DALTON
FULL PAPER

Chiral ruthenium–terpyridine based metallodendrimers: facile synthesis, characterization, and photophysical studies †

Hua Jiang, Suk Joong Lee and Wenbin Lin *

Department of Chemistry, CB#3290, University of North Carolina, Chapel Hill, North Carolina 27599, USA. E-mail: wlin@unc.edu

Received 26th June 2002, Accepted 30th July 2002
First published as an Advance Article on the web 16th August 2002

The new chiral ligand 4′-[6-(2,2′-diethoxy-1,1′-binaphthyl)]-2,2′:6′,2″-terpyridine ($\mathbf{L_1}$) was synthesized in three steps in 47% overall yield starting from 6,6′-dibromo-2,2′-diethoxy-1,1′-binaphthalene. $\mathbf{L_1}$ was quantitatively converted to 4′-[6-(2,2′-dihydroxy-1,1′-binaphthyl)]-2,2′:6′,2″-terpyridine ($\mathbf{L_2}$) by treatment with BBr_3, while $\mathbf{L_2}$ was treated with *tert*-butyldimethylsilyl chloride to give to 4′-{6-[2,2′-bis(*tert*-butyldimethylsiloxy)-1,1′-binaphthyl]}-2,2′:6′,2″-terpyridine ($\mathbf{L_3}$) in high yields. These new chiral terpyridine ligands $\mathbf{L_{1–3}}$ were coordinated to Ru(III) centers to generate Ru($\mathbf{L_{1–3}}$)Cl_3 which were then treated with the tetrakis(terpyridine) core in the presence of 4-ethylmorpholine to afford chiral Ru(terpy)$_2^{2+}$ based metallodendrimers containing enantiopure 1,1′-bi-2-naphthyl units in their peripheries. These chiral metallodendrimers were characterized by NMR, ESI-MS, and cyclic voltammetry, while their photophysical properties were studied using UV-Vis, luminescence, and circular dichroism spectroscopies.

Introduction

Interest in metal-containing dendrimers has continually grown in recent years because of their potential applications as catalysts,[1] synthetic light-harvesting antenna,[2] building blocks for tailor-made materials,[3] molecular supports for chemical catalysts,[4] and potential carriers for drug delivery.[5] Among many linkages used for the assembly of dendritic structures, metal–ligand coordination bonds offer an efficient synthetic pathway.[6] The incorporation of metal centers in the dendritic structures also offers tremendous synthetic versatility because metals can partake as branching centers, building block connectors, cores, terminal groups, and other structural auxiliaries.[7] Moreover, the metal centers in the dendritic structures can impart interesting properties such as the ability to absorb light, to give luminescence, and to undergo multielectron redox processes.[8] We have become interested in the construction of dendritic architectures containing exploitable chiral peripherals based on robust metal–ligand ligation. Herein we wish to describe facile synthesis of chiral metallodendrimers containing optically active 1,1-bi-2-naphthyl units in their peripheries. Such chiral supramolecular assemblies may find applications in enantioselective catalysis and sensing.[9,10]

Results and discussion

Syntheses

Enantiopure ligand 4-[6-(2,2′-diethoxy-1,1′-binaphthyl)]-2,2′:6′,2″-terpyridine, $\mathbf{L_1}$ was readily synthesized in three steps starting from 6,6′-dibromo-2,2′-diethoxy-1,1′-binaphthalene, **1** (Scheme 1). Lithiation of **1** with *n*-BuLi at –78 °C followed by hydrolysis afforded 6-bromo-2,2′-diethoxy-1,1′-binaphthalene, **2**, in 60% yield. **2** was then lithiated with *n*-BuLi at –78 °C and treated with trimethylstannyl chloride to give 6-trimethylstannyl-2,2′-diethoxy-1,1′-binaphthalene, **3**, in 90% yield. Stille coupling between **3** and 4′-triflato-2,2′:6′,2″-terpyridine in the presence of $Pd(PPh_3)_2Cl_2$ and LiCl afforded $\mathbf{L_1}$ in 87% yield. 4′-[6-(2,2′-dihydroxy-1,1′-binaphthyl)]-2,2′:6′,2″-terpyridine, $\mathbf{L_2}$, was obtained in quantitative yield by treating $\mathbf{L_1}$ with BBr_3, while 4′-{6-[2,2′-bis(*tert*-butyldimethylsiloxy)-1,1′-binaphthyl]}-2,2′:6′,2″-terpyridine, $\mathbf{L_3}$, was obtained in 89% yield by treating $\mathbf{L_2}$ with (*tert*-butyl)dimethylsilyl chloride. All the intermediates and ligands $\mathbf{L_{1–3}}$ have been characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy.

Ru(III) complexes Ru($\mathbf{L_{1–3}}$)Cl_3 were prepared in high yields (77–99%) by refluxing $RuCl_3$ and ligands $\mathbf{L_{1–3}}$ in ethanol overnight. As-prepared Ru(III) complexes Ru($\mathbf{L_{1–3}}$)Cl_3 were treated with tetrakis(2,2′:6′,2″-terpyridinyl-4′-oxymethyl)methane in ethylene glycol with 4-ethylmorpholine as the reducing agent at 120 °C to afford the crude products, whose chloride anions were metathesized with PF_6^- to give more soluble chiral metallodendrimers **4a**–**4c** in good overall yields (73–89%; Scheme 2).[11] Compounds **4a**–**4c** were characterized by ^1H, $^{13}C\{^1H\}$ NMR, COSY, ESI-MS, and microanalyses. We were able to assign almost all the aromatic proton signals based on the ^1H NMR and COSY spectra (Fig. 1). The integration ratio between the aromatic protons and the methylene protons for the tetrakis(2,2′:6′,2″-terpyridinyl-4′-oxymethyl)methane core provides an excellent diagnostic for the purity of **4a**–**4c**. ESI-MS spectra of **4a** and **4c** show *m*/*z* peaks for the cationic species

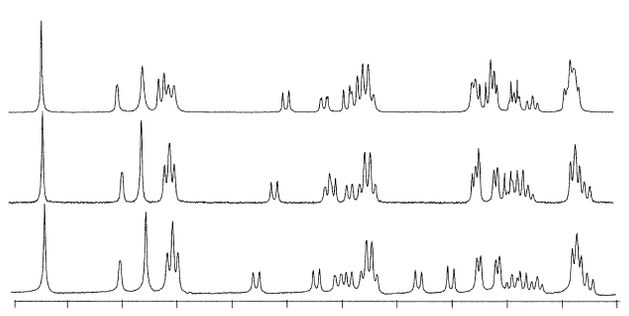
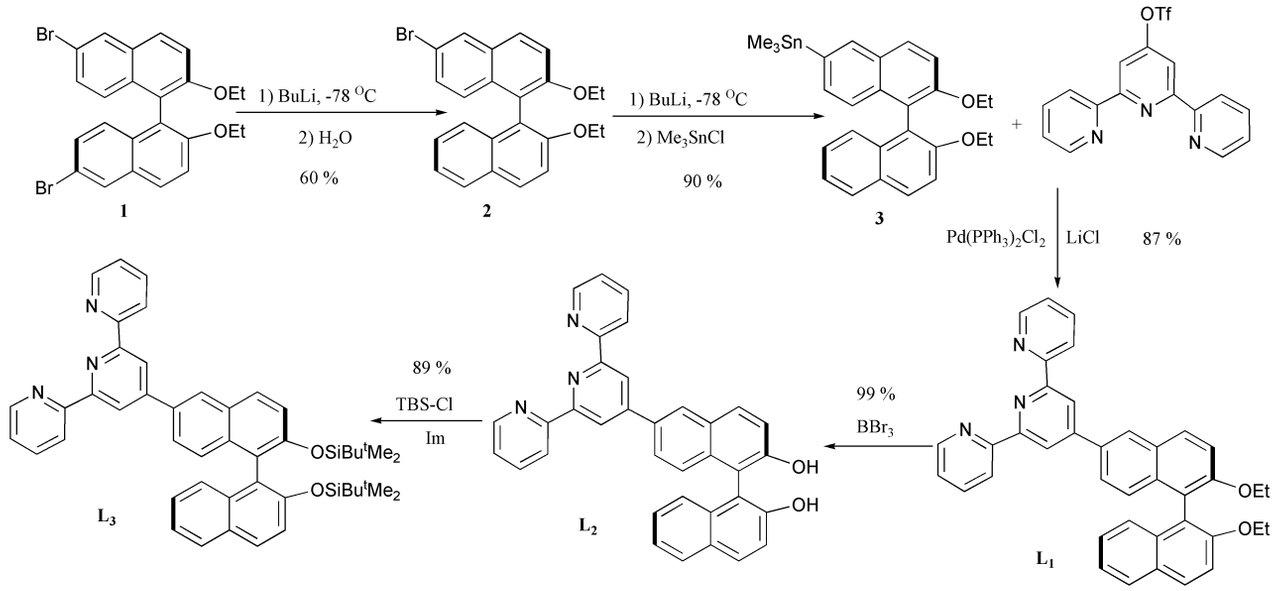


Fig. 1 ^1H NMR spectra for **4a**–**4c** (top to bottom). Only the aromatic regions are shown. See experimental section for detailed assignments.

† Electronic supplementary information (ESI) available: ^1H NMR and UV-Vis spectra of $\mathbf{L_{1–3}}$. See http://www.rsc.org/suppdata/dt/b2/b206159g/



Scheme 1

Table 1 ESI-MS peaks and their assignments

Compound	Assignment	Observed mass	Expected mass
4a	$[M - 3PF_6]^{3+}$	1495.5	1495.0
	$[M - 4PF_6]^{4+}$	1085.1	1085.0
	$[M - 5PF_6]^{5+}$	839.0	839.0
	$[M - 6PF_6]^{6+}$	675.1	675.0
	$[M - 7PF_6]^{7+}$	557.8	557.8
4b	$[M - 3PF_6]^{3+}$	1419.4	1420.2
	$[M - 4PF_6]^{4+}$	1028.7	1028.9
	$[M - 5PF_6]^{5+}$	793.9	794.1
	$[M - 6PF_6]^{6+}$	637.5	637.6
4c	$[M - 3PF_6]^{3+}$	1724.9	1724.9
	$[M - 4PF_6]^{4+}$	1257.4	1257.4
	$[M - 5PF_6]^{5+}$	976.8	976.9
	$[M - 6PF_6]^{6+}$	790.0	790.0
	$[M - 7PF_6]^{7+}$	656.8	656.4

after successive loss of three to seven PF_6^- anions, while the ESI-MS spectrum of **4b** exhibits *m*/*z* peaks for the cationic species after loss of three to six PF_6^- anions (Table 1). The combination of NMR, mass spectrometric data, and microanalysis results has thus unambiguously established the identities of **4a**–**4c**.

UV-Vis spectra of **4a**–**4c** exhibit broad peaks around 495 nm due to metal-to-ligand charge transfer excitation, in addition to those bands due to the ligands **4a**–**4c** and tetrakis(2,2′:6′,2″-terpyridinyl-4′-oxymethyl)methane core (Fig. 2). These ^{3}MLCT bands are slightly red-shifted from that of $[Ru(terpy)_2]^{2+}$ (*cf.* 476 nm), consistent with the presence of electron-donating groups in the 4′ positions of the modified terpy ligands.[12] Although ligands $\mathbf{L}_{1-3}$ are highly luminescent to give a broad peak at ~430 nm upon excitation at 320 nm, the chiral metallodendrimers **4a**–**4c** are non-emissive in solution at room temperature. It is well-established that low-lying metal-centered states can efficiently quench the luminescent ^{3}MLCT state in ruthenium(II) bis(terpyridine) complexes.[13] Compounds **4a**–**4c** exhibit one reversible $Ru^{II,III}$ oxidation process with $E_{1/2}$ values of 1.33, 1.34, and 1.29 V in acetonitrile, respectively. This trend is consistent with the increasing electron-donating ability of the hydroxy, ethoxy, and *tert*-butyldimethylsiloxy groups at the 4′ positions of the modified terpy ligands of **4b**, **4a**, and **4c**, respectively.

CD spectra of chiral terpy ligands $\mathbf{L}_1$–$\mathbf{L}_3$ exhibit three Cotton effects around 235, 270, and 330 nm, corresponding to the ^{1}B, ^1L_a, and ^1L_b transitions, respectively (Fig. 3). The Cotton effects

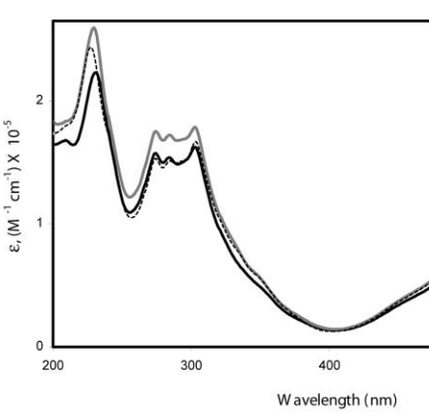


Fig. 2 UV-Vis spectra of **4a**–**4c** in acetonitrile.

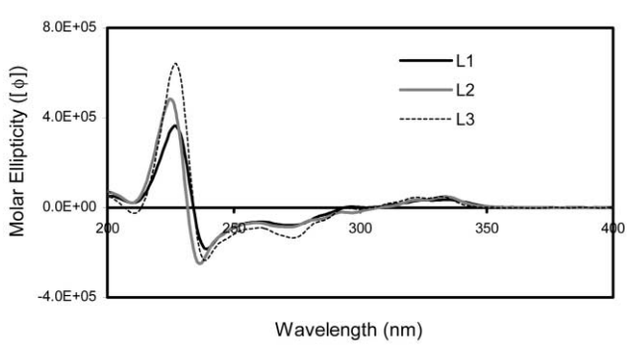
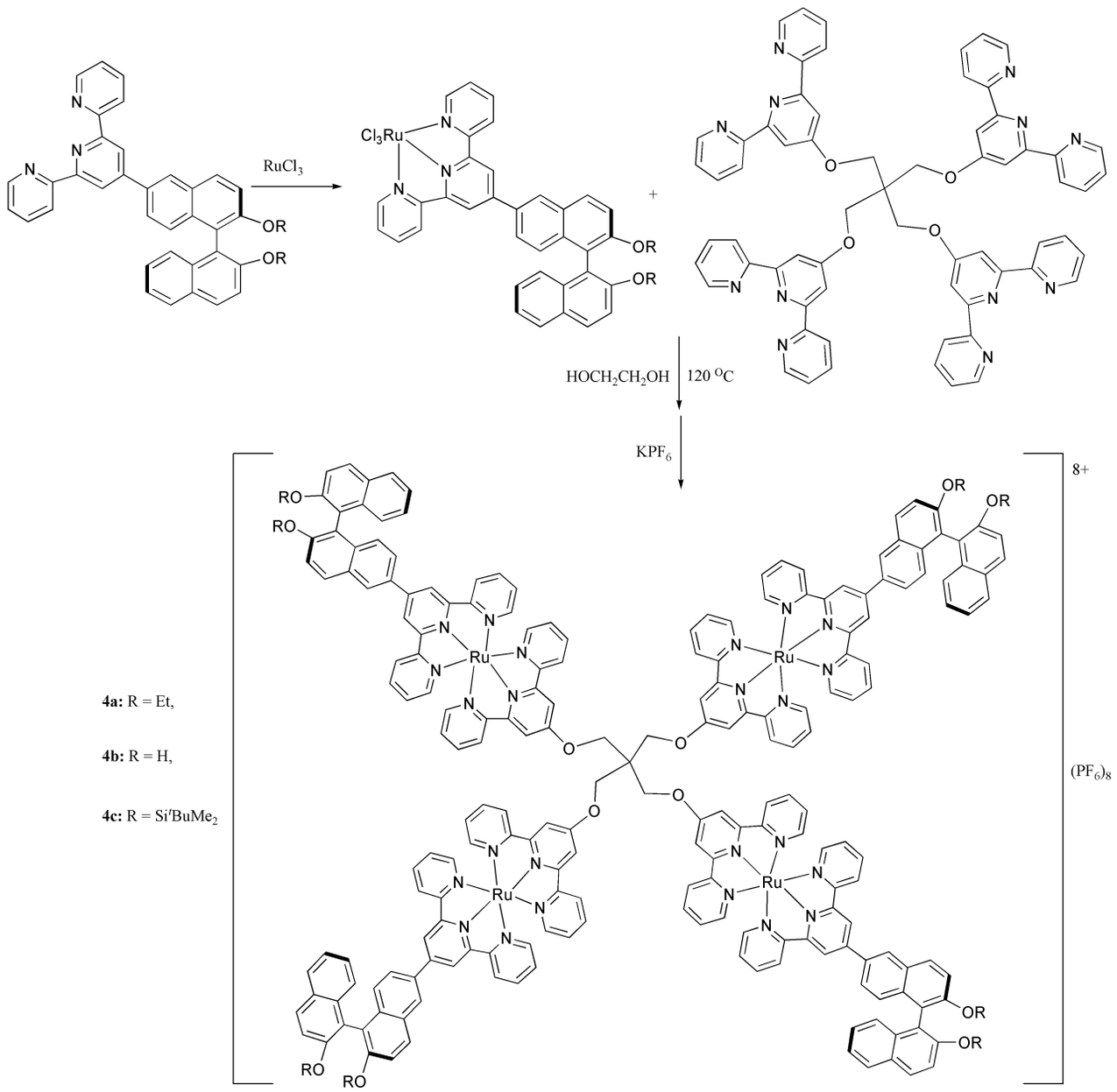


Fig. 3 Circular dichroism spectra of $\mathbf{L}_1$–$\mathbf{L}_3$ in acetonitrile.

due to the ^1L_a, and ^1L_b transitions have been previously observed in 1,1′-binaphthyl-based oligomers linked through their 6,6′-positions.[14] Interestingly, chiral metallodendrimers **4a**–**4c** exhibit CD signals similar to chiral terpy ligands $\mathbf{L}_1$–$\mathbf{L}_3$, indicating that no new chirality has resulted upon the formation of metallodendrimers (Fig. 4). The insolubility of **4a**–**4c** in non-polar organic solvents has precluded their use as chiral ligands for asymmetric catalysis. In summary, chiral Ru–terpy based metallodendrimers with enantiopure 1,1′-bi-2-naphthyl units in their peripheries have been readily synthesized. Current effort is focused on the introduction of solubilizing substituents into such chiral metallodendrimers so that their utility as chiral ligands for asymmetric catalysis can be explored.



4a-4c

Scheme 2

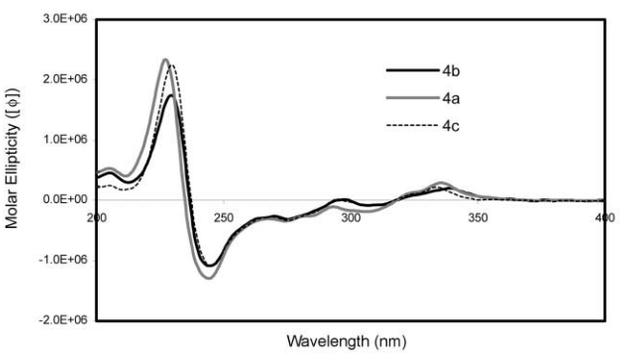


Fig. 4 Circular dichroism spectra of **4a**–**4c** in acetonitrile.

Experimental

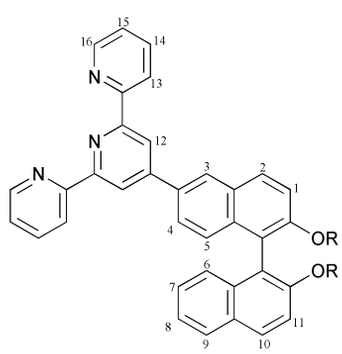
Materials and general procedures

All of the chemicals were obtained from commercial sources and used without further purification. All of the reactions and manipulations were carried out under N_2 with the use of standard inert atmosphere and Schlenk techniques. Solvents used in reactions were dried by standard procedures. UV-Visible spectra were obtained using a Hewlett Packard 8452A diode array spectrophotometer. Circular dichroism (CD) spectra were recorded on a JASCO J-810 spectropolarimeter. ^{1}H NMR spectra were recorded on Varian XL-400 spetrometer. ^{1}H-NMR spectra were recorded at 400 MHz and referenced to the proton resonance resulting from incomplete deuteration of the deuterated chloroform (δ 7.26), or acetonitrile (δ 1.93). ^{13}C{^{1}H} NMR spectra were recorded at 100 MHz, and all of the chemical shifts are reported downfield in ppm relative to the carbon resonance of the methyl group of acetone-d_6 (δ 29.8), or chloroform-d_1 (δ 77.0). Cyclic voltammetry (CV) experiments were carried out with a 0.5 mM solution of the desired compound under dried and deoxygenated acetonitrile on a BAS 100B electrochemical analyzer, with a platinum disk (1.0 mm diameter) working electrode, a platinum auxiliary electrode and a silver wire reference electrode. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was used as the electrolyte.

Syntheses

4′-[6-(2,2′-Diethoxy-1,1′-binaphthyl)]-2,2′:6′2″-terpyridine, L_1. To a 100 mL three-necked round bottom flask was added 4′-triflato-2,2′:6′,2″-terpyridine (2.613 g, 5.19 mmol), 6-trimethylstannyl-2,2′-diethoxy-1,1′-binaphthalene (1.978 g, 5.19 mmol), $Pd(PPh_3)_2Cl_2$ (0.409 mmol), LiCl (1.282 g, 30.2 mmol) and toluene (100 mL) under N_2. The mixture was refluxed for 48 h and then cooled to room temperature. After the solvent was removed in vacuum, methylene chloride was added to dissolve the solid, and the solution was washed with water. The organic layer was dried over $MgSO_4$. After removing solvent, the residue was purified *via* silica-gel chromatography with ethyl acetate–hexane (1 : 1 v/v) to afford a pure light yellow solid of L_1. Yield: 2.60 g (87%). ^{1}H NMR ($CDCl_3$): δ 8.83 (s, 2H, H12), 8.74 (d, 4.9 Hz, 2H, H16), 8.69 (d, 8.6 Hz, 2H, H13), 8.45 (d, 1.8 Hz, 1H, H3), 8.08 (d, 8.6 Hz, 1H, H2), 7.97 (d, 8.6 Hz, 1H, H10), 7.89 (m, 2H, H14), 7.88 (d, 8.6 Hz, 1H, H9), 7.75 (dd, 8.6 Hz, ^4J = 1.8 Hz, 1H, H4), 7.48 (d, 8.6 Hz, 1H, H1), 7.45 (d, 8.6 Hz, 1H, H11), 7.36 (m, 1H, H8), 7.35 (m, 2H, H15), 7.27 (d, 8.6 Hz, 1H, H5), 7.24 (m, 1H, H7), 7.18 (d, 8.6 Hz, 1H, H6), 4.08 (m, 4H, CH_2), 1.08 (m, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.7, 156.2, 155.4, 154.7, 150.7, 149.4, 137.2, 134.8, 134.5, 133.6, 130.2, 129.6, 128.2, 127.1, 126.7, 126.5, 125.8, 125.4, 124.1, 123.8, 121.7, 120.9, 120.6, 119.2, 116.6, 116.1, 65.6, 65.4, 15.4, 15.3.

4′-[6-(2,2′-Dihydroxy-1,1′-binaphthyl)]-2,2′:6′,2″-terpyridine, L_2. To a stirred solution L_1 (2.15 g, 3.76 mmol) in CH_2Cl_2 (90 mL) was added dropwise a solution of BBr_3 (15.9 g, 63.5 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The mixture was allowed to warm to r.t and stirred at r.t. for 2 h, then poured into a large amount of ice/water. A deep red precipitate was obtained. After filtration, the solid was treated with 5% NaOH aqueous solution, and the product was extracted with CH_2Cl_2 and dried over $MgSO_4$. The pure yellow solid of L_2 was obtained after the removal of the organic volatiles. Yield: 1.94 g (99 %). ^{1}H NMR ($CDCl_3$): δ 8.77 (s, 2 H, H16), 8.71 (d, 4.3 Hz, 2 H, H16), 8.67 (d, 7.9 Hz, 2 H, H13), 8.41 (s, 1 H, H3), 8.04 (d, 9.2 Hz, 1 H, H2), 8.00 (d, 9.2 Hz, 1 H, H10), 7.91 (d, 6.7 Hz, 1 H, H9), 7.88 (t, 7.9 Hz, 2 H, H14), 7.79 (d, 8.5 Hz, 1 H, H4), 7.42 (d, 9.2 Hz, 1 H, H11), 7.41 (d, 9.2 Hz, 1 H, H1), 7.38–7.30 (m, 4 H, H15, H7 and H8), 7.25 (d, 7.3 Hz, 1 H, H5), 7.17 (d, 8.5 Hz, 1 H, H6), 5.41 (br, 2 H, OH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.9, 155.3, 153.5, 153.1, 149.6, 148.7, 136.9, 133.9, 133.7, 133.1, 131.4, 130.9, 129.1, 128.1, 127.1, 126.8, 125.8, 125.3, 124.4, 123.7, 123.6, 121.5, 118.7, 118.5, 118.2, 112.4, 111.8.

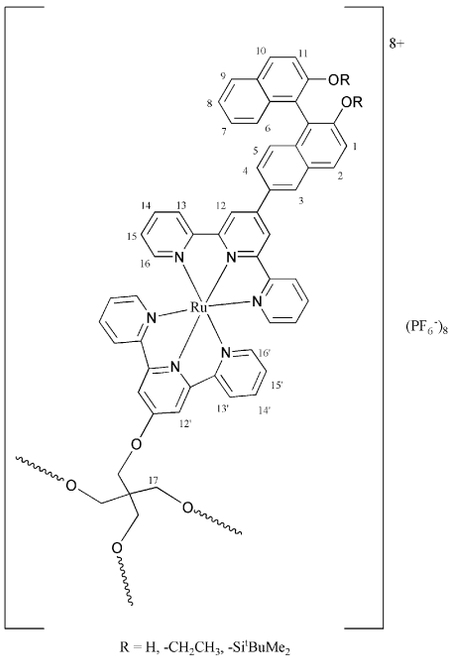


4′-[6-(2,2′-Di-*tert*-butyldimethylsiloxy-1,1′-binaphthyl)]-2,2′:6′,2″-terpyridine, L_3. A solution of L_2 (1.90 g, 3.68 mmol), *tert*-butyldimethylsilyl chloride (1.221 g, 8.10 mmol), and imidazole (1.254 g, 18.42mmol) in 6 mL of DMF was heated at 35 °C under N_2 overnight. After cooling to room temperature, the reaction mixture was poured into 5 % NaOH aqueous solution, and the product was extracted with CH_2Cl_2, washed twice with 5 % NaOH aqueous solution, and dried over $MgSO_4$. After filtration and evaporation, the solid residue was purified by column chromatography on silica gel (ethyl acetate–hexane: 1/1) to give the light yellow product L_3. Yield: 2.43 g (89 %). ^{1}H NMR ($CDCl_3$): δ 8.84 (s, 2 H, H12), 8.75 (d, 4.9 Hz, 2 H, H16), 8.69 (d, 7.9 Hz, 2 H, H13), 8.43 (d, 1.8 Hz, 1 H, H3), 7.96 (d, 8.5 Hz, 1 H, H9), 7.89 (t of d, 7.6 Hz, 1.8, 1 H, H14), 7.84 (d, 9.2 Hz, 2 H, H2 and H10), 7.78 (dd, 9.2 Hz, 1.8, 1 H, H4), 7.36 (td, 6.1 Hz, 1.2, 2 H, H15), 7.35 (d, 9.2 Hz, 1 H, H5), 7.30 (m, 2 H, H7 and H8), 7.25 (d, 6.7 Hz, 1 H, H6), 7.24 (d, 9.8 Hz, 1 H, H1), 7.21 (d, 8.5 Hz, 1 H, H11), 0.506 (s, 9 H, $C(CH_3)_3$), 0.497 (s, 9 H, $C(CH_3)_3$), 0.059 (s, 3 H, CH_3), 0.040 (s, 3 H, CH_3), −0.163 (s, 6 H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.3, 155.8, 152.0, 151.2, 150.3, 149.0, 136.8, 134.8, 134.5, 132.9, 129.5, 129.23, 129.21, 128.8, 127.7, 126.7, 126.6, 125.9, 125.7, 124.8, 123.7, 123.3, 122.2, 121.7, 121.4, 121.2, 120.5, 118.7, 25.04, 24.99, 17.58, 17.56, −4.26, −4.48, −4.58.

Ru($L_{1–3}$)Cl_3 complexes. Ligands L_1–L_3 were dissolved in ethanol, and an excess amount of $RuCl_3 \cdot xH_2O$ was added. The reaction mixture was refluxed overnight. After cooling to room temperature, the solvents were evaporated and the residue was washed with ethanol. Dark brown solids of Ru($L_{1–3}$)Cl_3 were obtained, and used for subsequent metallodendrimer syntheses without further purification. The yields for Ru(L_1)Cl_3, Ru(L_2)Cl_3, and Ru(L_3)Cl_3 were 77, 99 and 77%, respectively.

Metallodendrimer 4a. To a solution of tetrakis(2,2′: 6′,2″-terpyridinyl-4′-oxymethyl)methane (183 mg, 0.173 mg) and 4-ethylmorpholine (0.2 mL) in ethylene glycol (70 mL) was added Ru(L_1)Cl_3 (540 mg, 0.692 mmol) and the mixture was heated to 120 °C for 18 h after which period a deep red solution was obtained. This was concentrated to 10 mL *in vacuo*, cooled to room temperature, and treated with water (20 mL). The red solution was filtered and the filtrate was treated with potassium hexafluorophosphate to give a deep red solid. After crystallization by CH_3CN–methanol, the red solid was purified *via* silica-gel chromatography with acetone to afford pure red solid (583 mg, yield 73%). Anal. calc. for $C_{221}H_{200}F_{48}N_{24}O_{26}P_8Ru_4$, **4a**·$14H_2O$: C, 50.73; H, 3.57; N, 6.21%. Found: C, 50.91; H, 3.11; N, 6.35%. ^{1}H NMR (CD_3CN): δ 9.08 (s, 8 H, H12), 8.81 (s, 4 H, H3), 8.71 (s, 8 H, H12′), 8.63–8.60 (m, 16 H, H13 and H13′), 8.31 (d, 9.2 Hz, 4 H, H2), 8.09 (d, 9.2 Hz, 4 H, H10), 8.01 (d, 9.2 Hz, 4 H, H4), 7.97 (d, 7.9 Hz, 4 H, H9), 7.93–7.87 (m, 16 H, H14 and H14′), 7.72 (d, 9.2 Hz, 4 H, H1), 7.60 (d, 9.2 Hz, 4 H, H11), 7.50 (d, 5.5 Hz, 8 H, H16), 7.43 (d, 5.5 Hz, 8 H, H16′), 7.38 (t, 7.9 Hz, 4 H, H8), 7.34 (d, 9.2 Hz, 4 H, H5), 7.29 (t, 7.9 Hz, 4 H, H7), 7.16–7.13 (m, 16 H, H15 H15′), 7.10 (d, 8.5 Hz, 4 H, H6), 5.50 (s, br, 8 H, H17), 4.21–4.13 (m, 16 H, OCH_2), 1.12–1.09 (m, 24 H, CH_3). ^{13}C (Acetone-d_6): δ 167.4, 159.5, 159.3, 157.0, 156.8, 156.7, 155.4, 153.5, 153.4, 148.7, 138.8, 138.7, 135.6, 134.8, 132.2, 131.1, 130.3, 130.2, 130.1, 128.9, 128.7, 128.6, 128.4, 127.4, 126.9, 125.7, 125.5, 125.3, 124.2, 122.0, 120.9, 120.3, 120.2, 117.1, 116.3, 112.5, 69.1, 65.4, 65.3, 30.4, 15.3, 15.1.

Metallodendrimer 4b. By a procedure analogous to that described above, red solid **4b** was obtained in 80% yield. Anal. calc. for $C_{205}H_{148}F_{48}N_{24}O_{16}P_8Ru_4$, **4b**·$4H_2O$: C, 51.65; H, 3.13; N, 7.05%. Found: C, 51.26; H, 3.15; N, 6.74%. ^{1}H NMR (CD_3CN): δ 9.08 (s, 8 H, H12), 8.79 (d, 1.8 Hz, 4 H, H3), 8.72 (s, 8 H, H12′), 8.64–8.60 (m, 16 H, H13 and H13′), 8.24 (d, 8.6 Hz, 4 H, H2), 8.05 (dd, 9.2 Hz, 1.8 Hz, 4 H, H4), 8.03 (d, 8.5 Hz, 4 H, H10), 7.97 (d, 7.3 Hz, 4 H, H9), 7.93–7.88 (m, 16 H, H14 and H14′), 7.51 (d, 9.2 Hz, 4 H, H1), 7.50 (d, 4.3 Hz, 8 H, H16), 7.43 (d, 5.5 Hz, 8 H, H16′), 7.39 (d, 9.2 Hz, 4 H, H5), 7.37 (t, 6.7 H, H8), 7.34 (d, 8.5 Hz, 4 H, H11), 7.32 (t, 6.7 Hz, 4 H, H7), 7.16–7.13 (m, 16 H, H15 and H15′), 7.10 (d, 8.5 Hz, 4 H, H6), 5.50 (s, br, 8 H, H17). ^{13}C (Acetone-d_6): δ 167.2, 159.3, 159.2, 156.8, 156.7, 155.9, 154.4, 153.3, 148.6, 138.7, 138.5, 136.1, 135.2, 131.6, 131.4, 130.7, 129.8, 129.7, 128.8, 128.6, 128.4, 128.3, 127.0, 126.7, 125.6, 125.3, 125.1, 125.0, 123.5, 121.8, 120.5, 119.3, 117.4, 115.4, 114.3, 112.4, 59.1, 30.3.



Metallodendrimer 4c. By a procedure analogous to that described above, red solid **4c** was obtained in 89% yield. Anal. calc. for $C_{253}H_{260}F_{48}N_{24}O_{16}P_8Ru_4Si_8$, **4c**·$4H_2O$: C, 53.48; H, 4.61; N, 5.92%. Found: C, 53.23; H, 4.42; N, 5.59%. ^{1}H NMR (CD_3CN): δ 9.09 (s, 8 H, H12), 8.81 (d, 1.8 Hz, 4 H, H3), 8.72 (s, 8 H, H12′), 8.65 (d, 8.5 Hz, 8 H, H13), 8.61 (d, 8.5 Hz, 8 Hz, H13′), 8.19 (d, 9.2 Hz, 4 H, H2), 8.06 (dd, 9.2 Hz, 1.8 Hz, 4 H, H4), 7.98 (d, 9.2 Hz, 4 H, H10), 7.95 (d, 7.9 Hz, 4 H, H9), 7.94–7.88 (m, 16 H, H14 and H14′), 7.52 (d, 5.5 Hz, 8 H, H16), 7.48 (d, 9.2 Hz, 4 H, H1), 7.45 (d, 4.9 Hz, 8 H, H16′), 7.44 (d, 9.2 H, H5), 7.37 (d, 9.2 Hz, 4 H, H11), 7.36 (t, 6.7 Hz, 4 H, H8), 7.30 (t, 7.0 Hz, 4 H, H7), 7.198–7.13 (m, 20 H, H6, H15 and H15′), 5.51 (s, br, 8 H, H17), 0.55 and 0.51 (s and s, 72 H, $C(CH_3)_2$), 0.15 and 0.13 (s and s, 24 H, $SiCH_3$), 0.01 and −0.05 (s and s, 24 H, $SiCH_3$). ^{13}C (Acetone-d_6): 167.4, 159.5, 159.4, 157.0, 156.8, 153.7, 153.5, 152.1, 148.5, 138.8, 138.7, 136.1, 135.3, 132.2, 130.9, 130.4, 130.3, 130.1, 128.9, 128.6, 128.4, 127.7, 126.9, 126.0, 125.5, 125.3, 124.3, 123.1, 122.6, 122.1, 121.8, 121.4, 112.5, 69.2, 30.2, 25.5, 25.4, 18.2, 18.1, −4.0, −4.1, −4.2, −4.5.

Acknowledgements

We acknowledge NSF (CHE-0208930) for financial support and Dr Jian Zhang and Professor Royce W. Murray for help with electrochemical measurements. W. L. is an Alfred P. Sloan Fellow, an Arnold and Mabel Beckman Young Investigator, a Cottrell Scholar of Research Corp, and a Camille Dreyfus Teacher-Scholar.

References

1 (*a*) G. R. Newkome, C. N. Moorefield and F. Vögtle, *Dendritic Molecules: Concept, Synthesis, Perspectives*, VCH, Weinheim, 1996; (*b*) C. Köllner, B. Pugin and A. Togni, *J. Am. Chem. Soc.*, 1998, **120**, 10274; (*c*) F. J. Stoddart and T. Welton, *Polyhedron*, 1999, **18**, 3575; (*d*) M. T. Reetz and D. Giebel, *Angew. Chem., Int. Ed.*, 2000, **39**, 2498; (*e*) D. Astruc and F. Chardac, *Chem. Rev.*, 2001, **101**, 2991.
2 (*a*) A. Adronov and J. M.J. Fréchet, *Chem. Commun.*, 2000, 1701; (*b*) V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni and M. Venturi, *Acc. Chem. Res.*, 1998, **31**, 26.
3 O. Mongin and A. Gossauer, *Tetrahedron Lett.*, 1996, **37**, 3825.
4 (*a*) Y. Niu, L. K. Yeung and R. M. Crooks, *J. Am. Chem. Soc.*, 2001, **123**, 6840; (*b*) V. Chechik and R. M. Crooks, *J. Am. Chem. Soc.*, 2000, **122**, 1243; (*c*) J. W. J. Knapen, A. W. van der Made, J. C. de Wilde, P. W. N. M. van Leeuwen, P. Wijkens, D. M. Grove and G. van Koten, *Nature*, 1994, **372**, 659.
5 R. Duncan and J. Kopecek, *Adv. Polym. Sci.*, 1984, **57**, 51.
6 (*a*) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995; (*b*) V. Balzani and L. De Cola, *Supramolecular Chemistry*, Kluwer, Dordrecht, 1992.
7 G. R. Newkome, E. He and C. N. Moorefield, *Chem. Rev.*, 1999, **99**, 1689.
8 (*a*) C. B. Gorman and J. C. Smith, *Acc. Chem. Res.*, 2001, **34**, 60; (*b*) R. Wang and Z. Zheng, *J. Am. Chem. Soc.*, 1999, **121**, 3549; (*c*) F. Vögtle, M. Plevoets, M. Nieger, G. C. Azzellini, A. Credi, L. De Cola, V. De Machis, M. Venturi and V. Balzani, *J. Am. Chem. Soc.*, 1999, **122**, 6290.
9 S. B. Garber, J. S. Kingsbury, B. L. Gray and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2000, **122**, 8168.
10 V. J. Pugh, Q.-S. Hu and L. Pu, *Angew. Chem., Int. Ed.*, 2000, **39**, 3638.
11 (*a*) D. Armspach, M. Cattalini, E. C. Constable, C. E. Housecroft and D. Phillips, *Chem. Commun.*, 1996, 1823; (*b*) E. C. Constable, C. E. Housecroft, M. Cattalini and D. Phillips, *New. J. Chem.*, 1998, **22**, 193.
12 J.-P. Sauvage, J. P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola and L. Flamigni, *Chem. Rev.*, 1994, **94**, 993.
13 R. C. Young, J. K. Nagle, T. J. Meyer and D. G. Whitten, *J. Am. Chem. Soc.*, 1978, **100**, 4773.
14 L. Ma, P. S. White and W. Lin, *J. Org. Chem.*, in the press.