Construction of Dendritic Assemblies: A Tailored Approach to Isomeric Metallomacromolecules by Means of Bis(2,2′:6′,2″-terpyridine)ruthenium(II) Connectivity

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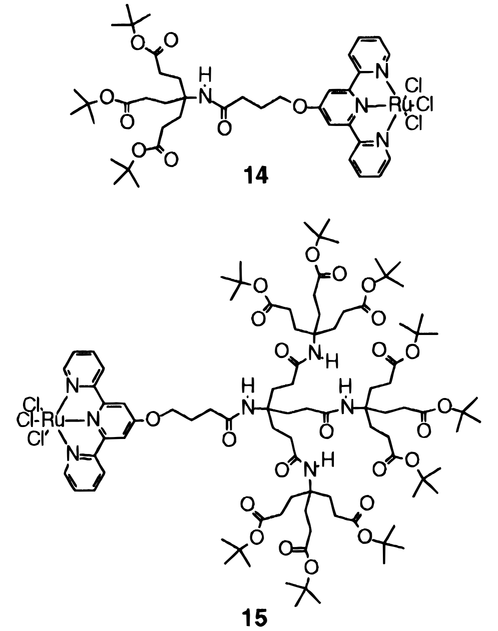
Received February 24, 1998
Revised Manuscript Received April 24, 1998

Routes to the assembly of metallomacromolecules have been widely investigated[1] due to their purported magnetic, electronic, photooptical, or catalytic properties.[2] An important feature of the use of branched monomers[3] in the construction of dendritic architectures[4] is the inherent synthetic control necessary to afford predetermined structures, which incorporate the desired utilitarian subunits into the superstructure. The incorporation of diverse dendritic subunits leads to the creation of a series of “dendritic assemblies”, which can, at least structurally, mimic molecular constructs but on the nanoscopic scale.

In our quest of new procedures to tailor-made supramolecular dendritic assemblies, we for the first time created two new isomeric metallomacromolecules **1**[5] and **2**.[6] The use of bis(2,2′:6′,2″-terpyridine)ruthenium(II) [−⟨*Ru*⟩−] connectivity[7] capitalizes on the formation of four stable complexes connecting the dendritic core with four similar dendritic molecules; thus the shape of CR_4 was created to generate an envisioned macromolecular “dendritic methane”-type of nanoscopic assembly.

The key building blocks, amines **10** and **11**, were prepared in the following manner (Scheme 1): nitroisophthalic acid was converted with 1 equiv of PCl_5 in cold Et_2O into the desired monoacyl chloride by a modified literature[8] procedure. Its treatment with amine[9] **8** afforded *N*-{tris[(2-*tert*-butoxycarbonyl)ethyl]-methyl}nitroisophthalamide monocarboxylic acid (**4**), which was subsequently reacted with 5-aminopentyl 4′-(2,2′:6′,2″-terpyridinyl) ether[10] (**5**) by DCC coupling[11] generating *N*-{tris[(2-*tert*-butoxycarbonyl)ethyl]methyl}-*N*′-[4′-oxa(2,2′:6′,2"-terpyridinyl)]nitroisophthalamide (**6**). Amidation of **4** was supported (^{13}C NMR) by the shift of the signal assigned to the quaternary carbon moiety (CONH*C*) of amine **8** from 52.8 to 58.7 ppm and the appearance (ESI-MS)[12] of a molecular peak at *m*/*z* 631.7 ($[M + Na^+]$ *m*/*z* 631.7). A downfield shift of (CONH*C*H_2) observed in the ^{13}C NMR spectrum of nitroterpyridyl **6** 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 supports its structural assignment. Hydrolysis of **6** by formic acid[13] gave the triacid **7**, which was iteratively amidated[14] to give nonaester **9**. The formation of **7** was supported by the signal at 174.6 ppm (*C*OOH) in the ^{13}C NMR spectrum and the molecular peak at *m*/*z* 757.3 ($[M + H^+]$ *m*/*z* 757.8) in ESI-MS. Structure **9** was confirmed by the new signal for the additional quaternary carbon (CONH*C*) at 57.5 ppm and the molecular peak (ESI-MS) at *m*/*z* 1972.0 ($[M + Na^+]$ *m*/*z* 1972.8). Reduction[15] of the aryl nitro moieties of both **6** and **9** under 10% Pd on C with a large excess of $HCOONH_4$ afforded the key arylamine monomers **10** and **11**, respectively, which were supported by the chemical shift (^{13}C NMR) for the aryl-*C* from 148.6 to 147.5 ppm and the molecular peaks at *m*/*z* 917.5 ($[M + Na^+]$ *m*/*z* 918.1) for **10** and at *m*/*z* 1942.8 ($[M + Na^+]$ *m*/*z* 1942.5) for **11**. Other standard spectral and analytical data further confirm the assigned structures.



14

15

Figure 1. First and second tier of metallodendrimers.

The first and second tier neutral Ru(III) metallodendrimers **14** and **15** were prepared by an established procedure[7b] (Figure 1). The first and second tier dendritic cores (**12** and **13**) were prepared via a coupling reaction of tetraacid chloride[16] (Scheme 2) with 4 equiv of **10** and **11**, respectively, in THF in the presence of Et_3N. ^{13}C NMR spectra of **12** and **13** showed a similar shift of the signal at about 147.5 to 139.2 ppm corresponding to Ar*C*−NHCO, which confirms the amidation. Both structures were further supported by the peaks (MALDI-TOF)[17] at *m*/*z* 1988.7 ($[M + 2Na^+]$ and *m*/*z* 8075 ($[M + 2Na^+ - H^+]$, respectively.

The complementary metallodonor and receptor dendritic molecules were readily assembled by four [−⟨*Ru*⟩−] connections to generate a methane-type motif. Reductive couplings were performed in boiling MeOH in the presence of 4-ethylmorpholine to afford the microcrystalline, red dendritic assemblies **1**−**3**[18] (Schemes 3 and 4). Based on ^{13}C NMR spectra, all three networks show the absence of any free terpyridine moiety and the presence of two similar but distinct complexed terpyridine moieties (i.e., core vs terminal directed terpyridines), indicative of the four symmetrical attachments. The UV−vis spectra showed four main absorption bands (λ_{max} = 242, 268, 306, 488 nm) for all three dendritic assemblies, in which the absorption intensity (ϵ) is proportional to the number of metal complexes, which is indicative that all three molecular assemblies have

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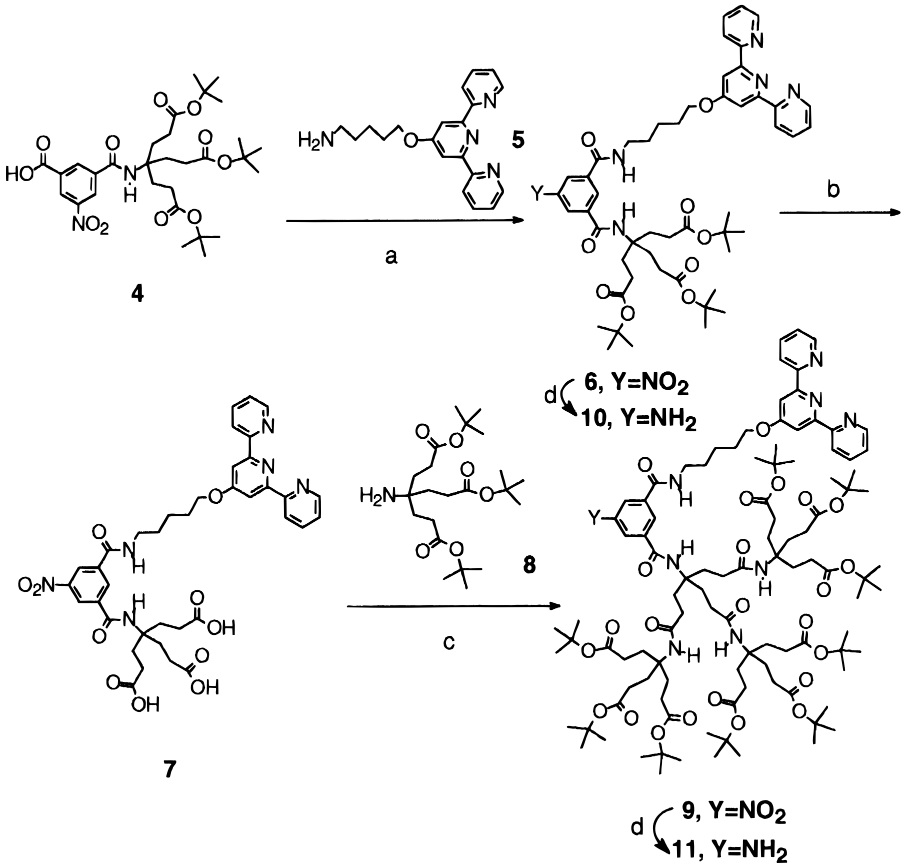
Scheme 1. Synthesis of the Functionalized Monomers[a]



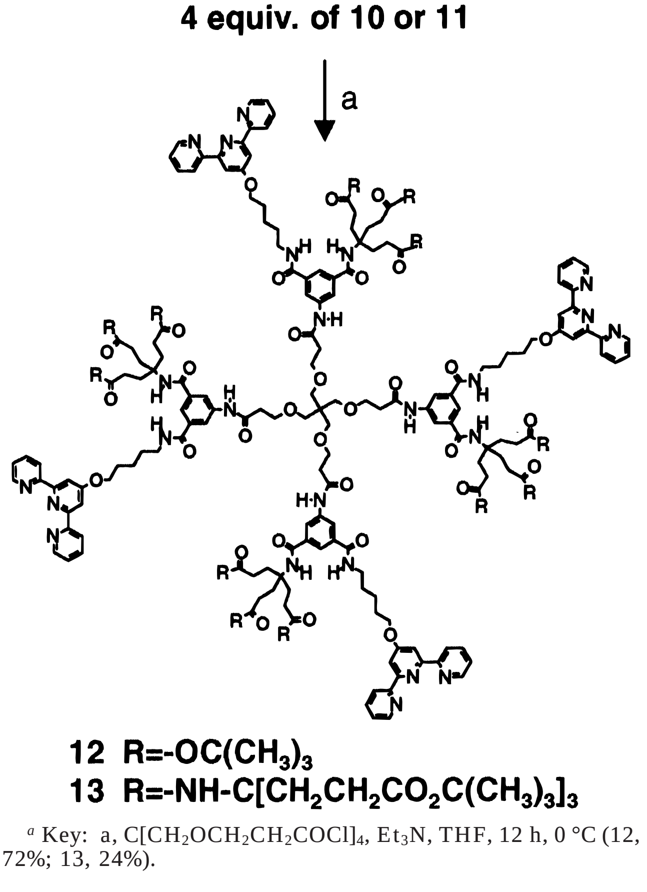
[a] Key: a, DCC, 1-HOBT, DMF, 24 h, 25 °C (84%); b, HCO_2H, 24 h, 25 °C (95%); c, 3.1 equiv **8**, DCC, 1-HOBT, DMF, 48 h, 25 °C (90%); d, 10% Pd/C, HCO_2NH_4, MeOH, 0.5 h, 50 °C (10, 87%; 11, 83%).

the same number of [−⟨*Ru*⟩−] connections. By comparison of these data with literature values,[7c,10,19] the four Ru(II) complexes are present in each of the dendritic constructs. The MALDI-TOF mass spectrum of each showed molecular peaks at *m*/*z* 8283 ([M − PF_6^-] *m*/*z* 8283) for **3**, at *m*/*z* 12 235 ([M − $2PF_6^-$] *m*/*z* 12 236) for **2**, and at *m*/*z* 12 234 ([M − $2PF_6^-$] *m*/*z* 12 236) for **1**.

A notable feature of these dendritic assemblies is that the design of the macromolecular architecture is controlled and the nanoscopic tetrahedral geometry of methane is mimicked. Most interestingly, structures **1** and **2** have an identical molecular formula ($C_{597}H_{880}F_{48}N_{52}O_{136}P_8Ru_4$) and are constitutional isomers. Unlike the characteristics of most structural isomers, which generally possess widely differing chemical and physical properties, these isomeric macromolecular assemblies share similar solubility and decomposition temperatures. Additionally, they are spectrally alike but are composed of different internal densities and void regions,[20] as depicted and shown by the following electrochemical data.

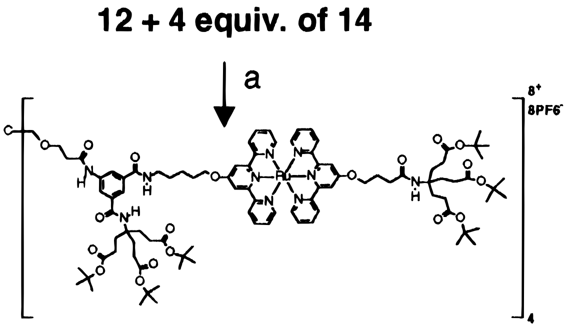
Cyclic voltammetry experiments of metallodendrimers **1** and **2** afforded insight concerning the chemical environments around the −⟨*Ru*⟩− moieties.[21] The voltammograms of both compounds are similar and exhibit two quasi-reversible waves (Figure 2) at negative potentials that correspond to redox processes on the two terpyridines.[7b] The $E_{1/2}$ values of the two waves of **2** are slightly more negative than those of **1** (Table 1). Since **2** features increasing dendritic character on the periphery of the molecule, the additional difficulty to reduce the terpyridines of **2** could be due to an increased

Scheme 2. Synthesis of the Dendritic Cores[a]



[a] Key: a, $C[CH_2OCH_2CH_2COCl]_4$, Et_3N, THF, 12 h, 0 °C (12, 72%; 13, 24%).

Scheme 3. Synthesis of Dendritic Assembly 3[a]



3

[a] Key: a, 4-Ethylmorpholine, MeOH, 4 h, reflux (97%).

inaccessibility of counterions.[22] In addition, the ΔE_p values for the two waves of **2** and for the most positive wave of **1** are similar and smaller than the ΔE_p for the most negative wave of **1**. This clearly indicates that the rate of electron transfer for one of the terpyridines in **1** is slower than that of the others.[23] The kinetic asymmetry should be expected on the basis of different chemical environments because of the different internal densities and void regions.[23,24] The voltammograms show one quasi-reversible pattern for the four Ru atoms of **2** (i.e., all the Ru atoms are electrochemically equivalent) and two waves for the metallic centers of **1**. This suggests that, as opposed to **2**, in which the bulky hyperbranched cluster is located on the periphery of the molecule, the internal dendritic structure of **1** may provide enough rigidity so that electrochemical communication between the Ru atoms is possible.[25]

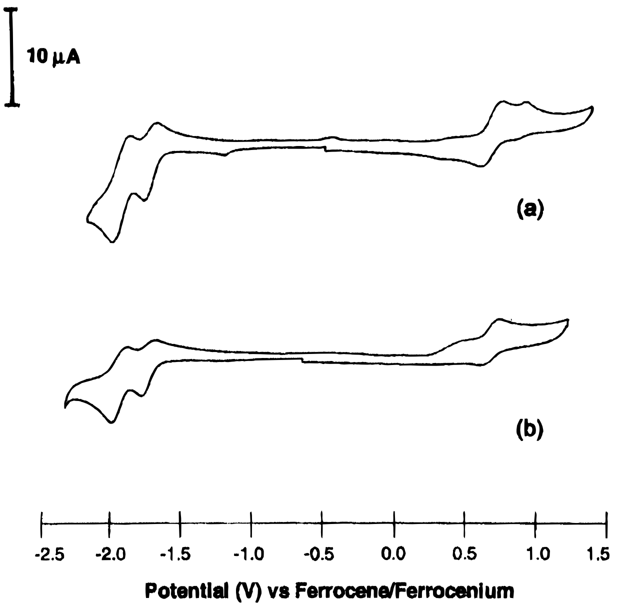
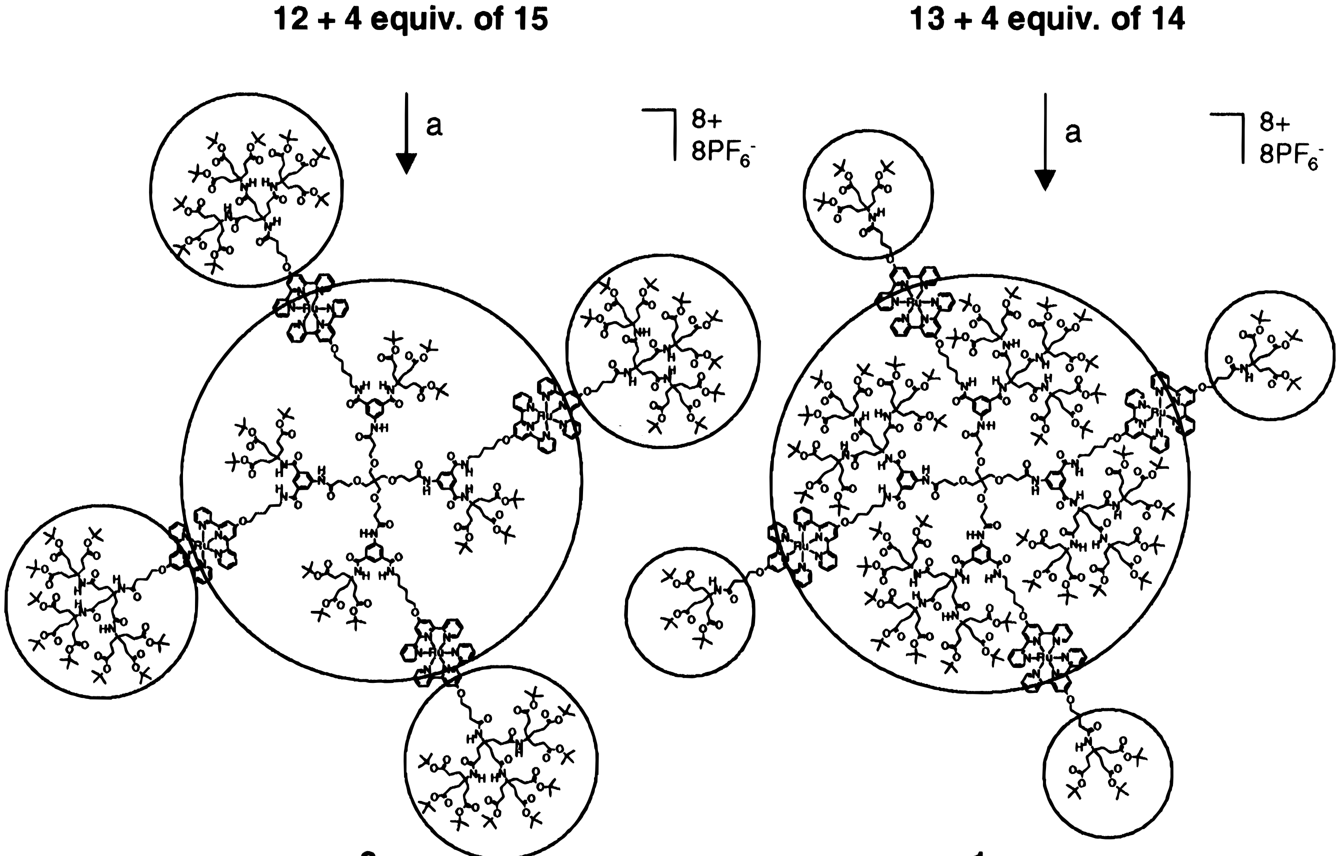


Figure 2. CV response of 1.0 mM solutions of dendrimers (a) **1** and (b) **2** in 0.1 M Et_4NTFB in CH_3CN at 298 K. Potentials are against internal ferrocene/ferrocenium. Scan rate: 200 mV/s.

In summary, the construction of structurally predetermined macromolecular components and their subsequent mutual attachment by established metal connectivity at precise loci afford a novel approach to the generation of dendritic assemblies with nanoscopic dimensions. This protocol, as conceived, geometrically mimics fundamental molecular structures. The den-

Scheme 4. Synthesis of Dendritic Assemblies 1 and 2[a]



2 **1**

[a] Key: a, 4-Ethylmorpholine, MeOH, 6 h, reflux (1: 80 %, 2: 93%).

Table 1. Electrochemical Parameters for Metallodendrimers 1 and 2 in CH_3CN at 298 K

compound	terpyridines		Ru^{3+}/Ru^{2+}	
	$E_{1/2}$ (ΔE_p)[a]	$E_{1/2}$ (ΔE_p)[a]	$E_{1/2}$ (ΔE_p)[a]	$E_{1/2}$ (ΔE_p)[a]
1	−1.923 (0.121)	−1.720 (0.087)	0.719 (0.170)	0.919 (0.092)
2	−1.951 (0.097)	−1.751 (0.093)	0.709 (0.109)	

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

dritic development of either the second or third tier either inside (core) or outside (appendage) of this construct will lead to new and different isomeric metallomacromolecules, which certainly will reveal interesting avenues to the creation of precisely coordinated, interrelated polymeric families. The application of this dendritic construction is currently being applied to nanoscopically mimicking other simple related hydrocarbon-like systems.

Acknowledgment is made to the National Science Foundation (DMR-96-22609; BIR-95-12208) and the Army Research Office (DAAH04-95-1-0373; DAAH04-96-1-0306). We gratefully thank Dr. Gregory R. Baker and Dr. Charles N. Moorefield for molecular modeling and constructive suggestions. We also thank Mr. Jason Hair for his expertise in computer graphics.

References and Notes

(1) For recent review, see: Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules: Concepts, Syntheses, Perspectives*; VCH: Weinheim, 1996. Recent metallodendrimers, see: Huck, W. T. S.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1213. Liao, Y.-H.; Moss, J. R. *Organometallics* **1996**, *15*, 4307. Lange, P.; Schier, A.; Schmidbaur, H. *Inorg. Chem.* **1996**, *35*, 637. Achar, S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 43. Loseda, J.; Cuadrado, I.; Morán, M.; Casado, C. M.; Alonso, B.; Barranco, M. *Anal. Chim. Acta* **1997**, *338*, 191. Constable, E. C. *J. Chem. Soc., Chem. Commun.* **1997**, 1073. Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26.

(2) Kleppinger, R.; Lillya, C. P.; Yang, C. *J. Am. Chem. Soc.* **1997**, *119*, 4097. Harriman, A.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1996**, 1707. Jiang, D. L.; Aida, T. *J. Chem. Soc., Chem. Commun.* **1996**, 1523. Hanan, G. S.; Arana, C. R.; Lehn, J.-M.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1122. Amoroso, A. J.; Thompson, A. M. W. C.; Maher, J. P.; McCleverty, J. A.; Ward, M. D. *Inorg. Chem.* **1995**, *34*, 4828.

(3) Newkome, G. R.; Moorefield, C. N.; Baker, G. R. *Aldrichim. Acta* **1992**, *25*, 31.

(4) Newkome, G. R.; Weis, C. D.; Moorefield, C. N.; Baker, G. R.; Childs, B. J.; Epperson, J. *Angew. Chem.* **1998**, *110*, 318. Huck, W. T. S.; Veggel, F. C. J. M. van; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1213. Armspach, D.; Cattalini, M.; Constable, E. C.; Housecroft, C. E.; Phillips, D. *J. Chem. Soc., Chem. Commun.* **1996**, 1823. Ardoin, N.; Astruc, D. *Bull. Soc. Chim. Fr.* **1996**, *132*, 875. Constable, E. C.; Thompson, A. M. W. C.; Harverson, P.; Macko, L.; Zehnder, M. *Chem. Eur. J.* **1995**, *1*, 360.

(5) All compounds were fully characterized by microanalysis, IR, ^1H NMR, and the following data. **1**: $C_{597}H_{880}F_{48}N_{52}O_{136}P_8Ru_4$; FM = 12 526; mp >152 °C dec; ^{13}C NMR (CD_3CN) δ 24.6 ($\mathrm{\mathit{C}H_2CH_2CH_2NH}$), 25.2 ($\mathrm{OCH_2\mathit{C}H_2CH_2CONH}$), 28.7 (d, $\mathrm{\mathit{C}H_3}$), 28.8, 29.0 ($\mathrm{\mathit{C}H_2CH_2\mathit{C}H_2CH_2NH}$), 30.8 (d, all $\mathrm{\mathit{C}H_2\mathit{C}H_2CO_2}$), 32.5 (d, $\mathrm{\mathit{C}H_2\mathit{C}H_2CONH}$), 32.9 ($\mathrm{OCH_2CH_2\mathit{C}H_2CONH}$), 38.8 ($\mathrm{OCH_2\mathit{C}H_2CONH}$), 41.2 ($\mathrm{CONH\mathit{C}H_2}$), 45.2 ($\mathit{C}$-core), 58.6 ($36\mathit{C}^{4\circ}$), 58.9, 59.8 ($4\mathit{C}^{4\circ}$, $12\mathit{C}^{4\circ}$), 66.1, 68.7, 70.7, 71.4 (all $\mathrm{O\mathit{C}H_2}$), 81.2, 81.3 ($\mathrm{\mathit{C}Me_3}$), 112.5 (d, py$\mathit{C}^{5,5''}$), 122.3 (ArC^4), 125.8 (d, py$\mathit{C}^{4,4''}$), 128.8 (d, py$\mathit{C}^{3,3''}$), 136.8, 137.6 (Ar$\mathit{C}^{2,3,5,6}$), 139.1 (d, py$\mathit{C}^{3',5'}$), 140.2 (ArCNHCO), 153.8 (d, py$\mathit{C}^{6,6''}$), 157.8 (d, py$\mathit{C}^{2,2''}$), 159.7 (d, py$\mathit{C}^{2',6'}$), 167.2 (d, py$\mathit{C}^{4'}$), 167.7, 168.3 ($\mathrm{\mathit{C}ONH, CH_2NH\mathit{C}O}$), 172.1 ($\mathrm{OCH_2CH_2\mathit{C}ONH}$), 173.3 ($\mathrm{OCH_2CH_2CH_2\mathit{C}ONH}$), 173.9, 174.4 ($\mathrm{\mathit{C}O_2}$); MALDI-TOF-MS *m/z* 12234 ($M - 2PF_6$); 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 ($6.73 \times 10^4$).

(6) **2**: $C_{597}H_{880}F_{48}N_{52}O_{136}P_8Ru_4$; FM = 12 526; mp >152 °C dec; ^{13}C NMR (CD_3CN) δ 23.2 ($\mathrm{\mathit{C}H_2CH_2CH_2NH}$), 24.8 ($\mathrm{OCH_2\mathit{C}H_2CH_2CONH}$), 28.1 (d, $\mathrm{\mathit{C}H_3}$), 28.6, 29.0 ($\mathrm{\mathit{C}H_2CH_2\mathit{C}H_2CH_2NH}$), 29.8 (d, $\mathrm{36\mathit{C}H_2\mathit{C}H_2CO_2}$), 31.5 (d, $\mathrm{12\mathit{C}H_2\mathit{C}H_2CO_2}$), 33.0 ($\mathrm{OCH_2CH_2\mathit{C}H_2CONH}$), 34.7 (d, $\mathrm{\mathit{C}H_2\mathit{C}H_2CONH}$), 37.8 ($\mathrm{OCH_2\mathit{C}H_2CONH}$), 40.2 ($\mathrm{CONH\mathit{C}H_2}$), 45.0 ($\mathit{C}$-core), 57.7 ($36\mathit{C}^{4\circ}$), 58.3, 58.4 ($4\mathit{C}^{4\circ}$, $12\mathit{C}^{4\circ}$), 66.0, 68.5, 69.3, 71.1 (all $\mathrm{O\mathit{C}H_2}$), 80.6, 81.4 ($\mathrm{\mathit{C}Me_3}$), 111.2 (d, py$\mathit{C}^{5,5''}$), 121.5 (ArC^4), 124.6 (d, py$\mathit{C}^{4,4''}$), 127.7 (d, py$\mathit{C}^{3,3''}$), 136.1, 136.4 (Ar$\mathit{C}^{2,3,5,6}$), 137.9 (d, py$\mathit{C}^{3',5'}$), 138.8 (ArCNHCO), 152.0 (d, py$\mathit{C}^{6,6''}$), 156.0 (d, py$\mathit{C}^{2,2''}$), 158.2 (d, py$\mathit{C}^{2',6'}$), 166.3 (d, py$\mathit{C}^{4'}$), 166.4, 166.5 ($\mathrm{\mathit{C}ONH, CH_2NH\mathit{C}O}$), 171.8 ($\mathrm{OCH_2CH_2\mathit{C}ONH}$), 172.4 ($\mathrm{CH_2CH_2\mathit{C}ONH}$), 172.8 ($\mathrm{\mathit{C}O_2}$), 173.5 ($\mathrm{\mathit{C}O_2}$); MALDI-TOF-MS *m/z* 12235 ($M - 2PF_6$); 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 ($6.54 \times 10^4$).

(7) (a) Newkome, G. R.; Cardullo, F.; Constable, E. C.; Moorefield, C. N.; Thompson, A. M. W. C. *J. Chem. Soc., Chem. Commun.* **1993**, 925. (b) Newkome, G. R.; Güther, R.; Moorefield, C. N.; Cardullo, F.; Echegoyen, L.; Perez-Cordero, E.; Luftmann, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2023. (c) Constable, E. C.; Thompson, A. M. W. C. *New J. Chem.* **1996**, *20*, 65.

(8) Landsteiner, K.; Van Der Scheer, J. *J. Exp. Med.* **1983**, *67*, 709.

(9) Newkome, G. R.; Weis, C. D. *Org. Prep. Proc. Int.* **1996**, *28*, 485.

(10) Newkome, G. R.; He, E. *J. Mater. Chem.* **1997**, *7*, 1237.

(11) Klausner, J.; Bodansky, B. *Synthesis* **1972**, 453.

(12) ESI-MS experiments were performed in MeOH with an accuracy of mass determination ±0.1%.

(13) Chandrasekaran, S.; Kluge, A. F.; Edwards, J. A. *J. Org. Chem.* **1977**, *42*, 3972.

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

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

(16) Newkome, G. R.; Lin, X. *Macromolecules* **1991**, *24*, 1443.

(17) MALDI-TOF experiments were conducted with a 340 nm laser, linear mode, 2,5-dihydroxylbenzoic acid matrix with an accuracy of mass determination of ±0.2%.

(18) **3**: $C_{381}H_{508}F_{48}N_{40}O_{76}P_8Ru_4$; FM = 8428.4; mp >182 °C dec; ^{13}C NMR (CD_3CN): δ 24.4 ($\mathrm{\mathit{C}H_2CH_2CH_2NH}$), 25.3 ($\mathrm{OCH_2\mathit{C}H_2CH_2CONH}$), 28.4 ($\mathrm{\mathit{C}H_3}$), 28.6, 29.0 ($\mathrm{\mathit{C}H_2CH_2\mathit{C}H_2CH_2NH}$), 30.8 (d, $\mathrm{\mathit{C}H_2\mathit{C}H_2CO_2}$), 33.0 ($\mathrm{OCH_2CH_2\mathit{C}H_2CONH}$), 37.9 ($\mathrm{OCH_2\mathit{C}H_2CONH}$), 40.2 ($\mathrm{CONH\mathit{C}H_2}$), 45.2 ($\mathit{C}$-core), 58.8 ($12\mathit{C}^{4\circ}$), 59.6 ($4\mathit{C}^{4\circ}$), 66.0, 68.5, 70.7, 71.7 (all $\mathrm{O\mathit{C}H_2}$), 81.2, 81.3 ($\mathrm{\mathit{C}Me_3}$), 112.6 (d, py$\mathit{C}^{5,5''}$), 122.8 (ArC^4), 125.8 (d, py$\mathit{C}^{4,4''}$), 128.8 (d, py$\mathit{C}^{3,3''}$), 136.7, 137.2, (Ar$\mathit{C}^{2,3,5,6}$), 139.1 (d, py$\mathit{C}^{3',5'}$), 140.9 (ArCNHCO), 153.7 (d, py$\mathit{C}^{6,6''}$), 157.7 (d, py$\mathit{C}^{2,2''}$), 159.7 (d, py$\mathit{C}^{2',6'}$), 167.2 (d, py$\mathit{C}^{4'}$), 167.2, 167.6 ($\mathrm{\mathit{C}ONH, CH_2NH\mathit{C}O}$), 171.8 ($\mathrm{OCH_2CH_2\mathit{C}ONH}$), 173.3 ($\mathrm{OCH_2CH_2CH_2\mathit{C}ONH}$), 174.0 (d, $\mathrm{\mathit{C}O_2}$); MALDI-TOF-MS *m/z* 8283 ($M - PF_6$); UV−vis λ_{max} 242 ($\epsilon = 2.74 \times 10^5$), 268 ($2.37 \times 10^5$), 306 ($2.32 \times 10^5$), 488 nm ($6.67 \times 10^4$).

(19) Vogler, L. M.; Jones, S. W.; Jensen, G. E.; Brewer, R. G.; Brewer, K. J. *Inorg. Chim. Acta* **1996**, *250*, 155.

(20) See ref 1a, Section 2.3.3.3, pp 28−30.

(21) CV experiments were carried out using a Princeton Applied Research (PAR) Model 173 potensiostat 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 carried out using a three-electrode standard setup (Cypress Systems, Lawrance, Kansas) in which a glassy carbon disk electrode (1 mm diameter), a platinum wire, and a Ag wire were properly fitted as the working, counter, and pseudoreference electrodes, respectively. All the solutions [1.0 mM of the electroactive dendrimer in 0.1 M of tetraethylammonium tetrafluoroborate (Et_4NTFB) in anhydrous MeCN] 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.

(22) Gorwan, C. B.; Parkhurst, B. L.; Su, W. Y.; Chen, K. Y. *J. Am. Chem. Soc.* **1997**, *119*, 1141. Chow, H. F.; Chan, I. Y.;

Chan, D. T. W.; Kwok, R. W. M. *Chem. Eur. J.* **1996**, *2*, 1085. Dandliker, P. J.; Diederich, F.; Gisselbrecht, J. P.; Louati, A.; Gross, M. *Angew Chem., Int. Ed. Engl.* **1995**, *34*, 2725.

(23) Newkome, G. R.; Narayanan, V. V.; Echegoyen, L.; Pérez-Cordero, E.; Luftmann, H. *Macromolecules* **1997**, *30*, 5187.

(24) Molecular simulations of the metallodendrimers **1** and **2** show that whereas the internal terpyridines of **1** are surrounded by the hyperbranched hydrocarbon environment, the other three terpyridines (the external terpyridine of **1** and both terpyridines of **2**) are characterized by a relatively similar solvent-exposed environment.

(25) Cuadrado, I.; Casado, C. M.; Alonso, B.; Morán, M.; Losada, J.; Belsky, V. *J. Am. Chem. Soc.* **1997**, *119*, 7613.

MA980280R