Nanometric dendritic macromolecules: stepwise assembly by double (2,2′:6′,2″-terpyridine)ruthenium(II) connectivity

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The construction of nanometric, dendritic macromolecules by bis(2,2′:6′,2″-terpyridine)ruthenium(II) connectivity is investigated. The assembly methodology, which incorporates both the control of metal complexation sites and degree of flexibility within the linkages, has been demonstrated.

Interest in specifically assembled, dendritic nanostructures has continued to escalate over the past decade[1] and will continue to do so due to the anticipation of their novel properties. Dendritic systems which incorporate metal centres are either of a random nature by simple molecular inclusion within the macrostructure,[2] or at a specific predetermined binding locus[3] either within the assembly or on its surface. Such metallo-macroassemblies afford entrance to materials capable of novel magnetic, electronic, photooptical or catalytic properties. As a prelude to the construction process, we previously reported[4–6] the use of bis(2,2′:6′,2″-terpyridine)ruthenium(II) (herein denoted by [—<Ru>—]), as the mode of connectivity, in order to combine preconstructed, pseudo-spherical dendritic fragments in a predetermined way. Such connectivity permitted the analysis of the final product by the easy quantification of the metal centre(s) by simple electrochemical procedures. This type of connectivity (*i.e.*, incorporation of multiple centres) gave rise to the dodecaruthenium complex[4] **1** and the single metal centre afforded the bisdendrimer[5] **2** (Fig. 1); these represent our initial approaches to the specific assembly of discrete dendritic networks by the connection of established constructs. We herein describe the use of two metal centres per appendage [—<Ru>—(×)—<Ru>—] for attachment to a four-directional core; this assembly methodology incorporates (i) positional control over the metal complexation sites and (ii) a variable flexibility within the linkages (×) between those connectivity sites.

Experimental

Equipment and materials

Melting points are uncorrected and were measured on a Mel-Temp apparatus. All reactions were conducted under a nitrogen atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC250 MHz spectrometer using $CDCl_3$ as solvent, unless otherwise indicated, with Me_4Si as the internal standard (d = 0). IR spectra were recorded on a Perkin-Elmer 621 grating IR spectrometer. UV–VIS spectra were recorded on a HP8452A diode array spectrophotometer. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

All reagents were purchased from Aldrich. Column chromatography was performed using activated basic aluminium oxide (150 mesh, Brockmann I; Aldrich).

Tetrakis(5-hydroxy-2-oxapentyl)methane 4

To a solution of 6,6-bis(carboxy-2-oxabutyl)-4,8-dioxaundecane-1,11-dicarboxylic acid[7] **3** (10 g, 23.6 mmol) in dry THF (50 cm^3) at 0 °C, was added dropwise a BH_3·THF[8] solution (104 cm^3, 4.4 equiv.) over 30 min. The solution was stirred for 1 h, then warmed to 25 °C and stirred for 3 h. Excess of a saturated aqueous $NaHCO_3$ solution was carefully added, then the solvent was removed *in vacuo* to afford a white solid, which was extracted with absolute EtOH (3 × 100 cm^3). The extract was concentrated *in vacuo* to give tetraol **4**, as a colourless oil. (8.26 g, 95%) (Found: C, 55.69; H, 9.61. $C_{17}H_{36}O_8$ requires C, 55.42; H, 9.85%); ^{1}H NMR (MeOD), d 1.78 (m, 2H, CH_2CH$_2$OH), 3.38 (s, 2H, CH$_2$O), 3.55 (t, *J* 5.0 Hz, 2H, OCH$_2$), 3.69 (t, *J* 5.1 Hz, 2H, CH$_2$OH); ^{13}C NMR (MeOD), d 31.8 (*C*H$_2$CH$_2$OH), 44.9 (C^{quat}), 60.5 (CH$_2$OH), 69.7 (OCH$_2$), 70.7 (CH$_2$O); IR (neat), 3364, 2948, 2879, 1493, 1424, 1363, 1109 cm^{-1}.

Tetrakis{5-[4′-oxa-(2,2′:6′,2″-terpyridinyl)]-2-oxapentyl}methane 5

To a suspension of powdered KOH (1.10 g) in dry Me_2SO (15 cm^3), was added tetraol **4** (600 mg, 1.63 mmol) in Me_2SO (5 cm^3). The suspension was heated to 60 °C for 30 min, then 4′-chloro-2,2′:6′,2″-terpyridine[9] (4′-Cl-tpy; 1.92 g, 4.4 equiv.) was added. After 24 h at 60 °C, the mixture was cooled and poured into cold water (300 cm^3). The resultant white solid was filtered, washed with water, and dried *in vacuo* to give a off-white solid, which was column chromatographed eluting with 15% EtOAc in CH_2Cl_2 to afford **5**, as a white solid (1.65 g, 78%), mp 161–164 °C (Found: C, 71.70; H, 5.57; N, 12.78; $C_{77}H_{72}N_{12}O_8$ requires C, 71.50; H, 5.61; N, 12.99%); ^{1}H NMR, d 1.98 (m, 8H, *J* 5.6 Hz, OCH$_2$CH_2), 3.42 (s, 8H, CH$_2$O), 3.52 (t, 8H, *J* 5.6 Hz, OCH$_2$), 4.18 (t, 8H, *J* 5.6 Hz, OCH$_2$CH$_2$CH_2), 7.24 (t, 8H, *J* 5.2 Hz, H$^{5,5''}$), 7.74 (t, 8H, *J* 7.6 Hz, H$^{4,4''}$), 7.94 (s, 8H, H$^{3',5'}$), 8.54 (d, 8H, *J* 7.9 Hz, H$^{3,3''}$), 8.62 (d, 8H, *J* 4.7 Hz, H$^{6,6''}$); ^{13}C NMR, d 29.4 (OCH$_2$*C*H$_2$), 45.6 (C^{quat}), 65.2 (OCH$_2$CH$_2$*C*H$_2$), 67.6 (OCH$_2$), 69.9 (CH$_2$O), 107.5 (C$^{5,5''}$), 121.3 (C$^{4,4''}$), 123.8 (C$^{3,3''}$), 136.7 (C$^{3',5'}$), 149.1 (C$^{6,6''}$), 156.2 (C$^{2,2''}$), 157.0 (C$^{2',6'}$), 167.2 (C$^{4'}$); IR (KBr), 3063, 2933, 2876, 1609, 1593, 1570, 1493, 1440, 1416, 1362, 1209, 1093, 801 cm^{-1}.

4-[4′-Oxa-(2,2′:6′,2″-terpyridinyl)]butanoic acid 6

To a solution of 4-hydroxybutanoic acid (942 mg, 7.47 mmol) and KOH (3 g) in dry Me_2SO (30 cm^3) at 60 °C, was added 4′-Cl-tpy (2.00 g, 7.47 mmol). The mixture was maintained for 36 h, then cooled to 25 °C and poured into water (600 cm^3) affording a yellow transparent solution. The pH was adjusted to neutral by the addition of 10% aqueous HCl resulting in the formation of a white precipitate, which after standing for at least 2 h, was filtered, washed with water, dried *in vacuo* to give the acid **6**, as a white solid (2.15 g, 86%); mp 173–175 °C (Found: C, 68.29; H, 5.29; N, 12.30. $C_{19}H_{17}N_3O_3$ requires C, 68.05; H, 5.11; N, 12.53%); ^{1}H NMR, d 2.21 (m, 2H, *J* 6.0 Hz, OCH$_2$CH_2CH$_2$), 2.57 (t, 2H, *J* 7.1 Hz, CH_2CO$_2$H), 4.31 (t, 2H, *J* 6.0 Hz, OCH$_2$), 7.38 (td, 2H, *J* 4.9, 1.0 Hz, H$^{5,5''}$), 7.88 (td,

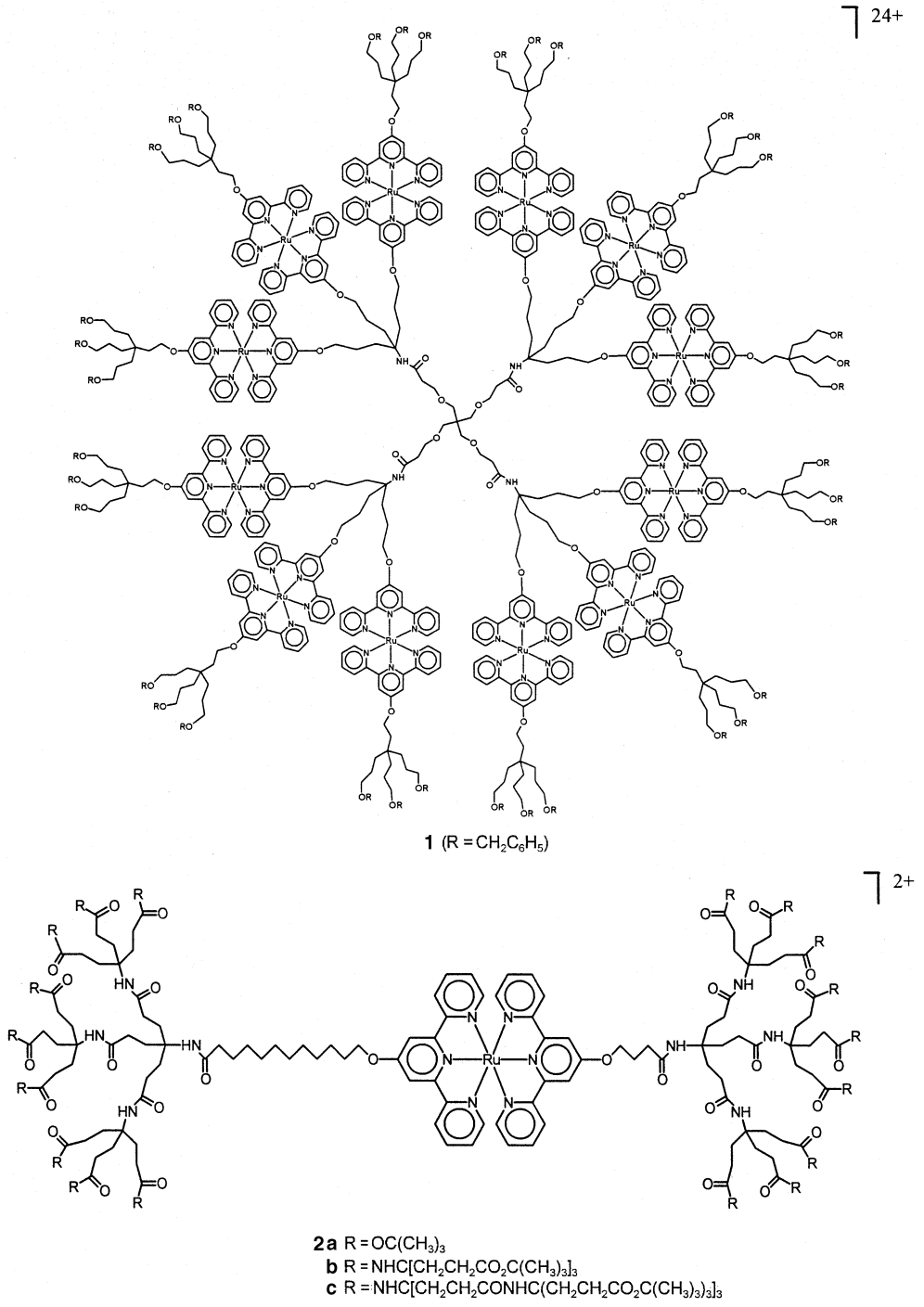
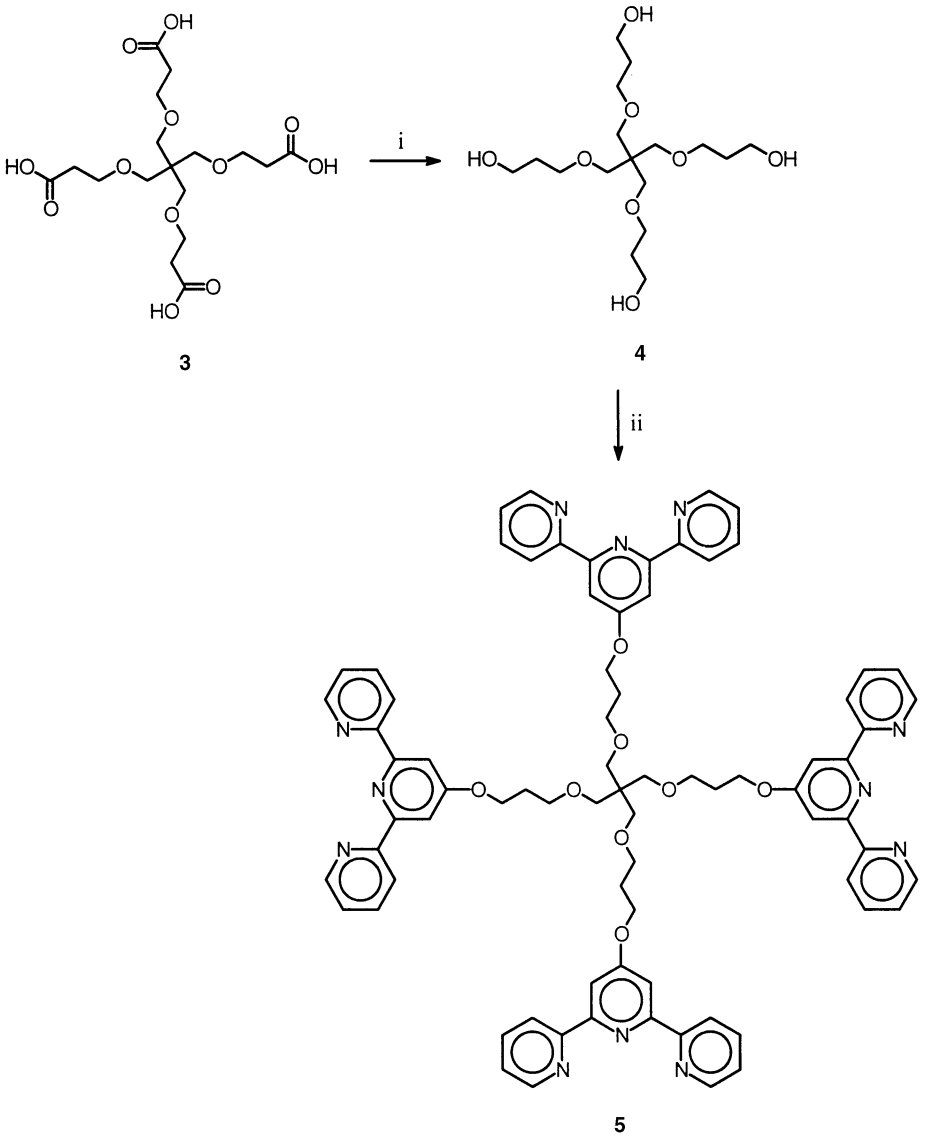


Fig. 1 Dendritic architectures incorporating (—<Ru>—) units

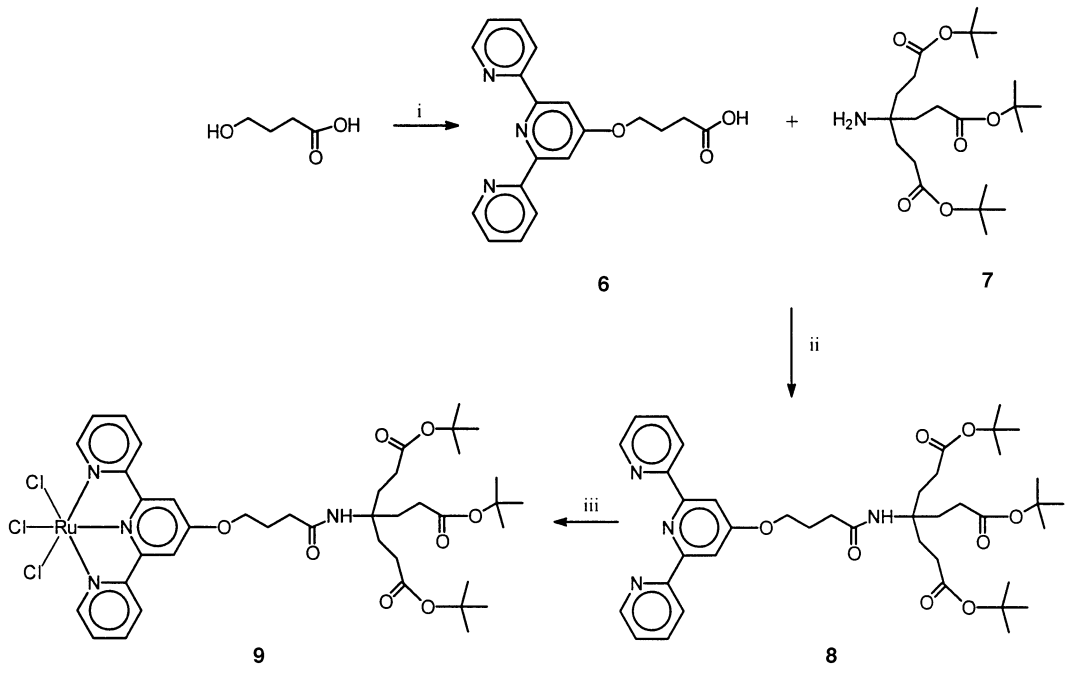
2H, *J* 7.8, 1.8 Hz, $H^{4,4''}$), 7.92 (s, 2H, $H^{3',5'}$), 8.61 (d, 2H, *J* 7.9 Hz, $H^{3,3''}$), 8.67 (d, 2H, *J* 4.3 Hz, $H^{6,6''}$); ^{13}C NMR, d 24.6 ($OCH_2CH_2CH_2$), 30.7 (CH_2CO_2H), 67.4 (OCH_2), 107.6 ($C^{5,5''}$), 121.9 ($C^{4,4''}$), 124.1 ($C^{3,3''}$), 137.3 ($C^{3',5'}$), 148.9 ($C^{6,6''}$), 156.1 ($C^{2,2''}$), 157.0 ($C^{2',6'}$), 167.2 ($C^{4'}$), 175.7 (CO_2H); IR (KBr), 3063, 2956, 2918, 2879, 1709, 1593, 1570, 1478, 1450, 1416, 1370, 1262, 1209, 1040, 801, 747 cm^{-1}.

N-{Tris[(2-*tert*-butoxycarbony)ethyl]methyl}[4′-oxa-(2,2′:6′,2″-terpyridinyl)]butamide 8

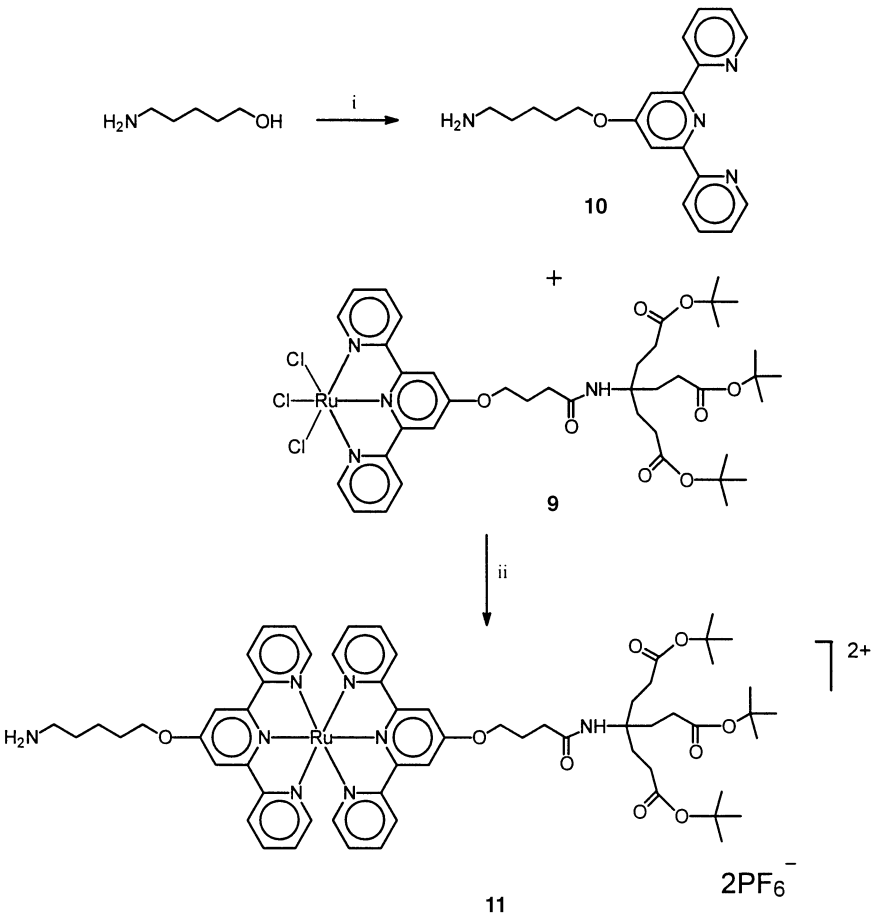
To a solution of acid **6** (2.0 g, 5.97 mmol) in dry DMF (30 cm^3), were added dicyclohexylcarbodiimide (DCC; 1.23 g, 5.97 mmol) and 1-hydroxybenzotriazole (1-HOBT; 806 mg, 5.97 mmol) at 25 °C. This mixture was stirred for 1 h, then di-*tert*-butyl 4-[(2-tert-butoxycarbonyl)ethyl]-4-aminoheptanedicarboxylate **7**[10] (2.48 g, 5.97 mmol) was added. The reaction mixture was stirred for 36 h, after which the white precipitate was filtered off. The filtrate was concentrated *in vacuo* affording a crude oil, which was dissolved in Et_2O (200 cm^3), washed with 10% aqueous Na_2CO_3 (2 × 100 cm^3), brine (2 × 100 cm^3), dried ($MgSO_4$), and concentrated *in vacuo* to afford a solid, which was recrystallized from cyclohexane (3.15 g, 72%); mp 146–149 °C (Found: C, 67.36; H, 7.51; N, 7.85. $C_{41}H_{56}N_4O_8$ requires C, 67.19; H, 7.70; N, 7.64%); ^1H NMR, d 1.42 (s, 27H, CH_3), 2.01 (t, 6H, *J* 8.2 Hz, CH_2CO_2), 2.23 (m, 8H, CH_2CH_2CONH, $CH_2CH_2CO_2$), 2.36 (t, 2H, *J* 7.1 Hz, CH_2CONH), 4.28 (t, 2H, *J* 5.9 Hz, OCH_2), 6.03 (s, 1H, NH), 7.32 (td, 2H, *J* 4.8, 1.8 Hz, $H^{5,5''}$), 7.84 (td, 2H, *J* 7.8, 1.7 Hz, $H^{4,4''}$), 8.01 (s, 2H, $H^{3',5'}$), 8.60 (d, 2H, *J* 8.0 Hz, $H^{3,3''}$), 8.68 (d,



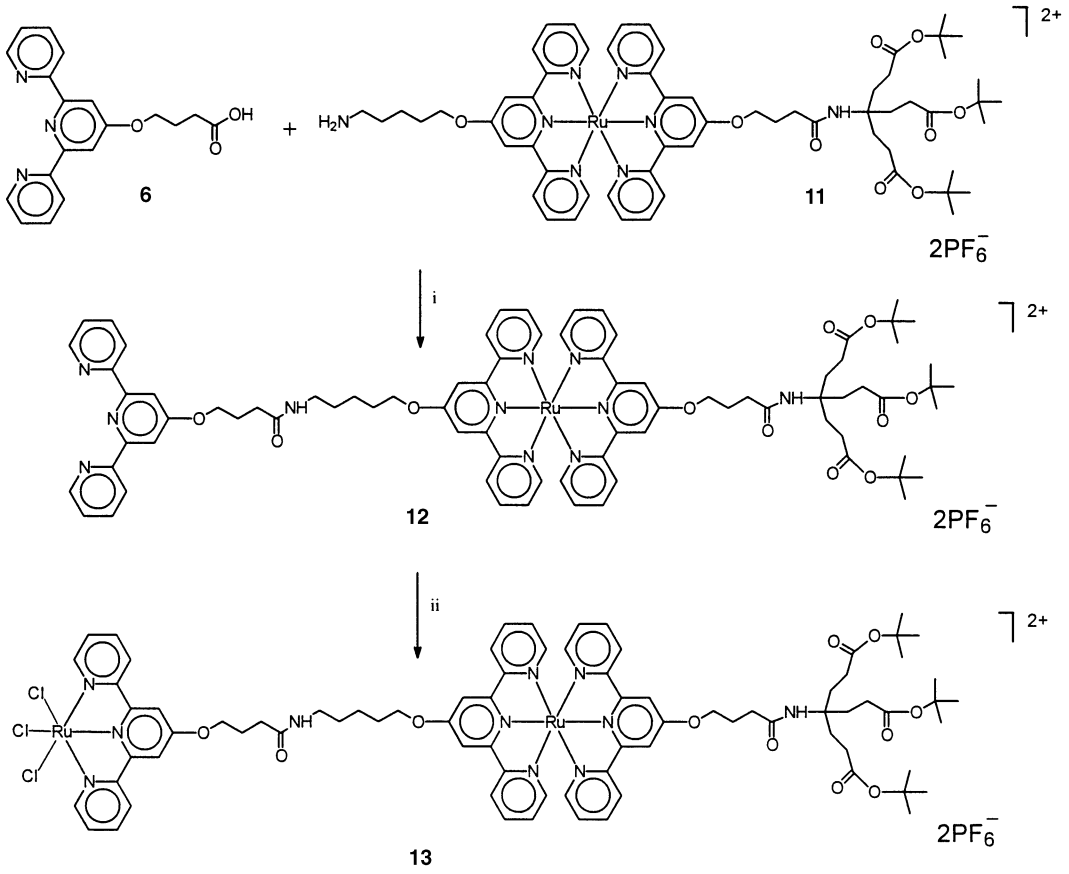
Scheme 1 *Reagents and conditions:* i, BH_3·THF, 1 h, 0 °C, then 3 h, 25 °C; ii, 4′-Cl-tpy, KOH, Me_2SO, 24 h, 60 °C



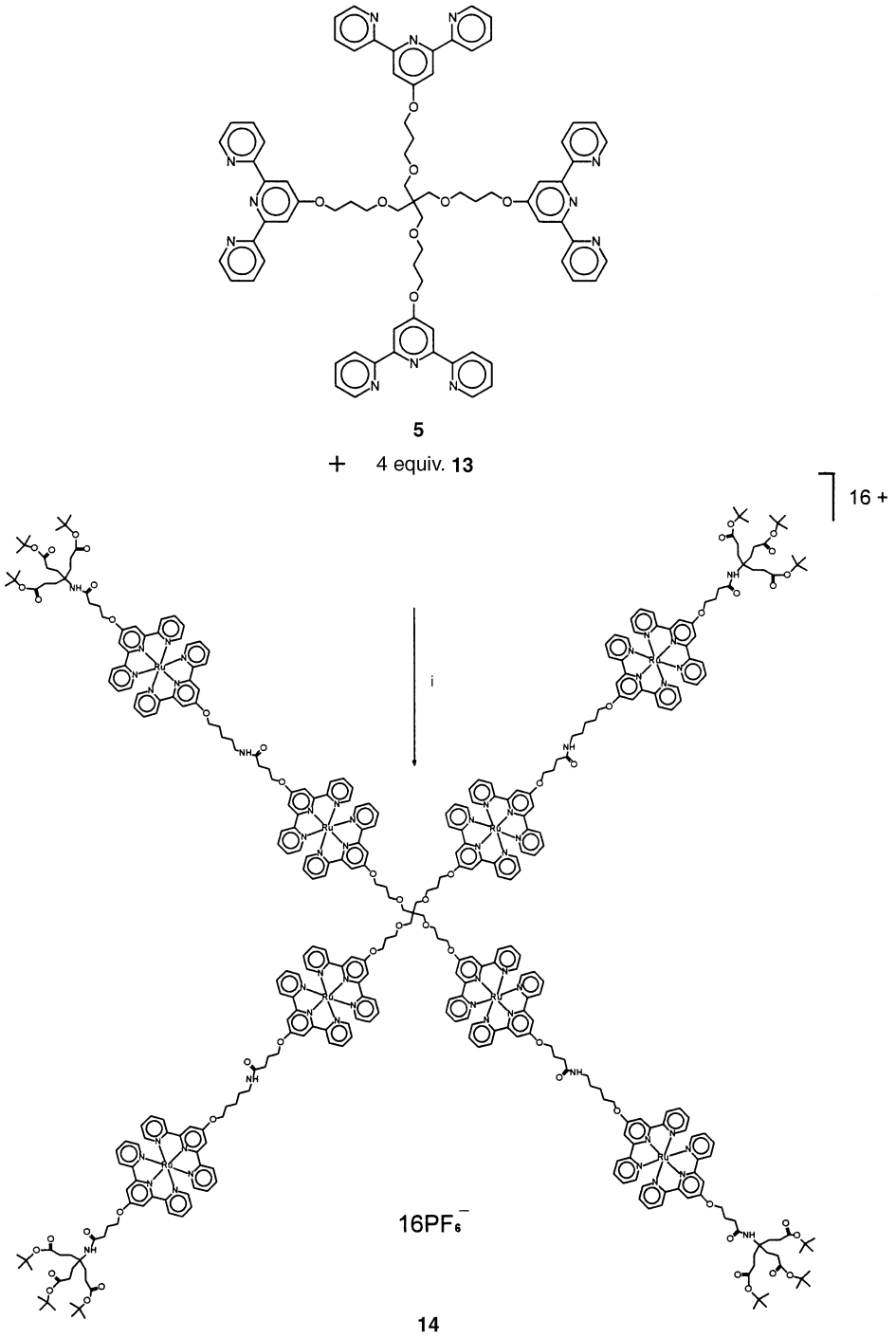
Scheme 2 *Reagents and conditions:* i, 4′-Cl-tpy, KOH, Me_2SO, 36 h, 60 °C; ii, DCC, 1-HOBT, DMF, 36 h, 25 °C; iii, $RuCl_3 \cdot 3H_2O$, MeOH, 3 h, reflux



Scheme 3 *Reagents and conditions:* i, 4′-Cl-tpy, KOH, Me_2SO, 36 h, 60 °C; ii, 4-ethylmorpholine, MeOH, 2 h, reflux



Scheme 4 *Reagents and conditions:* i, DCC, 1-HOBT, DMF, 48 h, 25 °C; ii, $RuCl_3 \cdot 3H_2O$, MeOH, 6 h, reflux



Scheme 5 *Reagents and conditions:* i, 4-ethylmorpholine, MeOH–$CHCl_3$, 4 h, reflux

2H, *J* 4.3 Hz, $H^{6,6''}$); ^{13}C NMR, d 25.2 (CH_2CH_2CON), 28.2 (CH_3), 29.9 (CH_2CO_2), 30.2 ($CH_2CH_2CO_2$), 33.6 (CH_2CON), 57.6 (NHC), 67.4 (OCH_2), 80.8 [$C(CH_3)_3$], 107.5 ($C^{5,5''}$), 121.4 ($C^{4,4''}$), 123.9 ($C^{3,3''}$), 136.9 ($C^{3',5'}$), 149.1 ($C^{6,6''}$), 156.2 ($C^{2,2''}$), 157.2 ($C^{2',6'}$), 167.2 ($C^{4'}$), 171.6 (CONH), 173.0 (CO_2); IR (KBr), 3341, 3063, 3010, 2987, 2933, 1732, 1671, 1586, 1563, 1478, 1452, 1362, 1155, 793 cm^{-1}.

Ruthenium(III) complex of *N*-{tris[(2-*tert*-butoxycarbony)ethyl]methyl}[4′-oxa-(2,2′:6′,2″-terpyridinyl)]butamide 9

A solution of $RuCl_3 \cdot 3H_2O$ (709 mg, 2.71 mmol) and **8** (2.0 g, 2.71 mmol) in MeOH (50 cm^3) was refluxed for 3 h. After cooling, the yellow–brown precipitate was filtered, washed sequentially with MeOH (5 cm^3), water (2×20 cm^3) and Et_2O (2×10 cm^3) then dried *in vacuo*, yielding **9**, as a yellow–brown solid (1.94 g, 76%); mp > 202 °C (decomp.); (Found C, 52.17; H, 5.95; N, 6.06. $C_{41}H_{56}Cl_3N_4O_8Ru$ requires C, 52.37; H, 6.00; N, 5.96%); IR (KBr), 3340, 3071, 2987, 2940, 1732, 1670, 1609, 1555, 1471, 1370, 1224, 1160, 1047, 801 cm^{-1}; UV–VIS, l_{max} = 232 ($e = 3.27 \times 10^4$), 278 (2.91×10^4), 312 (1.63×10^4), 402 (9.32×10^3), 466 nm (3.73×10^3 dm^3 mol^{-1} cm^{-1}).

5-Aminopentyl 4′-(2,2′:6′,2″-terpyridinyl) ether 10

To a suspension of powdered KOH (2.0 g) in dry Me_2SO (30 cm^3), was added 5-aminopentan-1-ol (770 mg, 7.47 mmol). The suspension was stirred at 60 °C for 30 min, then 4′-Cl-tpy (2.00g, 7.47 mmol) was added. The whole mixture was stirred at 60 °C for an additional 36 h. After cooling to 25 °C, the mixture was poured into water (600 cm^3), stirred, then allowed

to set for 3 h. The precipitate was filtered, washed with water, and dried *in vacuo* to give a crude product, which was column chromatographed eluting with 10% MeOH in CH_2Cl_2 to yield **10,** as a light yellow solid (1.78 g, 71%); mp 104–106 °C (Found: C, 72.04; H, 6.46; N, 16.60. $C_{20}H_{22}N_4O$ requires C, 71.83; H, 6.63; N, 16.75%); ^{1}H NMR, d 1.49–1.55 (m, 6H, NH_2, $NCH_2CH_2CH_2$), 1.82 (m, 2H, CH_2CH_2O), 2.67 (t, 2H, *J* 6.1 Hz, NCH_2), 4.17 (t, 2H, *J* 6.2 Hz, CH_2O), 7.29 (td, 2H, *J* 4.9, 1.6 Hz, $H^{5,5''}$), 7.78 (td, 2H, *J* 7.2, 1.4 Hz, $H^{4,4''}$), 8.01 (s, 2H, $H^{3',5'}$), 8.59 (d, 2H, *J* 7.9Hz, $H^{3,3''}$), 8.65 (d, 2H, *J* 4.4 Hz, $H^{6,6''}$); ^{13}C NMR, d 23.2 ($NCH_2CH_2CH_2$), 28.8 (CH_2CH_2O), 33.3 (NCH_2CH_2), 42.0 (NCH_2), 67.9 (CH_2O), 107.3 ($C^{5,5''}$), 121.2 ($C^{4,4''}$), 123.7 ($C^{3,3''}$), 136.6 ($C^{3',5'}$), 148.9 ($C^{6,6''}$), 156.0 ($C^{2,2''}$), 156.9 ($C^{2',6'}$), 167.1 ($C^{4'}$); IR (KBr), 3359, 3299, 3059, 3014, 2947, 2865, 1598, 1583, 1576, 1470, 1448, 1410, 1358, 1208, 1043, 803 cm^{-1}.

Amino-ruthenium(II) complex 11

To a suspension of complex **9** (300 mg, 318 mmol) in MeOH (20 cm^3) were added amine **10** (106 mg, 318 mmol) and 4-ethylmorpholine (73 mg). The mixture was refluxed for 2 h until it turned into a clear red solution. After cooling to 25 °C, saturated NH_4PF_6 in MeOH (10 cm^3) was added, then the methanol was removed *in vacuo*, the resulting red solid was dissolved in $CHCl_3$ (4 cm^3), which was then slowly added to Et_2O (100 cm^3) with stirring, to yield a red precipitate, which was filtered, and dried *in vacuo* to give complex **11**, as a red solid (336 mg, 72%); mp >152 °C (decomp.); (Found: C, 49.92; H, 5.29; N, 7.28. $C_{61}H_{78}F_{12}N_8O_9P_2Ru$ requires C, 50.24; H, 5.39; N, 7.68%); ^{1}H NMR (CD_3CN), d 1.11–1.45 (m, 31H, $NCH_2CH_2CH_2$, CH_3), 1.8–2.0 (m, 10H, CH_2CH_2O, OCH_2CH_2, $CH_2CH_2CO_2$), 2.22 (m, 6H, CH_2CO_2), 2.45 (t, 2H, *J* 7.0 Hz, CH_2CON), 3.00 (br s, 2H, H_2NCH_2), 4.52 (m, 4H, CH_2O, OCH_2), 6.67 (s, CONH), 7.16 (m, 4H, $H^{5,5''}$), 7.42 (m, 4H, $H^{6,6''}$), 7.88 (m, 4H, $H^{4,4''}$), 8.35–8.60 (m, 8H, $H^{3,3''}$, $H^{3',5'}$); ^{13}C NMR (CD_3CN), d 23.8 ($NCH_2CH_2CH_2$), 25.0 (CH_2CH_2CON), 28.4 (d, CH_3, CH_2CH_2O), 29.7 (d, $CH_2CH_2CO_2$), 32.7 (d, CH_2CON, $H_2NCH_2CH_2$), 41.7(H_2NCH_2), 58.6 (NHC), 70.3 (OCH_2), 71.1 (CH_2O), 112.2 ($C^{5,5''}$), 125.4 ($C^{4,4''}$), 128.5 ($C^{3,3''}$), 138.7 ($C^{3',5'}$), 153.5 ($C^{6,6''}$), 157.5 ($C^{2,2''}$), 159.4 ($C^{2',6'}$), 167.0 (d, $C^{4'}$), 172.9 (CONH), 173.7 (CO_2); IR (KBr), 3417, 3295, 3086, 2980, 2940, 1719, 1614, 1470, 1394, 1370, 1213, 1162, 1040, 840, 788, 754 cm^{-1}; UV–VIS, l_{max}=244 (e=4.76×10^4), 270 (5.17×10^4), 304 (6.08×10^4), 488 nm (1.81×10^4 dm^3 mol^{-1} cm^{-1}).

Complex 12

To a solution of 4-[4′-oxa-(2,2′:6′,2″-terpyridinyl)]butanoic acid **6** (207 mg, 618 mmol) in dry DMF (15 cm^3) were added DCC (128 mg, 618 mmol) and 1-HOBT (83.5 mg, 618 mmol) at 25 °C. The mixture was stirred for 1 h, then amine **11** (901 mg, 618 mmol) was added. The whole mixture was stirred for 48 h, after which the white precipitate was filtered. The red filtrate was concentrated *in vacuo* to afford a crude residue, which was dissolved in $CHCl_3$ (200 cm^3), washed with saturated aqueous $NaHCO_3$ (2×50 cm^3), then brine (2×100 cm^3), dried ($MgSO_4$), and concentrated *in vacuo*. The crude residue was column chromatographed eluting with 10% MeOH in CH_2Cl_2 to yield **12**, as a red solid (465 mg, 42%); mp 90–94 °C (Found: C, 53.95; H, 5.50; N, 9.47. $C_{80}H_{93}F_{12}N_{11}O_{11}P_2Ru$ requires C, 54.11; H, 5.28; N, 8.68%); ^{1}H NMR, d 1.11–1.45 (m, 31H, $NCH_2CH_2CH_2$, CH_3), 1.8–2.0 (m, 12H, OCH_2CH_2, CH_2CH_2O, OCH_2CH_2, $CH_2CH_2CO_2$), 2.22 (m, 6H, CH_2CO_2), 2.40–2.46 (m, 4H, CH_2CONH, CH_2CONH), 3.10 (m, 2H, $CONHCH_2$), 4.52 (m, 6H, OCH_2, CH_2O, OCH_2), 6.56 (s, CONHC), 7.16–8.70 (m, tpy H); ^{13}C NMR, d 23.1 ($NCH_2CH_2CH_2$), 25.0 (d, CH_2CH_2CONH, CH_2CH_2CONH), 28.0 (d, CH_3, CH_2CH_2O), 29.8 (d, $CH_2CH_2CO_2$), 31.7, 32.3, 32.7 (CH_2CONH, $H_2NCH_2CH_2$, CH_2CONH), 39.2 ($CONHCH_2$), 57.4 (CONHC), 67.4 (free tpy-OCH_2,), 69.3 (OCH_2), 71.0 (CH_2O), 107.2 (free tpy $C^{5,5''}$), 111.1 ($C^{5,5''}$), 121.2 (free tpy $C^{4,4''}$), 123.9 (free tpy $C^{3,3''}$), 124.5 ($C^{4,4''}$), 127.8 ($C^{3,3''}$), 136.9 (free tpy $C^{3',5'}$), 137.7 ($C^{3',5'}$), 148.9 (free tpy $C^{6,6''}$), 152.0 ($C^{6,6''}$), 153.7 ($C^{2,2''}$), 156.7, 156.8 ($C^{2',6'}$, free tpy $C^{2,2''}$), 158.0 (free tpy $C^{2',6'}$), 162.5 ($CONHCH_2$), 165.9, 166.2, 166.8 ($C^{4'}$, free tpy $C^{4'}$), 172.1 (CONHC), 172.9 (CO_2); IR (KBr), 3418, 3333, 3071, 2980, 2940, 2851, 1724, 1678, 1616, 1563, 1470, 1393, 1370, 1216, 1162, 847, 790, 754 cm^{-1}; UV–VIS, l_{max}=244 (e=6.86×10^4), 270 (7.13×10^4), 304 (7.19×10^4), 488 nm (1.99×10^4 dm^3 mol^{-1} cm^{-1}).

Ruthenium(II) ruthenium(III) complex 13

A solution of $RuCl_3\cdot3H_2O$ (80 mg, 306 mmol) and **12** (542 mg, 306 mmol) in MeOH (20 cm^3) was refluxed for 6 h. After cooling to 25 °C, the red precipitate was filtered, washed with cold MeOH (2 cm^3), water (2×10 cm^3), and dried *in vacuo* to yield crude product **13**, as a dark-red solid (206 mg, 34% crude yield); mp >152 °C (decomp.); IR (KBr), 3425, 3071, 2980, 2940, 1724, 1655, 1617, 1547, 1470, 1371, 1163, 847, 793 cm^{-1}; UV–VIS, l_{max}=232 (e=7.25×10^4), 270 (7.53×10^4), 304 (7.49×10^4), 488 nm (2.06×10^4 dm^3 mol^{-1} cm^{-1}). This product was not purified but carried on to the next reaction.

Dendritic complex 14

To a suspension of complex **13** (429 mg, 216 mmol, 4.4 equiv.) in MeOH (30 cm^3) were added tetrakisterpyridine core **5** (63.5 mg, 49 mmol) and 4-ethylmorpholine (45 mg) in MeOH–$CHCl_3$ (2:1, v/v, 5 cm^3). The mixture was refluxed for 4 h until it turned into a clear red solution. After cooling to 25 °C, an excess of NH_4PF_6 was directly added to the solution to form a red precipitate, which was filtered, washed sequentially with cold MeOH (2×5 cm^3), water (2×15 cm^3), Et_2O (2×5 cm^3), and dried *in vacuo* to yield **14**, as a red solid (416 mg, 85%); mp 219–221 °C (Found: C, 47.66; H, 4.32; N, 7.95. $C_{397}H_{444}F_{96}N_{56}O_{52}P_{16}Ru_8$ requires C, 47.87; H, 4.49; N, 7.88%); ^{1}H NMR (CD_3CN), d 1.30–3.90 (br m, 236H, CH_2, CH_3), 4.53 (m, 40H, OCH_2, CH_2O), 6.47 (s, 4H, CONH), 7.15 (m, 32H, $H^{5,5''}$), 7.40 (m, 32H, $H^{6,6''}$), 7.86 (m, 32H, $H^{4,4''}$), 8.35–8.60 (m, 64H, $H^{3,3''}$, $H^{3',5'}$); ^{13}C NMR (CD_3CN), d 23.1, 25.0, 25.9, 28.4 (CH_3), 29.8, 29.9, 30.5, 30.6, 32.7, 32.8, 40.0 ($CONHCH_2$), 58.0 (CONHC), 68.0–70.0 (m, all CH_2O, OCH_2), 81.3 (CO_2C), 112.1 (d, $C^{5,5''}$), 125.5 (d, $C^{4,4''}$), 128.5 ($C^{3,3''}$), 138.8 ($C^{3',5'}$), 153.5 ($C^{6,6''}$), 157.4 ($C^{2,2''}$), 159.4 ($C^{2',6'}$), 167.1 (d, $C^{4'}$), 172.4 (CONHC), 174.0 (CO_2); IR (KBr), 3425, 3118, 3079, 2979, 2941, 1724, 1671, 1617, 1547, 1470, 1425, 1217, 848, 786 cm^{-1}; UV–VIS, l_{max}=244 (e=3.68×10^5), 270 (3.99×10^5), 304 (4.77×10^5), 488 nm (1.41×10^5 dm^3 mol^{-1} cm^{-1}).

Results and Discussion

Synthesis of the tetrakisterpyridine core 5

The synthesis of tetrakisterpyridine core **5** was initiated from the readily available tetracarboxylic acid **3**, which has been demonstrated to be an ideal core for the construction of a four-directional dendritic materials.[7] Acid **3**, prepared[10] in high yield and purity from pentaerythritol and acrylonitrile, followed by hydrolysis, was reacted[8] with BH_3 in THF at 0 °C to afford tetraol **4**, which was then treated with at least 4 equivalents of 4′-chloro-2,2′:6′,2″-terpyridine[9] (4′-Cl-tpy) in the presence of powered KOH in anhydrous Me_2SO at 60 °C to give the desired tetrakisterpyridine core **5** in 74% yield after purification, Scheme 1. The structure of core **5** was confirmed (^{1}H NMR) by the definitive upfield shift (Dd=−0.52 ppm) for the singlet for the 3′,5′-terpy H upon the 4′-terpy Cl to 4′-terpy OR conversion. In ^{13}C NMR, the peak shifts for the $C^{5,5''}$ from

d 121.1 to 107.3 and for $C^{4'}$ from d 146.5 to 167.1 further support the transformation.

Synthesis of ruthenium(II) complex connectors

4-[4′-Oxa-(2,2′:6′,2″-terpyridinyl)]butanoic acid **6,** was prepared by the reaction of 4′-Cl-tpy with 4-hydroxybutanoic acid in the presence of solid KOH in anhydrous Me_2SO at 60 °C in 86% yield. The structure of **6** can be supported (NMR) by the shift of $H^{3',5'}$ at d 8.46 to 7.92 denoting the formation of the 4′-ethereal bond. By taking advantage of the peptide coupling method[11] (Scheme 2) using dicyclohexylcarbodiimide (DCC) and 1-hydroxybenzotriazole (1-HOBT) in DMF, acid **6** was reacted with 'Behera's amine' **7**[10] to afford terpyridine amide **8** in 72% yield. The new peak (^{1}H NMR) at d 6.03 denotes the formation of the amide bond. In ^{13}C NMR, the formation of the ethereal bond can be concluded based on the significant shifts of $C^{5,5''}$ and $C^{4'}$; the successful amidation is supported by the shift of the signal assigned to newly introduced quaternary carbon moiety (CONH*C*) from d 52.8 to 57.6. The yellow–brown microcrystalline, paramagnetic ruthenium(III) complex **9** was prepared by refluxing 1 equivalent of **8** with $RuCl_3 \cdot 3H_2O$ in methanol to give 76% yield, which was used without further purification.

Preferential *O- vs. N*-arylation was realized when 5-aminopentan-1-ol was reacted with 4′-Cl-tpy in the presence of powered KOH in dry Me_2SO to afford the free 5-aminopentyl 4′-(2,2′:6′,2″-terpyridinyl) ether **10** in 71% conversion, Scheme 3. The structure of **10** was readily confirmed by the lack of change for the signals of H_2N-CH_2 in both ^{1}H and ^{13}C NMR spectra. The significant chemical shifts (^{1}H NMR) for $H^{3',5'}$ and $C^{5,5''}$, as well as for $C^{4'}$ (^{13}C NMR) confirmed the free amino group and the preferential formation of the 4′-ethereal bond. The aminoterpyridine **10** was then reacted with 1 equivalent of the ruthenium(III) complex **9** in boiling methanol and *N*-ethylmorpholine, as the reducing agent, followed by addition of an excess of NH_4PF_6, to afford the amino complex **11,** as a red hexafluorophosphate salt in 72% yield. Confirmation of the structure of this ruthenium(II) complex was demonstrated by the upfield shift ($\Delta\delta = -1.23$ ppm) for $H^{6,6''}$ in ^{1}H NMR, and all downfield shifts of $C^{5,5''}$ from d 107.3 to 112.2, $C^{4,4''}$ from d 121.2 to 125.4, $C^{3,3''}$ from d 123.7 to 128.5, $C^{3',5'}$ from d 136.6 to 138.7, $C^{6,6''}$ from d 148.9 to 153.5, $C^{2,2''}$ from d 156.0 to 157.5, $C^{2',6'}$ from d 156.9 to 159.4; notably the signal for $C^{4'}$ remained nearly constant.

Reaction of acid **6** with amine **11** was accomplished by using the DCC coupling method, as described above, to give (42%) the complex **12,** as a red solid. Any unreacted acid **6**, which contains the uncomplexed terpyridine moiety, was eliminated by column chromatography so that no unexpected metal complexation sites would be carried to the subsequent reaction. An equimolar solution of ligand **12** with $RuCl_3 \cdot 3H_2O$ in methanol was refluxed to give the red paramagnetic complex **13**, which was filtered from the mixture in 34% crude yield, Scheme 4.

Synthesis of the dendritic complex 14

The synthesis of the final product, the dendritic macromolecule with two layers of ruthenium(II) terpyridine complexes, is shown in Scheme 5. The tetrakisterpyridine core **5** was treated with 4.4 equivalents of complex **13** in the presence of 4-ethylmorpholine in methanol–chloroform, followed by addition of a slight excess NH_4PF_6 to afford the red, microcrystalline, dendritic complex **14** in 85% yield. At this point, the traces of impurities, which were present in the reaction mixture due to the lack of purification of complex **13**, conveniently remained in solution. The structure of the dendritic complex **14** was confirmed by elemental analysis and NMR spectroscopy. The ^{1}H NMR spectrum of **14** demonstrated the absence of paramagnetic species as well as terminal terpyridines and the complex heteroaryl H region supports the presence of structurally dissimilar terpyridine environments. Whereas in its ^{13}C NMR spectrum, the two pairs of different terpyridines afforded complex patterns with peaks for each carbon atom due to the small difference caused by the two layers of ruthenium(II) terpyridines centres connected by the slightly different organic linkages. All signals (^{13}C NMR) were, however, resolved to show each moiety of the dendritic complex, with the exception of the quaternary core carbon, which should have appeared at d 45.6; the absence of this signal is reasonable since it is the only unique atom in the dendritic assembly.

Hydrolytic or thermal deprotection, followed by subsequent formation of a larger 'dendritic' surface can be accomplished at either the appendage stage (**8** or **12**) or the four-directional dendrimer (**14**). The former offers solubility advantages as well as the ability to conveniently attach these metallo-modules to other macromolecular materials; applications of these metallo-macromolecules are in progress and will be reported elsewhere.

Conclusion

The construction of this new type of double tiered metallodendrimer shows the importance of the stepwise construction by means of controlled metal complexation. This modular approach also provides a much more versatile methodology for the synthesis of specifically assembled metallodendrimers and related polymers by using a combination of divergent and convergent approaches.

This work was supported, in part, by the National Science Foundation (DMR-96–22609) and the Army Research Office (DAAH04–93-G-0448).

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Paper 7/00127D; *Received* 6*th January*, 1997