*Ru*⟩−] complex.[42] Though the values of ϵ in this series of related complexes are smaller than that of Constable's, our metal complexes are heavily hindered by branched organic moieties, which may slightly affect the UV absorption. Comparison of these data with previous results[37] indicated that four −⟨*Ru*(II)⟩− complexes are present in each of the dendritic constructs, further supporting the desired structures.

According to the present data, the UV absorption of the metal complexes is relatively independent of the dendritic structures. The bulkiness of the internal and external branches may slightly shift (2−4 nm) the absorption (λ_{max}) to longer wavelengths, as evidenced by the larger dendrimers **15**, **16**, and **17**. The loss of external counterions does affect the UV absorption; both of the neutral species shifted the signals to longer wavelengths and slightly decreased the absorptivities. This effect may be related to their unimolecular behavior and the stability of these neutral species.

Electrochemistry of Isomeric and Neutral Metallodendrimers

Isomeric Metallodendrimers. Despite the similarity of these isomers, the different distributions of the branched building blocks for the two isomers **16** and **17** should result in different chemical environments around the [−⟨*Ru*⟩−] moieties. The cyclic voltammograms of both compounds (Figure 4) were

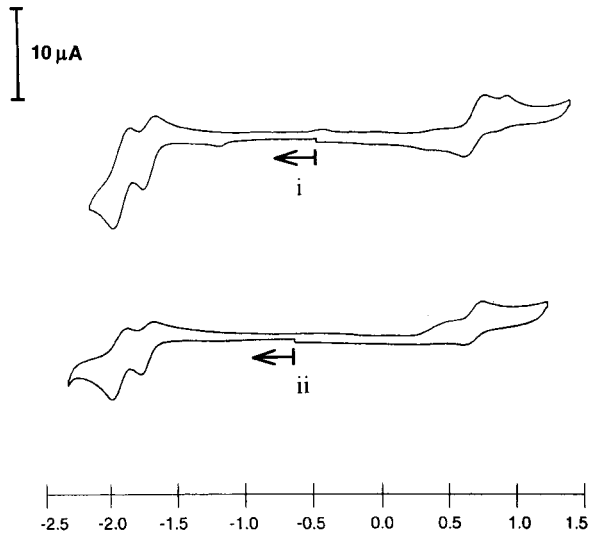


Figure 4. CV response of 1.0 mM solutions of the isomeric metallodendrimers. (i) **17** and (ii) **16** in 0.1 M Et_4NTFB in CH_3CN at 298 K. Potentials are against internal ferrocene/ferrocenium. Scan rate: 200 mV/s.

similar and exhibited two quasi-reversible waves at negative potentials that correspond to redox processes on two electroactive terpyridine groups.[15] Inspection of the corresponding electrochemical parameters, that is, the half-wave potential $E_{1/2}$ and the peak-to-peak splitting ΔE_p (Table 1), revealed interesting differences between the two structural isomers. On one hand, the $E_{1/2}$ values of the two waves of **16** were about 30 mV more negative than that of **17**. Since the reduction of these metallodendrimers generates neutral species that do not require (or incorporate) counterions from solution, but instead tend to get rid of them, the observed half-wave potential displacement may result from either differences of accessibility of counterions, or from differences in the solvent environment of the electroactive terpyridine groups. Metallodendrimer **16** features increased dendritic character on the periphery of the molecule; thus, the additional thermodynamic difficulty to reduce the terpyridine groups of **16** compared to **17** coupled with the necessary participation (loss) of counterions during reduction is consistent with decreased accessibility of counterions for **16**.[43−45] Interestingly, the ΔE_p values for two terpyridine redox processes in **16** and for the most positive wave of **17** were similar (within a 10 mV range) and ∼30 mV smaller than the ΔE_p for the most negative wave of **17**. This clearly indicated that the kinetic rate of electron transfer for one of the terpyridines in **17** was slower than that of the other terpyridine in **17** and both terpyridines in **16**.[46] According to the chemical structures of both dendrimers, the electron-transfer kinetic asymmetry showed by **17** should be expected on the basis of different chemical environments. As can be seen in Scheme 5, a dense branched cluster must surround the internal terpyridine groups in **17**, whereas the other three terpyridines (the external terpyridine of **17** and both terpyridines of **16**) were characterized by a relatively similar solvent-exposed environment. Furthermore, the asymmetry reflected on the ΔE_p values, presented in Table 1, was also consistent with the previous studies of similar compounds.[15]

(43) Dandliker, P. J.; Diederich, F.; Gisselbrecht, J.-P.; Louati, A.; Gross, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2725−2728.
(44) Chow, H.-F.; Chan, I. Y. K.; Chan, D. T.; Kwok, R. W. *Chem. Eur. J.* **1996**, *2*, 1085−1091.
(45) Gorman, C. B.; Parkhurst, B. L.; Su, W. Y.; Chen, K.-Y. *J. Am. Chem. Soc.* **1997**, *119*, 1141−1142.
(46) Newkome, G. R.; Narayanan, V. V.; Echegoyen, L.; Pèrez-Cordero, E.; Luftmann, H. *Macromolecules* **1997**, *30*, 5187−5191.

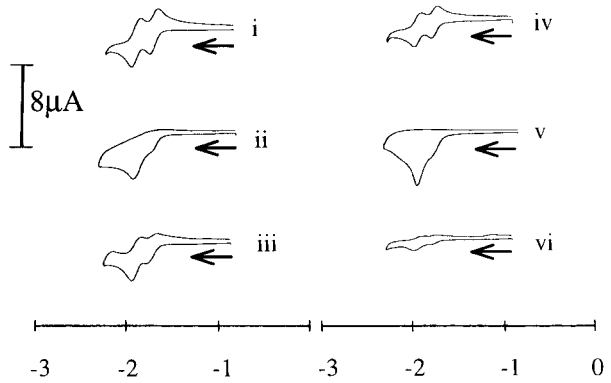


Figure 5. CV response of 1.0 mM solutions of dendrimers. (i) **34**, (ii) **35**, (iii) **36**, (iv) **31**, (v) **32**, (vi) **33** (the smaller current observed was due to the limited solubility of **33** that was presented in DMF) in 0.1 M Et_4NTFB in DMF at 298 K. Potentials are against internal ferrocene/ferrocenium. Scan rate: 200 mV/s.

Inspection of the positive region of the voltammograms also showed some interesting differences between the isomeric metallodendrimers **16** and **17**.[47] Figure 4ii, for instance, shows that the process involving the Ru^{3+}/Ru^{2+} couple of **16** corresponding to one quasi-reversible wave; that is, the four metallic centers were electrochemically equivalent. In contrast, Figure 4i shows that the wave corresponding to the Ru atoms in **17** had split into two waves with the more positive wave somewhat smaller. The apparent 3:1 ratio may arise from initial oxidation of three Ru atoms and oxidation of the fourth Ru atom at more positive potential, and may be indicative of reaction of the "tetrahedral" dendrimer at a fixed position on the electrode surface with three Ru centers close to the electrode and one Ru moiety oriented away from the electrode surface. In this regard, previous electrochemical studies on compounds bearing multiple equivalent electroactive units had shown that the corresponding redox waves split when these moieties were fixed at relatively short distances from each other. Further electrochemical studies of these materials are in progress.

Neutral Metallodendrimers. Electrochemical experiments with the neutral series of metallodendrimers give further insight to their electrocatalytic potential. The half-wave potentials for **31**−**36** in the metal oxidation region are very close to each other (Table 2); the only difference between the anodic redox waves of these compounds is a slightly larger peak-to-peak separation for the larger dendrimers. The terpyridine electrochemical responses are more varied and interesting; thus, the negative regions of the studied window are shown in Figure 5. For instance, Figure 5i shows the two reversible waves that characterize the cathodic CV response of the two-terpyridine ligands of **34**. After internal deprotection of the *tert*-butyl groups, the presence of the carboxylic acid moieties in **35** results in the merging of the two-redox waves and the virtual disappearance of the corresponding anodic signal (Figure 5ii). On the basis of previous studies of the electrochemical reduction of pyridine and its derivatives,[48,49] the irreversibility observed is due to an electrochemical−chemical reaction in which a proton uptaken by the aromatic anion radical from the vicinal carboxylic acid group upon a probable 1,4-reduction of one of the pyridine rings of each terpyridine ligand. This explanation is further supported by CV experiments with the second generation of neutral dendrimer **36** (as seen in Figure 5iii), where the lack of neighboring acidic protons, readily available in **35**, results in the recovery of the typical "two wave" reversible response of the terpyridine ligands.

CV experiments on the first generations of the related dendrimer series of **31**, **32** and **33**, exhibit similar voltammetric responses to those discussed above. By careful inspection of Table 2, however, the second generation complexes **34** and **36** show slightly larger ΔEp values than those corresponding to the first tier series **31** and **33**. This observation is in strong agreement with previous reports[43,45,50] and has been attributed to the slower electron-transfer kinetics that characterizes molecules featuring bulkier dendritic structures around their electroactive sites.

Conclusions

Two isomeric metallodendrimers were synthesized by a combination of divergent and convergent strategies. These two constitutional isomers clearly indicated the differences between dendrimers and traditional polymers. Due to the large molecular weight distribution of linear or branched polymers, no known methods can yield two structural isomeric polymers in pure form; however, two constitutionally isomeric metallodendrimers were constructed since each dendrimer possesses a single precise molecular mass of 12 526 Da. Another important aspect of construction of these two tailor-made metallomacromolecules is that we loosely mimicked the topology of simple organic molecules such as CR_4 or SiR_4 at nanoscopic scale by forming these simple dendritic networks. Thus, the dendritic network concept via envisioned "dendritic methane"-type of assembly was introduced. Despite their similar physical and chemical properties, these two isomers displayed distinct CV spectra that indicted the different internal density and void regions inside the dendritic networks.

Metallodendrimers are always in association with counterions that usually are external counterions, such as Cl^-, BF_4^-, NO_3^-, and PF_6^-, which may be interchangeable. The physical and chemical properties very often depend on the different associated counterions. Construction of metallodendrimers without external counterions not only added additional synthetic challenge, but also provided a better understanding of these materials. The PF_6^- salts are commonly used to make metal complexes more stable and less soluble for the purposes of storage and purification, but the Cl^- salts exhibited advantages in our materials. Due to the low solubilities of metallodendrimers, the Cl^- counterions maintained the solubilities to the point that measurement of NMR spectra was still quite convenient. The loss of external counterions in these metallomacromolecules had marginal effect on their spectra, as well as the stability and most of the physical properties. However, the solubilities of these neutral species decreased quite obviously in polar solvents, such as MeOH and H_2O, in comparison to those possessing external Cl^- counterions. These neutral metallodendrimers have internally balanced carboxylate moieties, which are weaker counterions than most others, like Cl^- and PF_6^-; the addition of inorganic salts to these neutral species conveniently gave the desired external counterions. One interesting and useful property of these neutral materials is that they tended to ionize more easily (lower laser power) and gave clearer signals

(47) The pre-waves at ~0.5 V were also present in background CV experiments performed on the solvent-supporting electrolyte system used. This signal remained unaffected by purification of the solvent and supporting electrolyte salt, and careful polishing of the electrode surface; thus, this signal does not arise from the electroactivity of the dendrimers studied, and its presence is not considered in the analysis and interpretation of the voltammetric responses.

(48) Elliott, C. M. *J. Chem. Soc., Chem. Commun.* **1980**, 261−262.

(49) Tokel-Takvoryan, N. E.; Hemingway, R. E.; Bard, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 6582−6589.

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in MALDI-TOF-MS than those possessing external Cl^- or PF_6^- counterions. This application could be a quite convenient method to obtain mass spectra of some less stable metal-containing macromolecules. The observed intramolecular proton transfer during the redox process also gives insight to the potential chemistry within such macromolecular constructs.

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