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Metallodendrimers: homo- and heterogeneous tier construction by bis(2,2′:6′,2″-terpyridinyl)Ru(II) complex connectivity☆

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Abstract—A convenient combinatorial-style route for the incorporation of multiple, differing functional groups, in a controllable ratio, onto a dendritic poly(propylene imine) scaffolding is described. Attachment of the functionality is accomplished by the connective formation of bis(2,2′:6′,2-terpyridine)Ru(II) complexes via reaction of a terpyridine-modified dendritic surface with 1→3 branched monomers each possessing a focal terpyridine moiety. This synthetic approach produces a heterogeneous surface coating that is compared and contrasted to that of analogous homogeneous surfaced constructs. UV–vis absorption and TGA data for the metallodendrimers are also reported.

1. Introduction

Since the initiation of dendrimer chemistry,[1,2] these molecules have been demonstrated to be well-defined and highly branched tree-like structures, which exhibit unique molecular properties and provide uniform architectural foundations for creative modification.[3,4] In addition, potential intra- and inter-dendrimer interactions provide an entry to the supramacromolecular regime,[5] which is exemplified in the metallodendrimer arena whereby metal complex formation has been extensively employed internally and peripherally for chemicophysical modifications; the catalytic potential of these multifunctional transition metal-constructs has been recently reviewed.[6] Notably, the use of polypyridyl-based[7] ligands, such as 2,2′:6′,2″-terpyridine[8–28] and 2,2′-bipyridine,[7,29–45] has allowed access to many new macromolecular materials. Thus, building on both the facile metal complex formation[22] afforded by the terpyridine moiety and our combinatorial-type 'mixed-monomer,' macromolecular property modification technology,[46] predicated on our isocyanate-based monomers,[46–52] we herein report the controlled attachment of fixed ratios of mixed functionality via bis(terpyridine)-metal ion-connectivity (–‹M›–) to dendrimers. This has been accomplished via the construction of new 1→3 branched monomers each possessing a focal terpyridinyl moiety for (–‹M›–) complex formation within the new macromolecular construct. Ramifications of this technique include the facile introduction of differing yet mutually compatible functionality to a dendritic core, incorporation of multiple internal metal centers, attachment of latent external functionality to be accessed after additional tier modification or growth, and the potential to easily manipulate surface characteristics as well as the overall macromolecular properties, such as solubility and viscosity.

This technique is in contrast to the well-known, combinatorial screening of small molecule libraries[53–56] and approaches to materials discovery[57,58] in addition to polymer[59] and catalyst design.[60–63] Dendrimer-supported combinatorial synthesis[64] and diverse combinatorial-based aminoacid dendrimers[65] have also been reported.

2. Results and discussion

Access to the combinatorial-styled materials began (Scheme 1) with the modification of the eight terminal amine groups of a 2nd generation poly(propylene imine)[66,67] (**1**) with the known 4-[4′-(2,2′:6′,2″-terpyridinyloxy)]butanoic acid[13,14] (**2**), by traditional peptide coupling conditions,[68] to give (81%) the desired octaterpyridinyl polyamide **3**, as a white solid. Confirmation of this core included the appearance (^{13}C NMR) of a new amide carbonyl absorption (*C*ONH) at 172.2 ppm, the shifted CH_2NH_2 signal to 37.8 ppm upon amidation, and the expected resonances attributed to the peripheral terpyridinyl moieties [key assignments: 148.5 ($C_{6,6''}$), 156.6 ($C_{2'}$), and 166.6 ppm ($C_{4'}$)]; the molecular ion peak at *m/z* 3312.06 $[M]^+$ (calcd *m/z* 3312.10 for $[M]^+$) in ESI-MS further supported the assignment.

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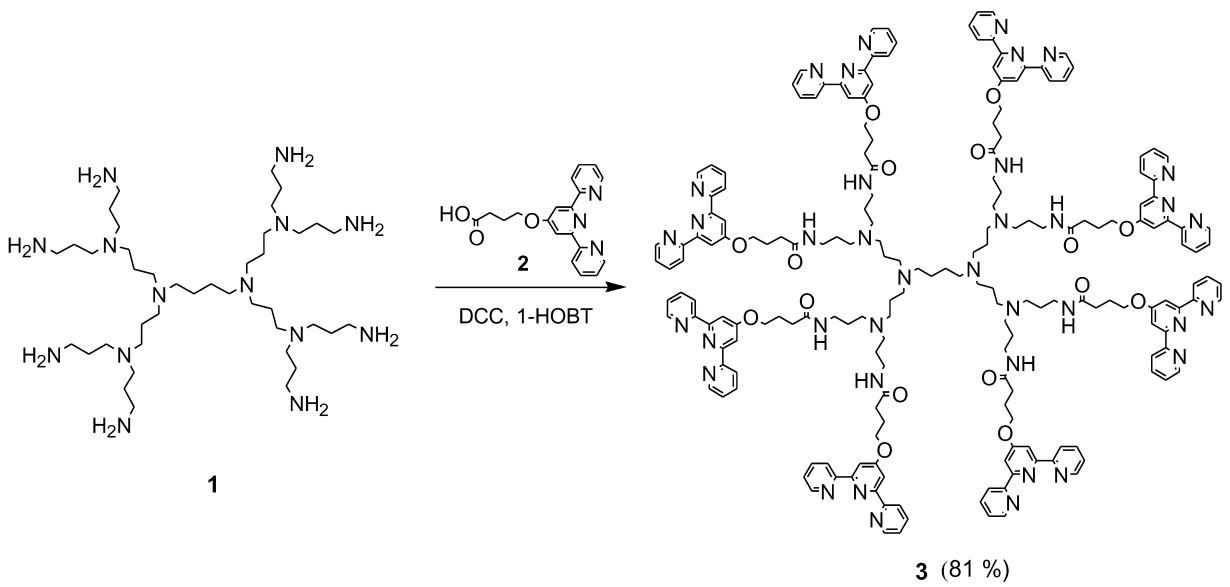


Scheme 1. Synthesis of the terpyridinyl core dendrimer **3**.

The 1→3 branched monomers (**4**–**6**) possessing the necessary focal Ru(III) terpyridine (Fig. 1) were similarly prepared using coupling reactions (DCC/HOBT) with the terpyridinyl acid **2** and the corresponding aminotrisbenzyl ether,[46,69] aminotris*tert*butyl ester,[70,71] and aminotrisethyl ester,[72,73] respectively, followed by treatment of each with Ru(III)·xH$_2$O (MeOH/reflux) to give (79–84%) the desired, paramagnetic building blocks. Characterization of the unmetallated terpyridine intermediates included the observation of the expected signals (^{13}C NMR) for each of the components in the amidation process: 171 ppm for the newly formed carbonyl and the appropriate downfield shift (ca. 5 ppm) for absorption attributed to the N$C_{4'}$ center. The subsequent Ru(III) adducts were used without further purification due to their low solubility in most organic solvents compared to the free ligands, their high yield of formation, and their paramagnetic character.

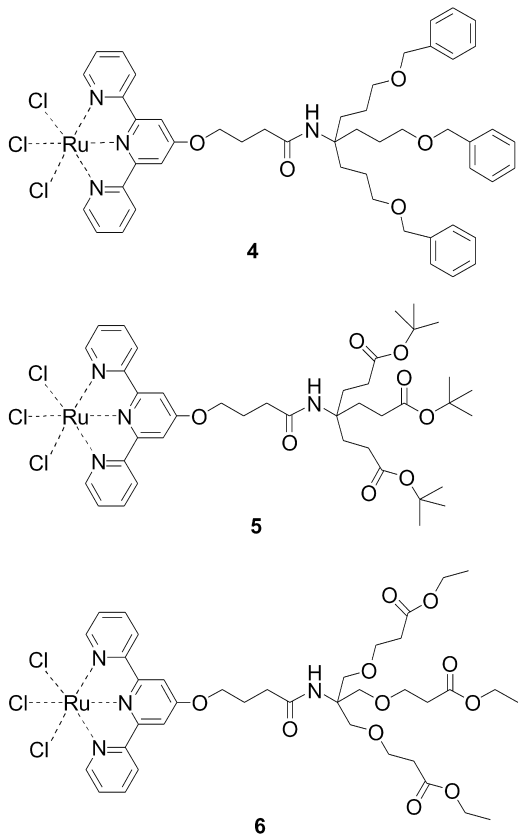
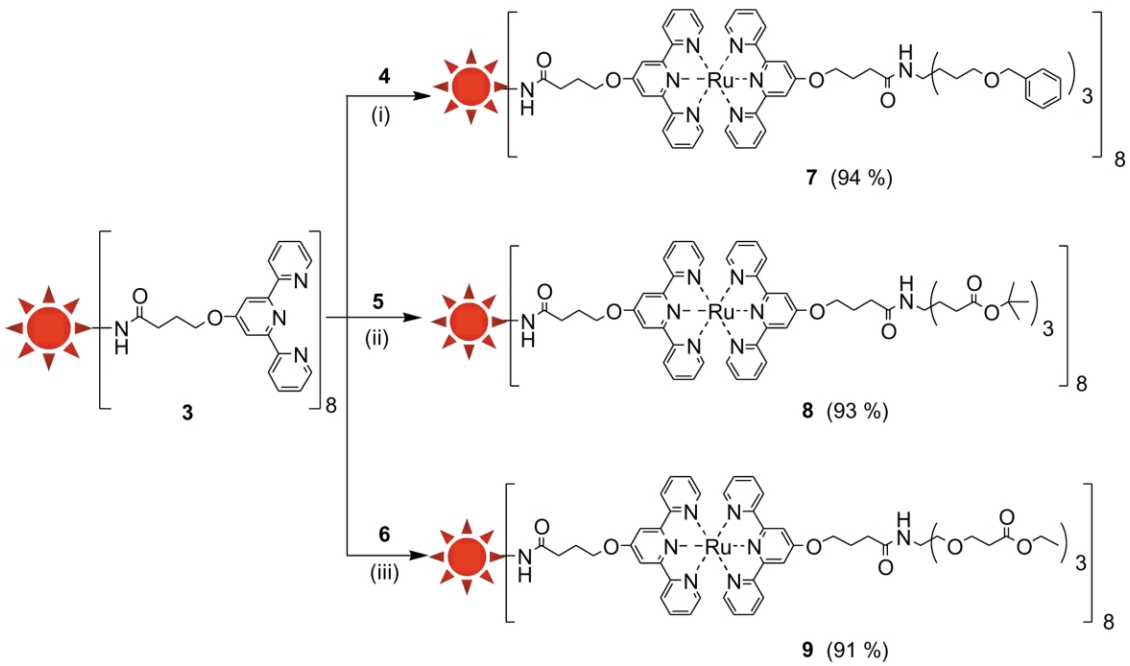


Figure 1. Structures of metalloadduct monomers **4**–**6**.

Reaction of each of these Ru(III) dendrons **4**–**6** with the terpyridinyl-terminated poly(propylene imine) core **3** in refluxing MeOH and 4-ethylmorpholine for 3 h afforded (>90%) the corresponding homogeneous surfaced 24-benzyl ether **7**, 24-*tert*-butyl ester **8**, and 24-ethyl ester **9**, respectively (Scheme 2). Following dialysis, (MeOH/5000 MWCO) these homometallodendrimers were characterized (^{13}C NMR) by the typical downfield chemical shifts of terpyridine carbons upon complexation, for example, $C_{6,6''}$ from 148.5 to 153.3 ppm, the notable absence of any uncomplexed terpyridine signals, and the presence of the expected indicative absorptions for each new dendrimer. Thus, pertinent resonances for **7**–**9** included: **7**: 139.7, 129.3, 128.7, 128.5 (*C*-aryl), 73.7 ($CH_2C_6H_5$), 71.6 (CH_2CH_2O); **8**: 174.3 (CO_2), 81.6 (CMe_3), 28.3 (CH_3); and **9**: 173.3 (CO_2), 69.8 (CCH_2O), 68.0 (OCH_2CH_2), 61.6 (CH_2CH_3), 35.9 (CH_2CO_2), 14.6 (CH_2CH_3), respectively; several of these characteristic resonance tags were used in the analysis of the mixed monomer generated heterometallodendrimers. Chemical shifts (^{13}C NMR) of resonances assigned to the dendritic core were slightly broadened [53.3 ($CH_2CH_2CH_2$, $CH_2CH_2CH_2CH_2$), 52.6 ($CH_2CH_2CH_2$-NHCO), 38.9 ($CH_2CH_2CH_2$NHCO), 27.8 ($CH_2CH_2CH_2$-NHCO), 25.8 ($CH_2CH_2CH_2$) ppm] relative to the uncomplexed precursor.

Treatment of the octameric dendritic core **3** with mixtures of the paramagnetic Ru(III) monomers **4**–**6** under similar reaction conditions as above, in stoichiometric ratios of 2:3:3, 1:2:1 and 2:1:1 (in the order of **4**–**6** for each ratio) gave (>90%) the corresponding combinatorial-style dendrimers **10**–**12**, respectively (Scheme 3). For each heterogeneous surfaced dendrimer, i.e. **10**–**12**, the observed ^{13}C



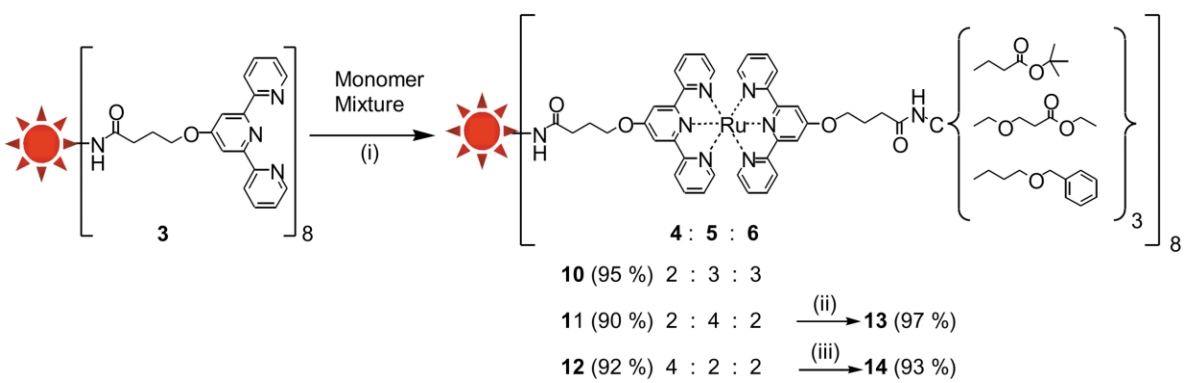
Scheme 2. Synthesis of the homogeneous metallodendrimers (i) **4**, 4-ethylmorpholine (6 drops), △>, 3 h; (ii) **5**, 4-ethylmorpholine (6 drops), △, 3 h; (iii) **6**, 4-ethylmorpholine (6 drops), △, 3 h.

NMR spectra exhibited all of the signals found in the homogeneous surfaced dendrimers, specifically, for the benzyl ether component: 71.6 ($CH_2OCH_2C_6H_5$), 73.7 ($CH_2OCH_2C_6H_5$), 128.5, 128.7, 129.3, 139.7 (*C*-aryl); for the *tert*-butyl ester: 28.3 (CH_3), 81.6 (CMe_3); and ethyl ester: 14.6 (CH_3), 61.5 (CH_2CH_3), 68.8 and 69.8 ppm (CH_2OCH_2). Qualitatively, the relative monomer ratios were reflected in the relative intensities of the various monomer subunit absorptions. Figure 2 compares the ^{13}C NMR of the combinatorially prepared metallodendrimer **10** to that of each homogeneous surfaced construct. Colored signals, corresponding to the benzyl ether (red), *tert*-butyl ester (blue), and ethyl ester (green) termini assignments of dendrimers **7**–**9**, respectively, are evident in the spectrum of dendrimer **10** at identical positions. Similar data are found for **11** and **12**; the peak intensity ratios mimic the relative reagent ratios. ^1H NMR data also confirm the distribution ratios as ascertained by integration.

The synthetic versatility associated with the surface groups coupled with the stability of the –‹Ru›– connectivity is exemplified via the selective hydrolysis (HCO_2H) of the *tert*-butyl esters in dendrimer **11** to carboxylic acid moieties thereby affording dendrimer **13** (Scheme 3 and Figure 3). Notably, absorptions (^{13}C NMR) corresponding to the *tert*-butyl groups are absent at 28.3 and 81.6 ppm; a downfield shift (Δ 3.2 ppm) of the former *tert*-butyl carbonyl carbon was also indicative of the ester to acid conversion.

Similarly, selective debenzylation of dendrimer **12** by treatment (Pd–C/EtOH/H_2/60 psi) afforded (93%) the desired metallodendrimer **14** possessing hydroxyl termini (ca. 50% of the termini), as supported by the appearance (^{13}C NMR) of a new peak attributed to the hydroxymethylene carbon (CH_2OH) at 63.3 ppm as well as the notable disappearance of the associated aromatic benzyl signals. Figure 3 is also color coded as in Figure 2 to facilitate peak matching of the various mixed monomer dendrimers.

Each homo- and heterogeneous surfaced dendrimer was



Scheme 3. Synthesis of the heterogeneous metallodendrimers **10**–**12** and deprotection reactions (hydrolysis and debenzylation). (i) mixtures of Ru(III) metalloappendages **4**–**6** [different ratios; 2:3:3, 1:2:1, and 2:1:1 for **4**–**5**–**6**, respectively], 4-ethylmorpholine (6 drops), △, 3 h; (ii) HCO_2H, 25°C, 12 h; (iii) Pd/C, MeOH, 60 psi H_2, 25°C, 24 h.

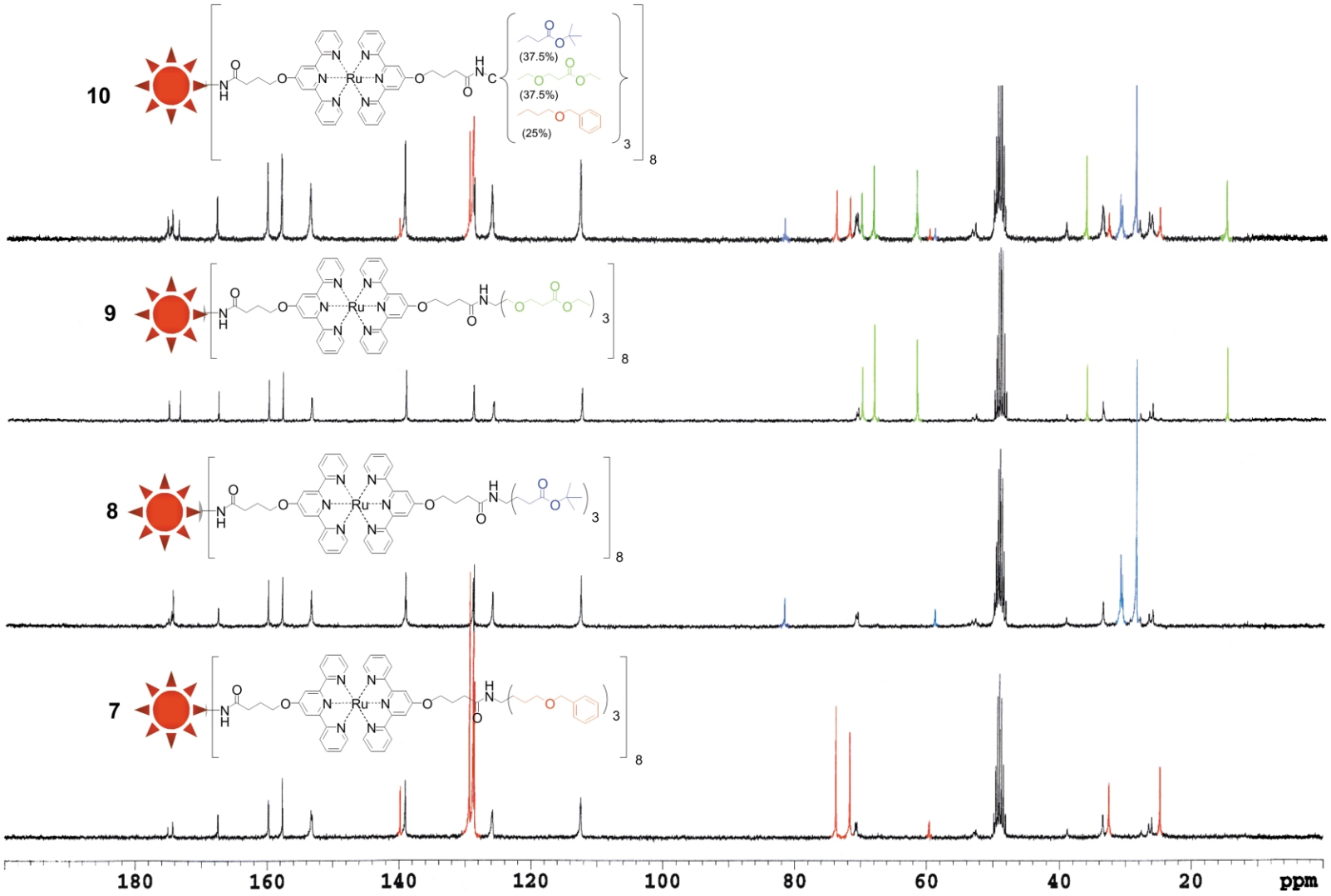


Figure 2. Color-coded ^{13}C NMR spectra for the peripherally homogeneous benzyl ether, *tert*-butyl ester, and ethyl ester metallodendrimers **7**–**9**, respectively, and heterogeneous dendrimer **10** (prepared using a 2:3:3 ratio of monomers **4**–**6**, respectively).

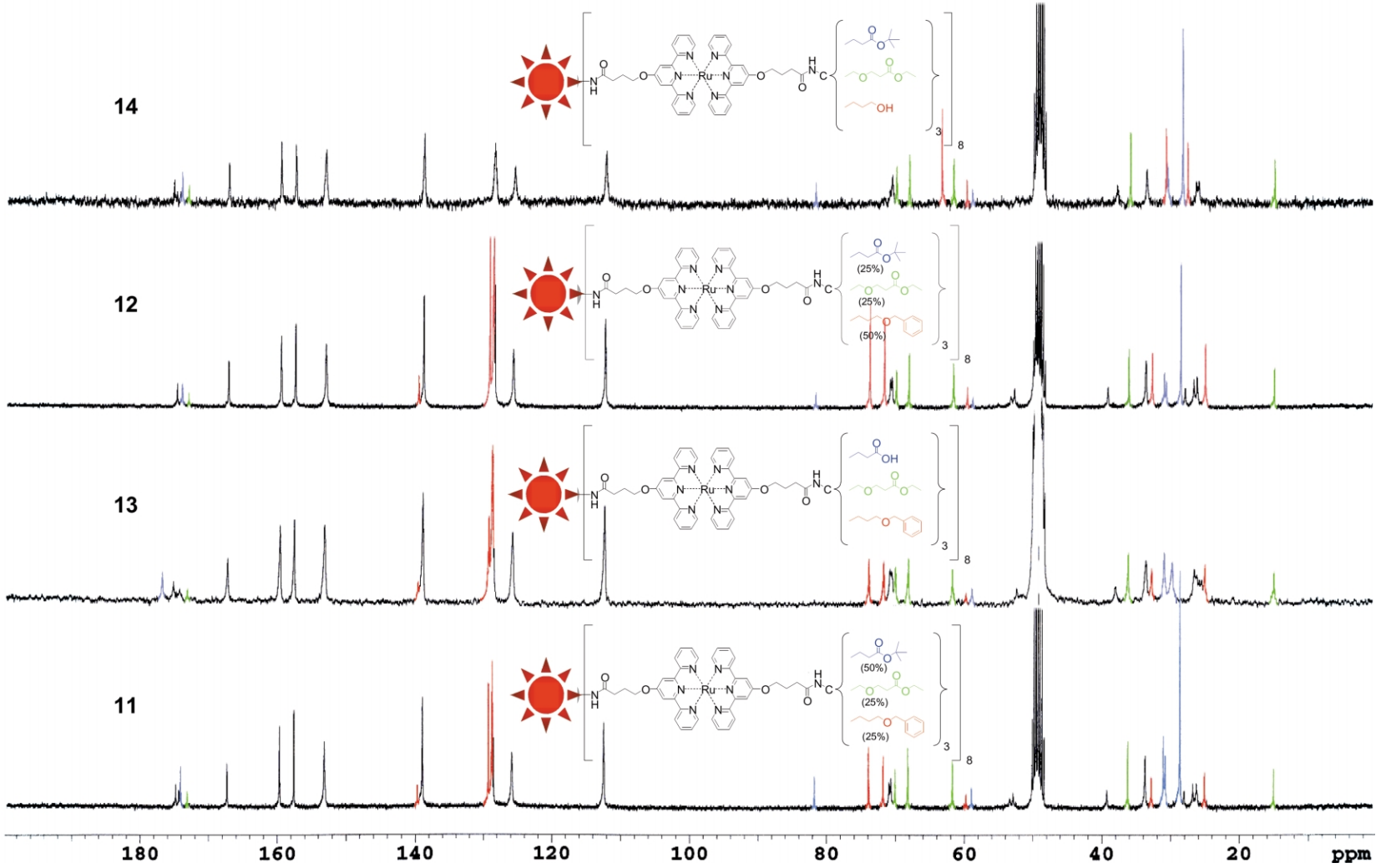


Figure 3. Color-coded ^{13}C NMR spectra of the peripherally heterogeneous dendrimers **11** [1:2:1 ratio of **4**–**5**–**6**] and **12** [2:1:1 ratio of **4**–**5**–**6**], respectively, and acid dendrimer **13** and alcohol dendrimer **14** from hydrolysis with HCO_2H and debenzylation under H_2 with Pd/C, respectively.

Table 1. Molar absorptivies (ε) of the Ru(II) complexes of the homo-and heterometallodendrimers at the specified wavelengths (λ_{max})

	Molar absorptivities[a] (ε)		
Metallodendrimer	267[b]	306[b]	486[b]
7	3.12	4.76	1.44
8	3.08	4.72	1.43
9	3.03	4.67	1.43
10	2.98	4.56	1.41
11	2.77	4.52	1.39
12	3.01	4.64	1.41
13	2.98	4.62	1.40
14	2.92	4.60	1.39

[a] $\varepsilon\times10^5$ dm^3 mol^{-1} cm^{-1}.
[b] λ_{max} (nm).

found to be highly soluble in common organic solvents, such as: MeOH, EtOH, DMF, and DMSO. Deprotected heterogeneous dendrimers **13** and **14** possessing carboxylic acid and hydroxyl groups, respectively, readily dissolved in H_2O due to the added hydrophilic character.

In order to elucidate and support the content of the Ru(II) metal complexes in the metallodendrimers, the UV–vis absorbance for each homogenous and heterogeneous construct was measured (MeOH). All spectra recorded exhibited four major absorption bands (Table 1) at λ_{max} 242, 267, 306, 486 nm and showed similar molar absorptivities (ε) indicative of the –‹Ru›– assemblies. For the strongest absorption in each octacomplex (λ_{max}=486 nm), the average ε value was found to be 1.42×10^5 dm^3 mol^{-1} cm^{-1}, which is approximately eight times as strong as Constable's monoRu(II) complex.[23] Notably, the molar absorptivity (ε) of polyacid **13** and polyalcohol **14**, after the deprotection reactions, also suggested an eight-fold absorptivity increase compared with that of a monoRu(II) complex. Application of this use of the –‹Metal›– connectivity to alternate metals will permit incorporation of mixed metals as well as mixed surface functionality for controlled solubility properties.

The thermogravimetric analysis (TGA) data for these metallodendrimers are shown in Figure 4. Although a small weight loss (ca. 4 wt%) occurred below 170°C, presumably due to the loss of associated waters of hydration. All metallodendrimers were found to be stable up to 170°C, but slightly above 190°C, those possessing the *tert*-butyl ester moiety were shown to eliminate isobutylene;[74,75] this has also been observed in a related dendritic series where isobutylene weight loss was used to quantity the surface dendrimerization of silica particles.[52] The weight loss of isobutylene from **8** was estimated to be ca. wt12%, which is close to the theoretical value (12.75 wt%). At 255°C, there appeared a shoulder, which correlates to the dehydration of the carbonyl termini and fragmentation processes associated with retro-Michael reactions. The benzyl-coated analogue **7** exhibited the highest beginning decomposition temperature value (>250°) whereas, the data for the ethyl ester **9** (not shown) was closely aligned to that of **8**. Thermal decomposition above 350°C was similar in all cases. As expected, the heterogeneous metallodendrimers have different onsets of decomposition depending on the average constitution of the terminal groups; their TGA values do not deviate from between the most thermally labile **8** and the most thermally stable **7**. Since these combinatorial-style heterometallodendrimers are actually a complex mixture with an average overall composition, one would expect a decomposition pattern related to the ratio of reactants. Incorporation of thermally stable termini to the poly(propylene imine) core leads to enhanced thermal stability in the resultant dendritic systems where the core is a common denominator.

3. Conclusion

In conclusion, the formation of the –‹Ru›– complexes was demonstrated to be a facile method for monomer connectivity. Use of this method has afforded entry to a series of heterogeneous metallomacromolecules possessing logically chosen, differing terminal functionality in a

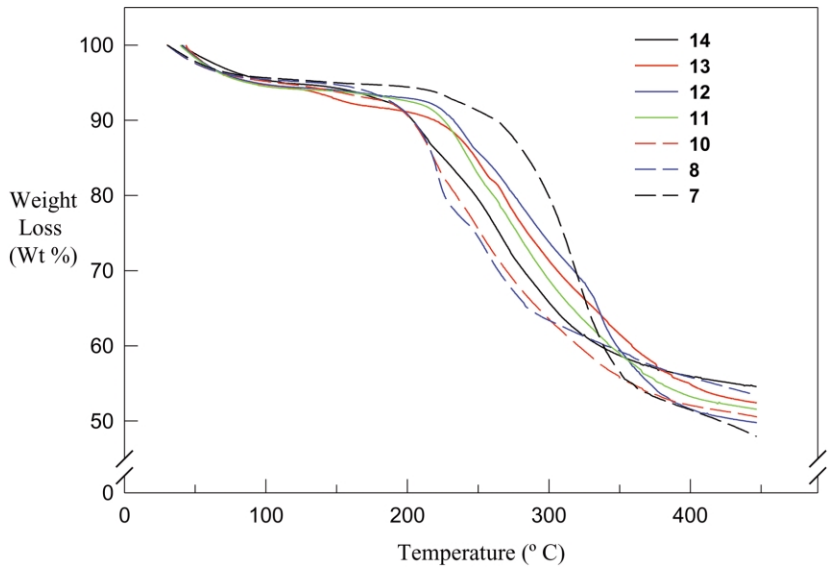


Figure 4. Thermal gravimetric analysis (TGA) of dendrimers **7** and **8**, and **10**–**14** showing weight loss (wt%) as a function of increasing temperature.

controllable ratio. This, in turn, leads to the incorporation of latent or masked regions of reactivity that can be accessed after further generational elaboration. In addition, the potential to easily modify macromolecular physical attributes, such as solubility (notably, all of these metallodendrimers possessed good organic solubility prior to selective deprotection), via this combinatorial-styled method was demonstrated. Thus, this protocol provides an advantageous synthetic flexibility between that of a completely directed approach whereby precise control over monomer attachment is strictly maintained and that of random, uncontrolled mixed monomer attachment via unequal building blocks to surface reactivity. Strict control over 'depth of placement' (i.e. generational placement) is maintained, while positioning of adjacent building blocks within a tier is statistical yet possesses an overall ratio determined by the initial reactant combination and near-equality of reactivity.[46]

4. Experimental

4.1. General procedures and instrumentation

Chemicals were purchased from Aldrich and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets precoated with Al_2O_3 IB-F or SiO_2 IB2-F (Baker–flex) and visualized by UV light. Column chromatography was conducted using neutral/basic Al_2O_3, Brockman Activity I (60–325 mesh) or SiO_2 (60–200 mesh) from Fisher Scientific. Melting points were determined on Electrothermal 9100 heater and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX250 NMR spectrometer. Mass spectra were obtained on a Bruker Esquire Electrospray Ion Trap mass spectrometer (ESI-MS). TGA data were determined with a Mettler-Toledo, TG 50 thermal analysis system, in which the TGA scans were recorded at 10°C/min under a nitrogen atmosphere from 30 to 450°C.

4.2. Experimental details

4.2.1. Octaterpyridinyl dendrimer 3. To a solution of 4-[4′-(2,2′:6′,2″-terpyridinyloxy)]butanoic acid[13,14] (**2**; 510 mg, 1.52 mmol) in dry DMF (10 mL), were added DCC (400 mg, 1.52 mmol) and 1-HOBT (300 mg, 1.52 mmol) at 25°C. The mixture was stirred for ca. 1 h, then the 2nd generation poly(propylene imine) (**1**; 125 mg, 161 μmol) was added. The stirred mixture was maintained at 40°C for 48 h, after which the white precipitate was filtered. The filtrate was concentrated in vacuo to afford a crude oil, which was dissolved in $CHCl_3$ (100 mL) washed (2×50 mL ea) sequentially with 10% aq. Na_2CO_3, H_2O, and brine, then dried (Na_2SO_4) and concentrated in vacuo to give a solid, which was column chromatographed (basic Al_2O_3) eluting with a mixture of EtOAc/hexane (2:1) to afford (81%) the dendritic core **3**, as a white solid: 450 mg; mp <200°C (dec.); ^{1}H NMR δ 1.30 (br s, $NCH_2CH_2CH_2CH_2N$, 4H), 1.45 (br s, $NHCH_2CH_2CH_2N$, 8H), 1.53 (br s, CH_2CH_2NHCO, 16H), 2.15 (br s, CH_2CH_2O, 16H), 2.29 (br s, $NHCOCH_2$, $NCH_2CH_2CH_2CH_2N$, $NCH_2CH_2CH_2N$, 36H), 2.39 (br s, $NCH_2CH_2CH_2NHCO$, 16H), 3.22 (br s, CH_2NHCO, 16H), 4.17 (t, CH_2O, 16H, J=6.4 Hz), 7.27 (td, Py$H_{5,5''}$, 16H, J=5.1, 1.5 Hz), 7.78 (td, Py$H_{4,4''}$, 16H, J=7.8, 1.5 Hz), 7.90 (s, Py$H_{3',5'}$, 16H), 8.52 (d, Py$H_{3,3''}$, 16H, J=8.1 Hz), 8.62 (d, Py$H_{6,6''}$, 16H, J=4.2 Hz); ^{13}C NMR δ 24.0 ($NCH_2CH_2CH_2N$), 24.6 (CH_2CH_2N), 24.8 ($NHCOCH_2CH_2$), 26.4 (CH_2CH_2NHCO), 32.3 ($NHCOCH_2$), 37.8 (CH_2NHCO), 51.2 ($NCH_2CH_2CH_2N$), 51.5 $NHCH_2CH_2CH_2NHCO$), 53.6 ($NCH_2CH_2CH_2CH_2N$), 66.9 (CH_2O), 106.9 (Py$C_{5,5''}$), 121.0 (Py$C_{4,4''}$), 123.6 (Py$C_{3,3''}$), 136.4 (Py$C_{3',5'}$), 148.5 (Py$C_{6,6''}$), 155.5 (Py$C_{2,2''}$), 156.6 (Py$C_{2',6'}$), 166.6 (Py$C_{4'}$), 172.2 ($CONH$); ESI-MS: m/z 3312.06 $[M]^+$ (calcd m/z 3312.10 for $[M]^+$).

4.2.2. Ru(III) adduct (4) of terpyridinyl benzyl ether monomer. To a solution of acid[13,14] **2** (300 mg, 895 μmol) in dry DMF (10 mL), were added DCC (200 mg, 969 μmol) and 1-HOBT (131 mg, 969 μmol) at 25°C. The mixture was stirred for ca. 1 h, then 4-amino-4-[3′-(benzyloxy)propyl]-1,7-di(benzyloxy)heptane[47] (436 mg, 917 μmol) was added. The mixture was stirred at 25°C for 18 h, then worked up as described above for **3**, to give a crude solid, which was column chromatographed eluting with a 1:1 mixture of EtOAc and hexane to give (82%) the monoether, as a white solid: 580 mg; ^{1}H NMR δ 1.54 (m, CH_2CH_2-CH_2OPh, 6H), 1.76 (m, $CH_2CH_2CH_2OPh$, 6H), 2.08 (m, $CH_2CH_2CH_2CONH$, 2H), 2.19 (t, CH_2CONH, 2H, J=6.9 Hz), 3.41 (t, CH_2OCH_2Ph, 6H, J=6.3 Hz), 4.15 (t, $PyOCH_2$, 2H, J=7.5 Hz), 4.43 (s, CH_2Ph, 6H), 5.84 (s, NH, 1H), 7.25 (td, Py$H_{5,5''}$, 2H, J=5.1, 1.5 Hz), 7.29 (s, Ph, 15H), 7.79 (td, Py$H_{4,4''}$, 2H, J=7.8, 1.5 Hz), 8.03 (s, Py$H_{3',5'}$, 2H), 8.60 (d, Py$H_{3,3''}$, 2H, J=8.1 Hz), 8.66 (d, Py$H_{6,6''}$, 2H, J=4.2 Hz); ^{13}C NMR δ 23.4 ($CH_2CH_2OCH_2Ph$), 24.7 (CH_2CH_2CONH), 31.5 ($C^{4°}CH_2$), 32.8 (CH_2CONH), 57.8 ($C^{4°}$), 66.9 ($PyOCH_2$), 70.4 (CH_2OCH_2Ph), 72.6 (OCH_2Ph), 107.0 (Py$C_{5,5''}$), 120.9 (Py$C_{4,4''}$), 123.5 (Py$C_{3,3''}$), 127.2, 127.3, 128.0, 138.1 (PhC), 136.4 (Py$C_{3',5'}$), 148.7 (Py$C_{6,6''}$), 155.7 (Py$C_{2,2''}$), 156.7 (Py$C_{2',6'}$), 166.7 (Py$C_{4'}$), 171.0 ($CONH$); ESI-MS: m/z 793.43 $[M+H^+]$ (calcd m/z 793.39 for $[M+H^+]$).

A solution of $RuCl_3 \cdot 3H_2O$ (171 mg, 654 μmol) and the above monomer (519 mg, 654 μmol) in MeOH (20 mL) was refluxed for 3 h. After cooling, the precipitate was filtered, washed (50 mL ea) sequentially with MeOH, water, and Et_2O, then dried in vacuo to yield (79%) **4**, as yellow-brown solid: 520 mg; the material was used directly in the next step.

4.2.3. Benzyl-ether homometallodendrimer 7. To a suspension of 8 equiv. of Ru-adduct **4** (136 mg, 136 μmol) in MeOH (10 mL), were added terpyridine core **3** (50 mg, 15.1 μmol) and 4-ethylmorpholine (6 drops). The mixture was refluxed for 3 h, during which, the solution turned clear dark red. After cooling to 25°C, the solution was filtered, then sealed into a membrane (cut off mass=3500) for dialysis over 24 h, then the solution was concentrated and dried in vacuo to afford (94%) the homogeneous benzyl ether metallodendrimer **7**, as a red solid: 156 mg; ^{1}H NMR (CD_3OD) δ 1.61 (br s, CH_2CH_2-OCH_2Ph, CH_2CH_2NHCO, CH_2CH_2N, 76H), 1.89 (br s, $CH_2CH_2CH_2OCH_2Ph$, CH_2CH_2OPy, 80H), 2.34 (br s, CH_2CO_2, 48H), 2.58–2.71 (br s, $NHCOCH_2$, $CH_2CH_2CH_2$-$NHCO$, CH_2N, 104H), 3.32 (br s, CH_2NHCO, 16H), 3.48 (br s, CH_2OCH_2Ph, 48H), 4.43 (s, CH_2Ph, 48H), 4.71 (br s,

CH_2OPy, 32H), 6.25 (s, CONH, 16H), 7.28 (s, PhH, 120H), 7.13–8.92 (br s, tpy$H$, 160H); ^{13}C NMR (CD_3OD) δ 24.7 ($CH_2CH_2OCH_2Ph$), 25.9 (CH_2CH_2CONH, $NHCOCH_2CH_2$), 26.4 ($NHCOCH_2CH_2$), 27.5 ($NCH_2CH_2CH_2NHCO$), 32.5 ($CH_2CH_2CH_2OCH_2Ph$), 33.4 ($NHCOCH_2$, CH_2CONH), 38.8 (CH_2NHCO), 52.5 ($NCH_2CH_2CH_2NCH_2$), 59.5 ($C^{4°}$), 70.5 (OCH_2Py), 70.7 ($PyCH_2O$), 71.6 (CH_2OCH_2Ph), 73.7 (OCH_2Ph),112.4 ($PyC_{5,5''}$), 125.8 ($PyC_{4,4''}$), 128.5 (PhC), 128.7 ($PyC_{3,3''}$), 129.3 (PhC), 139.0 ($PyC_{3',5'}$), 139.7 (PhC), 153.3 ($PyC_{6,6''}$), 157.7 ($PyC_{2,2''}$), 159.8 ($PyC_{2',6'}$), 167.5 ($PyC_{4'}$), 174.3, 175.0 ($CONH$). Anal. calcd for $C_{592}H_{664}N_{70}O_{56}Ru_8Cl_{16}\cdot 16H_2O$: C, 62.81; H, 6.20; N, 8.66. Found: C, 62.84; H, 6.17; N, 8.68.

4.2.4. *tert*-Butyl ester homometallodendrimer 8. To a suspension of 8 equiv. of Ru-adduct[76] **5** (128 mg, 136 μmol) in MeOH (10 mL), were added terpyridine core **3** (50 mg, 15.1 μmol) and 4-ethylmorpholine (6 drops). The mixture was refluxed for 3 h. After cooling to 25°C, the clear dark red solution was filtered, then was sealed into a membrane (cut off mass=3500) for dialysis for 24 h. The solution was concentrated and dried in vacuo to afford (93%) the homogeneous *tert*-butyl ester metallodendrimer **8**, as a red solid: 147 mg; ^{1}H NMR (CD_3OD) δ 1.43 (s, CH_3, 216H), 1.60 (br s, CH_2CH_2NHCO, CH_2CH_2N, 28H), 2.06 (br s, $CH_2CH_2CO_2$, 48H), 2.28 (br s, CH_2CO_2, 48H), 2.31 (br s, CH_2CH_2OPy, 32H), 2.46 (br s, CH_2CO_2, 48H), 2.63 (br s, $NHCOCH_2$, $CH_2CH_2CH_2NHCO$, CH_2N, 104H), 3.28 (br s, CH_2NHCO, 16H), 4.69 (br s, CH_2OPy, 32H), 6.24 (s, CONH, 16H), 7.30–8.81 (br s, tpy$H$, 160H); ^{13}C NMR (CD_3OD) δ 25.8 (CH_2CH_2CONH, $NHCOCH_2CH_2$), 26.4 ($NHCOCH_2CH_2$), 27.8 ($NCH_2CH_2CH_2NHCO$), 28.3 (CH_3), 30.4 (CH_2CO_2), 30.7 ($CH_2CH_2CO_2$), 33.4 ($NHCOCH_2$, CH_2CONH), 39.0 (CH_2NHCO), 52.5 ($NCH_2CH_2CH_2NCH_2$), 58.7 ($C^{4°}$), 70.5 (OCH_2Py), 70.7 ($PyCH_2O$), 81.6 (CMe_3), 112.4 ($PyC_{5,5''}$), 125.8 ($PyC_{4,4''}$), 128.8 ($PyC_{3,3''}$), 139.0 ($PyC_{3',5'}$), 153.3 ($PyC_{6,6''}$), 157.7 ($PyC_{2,2''}$), 159.8 ($PyC_{2',6'}$), 167.5 ($PyC_{4'}$), 174.3 (CO_2), 174.5, 175.0 ($CONH$). Anal. calcd for $C_{592}H_{664}N_{70}O_{56}Ru_8Cl_{16}\cdot 16H_2O$: C, 57.62; H, 6.47; N, 9.05. Found: C, 57.65; H, 6.46; N, 9.07.

4.2.5. Ethyl ester homometallodendrimer 9. To a suspension of 8 equiv. of Ru-adduct[77] **6** (127 mg, 136 μmol) in MeOH (10 mL), were added terpyridine core **3** (50 mg, 15.1 μmol) and 4-ethylmorpholine (6 drops), then the mixture was refluxed for 3 h. After cooling, the dark red solution was worked up as described above to afford (92%) the homogeneous benzyl ether metallodendrimer **9**, as a red solid: 145 mg; ^{1}H NMR (CD_3OD) δ 1.13 (t, CH_2CH_3, 72H, J=6.6 Hz), 1.60 (br s, CH_2CH_2NHCO, CH_2CH_2N, 28H), 2.17 (br s, CH_2CH_2OPy, 32H), 2.43 (br s, CH_2CO_2, 48H), 2.45 (br s, $NHCOCH_2$, $CH_2CH_2CH_2NHCO$, CH_2N, 104H), 3.18 (br s, CH_2NHCO, 16H), 3.58 (s, CH_2OCH_2, 48H), 3.63 (s, CH_2OCH_2, 48H), 4.01 (q, CH_2CH_3, 48H, J=6.9 Hz), 4.67 (br s, CH_2OPy, 32H), 6.24 (s, CONH, 16H), 7.13–8.92 (br s, tpy$H$, 160H); ^{13}C NMR (CD_3OD) δ 14.6 (CH_2CH_3), 25.9 (CH_2CH_2CONH, $NHCOCH_2CH_2$), 26.4 ($NHCOCH_2CH_2$), 27.8 ($NCH_2CH_2CH_2NHCO$), 33.5 ($NHCOCH_2$, CH_2CONH), 35.9 (CH_2CO_2), 38.9 (CH_2NHCO), 52.6 ($NCH_2CH_2CH_2NCH_2$), 61.4 ($C^{4°}$), 61.6 (CH_2CH_3), 68.0 ($OCH_2CH_2CO_2$), 69.8 (CH_2OCH_2), 70.4 (OCH_2Py), 70.7 ($PyCH_2O$), 112.3 ($PyC_{5,5''}$), 125.7 ($PyC_{4,4''}$), 128.8 ($PyC_{3,3''}$), 139.0 ($PyC_{3',5'}$), 153.3 ($PyC_{6,6''}$), 157.7 ($PyC_{2,2''}$), 159.8 ($PyC_{2',6'}$), 167.5 ($PyC_{4'}$), 173.3 (CO_2), 175.0, 175.1 ($CONH$). Anal. calcd for $C_{592}H_{664}N_{70}O_{56}Ru_8Cl_{16}\cdot 16H_2O$: C, 55.46; H, 5.93; N, 9.13. Found: C, 55.52; H, 5.91; N, 9.15.

4.2.6. Heterometallodendrimers 10–12. To a suspension of 8 equiv. of three Ru-adducts comprised of a 2:3:3 mixture of **4** (30.2 mg, 30.2 μmol), **5** (42.6 mg, 45.3 μmol), and **6** (42.2 mg, 45.3 μmol) in MeOH (10 mL), were added terpyridine core **3** (50 mg, 15.1 μmol) and 4-ethylmorpholine (6 drops). The mixture was refluxed for 3 h, then worked up as described above to afford (95%) the homogeneous octametallodendrimer **10**, as a red solid: 157 mg. Metallodendrimers **11** and **12** were prepared by addition of a different ratio (2:1:1 and 1:2:1) of the same combination of Ru-adducts [**11**: **4** (30.2 mg, 30.2 μmol), **5** (56.8 mg, 60.4 μmol), **6** (28.2 mg, 30.2 μmol); **12**: **4** (60.4 mg, 60.4 μmol), **5** (28.3 mg, 30.2 μmol), **6** (28.2 mg, 30.2 μmol)]; ^{1}H NMR (CD_3OD for **10**) δ 1.14 (br s, CH_2CH_3, 27H), 1.43 (s, $CH_{3[BA]}$, 81H), 1.61 (br s, CH_2CH_2NHCO, CH_2CH_2N, 28H), 1.61 (br s, $CH_2CH_2OCH_2Ph$, 12H), 1.84 (br s, $CH_2CH_2CH_2OCH_2Ph$, 12H), 2.06 (br s, $CH_2CH_2CO_2Et$, 18H), 2.28 (br s, $CH_2CH_2CO_2H$, 18H), 2.31 (br s, CH_2CH_2OPy, 32H), 2.35 (br s, CH_2CO_2Et, 18H), 2.46 (br s, CH_2CO_2H, 18H), 2.59 (br s, $NHCOCH_2$, $CH_2CH_2CH_2NHCO$, $CH_2N^{4°}$, 104H), 3.35 (br s, CH_2NHCO, 16H), 3.49 (br s, CH_2OCH_2Ph, 12H), 3.73 (s, $CH_2OCH_{2[Et]}$, 18H), 3.77 (s, $CH_2OCH_{2[Et]}$, 18H), 4.13 (br s m, CH_2CH_3, 18H), 4.43 (s, CH_2Ph, 12H), 4.68 (br s, CH_2OPy, 32H), 6.24 (s, CONH, 16H), 7.28 (s, PhH, 30H), 7.30–8.81 (br s, tpy$H$, 160H); ^{13}C NMR (CD_3OD for **10**) δ 14.6 (CH_2CH_3), 24.7 ($CH_2CH_2OCH_2Ph$), 25.9 (CH_2CH_2CONH, $NHCOCH_2CH_2$), 26.4 ($NHCOCH_2CH_2$), 27.8 ($NCH_2CH_2CH_2NHCO$), 28.3 ($CH_{3[BA]}$), 30.4 (CH_2CO_2H), 30.7 ($CH_2CH_2CO_2H$), 32.4 ($CH_2CH_2CH_2OCH_2Ph$), 33.5 ($NHCOCH_2$, CH_2CONH), 35.9 (CH_2CO_2Et), 38.9 (CH_2NHCO), 52.6 ($NCH_2CH_2CH_2NCH_2$), 58.7 ($C^{4°}_{[BA]}$), 59.5 ($C^{4°}_{[Bz]}$), 61.3 ($C^{4°}_{[Et]}$), 61.6 (CH_2CH_3), 68.0 ($OCH_2CH_2CO_2Et$), 69.8 ($CH_2OCH_{2[Et]}$), 70.5 (OCH_2Py), 70.7 ($PyCH_2O$), 71.6 (CH_2OCH_2Ph), 73.7 (OCH_2Ph), 81.5 (CMe_3), 112.4 ($PyC_{5,5''}$), 125.8 ($PyC_{4,4''}$), 128.5 (PhC), 128.7 ($PyC_{3,3''}$), 129.2 (PhC), 139.0 ($PyC_{3',5'}$), 139.7 (PhC), 153.3 ($PyC_{6,6''}$), 157.7 ($PyC_{2,2''}$), 159.8 ($PyC_{2',6'}$), 167.4 ($PyC_{4'}$), 173.2 (CO_2Et), 174.2 (CO_2H), 174.5, 175.0 ($CONH$). Spectral data for metallodendrimers **11** and **12** was analogous to that of **10** but with different peak intensities corresponding to the different monomer ratios.

4.2.7. Heterometallodendrimer 13. A solution of **11** (64 mg) in HCO_2H (20 mL) was stirred for 12 h at 25°C. After reaction, the formic acid was removed in vacuo. The resultant material was dissolved in MeOH, which was then placed into a membrane (cut off mass=3500) and dialyzed for 24 h, then the solution was concentrated and dried in vacuo to afford (97%) the acid metallodendrimer **13**, as a red solid: 63 mg; ^{1}H NMR δ ^{1}H NMR (CD_3OD) δ 1.14 (br s, CH_2CH_3, 18H), 1.61 (br s, CH_2CH_2NHCO, CH_2CH_2N, 28H), 1.62 (br s, $CH_2CH_2OCH_2Ph$, 12H), 1.83 (br s, $CH_2CH_2CH_2OCH_2Ph$, 12H), 2.06 (br s, $CH_2CH_2CO_2Et$, 12H), 2.29 (br s, $CH_2CH_2CO_2H$, 24H), 2.31 (br s, CH_2CH_2OPy, 32H), 2.34 (br s, CH_2CO_2Et, 12H), 2.48 (br s, CH_2CO_2H, 24H), 2.59 (br s, $NHCOCH_2$, $CH_2CH_2CH_2NHCO$, $CH_2N^{4°}$, 104H), 3.34 (br s,

CH_2NHCO, 16H), 3.49 (br s, CH_2OCH_2Ph, 12H), 3.75 (s, $CH_2OCH_{2[Et]}$, 12H), 3.77 (s, $CH_2OCH_{2[Et]}$, 12H), 4.12 (br m, CH_2CH_3, 12H), 4.43 (s, CH_2Ph, 12H), 4.67 (br s, CH_2OPy, 32H), 6.25 (s, CONH, 16H), 7.28 (s, PhH, 30H), 7.32–8.82 (br s, tpyH, 160H); ^{13}C NMR δ 14.6 (CH_2CH_3), 24.7 ($CH_2CH_2OCH_2Ph$), 25.9 (CH_2CH_2CONH, $NHCOCH_2CH_2$), 26.3 ($NHCOCH_2CH_2$), 27.8 ($NCH_2CH_2CH_2NHCO$), 29.5 (CH_2CO_2H), 30.7 ($CH_2CH_2CO_2H$), 32.5 ($CH_2CH_2CH_2OCH_2Ph$), 33.3 ($NHCOCH_2$, CH_2CONH), 35.9 (CH_2CO_2Et), 38.9 (CH_2NHCO), 52.6 ($NCH_2CH_2CH_2NCH_2$), 58.7 ($C^{4°}_{[BA]}$), 59.5 ($C^{4°}_{[Bz]}$), 61.3 ($C^{4°}_{[Et]}$), 61.6 (CH_2CH_3), 68.0 ($OCH_2CH_2CO_2Et$), 69.9 ($CH_2OCH_{2[Et]}$), 70.5 (OCH_2Py), 70.7 ($PyCH_2O$), 71.6 (CH_2OCH_2Ph), 73.8 (OCH_2Ph), 112.4 ($PyC_{5,5''}$), 125.8 ($PyC_{4,4''}$), 128.5 (PhC), 128.8 ($PyC_{3,3''}$), 129.3 (PhC), 139.0 ($PyC_{3',5'}$), 139.8 (PhC), 153.4 ($PyC_{6,6''}$), 157.8 ($PyC_{2,2''}$), 159.9 ($PyC_{2',6'}$), 167.5 ($PyC_{4'}$), 173.5 (CO_2Et), 174.7, 175.4 (CONH), 177.1 (CO_2H).

4.2.8. Heterometallodendrimer 14. A mixture of homogeneous metallodendrimer **12** (60 mg) in the presence of 10% Pd on activated carbon (300 mg) in MeOH (50 mL) was hydrogenated at 60 psi at 25°C for 24 h. The solution was cautiously filtered through celite (pyrophoric) and the solvent was reduced in vacuo to afford (93%) the alcohol metallodendrimer **14**, as a red solid: 56 mg; ^1H NMR δ ^1H NMR (CD_3OD) δ 1.14 (br s, CH_2CH_3, 18H), 1.43 (s, $CH_{3[BA]}$, 54H), 1.61 (br s, CH_2CH_2NHCO, CH_2CH_2N, 28H), 1.51 (br s, CH_2CH_2OH, 24H), 1.74 (br s, $CH_2CH_2CH_2OH$, 24H), 2.06 (br s, $CH_2CH_2CO_2Et$, 12H), 2.28 (br s, $CH_2CH_2CO_2H$, 12H), 2.31 (br s, CH_2CH_2OPy, 32H), 2.35 (br s, CH_2CO_2Et, 12H), 2.46 (br s, CH_2CO_2H, 12H), 2.59 (br s, $NHCOCH_2$, $CH_2CH_2CH_2NHCO$, $CH_2N^{4°}$, 104H), 3.35 (br s, CH_2NHCO, 16H), 3.53 (br s, CH_2OH, 24H), 3.73 (s, $CH_2OCH_{2[Et]}$, 12H), 3.77 (s, $CH_2OCH_{2[Et]}$, 12H), 4.13 (q, CH_2CH_3, 12H), 4.68 (br s, CH_2OPy, 32H), 6.24 (s, CONH, 16H), 7.30–8.81 (br s, tpyH, 160H); ^{13}C NMR (CD_3OD) δ 14.6 (CH_2CH_3), 26.0 (CH_2CH_2CONH, $NHCOCH_2CH_2$), 26.2 ($NHCOCH_2CH_2$), 27.5 ($NCH_2CH_2CH_2NHCO$, CH_2CH_2OH), 28.3 ($CH_{3[BA]}$), 30.5 (CH_2CO_2H), 30.7 ($CH_2CH_2CO_2H$), 32.5 ($CH_2CH_2CH_2OH$), 33.5 ($NHCOCH_2$, CH_2CONH), 35.9 (CH_2CO_2Et), 37.6 (CH_2NHCO), 52.6 ($NCH_2CH_2CH_2NCH_2$), 58.8 ($C^{4°}_{[BA]}$), 59.7 ($C^{4°}_{[OH]}$), 61.3 ($C^{4°}_{[Et]}$), 61.6 (CH_2CH_3), 63.3 (CH_2OH), 68.0 ($OCH_2CH_2CO_2Et$), 69.9 ($CH_2OCH_{2[Et]}$), 70.5 (OCH_2Py), 70.7 ($PyCH_2O$), 81.6 (CMe_3), 112.4 ($PyC_{5,5''}$), 125.8 ($PyC_{4,4''}$), 128.7 ($PyC_{3,3''}$), 139.0 ($PyC_{3',5'}$), 153.3 ($PyC_{6,6''}$), 157.8 ($PyC_{2,2''}$), 159.9 ($PyC_{2',6'}$), 167.5 ($PyC_{4'}$), 173.4 (CO_2Et), 174.4 (CO_2H), 174.6, 175.1 (CONH).

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