Design, Syntheses, Complexation, and Electrochemistry of Polynuclear Metallodendrimers Possessing Internal Metal Binding Loci

George R. Newkome,* Anil K. Patri, and Luis A. Godínez[a]

Abstract: Extended, branched monomers possessing bipyridine moieties were synthesized by the use of high dilution conditions, then utilized in the assembly of macromolecular constructs. Dendrimers with four internal bipyridine units at precise locations within the superstructure were transformed into their $[Ru(bpy')(bpy)_2]^{2+}$ (bpy = 2,2′-bipyridine) complexes. The absorption spectra and cyclic voltammetry measurements of these polynuclear dendritic bipyridine ruthenium(II) complexes were measured and used to confirm their composition.

Keywords: bipyridine · cyclic voltammetry · dendrimers · metallodendrimers · ruthenium

Introduction

Dendrimers offer a wide range of unique physical and chemical properties owing to the availability of different functional surface groups as well as their internal cavities. As a result, unimolecular micelles,[1, 2] novel amphiphiles,[3] complexation agents,[4] photocatalysts,[5, 6] and MRI contrast agents[7] are notable areas that utilize selected aspects of different regimes of these macromolecular constructs. Many of the original issues associated with the assembly of these uniform spherical macromolecules, such as characterization, purity, dense packing limits, and surface functionalization, have been addressed and reviewed.[8–12] After establishing the foundations for their design and construction, attention is now being focussed on different tailored approaches to prepare highly specific, application-oriented dendrimers.[13]

From Balzani et al.,[14] the utilization of internal metal centers has lead to metallodendrimers possessing a variety of metal centers, instilling different dimensions to their physiochemical properties.[15] Making use of metal ion coordination, hyperbranched 1,10-phenanthroline[16] and 2,2′-bipyridine[17] ligands were self-assembled with Cu^{I} and Ru^{II} metal ions, respectively, to form dendrimers with central metal cores. Dendrimers with metal porphyrins at the core[18–30] were synthesized by means of a divergent procedure and were reported to show interesting photophysical and electrochemical properties. In that metals were used as branching centers to prepare arborols, Balzani and co-workers[31] used ruthenium as a branching center through a protection/deprotection scheme; whereas, Puddephatt et al.[32–36] prepared Pt-branched organoplatinum dendrimers by an oxidative addition/complexation cycle. Veggel and Reinhoudt et al.[37, 38] reported the preparation of metallodendrimers based on branching with coordinated Pd^{II} and then used this strategy in the preparation[39] of building blocks containing a barbituric acid residue; these then formed a hexameric rosette upon hydrogen bonding with melamine. Numerous accounts explore the surface chemistry of dendrimers possessing ruthenium,[40] nickel,[41] cobalt,[42] and copper, zinc, or nickel,[43] as the coordinating metal. Based on nonbranching metal connectivity, we reported the stepwise assembly of dendrimers by means of tpy-Ru^{II}-tpy (tpy = 2,2′:6′,2″-terpyridine) internal connectivity;[44-47] such construction has given rise to isomeric, tetrahedral dendritic assemblies.[48, 49]

The controlled internal chemical modifications of preformed dendrimers has been, thus far, limited to the site- and depth-specific placement of dicobalt clusters[50] and *ortho* carborane,[51] electrochemical reduction and oxidation of porphyrin-based[21, 52] and Ru-containing[17, 53, 54] dendrimers, and bis-dendrimer formation.[46] Our interests in the incorporation of specific binding loci within the internal cavities[55-58] for covalent and noncovalent attachment of guests have lead to the development of various multicomponent monomers through a high-dilution, three-component synthetic procedure. By variation of the subunit and/or spacer, it is possible to define the number and location of these utilitarian units within the supramolecular architecture. As $[Ru(bpy)_3]^{2+}$ complexes show a unique combination of photophysical and redox properties, incorporation of multiple units of these metal centers within a dendritic environment is of current interest. We recently reported the synthesis of substituted 2,2′-bipyridines[59] for the incorporation of these ligands into

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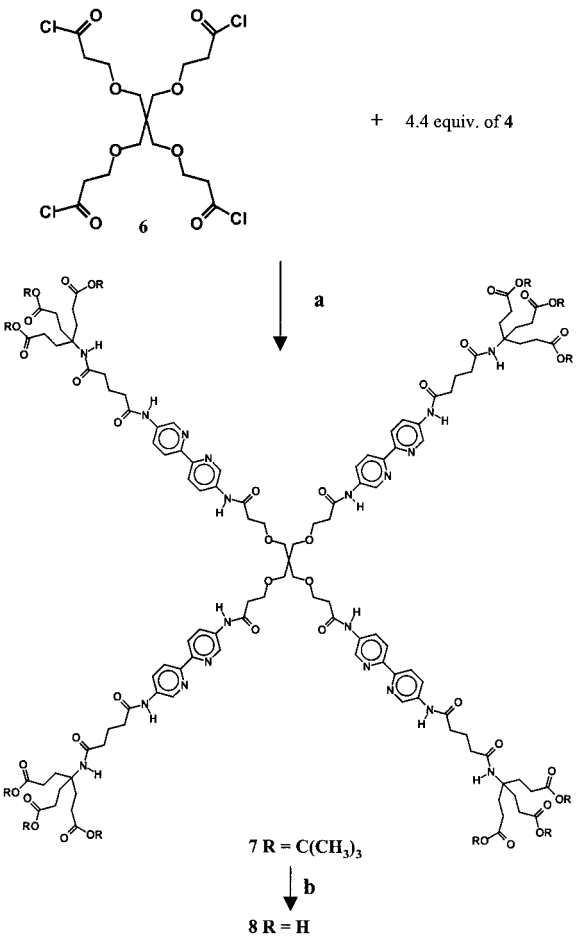
dendrimers. Herein we report the synthesis, metal complexation, and characterization using UV/VIS spectroscopy and electrochemistry of polynuclear $[Ru(bpy')(bpy)_2]^{2+}$ dendrimers.

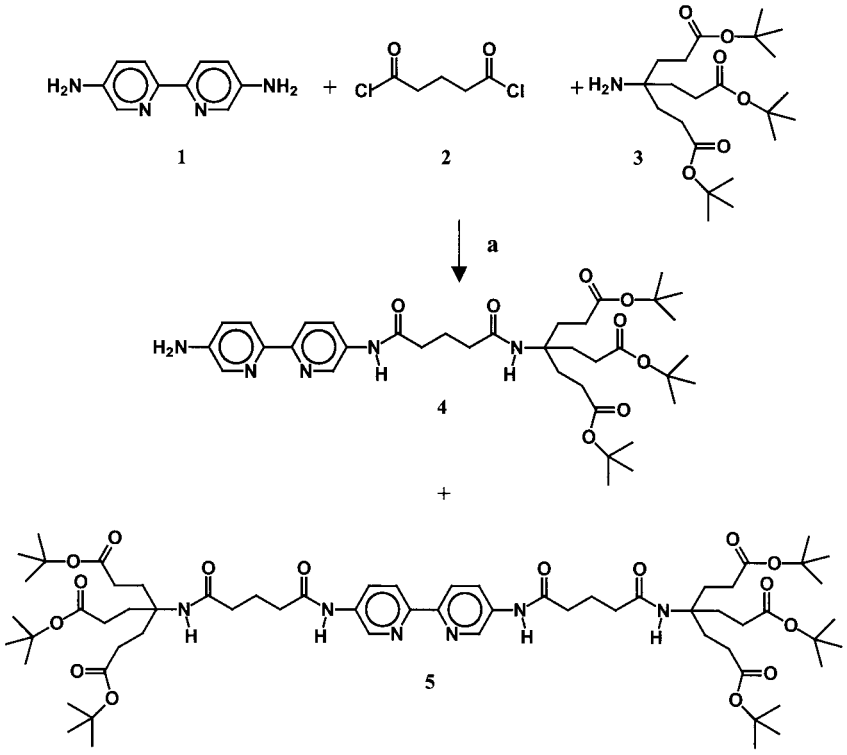
Results and Discussion

The key building block was prepared by treating glutaryl dichloride with one equivalent of Behera's amine (**3**),[60] followed by one equivalent of 2,2′-bipyridine-5,5′-diamine[61] (**1**) under high-dilution reaction conditions, with diisopropylethylamine as base, to afford the extended monomer **4** (54%; Scheme 1). The reaction mixture also afforded another useful byproduct, the 2-directional hexaester **5** (6%); these materials were easily separated by column chromatography over basic alumina. The structure of monomer **4** was supported by ^{13}C NMR spectrum, which showed ten distinct heteroaromatic signals including $\delta = 134.4$ and 136.3 for the different 6,6′-carbon atoms, in addition to the other expected signals. This pattern is characteristic of an unsymmetrically substituted bipyridine ring system[59] in contrast to the starting symmetrical bipyridine diamine **1**, which shows only five signals in the aromatic region. Notably, the ^{13}C NMR spectrum of hexaester **5** displayed only five signals in the aromatic region at $\delta = 120.4$, 127.0, 135.2, 140.1, and 150.8, confirming its symmetrical composition.

A slight excess (4.4 equiv) of pure monomer **4** was treated with tetrakis(acyl chloride) core **6**[62] in scrupulously anhydrous THF to give (94%) the first tier four-directional dodecaester **7** (Scheme 2). Formation of **7** was readily monitored by thin-layer chromatography (TLC). Structural



Scheme 2. Synthesis of first generation dendrimers **7** and **8**. a) THF, 0–25 °C, diisopropylethylamine; b) HCO_2H.



Scheme 1. Synthesis of building block **4**. a) THF, 0–25 °C, diisopropylethylamine.

proof for **7** is derived from its ^{13}C NMR spectrum, which displays only five signals in the aromatic region at $\delta = 120.4$, 127.5, 134.9, 140.4, and 150.4, similar to the hexaester **5**, indicating the desired bisamidation; however, upon close scrutiny, the data showed that two nearly identical sets of signals existed, for example, $\delta = 150.4$ and 150.7 for the 5,5′-carbons of bipyridine, supporting its inherent dissymmetry. Deprotection of the twelve peripheral *tert*-butyl ester groups of **7** was effected by the treatment with formic acid at 25 °C for 36 h affording (80%) the dodecacarboxylic acid **8**. Residual formic acid was removed by dialysis of **8** in a methanol and water mixture. The structure of **8** was established (^{13}C NMR) by the total absence of the distinctive

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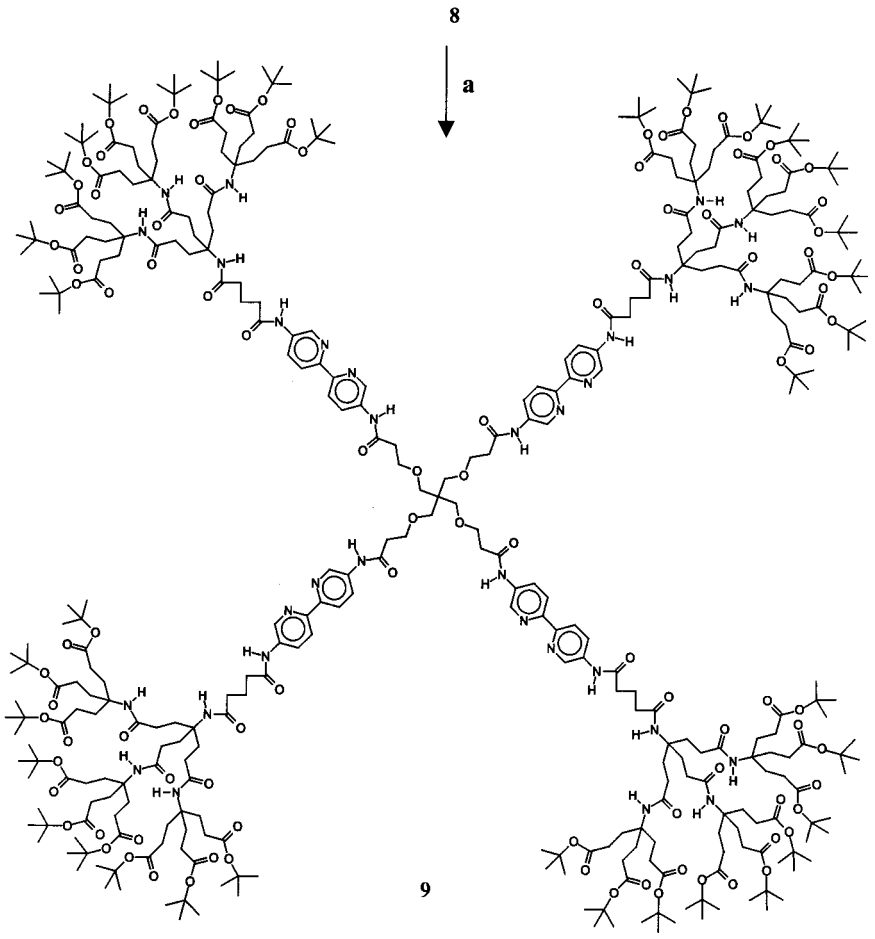
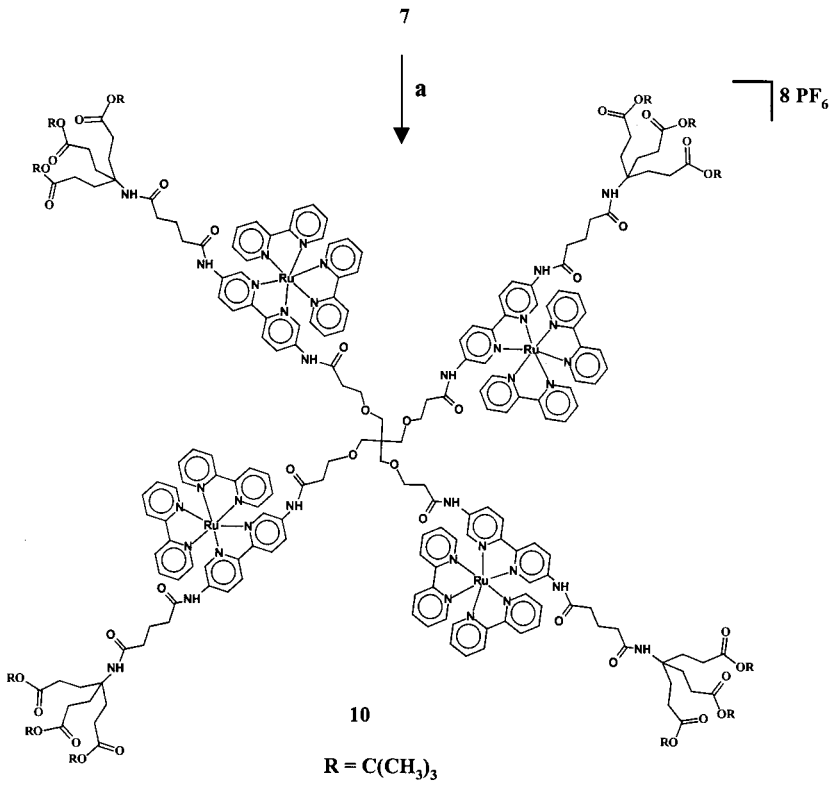
signals for the *tert*-butyl group carbons at δ 27.8 and 80.6, and appearance of a downfield signal at δ 183.7 for the terminal acid carbon atom.

Dodecaacid **8** was coupled[63] with **3** in the presence of DCC(DCC = dicyclohexyl carbodiimide) and 1-HBT (HBT = 1-hydroxybenzotriazole) in dry DMF to afford the second generation dendrimer **9** (38%; Scheme 3), which was spectroscopically supported (^{13}C NMR) by the broadening of signals, the difference in the relative intensities of the signals, and the appearance of additional signals at $\delta = 57.5$ (corresponding to $^{4^\circ}$*C*NH of new generation; 4° = quaternary) and $\delta =$ 172.8 (for *C*O$_2$*t*Bu). Absence of the distinctive carbonyl signal at $\delta = 183.7$ for the carboxylic acid moieties also supported the transformation.

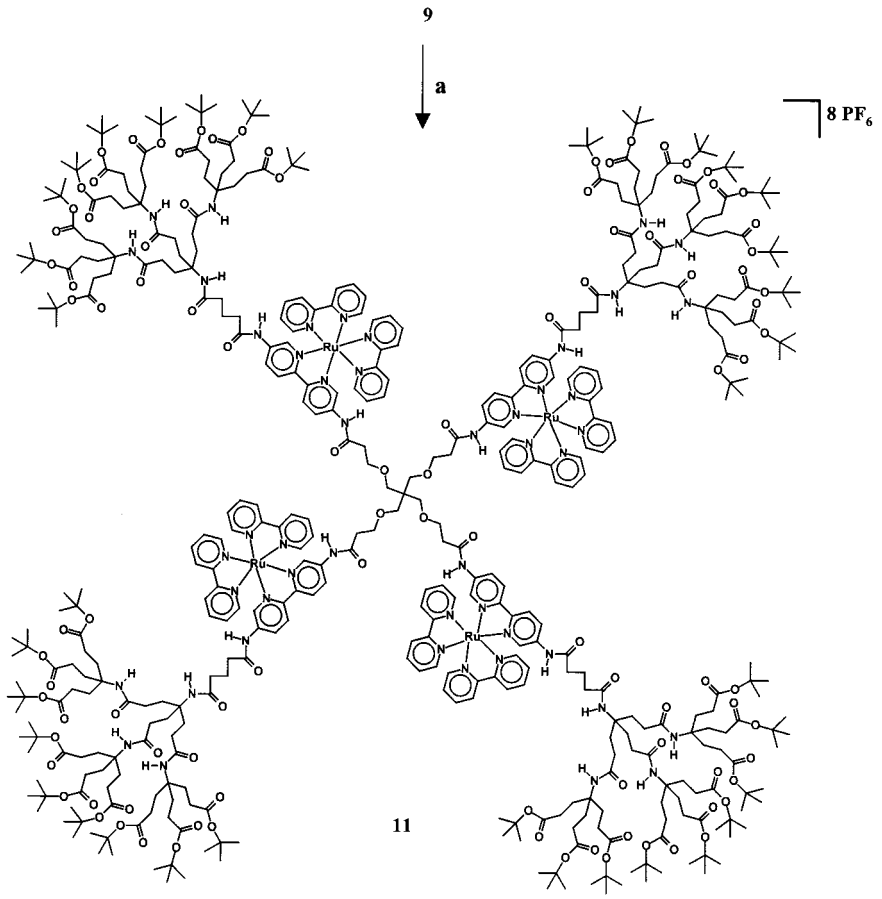
The ruthenium complexes of first and second generation esters, **10** and **11**, respectively, were prepared by refluxing the corresponding esters with [Ru(bpy)$_2$Cl$_2$] in ethanol under nitrogen for three days (Schemes 4 and 5); the chloride counter ions were exchanged with PF_6 ions by the addition of NH_4PF_6. Either column chromatography or dialysis was used to purify these salts. The aromatic region of the ^{13}C NMR spectra of these complexes is very complicated as a result of overlapping peaks; thus, proof of the structure was obtained from UV/visible spectroscopy, mass spectrometry, and cyclic voltammetry. The absorption spectra of **10** and **11** in acetonitrile solution at 25 °C are displayed in Figure 1. The absorption spectra show bipyridine-centered bands in the UV region and the metal-to-ligand charge-transfer (MLCT) bands in the visible region, characteristic of Ru^{II}-polypyridine complexes. The charge-transfer band shows λ_{max} at 448 nm due to MLCT with ε of 49900 and



Scheme 3. Synthesis of second generation dendrimer **9**. a) DMF, DCC, 1-HBT, amine **3**, 25 °C, 48 h.



Scheme 4. Synthesis of metallodendrimer **10**. a) Ethanol, [Ru(bpy)$_2$Cl$_2$], reflux 3 d, NH_4PF_6.



Scheme 5. Synthesis of metallodendrimer **11**. a) Ethanol, $[Ru(bpy)_2Cl_2]$, reflux 3 d, NH_4PF_6.

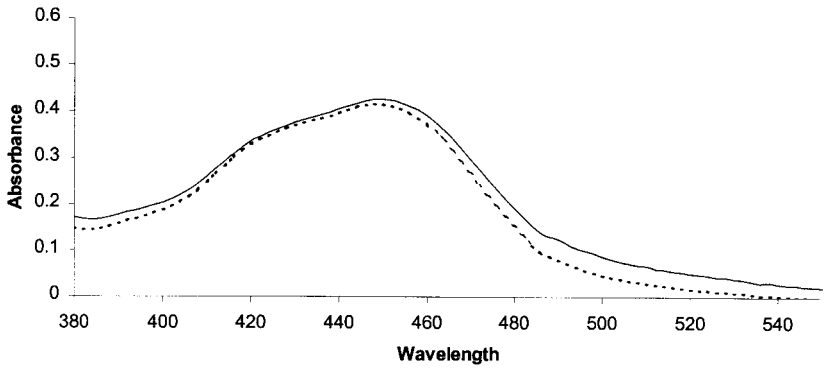


Figure 1. Absorption spectra in the charge transfer band for **10** (- - -) and **11** (—) at 25 °C in MeCN solution. The concentration is 8.0×10^{-6} M. Wavelength is in nm.

$53\,500\,M^{-1}cm^{-1}$ for first and second generation complexes, respectively; these values compare favorably with the ε of $[Ru(bpy)_3]^{2+}$ of $13\,400\,M^{-1}cm^{-1}$ at 450 nm;[64] thus, these facts afford evidence for **10** and **11** possessing four $[Ru(bpy')(bpy)_2]^{2+}$ per molecule.

The structure of the polynuclear ruthenium complexes **10** and **11** were further established by matrix-assisted laser desorption ionization (MALDI) mass spectrometry. The mass spectra were measured in the linear mode with the use of a 9-nitroanthracene matrix. Figure 2 shows the molecular ion region of the MALDI mass spectrum for **10**. The peaks at $m/z = 5812$, 5667, 5522 and 5377 were assigned to $[M-(PF_6)_n]^+$ cations (where $n = 1-4$, respectively). This pattern of loss of PF_6 ions with highly reduced, singly charged cations has been observed[46, 48, 65] in related polypyridine ruthenium complexes. A similar pattern caused by the loss of PF_6 ions was observed for **11** with peaks at $m/z = 9907$, 9762, 9617 and 9472 for $[M-(PF_6)_n]^+$ cations.

Further support for the proposed structures of metallodendrimers **10** and **11** was achieved by exploratory cyclic voltammetry experiments in DMF at 25 °C. As seen in Figure 3a, the voltammetric response of a 1.0 mM solution of the starting reagent $[Ru(bpy)_2Cl_2]$ is characterized by a chemically irreversible signal for the two bipyridine units (see the negative potential region) and by a reversible wave for the Ru^{III}/Ru^{II} couple. On the other hand, the formation of the mixed $[Ru(bpy')(bpy)_2]^{2+}$ complex incorporated within the dendritic structure of **10** and **11** should be characterized by an electrochemical response that reveals the presence of a third, albeit different, bipyridine ligand around each one of the metallic centers. As can be seen in Figures 3b and 3c, the voltammetric signals for both dendrimers show at least three waves in the negative potential region, corresponding to each of the bipyridine ligands in the organometallic complex. This wave pattern is consistent with the proposed structure of metallodendrimers **10** and **11** and opposed to the presence of starting material $[Ru(bpy)_2Cl_2]$. The appearance of three cathodic signals for each bipyridine ligand has been observed for the similar $[Ru(bpy)_3]^{2+}$ complex[46, 66, 67] and for mixed $[Ru(bpy')(bpy)_2]^{2+}$ complexes.[68]

Inspection of Table 1 reveals that the electrochemical reduction processes of the $[Ru(bpy)_3]^{2+}$ complex take place at more positive potentials than those of the metallodendrimers, possessing the $[Ru(bpy')(bpy)_2]^{2+}$ moieties. This negative potential shift for compounds **10** and **11** when compared with their $[Ru(bpy)_3]^{2+}$ analogue is consistent with the electron donating character of the pyr–NHCO linkages[69] that characterize the substituted bipyridine ligand of the macromolecular skeleton.[68]

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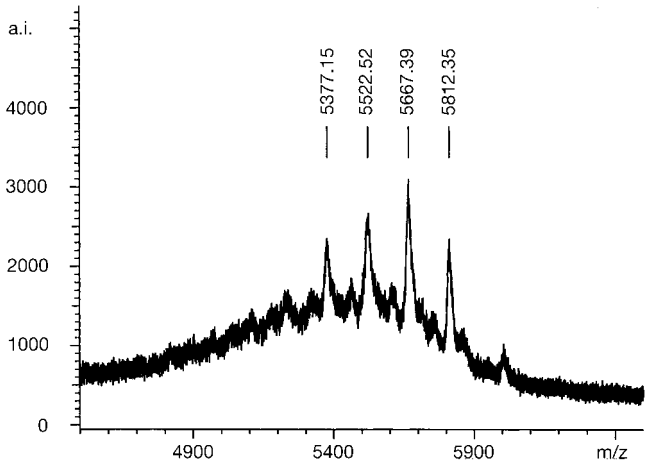

Figure 2. Molecular ion region of MALDI-TOF mass spectrum of **10**.

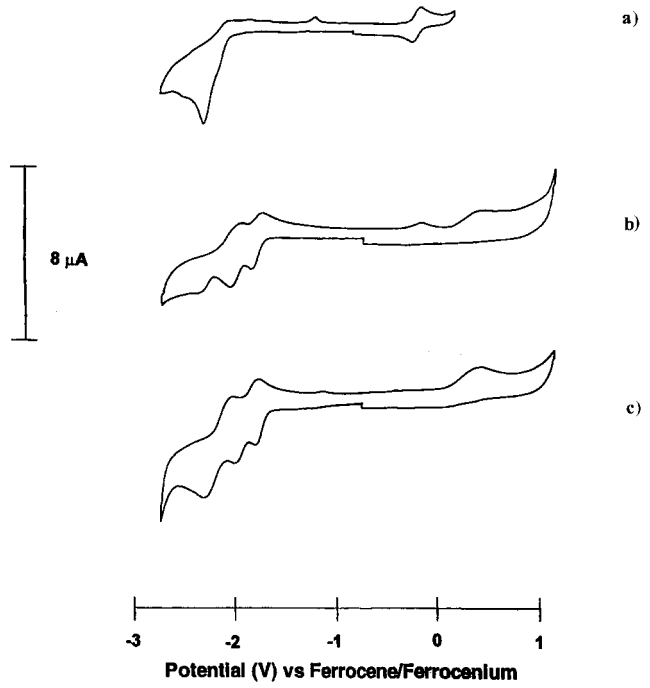

Figure 3. Cyclic voltammetry responses for 1.0 mM solutions of a) $[Ru(bpy)_2]Cl_2$, b) **10**, and c) **11** in 0.1 M Et_4NTFB in DMF at 25 °C. Scan rates 200 mV s^{-1}.

Table 1. Electrochemical parameters for $[Ru(bpy)_2Cl_2]$, $[Ru(bpy)_3]^{2+}$ and ruthenium metallodendrimers **10** and **11** (see experimental section for details). Potentials in V against the ferrocene/ferrocenium couple.

	Bipyridines						Ru	
	Cathodic peak potentials			Anodic peak potentials				
	Ec_1	Ec_2	Ec_3	Ea_1	Ea_2	Ea_3	$E_{1/2}$,(ΔEp)	Ea
$[Ru(bp)_2Cl_2]$	−2.24						−0.15 (0.06)	
$[Ru(bp)_3]^{2+}$	−1.77	−1.96	−2.2	−1.71	−1.89	−2.14	0.87 (0.06)	
10	−1.81	−2.02	−2.36	−1.91	−1.71			0.49
11	−1.80	−2.00	−2.31	−2.02	−1.74			0.49

Another important feature of the CV response of dendrimers **10** and **11** must include the impact that the structural change in the dendritic framework has on the electrochemistry of the ruthenium center when compared with the reversible response in the free $[Ru(bpy)_2Cl_2]$ and $[Ru(bpy)_3]^{2+}$ complexes.[65] As we[46, 58] and others[21, 22, 70, 71] have observed by studying dendritic systems, in which the electroactive units are positioned inside the branched structure, there is a marked decrease in the kinetics of electron transfer that usually translates into electrochemical irreversible behavior. The question of whether this irreversible voltammetric response of the ruthenium center in metallodendrimers **10** and **11**, when compared with their nondendritic analogues, is due to dendrimerization or whether there is an electrochemically induced chemical reaction that can break apart the organometallic complex remains unanswered. Studies on the photo- and electro-induced chemical reactions that take place inside the hyperbranched structures of these novel types of dendrimers are currently under investigation in our laboratory.

Conclusions

We have achieved the synthesis of polynuclear dendrimers with specific internal attachment of bipyridine units. The corresponding $[Ru(bpy')(bpy)_2]^{2+}$ complexes were prepared and characterized by means of UV/visible spectroscopy, mass spectrometry, and cyclic voltammetry. These internally positioned metal centers offer insight into the use of metallodendrimers as electrochemical and photochemical devices. Similar use of dendrimers with internal biquinoline ligands to form ordered dendritic networks is currently under investigation.

Experimental Section

Materials and methods: Chemicals were purchased from Aldrich and used as received, except for THF, which was dried, distilled, and stored on molecular sieves 4 Å. 2,2′-Bipyridine-5,5′-diamine **1**,[61] amine **3**,[62] and $[Ru(bpy)_2]Cl_2$[72] were prepared using literature procedures. Thin layer chromatography (TLC) was conducted on flexible sheets precoated with aluminum oxide IB-F (Baker-flex). Column chromatography was conducted with neutral/basic alumina, Brockman Activity I, 60–325 mesh (Fisher Scientific). Melting points were determined with an Electrothermal 9100 and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX250 spectrometer with $CDCl_3$, except where noted. IR spectra were recorded on ATI Matheson Genesis FTIR spectrophotometer. Absorption spectra were measured on a Hewlett Packard 8452A Diode Array spectrophotometer in MeCN solution at 25 °C. Mass spectra were obtained on either a Bruker Esquire electrospray ion-trap mass spectrometer or Bruker Reflex II MALDI-TOF mass spectrometer. The electrochemical experiments were performed with 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 with a PAR digital coulometer module (model 179) integrated to the potentiostat. All the cyclic voltammetry measurements were conducted in anhydrous DMF solutions (1.0 mM of the electroactive compound) with 0.1 M of tetraethylammonium tetrafluoroborate (Et_4NTFB) as supporting electrolyte. Dry N_2 gas was bubbled carefully through the electroactive solution for at least 10 minutes before the measurements to deoxygenate the solution. The electrochemical cell consisted of a 2.0 mL conical vial fitted with a graphite working electrode (previously polished in sequential steps with alumina and diamond polishing compound on a felt surface), a silver pseudo-reference electrode, and a platinum wire as a counter electrode (Cypress

Systems, Lawrance, KS). All the potentials reported in this work were measured against the ferrocene/ferrocenium redox couple.

Preparation of the extended monomer (4): A mixture of amine **3** (1.869 g, 4.5 mmol) and Et(*i*Pr)$_2$N (1.16 g, 9 mmol) in THF (25 mL) was added dropwise over 30 min to a stirred cold solution of glutaryl dichloride **2** (761 mg, 4.5 mmol) in dry THF (60 mL). The mixture was then allowed to warm to 25 °C and stirred for an additional 4 h. Excess 2,2′-bipyridine-5,5′-diamine **1** (2 equiv, 2 g, 9 mmol) in THF (50 mL) was added at once and stirring was continued at 25 °C for 12 h. The resultant yellow insoluble salt was filtered and the solvent was removed in vacuo. The residue was dissolved in EtOAc and was washed successively with aq. K_2CO_3, deionized water, and finally a saturated brine solution. The organic layer was dried ($MgSO_4$), filtered, and concentrated in vacuo to give a reddish-orange residue, which was column chromatographed (basic Al_2O_3) eluting with a mixture of EtOAc/MeOH (95:5). Two pure products were isolated; the aminobipyridine **4**, as a light yellow solid (1.7 g, 54 %) and hexaester **5**, as white powder (320 mg, 6 %). Amine **4** was recrystallized from chloroform: m.p. 88 – 90 °C; ^{1}H NMR: $\delta = 1.42$ (s, 27H, C(CH_3)$_3$), 1.96 (t, 6H, CH_2CH$_2$CO$_2$), 2.06 (m, 2H, CH$_2$CH_2CH$_2$), 2.21 (t, 8H, CH$_2$CH_2CO$_2$, CH_2CO) 2.47 (t, 2H, COCH_2), 6.13 (s, 1H, CONHC^{4}), 7.12 (dd, 1H, ArH), 8.04 – 8.24 (m, 4H, ArH), 8.74 (s, 1H, ArH), 9.29 (s, 1H, ArNHCO); ^{13}C NMR: $\delta = 21.6$ (CH$_2$CH$_2$CH$_2$), 28.0 (C(CH$_3$)$_3$), 29.8, 29.9 (CH$_2$CH$_2$CO$_2$), 35.6, 35.8 (CH$_2$CH$_2$CH$_2$), 57.7 (^{4}CNH), 80.9 (C(CH$_3$)$_3$), 119.8, 121.2, 122.0, 127.4, 134.4, 136.3, 140.1, 142.5, 146.6, 151.7 (C_{Ar}), 171.5, 172.2 (CONH), 173.0 (CO_2); IR: $\tilde{\nu} = 3437$, 3362, 2978, 2928, 1726, 1657, 1154 cm^{-1}; ESI-MS: m/z: 698.8 [M^++1]; calcd $C_{37}H_{55}N_5O_8$ (697.8).

Hexaester 5: mp 217 – 218 °C; ^{1}H NMR: $\delta = 1.43$ (s, 54H, CH_3), 1.97 (t, 12H, CH_2CH$_2$CO$_2$), 2.06 (m, 4H, CH$_2$CH_2CH$_2$), 2.21 (t, 16H, CH$_2$CH_2CO$_2$, CH$_2$CH_2CO), 2.45 (t, 4H, COCH_2), 6.04 (s, 2H, NHC^{4}), 8.24 (brs, 4H, ArH), 8.70 (s, 2H, ArH), 9.09 (s, 2H, ArNHCO); ^{13}C NMR: $\delta = 21.5$ (CH$_2$CH$_2$CH$_2$), 27.8 (C(CH$_3$)$_3$), 29.5, 29.7 (CH$_2$CH$_2$CO$_2$), 35.5, 35.8 (CH$_2$CH$_2$CH$_2$), 57.4 (NHC^{4}), 80.4 (OC(CH$_3$)$_3$), 120.4, 127.0, 135.2, 140.1, 150.8 (C_{Ar}), 171.6, 172.3 (CONH), 172.7 (CO_2); IR: $\tilde{\nu} = 3334$, 2976, 2934, 1728, 1651, 1154 cm^{-1}; ESI-MS: m/z: 1210.6 [M^++1]; calcd $C_{64}H_{100}N_6O_{16}$ (1209.5).

Preparation of dodecaester 7: Tetraacid chloride **6** (139 mg, 279 μmol) in THF (10 mL) was added dropwise to a stirred cold (0 °C) THF (20 mL) solution containing amine **4** (865 mg, 1.23 mmol) and Et(*i*Pr)$_2$N (158 mg, 1.23 mmol) under nitrogen. The mixture was stirred at 0 °C for 30 min, allowed to warm to 25 °C, and maintained for 12 h. The solvent was removed in vacuo, and the residue was dissolved in EtOAc, then washed sequentially with aq. K_2CO_3, deionized water, and brine, and then dried ($MgSO_4$). The EtOAc was removed in vacuo and the residue was chromatographed (basic Al_2O_3) eluting with a EtOAc/MeOH (9:1) solution to afford the dodecaester **7**, as a light yellow solid: 825 mg (94 %), mp 142 – 144 °C; ^{1}H NMR: $\delta = 1.4$ (s, 108H, C(CH_3)$_3$), 1.95 (brs, 8H, CH$_2$CH_2CH$_2$), 2.00 (m, 24H, CH_2CH$_2$CO$_2$), 2.23 (m, 32H, CH$_2$CH_2CO$_2$, CH_2CONHC^{4}), 2.42 (brs, 8H, ArNHCOCH_2), 2.53 (brs, 8H, OCH$_2$CH_2CO), 3.34 (brs, 8H, OCH_2CH$_2$), 3.67 (brs, 8H, C$_{Core}$CH_2O), 6.23 (brs, 4H, CONHC^{4}), 8.07, 8.15 (brs, 16H, ArH), 8.64, 8.66 (brs, 8H, ArH), 9.23, 9.35 (brs, 8H, ArNHCO); ^{13}C NMR: $\delta = 21.5$ (CH$_2$CH$_2$CH$_2$), 27.8 (C(CH$_3$)$_3$), 29.7 (CH$_2$CH$_2$CO$_2$), 35.7 (CH$_2$CH$_2$CH$_2$), 37.5 (OCH$_2$CH$_2$), 45.0 (^{4}C$_{Core}$), 57.4 (^{4}CNH), 67.0, 69.2 (CH$_2$OCH$_2$), 80.6 [C(CH$_3$)$_3$], 120.4, 127.5, 134.9, 140.4, 150.4, 150.7 (C_{Ar}), 171.0, 171.6, 172.2 (CONH), 172.7 (CO_2); IR: $\tilde{\nu} = 3332$, 2976, 2934, 1728, 1656, 1154 cm^{-1}; MALDI-TOF-MS (*trans*-3-indoleacrylic acid): m/z: 3167.4 ([M^++Na]); calcd $C_{165}H_{240}N_{20}O_{40}$ (3143.83).

Preparation of dodecaacid 8: A stirred mixture of dodecaester **7** (400 mg, 127 μmol) and formic acid (15 mL) was maintained at 25 °C for 36 h. The formic acid was removed in vacuo to give a residue, which was dissolved in a water/MeOH mixture and dialyzed in a Spectra/Por CE membrane (MWCO: 500) for 24 h. The solvent was removed in vacuo to afford the desired dodecaacid **8**, as orange red solid: 250 mg (80 %), m.p. 70 – 72 °C; ^{1}H NMR (D$_2$O/NaOD): $\delta = 1.6$ (8H, CH$_2$CH_2CH$_2$), 1.8, 1.9 (m, 48H, CH_2CH$_2$COO), 2.0, 2.1 (m, 24H, CH_2CH$_2$CH_2, CH_2CONH), 3.1, 3.3 (16H, CH_2OCH_2); ^{13}C NMR (D$_2$O/NaOD): $\delta = 22.4$ (CH$_2$CH_2CH$_2$), 31.6, 32.6 (CH$_2$CH$_2$COO), 36.6 (CH$_2$CONH), 45.3 (C_{Core}), 59.2 (^{4}CNH), 67.4, 67.9 (CH$_2$OCH$_2$), 122.0, 129.1, 136.1, 140.8, 149.8 (C_{Ar}), 173.1, 174.8, 175.7 (CONH), 183.7 (CO_2); IR: $\tilde{\nu} = 3500 – 3000$ (br, acid OH), 1700 cm^{-1}; ESI-MS: m/z: 2494; calcd $C_{117}H_{144}N_{20}O_{40}$ (2470.5).

Preparation of 36-cascade 9: A stirred mixture of dodecaacid **8** (113 mg, 45 μmol), DCC (135 mg, 658 μmol), and 1-HBT (88 mg, 658 μmol) in dry DMF (20 mL) was maintained at 25 °C for 1 h under anhydrous conditions. Formation of dicyclohexyl-urea, as a white precipitate, was noted. Amine **3** (273 mg, 658 μmol) was added and stirring was continued for 48 h at 25 °C. After filtration, DMF was removed in vacuo to give a yellow residue, which was dissolved in EtOAc. The organic layer was washed sequentially with 10 % HCl, deionized water, aq. $NaHCO_3$, and saturated brine solution, and then dried ($MgSO_4$). The EtOAc was removed in vacuo affording a residue, which was column chromatographed (basic Al_2O_3) eluting with an EtOAc/MeOH (9:1) mixture affording **9**, as a light yellow solid: 125 mg (38 %), m.p. 64 – 67 °C; ^{1}H NMR: $\delta = 1.42$ (324H, CH_3), 1.94 (8H, CH$_2$CH_2CH$_2$), 2.00 (96H, CH_2CH$_2$CO$_2$), 2.20 (104H, CH$_2$CH_2CO, CH_2CONH), 2.42 (8H, ArNHCOCH_2), 2.52 (8H, OCH$_2$CH_2), 3.34 (8H, OCH_2CH$_2$), 3.68 (8H, C$_{Core}$CH_2O), 6.2 (16H, C^{4}NH), 8.10, 8.75 (24H, ArH), 9.30 (8H, ArNH); ^{13}C NMR: $\delta = 21.5$ (CH$_2$CH$_2$CH$_2$), 27.9 (C(CH$_3$)$_3$), 29.8 (CH$_2$CH$_2$COO), 35.7, 37.2 (CH$_2$CONH), 45.2 (C_{Core}), 57.5, 60.2 (^{4}CNH), 67.2, 69.8 (CH$_2$OCH$_2$), 80.7 (C(CH$_3$)$_3$), 120.5, 127.4, 134.9, 140.5, 150.9 (C_{Ar}), 170.8, 171.7, 172.2 (CONH), 172.8 (COO); IR: $\tilde{\nu} = 3321$, 2977, 2934, 1729, 1657, 1542, 1463, 1154 cm^{-1}; MALDI-TOF-MS (*trans*-3-indoleacrylic acid): m/z: 7264.19 ([M^++Na]); calcd $C_{381}H_{612}N_{32}O_{100}$ (7241.20).

Ruthenium complex 10: [Ru(bpy)$_2$Cl$_2$] (101 mg, 200 μmol) was added to a stirred solution of **7** (150 mg, 40 μmol) in absolute ethanol (50 mL), and refluxed under nitrogen for 3 days. The ethanol was removed in vacuo, and excess NH_4PF_6 in water was added. The precipitated PF_6 salt was filtered and washed with water until the filtrate was colorless. The crude residue was column chromatographed (neutral alumina) eluting with EtOAc/MeOH (8:2) to yield **10** as a red crystalline solid: 160 mg (57 %); ^{1}H NMR: $\delta = 1.4$ (108H, CH_3), 1.9 – 2.4 (m, 72H, CH_2CH$_2$CH$_2$, CH$_2$CH$_2$CO$_2$), 2.5 – 3.7 (24H, CH$_2$OCH$_2$CH$_2$), 6.30 (4H, C^{4}NH), 7.0 – 9.0 (88H, ArH), 10.0 (8H, ArNH); ^{13}C NMR: $\delta = 21.2$ (CH$_2$CH$_2$CH$_2$), 27.8 (CH$_3$), 29.5 (CH$_2$CH$_2$CO$_2$), 35.6 (CH$_2$CH$_2$CH$_2$), 36.7 (OCH$_2$CH$_2$), 45.0 (^{4}C$_{Core}$), 57.9 (^{4}CNH), 67.0, 69.0 (CH$_2$OCH$_2$), 80.5 (C(CH$_3$)$_3$), 123.9, 127.3, 138.0, 150.8, 156.5 (br, C_{Ar}), 171.0, 172.2, 172.8 (C=O); IR: $\tilde{\nu} = 3397$, 2976, 1722, 1533, 1482, 1156, 843 cm^{-1}; UV/VIS: λ_{max} (ε) = 448 nm (49900); MALDI-TOF-MS (9-nitroanthracene): m/z: 5812.3 ([M – PF$_6$]$^+$); calcd $C_{245}H_{304}F_{48}N_{36}O_{40}P_8Ru_4$ (5957.3).

Ruthenium complex 11: [Ru(bpy)$_2$Cl$_2$] (40 mg, 82 μmol) was added to a stirred solution of **9** (125 mg, 17 μmol) in absolute ethanol (50 mL) and refluxed under nitrogen for 3 days. The ethanol was removed in vacuo, and excess NH_4PF_6 in water was added to precipitate the PF_6 salt. The isolated solid was washed with water, dissolved in a MeOH/water mixture and dialyzed in a CE membrane (MWCO: 3500) for 2 days. Solvent was removed in vacuo to give **11** as a red solid: 70 mg (40 %), ^{1}H NMR: $\delta = 1.4$ (324H, CH_3), 1.9 – 2.5 (m, 216H, CH_2CH$_2$CH$_2$, CH$_2$CH$_2$CO$_2$), 2.5 – 3.8 (24H, CH$_2$OCH$_2$CH$_2$), 6.5 (16H, C^{4}NH), 7.0 – 9.0 (88H, ArH), 10.0 (8H, ArNH); ^{13}C NMR: $\delta = 21.5$ (CH$_2$CH$_2$CH$_2$), 28.0 (CH$_3$), 29.7 (CH$_2$CH$_2$CO$_2$, CH$_2$CH$_2$CONH), 31.6, 34.6 (CH$_2$CH$_2$CH$_2$), 57.4 (^{4}CNH), 80.6 (C(CH$_3$)$_3$), 124.2, 128.0, 138.1, 151.1, 156.9 (C_{Ar}), 172.4, 172.9, 173.4 (C=O); IR: $\tilde{\nu} =$ 3400, 3329, 2977, 2932, 1725, 1155, 844 cm^{-1}; UV/VIS: λ_{max} (ε) = 448 nm (53500); MALDI-TOF-MS (9-nitroanthracene): m/z: 9907.0 ([M^+ – PF$_6$]); calcd $C_{461}H_{676}N_{48}N_{48}O_{100}P_8Ru_4$ (10054.6).

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