Routes to Metallodendrimers: Synthesis of Isomeric Neutral Metallomacromolecules Based on Bis(2,2′:6′,2″-terpyridine)ruthenium(II) Connectivity

George R. Newkome,*[a] Kyung Soo Yoo,[a] Hyung Jin Kim,[b] and Charles N. Moorefield[a]

Abstract: Routes for the syntheses of isomeric, zwitterionic, bisterpyridine – Ru^{II}-based macromolecules are described. Access to these novel architectures is facilitated by the construction of terpyridine-modified, $1 \rightarrow 3$ *C*-branched, ester-terminated building blocks. Constitutional isomers result from the interchangable placement of methyl and *tert*-butyl ester groups on both the branched framework near the Ru^{II} centers and the termini of the branched construct. Water solubility is imparted to each isomer through selective transformation of the *tert*-butyl esters to their corresponding carboxylates. Along with the standard characterization techniques, electrochemical and spectroscopic data also support the structural formation.

Keywords: constitutional isomer · dendrimers · nanostructures · ruthenium · zwitterions

Introduction

For a number of years, the 2,2′:6′,2″-terpyridine ligand[1, 2] has been of interest in the assembly of metallomacromolecules and metallosupramolecules,[3–12] owing to its metal-coordinating ability and the subsequent application in areas such as magnetic, electronic, electrochemical, photooptical, and catalytic potential.[12–31] In general, these positively charged, terpyridine – metal – terpyridine assemblies are counter balanced with ions, such as Cl^-, BF_4^-, PF_6^-; however, to date, there has been a derth of study relating to the zwitterionic forms of these types of complexes and their effects on macromolecular architecture. Recently, we have reported the construction of neutral dendritic metallomacromolecules without external counterions that incorporate bis(2,2′:6′,2″-terpyridine)ruthenium(II) ([–<Ru>–]) complexes with internally off-setting charges.[32–34] Goals related to the construction of metallodendrimers[35, 36] possessing covalently bound counterions include the investigation and modification of such physicochemical properties as solubility, charge density, and electrochemical behavior. Herein, we report the synthesis and electrochemical behavior for isomeric, neutral, Ru^{II}-based metallomacromolecules (**19** and **22**) that possess the requisite number of covalently bound internal or terminal charge-compensating carboxylate ions as well as limited sites for surface modification or dendritic growth.

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Results and Discussion

With respect to the assembly the isomeric neutral metallomacromolecules with four bis(terpyridine) – ruthenium connections ([–<Ru>–]), it was of interest to evaluate the juxtaposition of appended counterions. In essence, either an internal or external relative disposition of the eight carboxylate moieties was necessary to compensate for the overall 8+ charge of the four connective Ru^{II} centers; thus, simple routes to dendritic macromolecules possessing eight *tert*-butyl and methyl ester moieties, assembled by means of four [–<Ru>–] metallo-connections, were devised. The initial $1 \rightarrow (2+1)$ branched monomers, for example, **4**, were devised so that easy hydrolysis of the *tert*-butyl ester could be achieved, thus generating the desired internal counterions for the adjacent divalent metal, and the unique remaining surface arm could be used to continue the branched construction motif.

Recently, a series of $1 \rightarrow (2+1)$ C-branched monomers, possessing either ester and protected hydroxy or mixed esters, has been reported as an initial study on selectively functionalized hyperbranched and dendritic frameworks.[37] As a continuation of that series, amines **4** and **14**, which contain a single [–<Ru>–] site of connection within each dendron as well as introduce a terminal hydroxy site for later surface modification, have been isolated. The treatment of *tert*-butyl (or alkyl) acrylate with $MeNO_2$ in the presence of a catalytic amount of Triton B ($BnMe_3N^+OH^-$) gave an alkyl 4-nitro-

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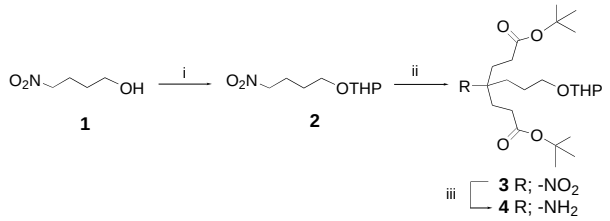
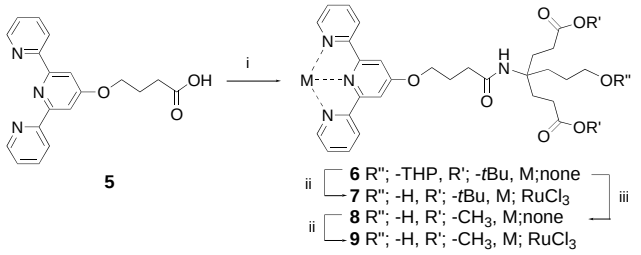
butanoate, which after hydrolysis and reduction with $BH_3 \cdot THF$ afforded (85%) 4-nitrobutan-1-ol (**1**; Scheme 1),[37, 38] which was confirmed (^{13}C NMR spectroscopy) by the appearance of a new peak for primary CNO_2 at $\delta =$ 75.2 ppm. Protection of hydroxy terminus with dihydropyran



Scheme 1. i) Dihydropyran, TsOH, CH_2Cl_2, 25 °C, 4 h; ii) 2 equiv *tert*-butyl acrylate, Triton B, THF, 25 °C, 24 h; iii) T1 Raney Ni, EtOH, 60 psi, 24 h.

afforded (97%) the corresponding ether **2**, which was identified by the downfield chemical shift (^{13}C NMR spectroscopy) for CH_2O from 61.0 to 62.2 ppm and appearance of the appropriate peaks for the THP moiety. Treatment of ether **2** with two equivalents of *tert*-butyl acrylate, in the presence of Triton B, in THF at 60 °C for 24 h gave the bis-*C*-functionalized dendron **3**, the structure of which was supported by the appearance of the new $C^{4\circ}NO_2$ signal at $\delta = 92.8$ ppm, which is shifted downfield from the signal ($\delta = 75.2$ ppm) assigned to the $C^{1\circ}NO_2$ group in **2**. Reduction of the nitro moiety with Raney-Ni in absolute EtOH at 40 °C for 24 h afforded (96%) the desired starting $1 \rightarrow (2+1)$ monomer **4** in an overall 80% yield from $MeNO_2$. The use of alternative O-protecting moieties, such as acetate (selectively deprotected with base) and benzyl (deprotected by hydrogenolysis), has been demonstrated;[37] the THP derivative can be deprotected under acidic conditions. The structure of **4** was confirmed by the upfield chemical shift (^{13}C NMR) for $C^{4\circ}$ from 92.8 to 52.2 ppm; the molecular peak (ESI-MS) *m*/*z* 430.4 [M^++H] (calcd 430.4 [M^++H]) further supported the assignment.

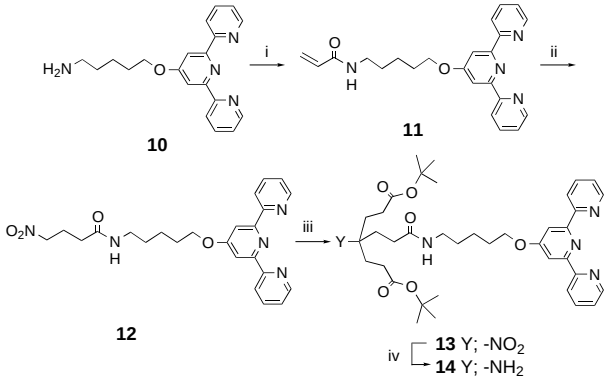
Amine **4** was then coupled with 4-[4′-(2,2′:6′,2″-terpyridinyloxy)]butanoic acid (**5**), prepared from 4′-chloro-2,2″:6′,2″-terpyridine and 4-hydroxybutanoate,[39, 40] by means of traditional peptide coupling conditions[41] to afford (82%) **6**, which was identified by the formation of a new peak assigned to the amide carbonyl carbon at $\delta = 170.9$ ppm (*C*ONH); the ESI-MS further confirmed the assignment by a peak at *m*/*z* 769.8 [M^++Na] (calcd: 769.4 [M^++Na]). Next, treatment of **6** with one equivalent of $RuCl_3$ in MeOH at reflux afforded the paramagnetic, THP-free, Ru^{III} complex **7**. The THP moiety was lost upon treatment with $RuCl_3 \cdot H_2O$, which presumably acted as a Lewis acid under the reaction conditions. The corresponding methyl ester **8** was obtained (98%) by the facile transesterification and deprotection of **6** in absolute MeOH with a trace of acid at 60 °C for 24 h. Its structure was confirmed (^{13}C NMR spectroscopy) by the presence of a peak at $\delta = 51.7$ ppm for the new methyl ester groups, as well as the complete disappearance of *tert*-butyl signals; peaks at *m*/*z* 601.3 [M^++Na] (calcd: 601.3 [M^++Na]) in its ESI-MS further establish its identity. The Ru^{III} adduct **9** was subsequently obtained (68%) by treatment with $RuCl_3 \cdot 3H_2O$ in MeOH (Scheme 2). Both adducts **7** and **9** were used without further



Scheme 2. i) **4**, DCC, 1-HOBt, DMF, 25 °C; ii) $RuCl_3 \cdot H_2O$, MeOH, Δ, 2 h; iii) MeOH, H_2SO_4 (cat.), 25 °C.

purification or characterization due to their poor solubility in most organic solvents and their inherent paramagnetic character.

Synthesis of the $1 \rightarrow (2+1)$ dendron **14**, which possesses a single terpyridine moiety, was accomplished as depicted in Scheme 3. The pentylamine **10**, previously synthesized,[40] was treated with one equivalent of acryloyl chloride in the

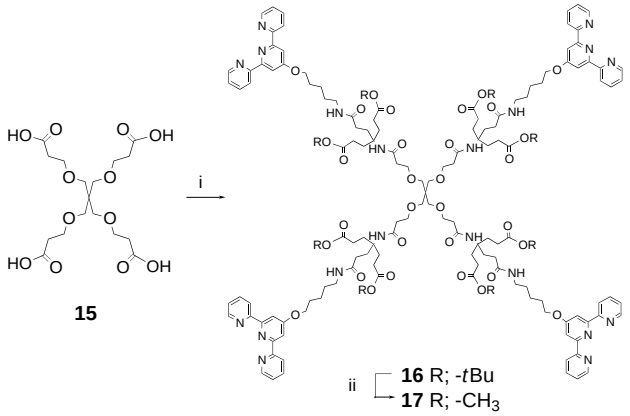


Scheme 3. i) Et_3N, THF, CH_2=CHCOCl, O° C; ii) $MeNO_2$, $CHCl_3$, Triton B, 25 °C, 24 h; iii) CH_2=$CHCO_2CMe_3$, 2 equiv), CH_2Cl_2, Triton B, 25 °C, 24 h; iv) T1 Raney Ni, EtOH, 120 psi H_2, 40 °C, 24 h.

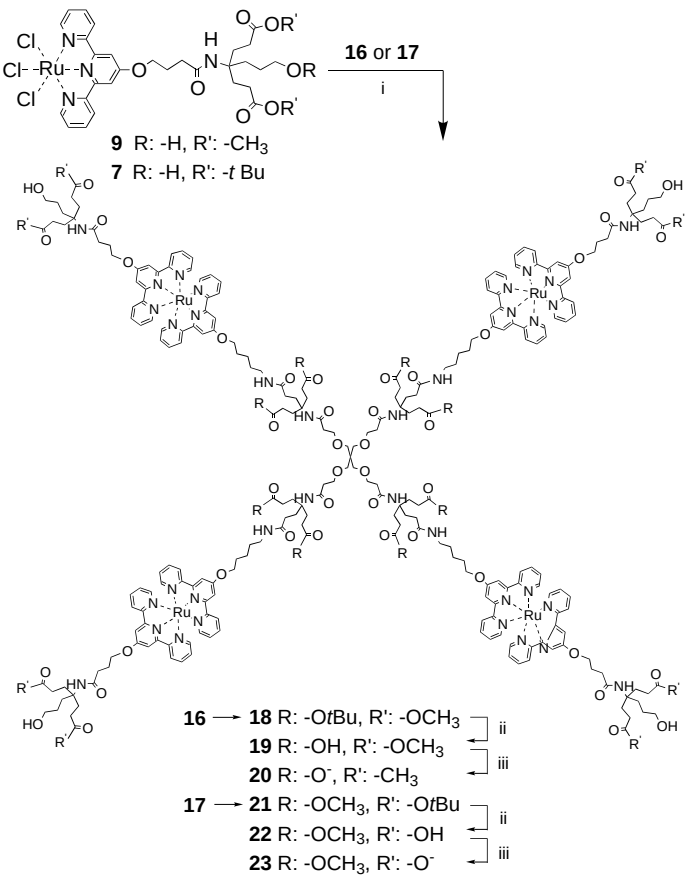
presence of Et_3N in THF to give the N-substituted amide **11** (91%), which was confirmed (^{13}C NMR spectroscopy) by the observation of new peaks assigned to the acrylamido group at $\delta = 126.3$ (CH_2=), 130.8 (=*C*H), and 165 ppm (*C*=O), as well as the expected chemical shift change for the NCH_2 peak (42.0 to 39.4 ppm) upon amidation; ESI-MS further confirmed the assignment by a peak at *m*/*z* 789.2 [M^++H] (calcd: 789.3 [M^++H]). Michael addition of $MeNO_2$ to **11** in the presence of Triton B afforded the amide **12** (75%), whose structure was supported (^{13}C NMR spectroscopy) by the appearance of a new resonance for primary CH_2NO_2 group at $\delta = 74.5$ ppm, as well as loss of signals associated with the unsaturated center. Attachment of the two ester units to the carbon α to the nitro moiety in amide **12** was accomplished through the use of Michael-type conditions by reaction with two equivalents of *tert*-butyl acrylate in the presence of Triton B in $CHCl_3$ at 25 °C for 24 h to generate the diester **13** (70%). Characterization of the product (^{13}C NMR spectroscopy) included an expected change in chemical shift for the resonance assigned to the CH_2NO_2 group from $\delta = 74.5$ ppm to $\delta = 92.3$ ppm, corresponding to the $(alkyl)_3CNO_2$ transformation. An alternate approach to diester **13** was realized by treatment of

4-nitro-4-di(2-*tert*-butoxycarbonylethyl)butanoic acid[37] with 1-amino-(4′-terpyridinyloxy)pentane[33, 42] by means of standard, DCC-type, peptide-coupling conditions. Reduction of the nitro moiety in diester **13** with Raney-Ni in absolute EtOH at 40 °C smoothly afforded the desired aminodiester monomer **14** (87 %), as evidenced by the traditional upfield chemical shift (^{13}C NMR spectroscopy) of the signal assigned to the $C^{4\circ}$ from $\delta = 92.3$ ppm to $\delta = 52.3$ ppm; the remaining NMR peaks were essentially unchanged, and the molecular peak at *m*/*z* 677.8 [M^++H] (calcd: 677.8 [M^++H]) in the ESI-MS further supported the assignment.

The first-generation dendrimer **16**, which has a single terpyridine group and two internal hydrolyzable *tert*-butyl groups per arm (Scheme 4), was accessed by treatment of the



Scheme 4. i) **15** (4 equiv), HOBt, DCC, DMF, 25 °C, 3 d; ii) MeOH, H_2SO_4 (cat.), 25 °C, 24 h.



Scheme 5. i) MeOH, 4-ethylmorpholine, Δ, 3 h; ii) HCO_2H, 25 °C, 12 h; iii) KOH (8 equiv), MeOH/H_2O, dialysis.

known tetraacid core **15**[43] with four equivalents of dendron **14** with DCC-promoted coupling in anhydrous DMF at 25 °C for 72 h. The ^{13}C NMR spectrum of poly(*tert*-butyl ester) **16** revealed a notable downfield shift of the signal at $\delta =$ 52.3 ppm to $\delta = 57.3$ ppm, corresponding to the formation of the new $C^{4\circ}$NHCO group; this corroborated the amidation. As well, the peak (MALDI-TOF) at *m*/*z* 3077.1 [M^++Na] (calcd: 3077.7 [M^++Na]) provided further support for this structure. The related dendrimer **17**, which has internal acid-stable methyl esters, was obtained (78 %) by simple transesterification of poly(*tert*-butyl ester) **16** by reaction with absolute MeOH promoted by a trace of acid at 60 °C for 24 h; the amide and ether bonds are unperturbed by these conditions. The structure of poly(methyl ester) **17** was identified by the presence of a new methyl ester peak at $\delta = 51.5$ ppm, a slight downfield shift ($\Delta = 1$ ppm) for the ester carbonyl peak, and the complete disappearance of *tert*-butyl peaks; the peak observed at *m*/*z* 2720.6 [M^++H] (calcd: 2719.2 [M^++H]) in the MALDI-TOF MS also supports the assignment.

The *tert*-butyl ester core **16** was then refluxed with four equivalents of the paramagnetic Ru^{III} adduct **9** in MeOH in the presence of an equivalent amount of 4-ethylmorpholine, as reducing agent, to afford the mixed alkyl hexadecaester **18** (76 %; Scheme 5). After dialysis (MeOH, membrane molecular weight cut Off (MWCO) 3500 amu), the isolated material exhibited (^{13}C NMR spectroscopy) an absence of any free terpyridine moieties based on the expected shifts of all terpyridine carbon signals as well as the assignable, symmetric pattern of the alkyl region. Further corroboration was provided by the expected upfield chemical shift (^{1}H NMR spectroscopy) of the resonance assigned to the 6,6″ terpyridine protons upon complexation (i.e., from $\delta = 8.64$ ppm to $\delta = 7.56$ ppm). MALDI-TOF mass spectra revealed a broad signal at the correct molecular mass; notably, better mass spectra were obtained for the corresponding acid and carboxylate. Hydrolysis of the *tert*-butyl moieties from ester **18** was readily accomplished by treatment with HCO_2H affording complex **19** (95 %). The characteristic downfield shift (^{13}C NMR spectroscopy) of the carbonyl carbon atom ($\Delta = 2.7$ ppm) clearly indicated the complete transformation to the acid with retention of the external methoxycarbonyl groups, as confirmed by the presence of the signals at $\delta = 52.2$ and 175.4 ppm (Figure 1). The structure of octaacid **19** was further confirmed by the molecular ion peak (MALDI-TOF) at *m*/*z* 5609 [M^++H] (calcd: 5610) and *m*/*z* 2771 [$M^{2+} - 2$Cl] (calcd: 2769). The addition of a slight excess of KOH to the free acid **19** in H_2O/MeOH gave, after dialysis for 24 h, the neutral octacarboxylate **20**, as characterized by the downfield shift (^{13}C NMR spectroscopy) for acid carbonyl carbon atom ($\Delta = 3.3$ ppm) and the mass peak (MALDI-TOF) at *m*/*z* 5355 [M^++K] (calcd: 5357) for the molecular ion.

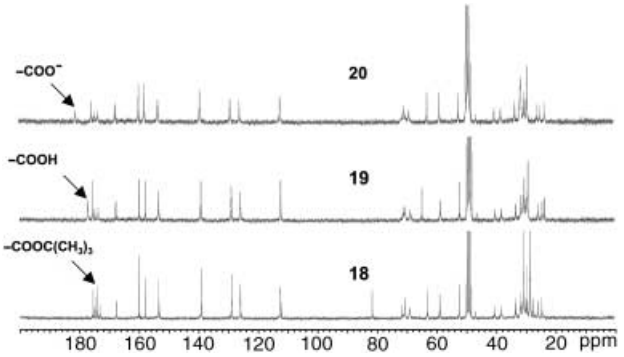


Figure 1. ^{13}C NMR spectra of the metallodendrimers **18**–**20** showing the progressive changes of the *tert*-butyl carbonyl carbon atom as it is transformed to the corresponding acid and carboxylate.

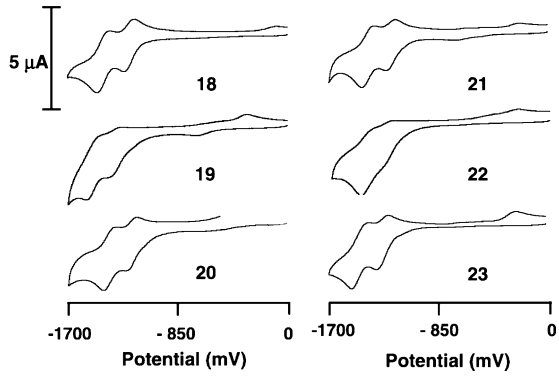


Figure 2. Cyclic voltammetry responses of the isomeric metallodendrimers **18**–**23**.

Utilizing the same procedure, one equivalent of core **17** with methyl esters was refluxed with four equivalents of Ru^{III} adduct **9** in MeOH in the presence of 4-ethylmorpholine to assemble dendrimer **21** (82%), which, after dialysis, was characterized by similar ^1H and ^{13}C NMR absorption patterns as observed for the isomeric polyester **18**. Hydrolysis of the terminal *tert*-butyl groups of ester **21** by treatment with HCO_2H at 25 °C quantitatively afforded the free octaacid **22**. Observation of a similar characteristic downfield shift (^{13}C NMR spectroscopy) of the carbonyl carbon atom ($\Delta =$ 2.5 ppm) supported the transformation to the polyacid along with the molecular ion peak (MALDI-TOF) at m/z 5573 [$M^+ - Cl$] (calcd: 5575). The neutral terminal octacarboxylate **23** (87%) was then synthesized by adding a slight excess of KOH into an H_2O/MeOH solution of acid **22**. After dialysis in MeOH for 24 h, the neutral complex **23**, identified by the downfield shift (^{13}C NMR spectroscopy) for the external acid carbonyl carbon ($\Delta = 3.5$ ppm), was isolated. The mass peak (MALDI-TOF) at m/z 5355 [M^++K] (calcd: 5357) for the molecular ion further supported the transformation.

Four major absorption bands (λ_{max} 241, 267, 304, 486 nm), in UV-visible spectra were observed for these [–<Ru>–] connected constructs. The molar absorptivities (ε) of the complexes have similar values (Table 1); this suggests that the isomeric neutral assembles **20** and **23** have the same number of [–<Ru>–] units. Notably, for the highest absorption ($\lambda_{max} =$ 486 nm), the molar absorptivites ($\varepsilon = 6.03 \times 10^4$ and 5.91×10^4 $dm^3\,mol^{-1}\,cm^{-1}$ for **20** and **23**, respectively) are approximately four times as strong as Constable's [Ar–<Ru>–Ar] complex.[44]

Cyclic voltammetry experiments showing the half-wave potentials in the metal oxidation region for each isomeric dendrimer pair (**18**–**23**) are shown in Figure 2. The cyclic responses of the terpyridine ligands of isomers **18** and **21** show the typical two reversible waves due to successive monoelectronic reduction events. Removal of the *tert*-butyl groups to give the free carboxylic acid moieties in **19** and **22** results in the merging of the two redox waves and the virtual disappearance of the corresponding anodic signal. Based on previous studies of the electrochemical reduction of pyridine and its derivatives,[33] this is due to an electrochemical reaction in which an aromatic anion radical abstracts a proton from the adjacent carboxylic acid group. The explanation is further supported by CV experiments with the neutral dendrimer **20** and **23**, whereby the lack of neighboring acidic protons results in the recovery of the typical two-wave reversible response of the terpyridine ligands.

Table 1. Molar absorptivies of [–<Ru>–] metallodendrimers.

	$\varepsilon \times 10^4$ [$dm^3\,mol^{-1}\,cm^{-1}$]			
λ_{max} [nm]	241	267	304	486
18	18.51	17.19	21.27	6.11
19	18.81	17.05	20.73	6.05
20	18.43	16.81	20.22	6.03
21	19.04	17.71	21.31	5.94
22	18.99	17.59	21.04	5.92
23	18.87	17.29	20.92	5.91

Observed solubilities of the all-ester, metalloterpyridine constructs **18**, **19**, **21**, and **22** follow that expected for polyionic species in that they are freely soluble in solvents such as MeOH, EtOH, and DMSO and insoluble in ethereal solvents such as THF. Both carboxylate-based materials **20** and **23**, however, exhibited good solubility in H_2O as well as alcoholic solvents.

Conclusion

In summary, we have prepared isomeric, mixed ester, first-generation dendrimers and converted them to their corresponding octacarboxylate derivatives, thus allowing access to the overall neutral, zwitterionic forms. Solubilities were observed to be those expected for these types of molecules. The observed electrochemistry followed trends associated with protic-functionalized polypyridinyl moieties and was shown to display typical reversible redox behavior upon deprotonation. Investigation of these novel materials with respect to charge densities and electron storage potential as well as their use as cores for dendritic surface growth is ongoing.

Experimental Section

General: The melting points were determined in capillary tubes with an Electrothermal 9100 apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 300 and 71 MHz, respectively, on a Varian GEMINI 300 MHz spectrometer and were obtained in $CDCl_3$, unless

otherwise stated. Mass spectral data were obtained on either a Bruker Esquire electrospray ion-trap mass spectrometer (ESI-MS) or Bruker Reflex-III MALDI-TOF mass spectrometer. All reagents were obtained from Aldrich and used without further purification. THF was distilled under nitrogen with $LiAlH_4$, as drying agent, and triphenylmethane, as indicator.

1-Nitro-4-(2′-tetrapyranyloxy)butane (2): A catalytic amount of *p*-TsOH was added to a stirred solution of 4-nitrobutan-1-ol[37] (**1**; 5.5 g, 46.2 mmol) and dihydropyran (7.76 g, 92.3 mmol) in anhydrous CH_2Cl_2 (50 mL). The mixture was maintained for 4 h at 25 °C, then a satd. $NaHCO_3$ solution (50 mL) was added; the organic layer was separated and washed with water (3 ×), and satd. brine. The organic solution was dried (Na_2SO_4), filtered, and reduced in vacuo to give **2** (8.3 g, 97 %), as colorless liquid. ^{1}H NMR: $\delta = 1.43$ (m, 6H; THP$H_{4,5}$, CH_2CH$_2$O), 1.58 (q, $J = 8$ Hz, 2H; THPH_3), 2.01 (quintet, $J = 8.7$ Hz, 2H; O$_2$NCH$_2$CH_2), 3.34 (td, $J = 7$, 6 Hz, 2H; CH_2O), 3.69 (td, $J = 7.4$, 6.7 Hz, 2H; THPH_6), 4.36 (t, $J = 8.4$ Hz, 2H; O$_2$NCH_2), 4.45 ppm (s, 1H; THPH_2); ^{13}C NMR: $\delta = 19.4$ (THPC_4), 24.5 (O$_2$NCH$_2$CH_2), 25.3 (THPC_5), 26.2 (CH_2CH$_2$O), 30.5 (THPC_3), 62.1 (CH_2O), 66.1 (THPC_6), 75.2 (O$_2$NCH_2), 98.7 ppm (THPC_2); ESI-MS: *m*/*z* calcd: 201.2 [M^++H]; found: 201.2

Di-*tert*-butyl 4-nitro-4-[3′-(tetrahydropyran-2″-yloxy)propyl]heptanedioate (3): Triton B (600 μL of a 40 % MeOH solution) was added to a stirred solution of ether **2** (4.1 g, 20.4 mmol) in *tert*-butyl acrylate (6.57 mL, 44.8 mmol) in THF (80 mL), and then the mixture was stirred for 24 h at 60 °C. Then the mixture was reduced in vacuo, and the residue was dissolved in CH_2Cl_2 and sequentially washed with dilute HCl, water, and satd. brine. The organic solution was dried (Na_2SO_4), filtered, and reduced in vacuo to give a yellow oil, which was purified by column chromatography (SiO_2) eluting with a 20 % EtOAc/hexane solution to give **3** (5.9 g, 63 %), as colorless liquid. ^{1}H NMR: $\delta = 1.33$ (s, 18H; CH_3), 1.38–1.51 (m, 8H; CH_2CH$_2$CO$_2$, CH$_2$CH_2CH$_2$O), 1.59–1.66 (m, 6H; THP$H_{3\text{-}5}$), 2.11 (m, 4H; CH$_2$CH_2CO$_2$), 3.26, 3.37 (m, 2H; CH_2O), 3.61, 3.68 (m, 2H; THPH_6), 4.33 ppm (s, 1H; THPH_2); ^{13}C NMR: $\delta = 19.7$ (THPC_4), 24.2 (CH_2CH$_2$O), 25.5 (THPC_5), 28.1 (CH_3), 29.8 (CH_2CO$_2$), 30.6 (CH$_2$CH$_2$CO$_2$), 30.7 (CH_2CH$_2$CH$_2$O), 32.0 (THPC_3), 62.5 (CH_2O), 66.6 (THPC_6), 81.0 (CMe$_3$), 92.8 (O$_2$NC), 99.0 (THPC_2), 171.3 ppm (CO_2); ESI-MS: *m*/*z* calcd: 482.4 [M^++Na]; found: *m*/*z* 482.4.

Di-*tert*-butyl 4-amine-4-[3′-(tetrahydropyran-2″-yloxy)propyl]heptanedioate (4): The diester **3** (1.2 g, 2.62 mmol) was hydrogenated with T1 Raney Ni (3 g) in absolute EtOH (100 mL) at 60 psi for 24 h. The solution was cautiously filtered through Celite (*pyrophoric*), after which the solvent was concentrated in vacuo. The mixture was dissolved in EtOAc, then sequentially washed with a 5 % NH_4OH solution, water, and satd. brine. The organic solution was dried (Na_2SO_4), filtered, and reduced in vacuo to give **4** (1.08 g, 96 %), as colorless oil. ^{1}H NMR: $\delta = 1.19$ (s, 18H; CH_3), 1.37–1.50 (m, 8H; CH_2CH$_2$CO$_2$, CH$_2$CH_2CH$_2$O), 1.59–1.66 (m, 6H; THP$H_{3\text{-}5}$), 2.02 (m, 4H; CH$_2$CH_2CO$_2$), 3.12, 3.25 (m, 2H; CH_2O), 3.48, 3.60 (m, 2H; THPH_6), 4.33 ppm (s, 1H; THPH_2); ^{13}C NMR: $\delta = 19.1$ (THPC_4), 23.3 (CH_2CH$_2$O), 24.9 (THPC_5), 27.5 (CH_3), 29.4 (CH_2CO$_2$), 30.1 (CH$_2$CH$_2$CO$_2$), 33.8 (THPC_3), 35.2 (CH_2CH$_2$CH$_2$O), 52.2 (H$_2$NC), 61.6 (CH_2O), 67.0 (THPC_6), 79.4 (CMe$_3$), 98.1 (THPC_2), 172.5 ppm (CO_2); ESI-MS: *m*/*z* calcd: 430.4 [M^++H]; found: 430.4.

Di-*tert*-butyl 4-{4-[(2,2′:6′,2″)terpyridin-4′-yloxy]butyrylamino}-4-[3-(tetrahydropyran-2-yloxy)propyl]heptanedioate (6): DCC (700 mg, 3.44 mmol) and 1-HOBt (470 mg, 3.44 mmol) were added at 25 °C to a solution of **5**[39] (770 mg, 2.29 mmol) in dry DMF (10 mL). This mixture was stirred for 2 h, and then amine **4** (986 mg, 2.29 mmol) was added. The mixture was stirred for 36 h at 25 °C, after which the white precipitate was filtered. The filtrate was concentrated in vacuo affording a crude oil, which was dissolved in CH_2Cl_2 (100 mL), and washed with water and satd. brine. The organic solution was dried (Na_2SO_4), filtered, and reduced in vacuo to give a crude product, which was purified by column chromatography (Al_2O_3), eluting with a 50 % EtOAc/hexane solution to give **6** (1.41 g, 82 %), as a spongy white solid. ^{1}H NMR: $\delta = 1.38$ (s, 18H; CH_3), 1.42–1.51 (m, 6H; CH_2CH_2CH$_2$OTHP, THP$H_{4,5}$), 1.73 (m, 4H; THPH_3, CH_2CH$_2$CONH), 1.96 (m, 4H; CH_2CH$_2$CO$_2$), 2.17 (m, 4H; CH_2CO$_2$), 2.34 (m, 2H; CH_2CONH), 3.30, 3.43 (m, 2H; CH_2O), 3.67, 3.79 (m, 2H; THPH_6), 4.23 (t, $J = 6$ Hz, 2H; tpyOCH_2), 4.48 (s, 1H; THPH_2), 5.75 (s, 1H; CONH), 7.25 (td, $J = 5.1$, 1.5 Hz, 2H; tpy$H_{5,5''}$), 7.80 (td, $J = 7.8$, 1.5 Hz, 2H; tpy$H_{4,4''}$), 7.98 (s, 2H; tpy$H_{3',5'}$), 8.57 (d, $J = 8.1$, 2H; tpy$H_{3,3''}$), 8.64 ppm (d, $J = 4.2$ Hz, 2H; tpy$H_{6,6''}$); ^{13}C NMR: $\delta = 19.1$ (THPC_4), 23.0 (CH_2CH$_2$O), 24.5 (CH_2CH$_2$CONH), 24.8 (THPC_5), 27.4 (CH_3), 29.2 (CH_2CO$_2$), 29.5 (CH$_2$CH$_2$CO$_2$), 30.1 (THPC_3), 30.8 (CH_2CONH), 32.6 (CH_2CH$_2$CH$_2$O), 57.1 (CONHC), 61.7 (CH_2O), 66.6 (THPC_6), 66.8 (tpyOCH_2), 79.7 (CMe$_3$), 98.3 (THPC_2), 106.7 (tpy$C_{5,5''}$), 120.6 (tpy$C_{4,4''}$), 123.2 (tpy$C_{3,3''}$), 136.1 (tpy$C_{3',5'}$), 148.3 (tpy$C_{6,6''}$), 155.3 (tpy$C_{2,2''}$), 156.4 (tpy$C_{2',6'}$), 166.3 (tpy$C_{4'}$), 170.9 (CONH), 172.3 ppm (CO_2); ESI-MS: *m*/*z* calcd: 769.4 [M^++Na]; found: 769.8.

Ru^{III}-metalloappendage of ligand 6 (complex 7): A solution of $RuCl_3 \cdot 3H_2O$ (178 mg, 680 μmol) and ether **6** (510 mg, 680 μmol) in MeOH (20 mL) was refluxed for 2 h. After cooling, the precipitate was filtered, washed sequentially with MeOH (50 mL), water (50 mL), and Et_2O (50 mL), then dried in vacuo to afford **7** (520 mg, 88 %), as yellow-brown solid. The material was used directly without further purification in the next step.

Dimethyl 4-(3-hydroxypropyl)-4-{4-[(2,2′:6′,2″)terpyridin-4′-yloxy]butyrylamino}heptanedioate (8): A few drops of conc. H_2SO_4 were added at 25 °C to a solution of the THP ether **6** (700 mg, 940 μmol) in MeOH (50 mL). The mixture was refluxed for 24 h, and then reduced in vacuo; the residue was dissolved in CH_2Cl_2 and washed sequentially with a satd. $NaHCO_3$ solution, water (3 ×), and satd. brine. The organic solution was dried (Na_2SO_4), filtered, and reduced in vacuo to give an oil, which was purified by column chromatography (Al_2O_3), eluting with a 10 % MeOH/EtOAc solution to give (530 mg; 98 %) **8**, as a spongy white solid. ^{1}H NMR: $\delta = 1.48$ (m, 2H; CH_2CH$_2$OTHP), 1.73 (m, 2H; tpyOCH$_2$CH_2), 2.03 (m, 4H; CH_2CH$_2$CO$_2$), 2.16 (m, 2H; CH_2CH$_2$CH$_2$OH), 2.26 (m, 4H; CH_2CO$_2$), 2.38 (t, $J = 7.2$ Hz, 2H; CH_2CONH), 3.55 (m, 2H; CH_2OH), 3.57 (s, 6H; CH_3), 4.26 (t, $J = 6$ Hz, 2H; tpyOCH_2), 5.98 (s, 1H; CONH), 7.33 (td, $J = 5.1$, 1.5 Hz, 2H; tpy$H_{5,5''}$), 7.84 (td, $J = 7.8$, 1.5 Hz, 2H; tpy$H_{4,4''}$), 7.97 (s, 2H; tpy$H_{3',5'}$), 8.58 (d, $J = 8.1$, 2H; tpy$H_{3,3''}$), 8.65 (d, $J = 4.2$ Hz, 2H; tpy$H_{6,6''}$); ^{13}C NMR: $\delta =$ 24.8 (CH_2CH$_2$OH), 26.1 (CH_2CH$_2$CONH), 28.4 (CH_2CO$_2$), 30.0 (CH_2CH$_2$CO$_2$), 31.2 (CH_2CONH), 33.3 (CH_2CH$_2$CH$_2$OH), 51.7 (CH_3), 57.5 (CONHC), 62.1 (CH_2O), 67.1 (tpyOCH_2), 107.4 (tpy$C_{5,5''}$), 121.4 (tpy$C_{4,4''}$), 123.8 (tpy$C_{3,3''}$), 136.8 (tpy$C_{3',5'}$), 148.9 (tpy$C_{6,6''}$), 155.9 (tpy$C_{2,2''}$), 157.04 (tpy$C_{2',6'}$), 166.9 (tpy$C_{4'}$), 171.6 (CONH), 173.9 ppm (CO_2); ESI-MS: calcd *m*/*z*: 601.3 [M^++Na]; found: *m*/*z*: 601.3.

Ru^{III}-metalloappendage of dimethyl ester 8 (complex 9): A solution of $RuCl_3 \cdot 3H_2O$ (136 mg, 520 μmol) and **8** (300 mg, 520 μmol) in MeOH (20 mL) was refluxed for 2 h. After cooling, the precipitate was filtered, washed sequentially with MeOH (50 mL), water (50 mL), and Et_2O (50 mL), and then dried in vacuo yielding **9** (280 mg, 68 %) as yellow-brown solid.

***N*-{5-[4′-(2,2′:6′,2″)Terpyridinyloxy]pentyl}acrylamide (11)**: Acryloyl chloride (1.17 mL, 14.4 mmol) was added to a stirred solution of 5-[4′-(2,2′:6′,2″)terpyridinyloxy]pentylamine[40] (**10**; 4.1 g, 12.2 mmol) and Et_3N (2.01 mL, 14.4 mmol) in dried THF (100 mL) at 0 °C. After the mixture was stirred for 2 h at 25 °C, the solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2 and washed with the water and satd. brine. The organic solution was dried ($MgSO_4$), filtered, and reduced in vacuo to give a crude solid, which was purified by column chromatography (Al_2O_3), eluting with a 66 % EtOAc/hexane solution to give amide **11** (4.3 g, 91 %) as white solid. ^{1}H NMR: $\delta = 1.62$ (m, 4H; NHCH$_2$CH_2CH_2), 1.90 (t, 2H; $J = 6.3$ Hz, CH_2CH$_2$O), 2.07 (s, 2H; NH_2), 3.40 (q, $J = 6.3$ Hz, 2H; NHCH_2), 4.24 (t, $J = 6.2$ Hz, 2H; CH_2O), 5.65 (dd, $J = 10.0$, 1.4 Hz, 1H; CH_2=CH), 6.09 (br, 1H; CONH), 6.10 (dd, $J = 17.0$, 10.0 Hz, 1H; CH$_2$=CH), 6.32 (dd, $J = 17.0$, 1.4 Hz, 1H; CH_2=CH), 7.36 (td, tpy$H_{5,5''}$, 2H; $J = 5.8$, 1.4 Hz), 7.88 (td, 2H; $J = 7.8$, 1.2 Hz, tpy$H_{4,4''}$), 8.01 (s, 2H; tpy$H_{3',5'}$), 8.63 (d, $J = 7.9$ Hz, 2H; tpy$H_{3,3''}$), 8.71 ppm (d, $J = 4.5$ Hz, 2H; py$H_{6,6''}$); ^{13}C NMR: $\delta = 23.4$ (CH_2CH$_2$CH$_2$O), 28.5 (CH_2CH$_2$O), 29.1 (CONHCH$_2$CH_2), 39.4 (CONHCH_2), 67.9 (CH_2O), 107.3 (tpy$C_{5,5''}$), 121.4 (tpy$C_{4,4''}$), 123.8 (tpy$C_{3,3''}$), 126.3 (CH_2=CH), 130.8 (CH$_2$=CH), 136.8 (tpy$C_{3',5'}$), 148.9 (tpy$C_{6,6''}$), 156.0 (tpy$C_{2,2''}$), 156.9 (tpy$C_{2',6'}$), 165.6 (CONH), 167.1 ppm (tpy$C_{4'}$); IR: $\tilde{\nu} = 3296$, 1654, 1622 cm^{-1}; ESI-MS: *m*/*z* calcd: 389.3 [M^++H]; found: 389.2.

***N*-{5-[4′-(2,2′:6′,2″)Terpyridinyloxy]pentyl} 4-nitrobutanoyl amide (12)**: Triton B (600 μL of a 40 % MeOH solution) was added to a solution of acrylamide (**11**) (3.7 g, 9.52 mmol) in a $CH_3NO_2/CHCl_3$ (1:1; 200 mL); then the mixture was stirred for 24 h at 25 °C. The mixture was then reduced in vacuo to give a residue, which was dissolved in $CHCl_3$ and then washed with dilute aq. HCl, water, and satd. brine. The organic solution was dried (Na_2SO_4), filtered, and reduced in vacuo to give a crude oil, which was purified by column chromatography (Al_2O_3), eluting with a 33 % EtOAc/

hexane solution to give amide **12** (3.2 g, 75%) as a colorless oil: ^{1}H NMR: $\delta = 1.38$ (m, 4H; NHCH$_2$CH_2CH_2), 1.89 (t, $J = 5.6$ Hz, 2H; CH_2CH$_2$O), 2.32 (m, 4H; CH_2CH_2CONH), 3.30 (t, $J = 5.7$ Hz, 2H; NHCH_2), 4.24 (t, $J = 5.7$ Hz, 2H; CH_2O), 4.48 (t, $J = 4.7$ Hz, 2H; O$_2$NCH_2), 5.85 (s, 1H; CONH), 7.35 (td, $J = 6.3$, 1.5 Hz, 2H; tpy$H_{5,5''}$), 7.87 (t, $J = 7.4$ Hz, 2H; tpy$H_{4,4''}$), 8.01 (s, 2H; tpy$H_{3',5'}$), 8.62 (d, $J = 7.8$ Hz, 2H; tpy$H_{3,3''}$), 8.69 ppm (d, $J = 5.2$ Hz, 2H; tpy$H_{6,6''}$); ^{13}C NMR: $\delta = 22.8$ (O$_2$NCH$_2$CH_2), 23.1 (CH_2CH$_2$CH$_2$O), 28.3 (CH_2CH$_2$O), 28.9 (CONHCH$_2$CH_2), 31.9 (CH_2CONH), 39.2 (CONHCH_2), 67.7 (CH_2O), 74.5 (O$_2$NCH_2), 107.1 (tpy$C_{5,5''}$), 121.2 (tpy$C_{4,4''}$), 123.7 (tpy$C_{3,3''}$), 136.7 (tpy$C_{3',5'}$), 148.7 (tpy$C_{6,6''}$), 155.7 (tpy$C_{2,2''}$), 156.7 (tpy$C_{2',6'}$), 166.9 (tpy$C_{4'}$), 170.8 ppm (C=ONH); IR: $\tilde{\nu} = 3300$, 1550, 1377 cm^{-1}; ESI-MS: m/z calcd: 472.2 [M^++Na]; found: 472.2.

Di-*tert*-butyl 4-{2-[5-(4′-(2,2′:6′,2″)terpyridinyloxy)pentylcarbamoyl]ethyl}-4-nitroheptanedioate (13): *tert*-Butyl acrylate (2.5 mL, 17.04 mmol) and Triton B (600 μL of a 40% MeOH solution) were added to a stirred solution of amide **12** (3.2 g, 7.12 mmol) in dry CHCl$_3$ (100 mL). After the mixture was stirred for 24 h at 25 °C, it was reduced in vacuo to give a residue, which was dissolved in CH$_2$Cl$_2$ and then sequentially washed with dilute aq. HCl, water, and satd. brine. The organic solution was dried (Na$_2$SO$_4$), filtered, and reduced in vacuo to give a oil, which was purified by column chromatography (Al$_2$O$_3$), eluting with a 25% EtOAc/hexane mixture to give **13** (3.5 g, 70%) as a white solid:. The spectral data were identical to that prepared by using the $1 \rightarrow 2$ branched monomer approach.[37]

Di-*tert*-butyl 4-{2-[5-(4′-(2,2′:6′,2″)terpyridinyloxy)pentylcarbamoyl]ethyl}-4-aminoheptanedioate (14): The diester **13** (3.0 g, 4.25 mmol) was hydrogenated with T1 Raney Ni (10 g) in absolute EtOH (100 mL) at 120 psi at 40 °C for 24 h. The solution was cautiously filtered (*pyrophoric*) through Celite, after which the solvent was removed in vacuo to give a residue, which was dissolved in EtOAc and then washed with dilute aq. NaOH, water, and satd. brine. The organic solution was dried (Na$_2$SO$_4$), filtered, and reduced in vacuo to give **14** (87%), as a yellow oil. The spectral data are identical to that prepared by using the $1 \rightarrow 2$ branched monomer approach.[37]

First-generation dendrimer (16): Dendrimer **16** was prepared from the tetraacid **15**[43] (97 mg, 230 μmol) and amine **14** (683 mg, 1.01 mmol) as previously reported.[37] MALDI-TOF: m/z calcd: 3077.7 [M^++Na]; found: 3077.1.

Transesterification of octa(*tert*-butyl ester) 16 (formation of the octamethyl ester 17): Conc. H$_2$SO$_4$ (100 μL) was added to a solution of octaester **16** (250 mg, 81.8 μmol) in MeOH (100 mL) at 25 °C. The mixture was refluxed for 24 h, then concentrated in vacuo to afford a residue, which was dissolved in CH$_2$Cl$_2$, and then washed with satd. aq. NaHCO$_3$, water (3 ×), and satd. brine. The organic solution was dried (Na$_2$SO$_4$), filtered, and reduced in vacuo to give an oil, which was purified by column chromatography (Al$_2$O$_3$), eluting with a 5% MeOH/EtOAc mixture to give **17** (175 mg, 78%) as a spongy white solid. ^{1}H NMR: $\delta = 1.51$ (m, 16H; CH_2CH_2CH$_2$CH$_2$O), 1.82 (m, 8H; CH_2CH$_2$O), 1.98 (m, 24H; CH_2CH$_2$CO$_2$), 2.19 (m, 24H; CH_2CO$_2$), 2.34 (m, 8H; CH_2CONHC$^{4\circ}$), 3.20 (m, 8H; CONHCH_2), 3.30 (s, 8H; CCH_2O), 3.61 (s, 24H; CH_3), 3.63 (s, 8H; CH$_2$OCH_2), 4.15 (m, 8H; CH_2Opy), 7.29 (t, $J = 5.0$ Hz, 8H; tpy$H_{5,5''}$), 7.80 (t, 8H; $J = 7.5$ Hz, tpy$H_{4,4''}$), 7.95 (s, 8H; tpy$H_{3',5'}$), 8.57 (d, $J = 7.9$ Hz, 8H; tpy$H_{3,3''}$), 8.64 ppm (d, $J = 4.2$ Hz, 8H; tpy$H_{6,6''}$); ^{13}C NMR: $\delta = 23.2$ (NHCH$_2$CH$_2$CH_2), 27.8 (CH_2CH$_2$O), 28.4 (NHCH$_2$CH_2), 29.0 (CH_2CH$_2$CO$_2$), 29.7 (CH_2CH$_2$CONH), 30.4 (CH_2CO$_2$), 34.6 (CH_2CONH), 37.3 (OCH$_2$CH_2CONH), 39.3 (CONHCH_2), 45.1 (C$^{4\circ}$), 51.5 (CO$_2$CH_3), 57.2 (CONHC), 67.5 (OCH_2CH$_2$CONH), 67.7 (CH_2O), 68.9 (CCH_2O), 107.1 (tpy$C_{5,5''}$), 121.1 (tpy$C_{4,4''}$), 123.6 (tpy$C_{3,3''}$), 136.6 (tpy$C_{3',5'}$), 148.8 (tpy$C_{6,6''}$), 155.8 (tpy$C_{2,2''}$), 156.8 (tpy$C_{2',6'}$), 166.9 (tpy$C_{4'}$), 171.0 (CONHC), 172.6 (CONH), 173.6 ppm (CO$_2$); MALDI-TOF: m/z calcd: 2719.2 for [M^++H]; found: 2720.6.

Inside octa(*tert*-butyl ester) metallodendrimer (18): Tetrakisterpyridine core **16** (120 mg, 39.3 μmol) and 4-ethylmorpholine (6 drops) were added to a suspension of four equivalents of **9** (134 mg, 170 μmol) in MeOH (10 mL). The mixture was refluxed for 3 h; during this time, the solution turned dark red. After cooling to 25 °C, the solution was filtered to remove any insoluble materials. The solution was sealed into a membrane (MWCO = 3500) to dialyze for 24 h, and was then concentrated and dried in vacuo to afford complex **18** (180 mg, 76%) as a red solid. ^{1}H NMR (CD$_3$OD): $\delta =$ 1.29 (s, 8H; CH_2CH$_2$OH), 1.43 (s, 72H; C(CH_3)$_3$), 1.45 (m, 8H; CH_2CH$_2$CH$_2$Otpy), 1.75 (m, 24H; CH_2CH$_2$CH_2CH$_2$Otpy, tpyOCH$_2$CH_2), 2.05 (m, 48H; C$^{4\circ}$CH_2CH$_2$CO$_2$, C$^{4\circ}$CH_2CH$_2$CONH, CH_2CH$_2$CH$_2$OH), 2.34 (m, 56H; CH_2CONH, C$^{4\circ}$CH$_2$CH_2CO$_2$, C$^{4\circ}$CH$_2$CH_2CONH), 3.33 (s, 16H; C$^{4\circ}$CH_2OCH$_2$, CONHCH_2), 3.58 (m, 16H; C$^{4\circ}$CH$_2$OCH_2, CH_2OH), 3.64 (s, 24H; CH_3), 4.66 (br s, 16H; CH_2Otpy), 7.30 (dd, $J = 5.0$ Hz, 16H; tpy$H_{5,5''}$), 7.56 (d, $J = 7.5$ Hz, 16H; tpy$H_{6,6''}$), 8.01 (dd, 16H; tpy$H_{4,4''}$), 8.68 (s, $J = 7.9$ Hz, 16H; tpy$H_{3',5'}$), 8.81 ppm (d, $J = 4.2$ Hz, 16H; tpy$H_{3,3''}$); ^{13}C NMR (CD$_3$OD): $\delta = 24.4$ (NHCH$_2$CH$_2$CH_2), 25.8 (CH_2CH$_2$OH), 27.2 (tpyOCH$_2$CH_2CH$_2$CONH), 28.4 (C(CH_3)$_3$), 29.3 (CH_2CO$_2$), 29.6 (C$^{4\circ}$CH$_2$CH$_2$CONH), 30.1 (CH_2CH$_2$Otpy), 30.6 (CH_2CH$_2$CO$_2$), 31.3 (OCH$_2$CH$_2$CH_2CONH), 31.7 (CONHCH$_2$CH_2), 33.1 (C$^{4\circ}$CH$_2$CH_2CONH), 33.3 (CH_2CH$_2$CH$_2$OH), 38.1 (OCH$_2$CH_2CONH), 40.3 (CONHCH_2), 46.6 (C$^{4\circ}$), 52.1 (CO$_2$CH_3), 58.7, 58.8 (CONHC), 62.9 (CH_2OH), 68.7 (OCH_2CH$_2$CONH), 70.4 (CCH_2O), 71.3 (tpyOCH_2), 81.4 (CMe_3), 112.4 (tpy$C_{5,5''}$), 125.8 (tpy$C_{4,4''}$), 128.9 (tpy$C_{3,3''}$), 139.0 (tpy$C_{3',5'}$), 153.3 (tpy$C_{6,6''}$), 157.7 (tpy$C_{2,2''}$), 159.8 (tpy$C_{2',6'}$), 167.4, 167.7 (tpy$C_{4'}$), 173.2 (CONH), 174.3 (CO$_2$C(CH$_3$)), 174.5 (CONH), 175.3 (CONH), 175.5 ppm (CO$_2$CH$_3$); MALDI-TOF: a broad signal at correct formula mass, the precise MS analyses were conducted on the corresponding free acid **19** and subsequent carboxylate **20**.

Inside octaacid tetra-Ru^{II}-metallodendrimer (19) A solution of **18** (120 mg, 19.8 μmol) in HCO$_2$H (20 mL) was stirred for 12 h at 25 °C. After reaction, the formic acid was removed in vacuo. A mixture of MeOH and H$_2$O was added to dissolve the resultant material, which was then placed into a membrane (cut off mass = 3500) to dialyze for 24 h; the solution was then concentrated and dried in vacuo to afford the complex **19** (101 mg, 95%) as a red solid; ^{1}H NMR (CD$_3$OD): $\delta = 1.39$ (m, 8H; CH_2CH$_2$CH$_2$Otpy), 1.73 (m, 24H; CH_2CH$_2$CH_2CH$_2$Otpy, tpyOCH$_2$CH_2), 1.79 (m, 8H; CH_2CH$_2$OH), 2.09 (m, 48H; C$^{4\circ}$CH_2CH$_2$CO$_2$, C$^{4\circ}$CH_2CH$_2$CONH, CH_2CH$_2$CH$_2$OH), 2.39 (m, 56H; CH_2CONH, C$^{4\circ}$CH$_2$CH_2CO$_2$, C$^{4\circ}$CH$_2$CH_2CONH), 3.33 (s, 8H; C$^{4\circ}$CH_2OCH$_2$), 3.37 (s, 8H; CONHCH_2), 3.59 (m, 16H; C$^{4\circ}$CH$_2$OCH_2, CH_2OH), 3.61 (s, 24H; CH_3), 4.63 (br s, 16H; CH_2Otpy), 7.28 (dd, $J = 5.0$ Hz, 16H; tpy$H_{5,5''}$), 7.52 (d, $J = 7.5$ Hz, 16H; tpy$H_{6,6''}$), 7.99 (dd, 16H; tpy$H_{4,4''}$), 8.65 (s, $J = 7.9$ Hz, 16H; tpy$H_{3',5'}$), 8.76 ppm (dd, $J = 4.2$ Hz, 16H; tpy$H_{3,3''}$); ^{13}C NMR (CD$_3$OD): $\delta = 23.5$ (NHCH$_2$CH$_2$CH_2), 24.4 (CH_2CH$_2$OH), 25.8 (tpyOCH$_2$CH_2), 29.2 (CH_2CO$_2$), 29.6 (C^{4}CH$_2$CH$_2$CONH), 30.0 (CH_2CH$_2$Otpy), 30.5 (CH_2CH$_2$CO$_2$), 31.5 (OCH$_2$CH$_2$CH_2CONH, CONHCH$_2$CH_2), 33.4 (CH_2CH$_2$CH$_2$OH, C$^{4\circ}$CH$_2$CH_2CONH), 38.3 (OCH$_2$CH_2CONH), 40.3 (CONHCH_2), 46.6 (C$^{4\circ}$), 52.2 (CO$_2$CH_3), 58.8, 58.9 (CONHC), 64.9 (CH_2OH), 68.8 (OCH_2CH$_2$CONH), 70.5 (CCH_2O), 71.3 (tpyOCH_2), 112.3 (tpy$C_{5,5''}$), 125.8 (tpy$C_{4,4''}$), 128.8 (tpy$C_{3,3''}$), 139.0 (tpy$C_{3',5'}$), 153.3 (tpy$C_{6,6''}$), 157.7 (tpy$C_{2,2''}$), 159.8 (tpy$C_{2',6'}$), 167.4, 167.6 (tpy$C_{4'}$), 173.5 (CONH), 174.6 (CONH), 175.3 (CONH), 175.4 (CO$_2$CH$_3$), 177.0 ppm (CO$_2$H); MALDI-TOF: m/z calcd: 5610 [M+H]$^+$, 2769 [M − 2Cl]$^{2+}$; found: 5609, 2771.

Neutral (inside octacarboxylate) tetra-Ru^{II}-metallodendrimer (20): KOH (463 μg, 8.26 μmol) in H$_2$O (20 mL) was added to a solution of acid dendrimer **19** (44 mg, 8.26 μmol) in MeOH/H$_2$O (2/20 mL). The solution was sealed into a membrane (cutoff mass = 3500) to dialyze for 24 h, and was then concentrated and dried in vacuo to give the desired neutral metallodendrimer **20** (37 mg, 80%) as a red solid. ^{1}H NMR (CD$_3$OD): $\delta =$ 1.29 (m, 8H; CH_2CH$_2$CH$_2$Otpy), 1.71 (m, 24H; CH_2CH$_2$CH_2CH$_2$Otpy, tpyOCH$_2$CH_2), 1.92 (m, 8H; CH_2CH$_2$OH), 2.06 (m, 48H; C$^{4\circ}$CH_2CH$_2$CO$_2$, C$^{4\circ}$CH_2CH$_2$CONH, CH_2CH$_2$CH$_2$OH), 2.34 (m, 56H; CH_2CONH, C$^{4\circ}$CH$_2$CH_2CO$_2$, C$^{4\circ}$CH$_2$CH_2CONH), 3.32 (s, 8H; C$^{4\circ}$CH_2OCH$_2$), 3.36 (s, 8H; CONHCH_2), 3.60 (m, 16H; C$^{4\circ}$CH$_2$OCH_2, CH_2OH), 3.61 (s, 24H; CH_3), 4.60 (br s, 16H; CH_2OPy), 7.29 (dd, $J = 5.0$ Hz, 16H; tpy$H_{5,5''}$), 7.49 (d, $J = 7.5$ Hz, 16H; tpy$H_{6,6''}$), 8.00 (dd, 16H; tpy$H_{4,4''}$), 8.54 (s, $J = 7.9$ Hz, 16H; tpy$H_{3',5'}$), 8.67 ppm (d, $J = 4.2$ Hz, 16H; tpy$H_{3,3''}$); ^{13}C NMR (CD$_3$OD): $\delta =$ 24.0 (NHCH$_2$CH$_2$CH_2), 25.8 (CH_2CH$_2$OH), 26.2 (tpyOCH$_2$CH_2), 29.2 (CH_2CO$_2$), 29.6 (C$^{4\circ}$CH$_2$CH$_2$CONH), 30.2 (CH_2CH$_2$OPy), 30.5 (CH_2CH$_2$CO$_2$), 31.3 (OCH$_2$CH$_2$CH_2CONH, CONHCH$_2$CH_2), 33.4 (CH_2CH$_2$CH$_2$OH, C$^{4\circ}$CH$_2$CH_2CONH), 38.3 (OCH$_2$CH_2CONH), 40.3 (CONHCH_2), 46.3 (C$^{4\circ}$), 52.8 (CO$_2$CH_3), 58.7, 58.8 (CONHC), 62.6 (CH_2OH), 68.8 (OCH_2CH$_2$CONH), 70.5 (CCH_2O), 71.3 (tpyOCH_2), 111.9 (tpy$C_{5,5''}$), 125.6 (tpy$C_{4,4''}$), 128.7 (tpy$C_{3,3''}$), 139.1 (tpy$C_{3',5'}$), 153.0 (tpy$C_{6,6''}$), 157.5 (tpy$C_{2,2''}$), 159.4 (tpy$C_{2',6'}$), 167.0, 167.3 (tpy$C_{4'}$), 173.5 (CONH), 175.2 (CONH), 176.2 (CONH), 176.7 (CO$_2$CH$_3$), 180.3 ppm (CO$_2^-$); MALDI-TOF: m/z calcd: 5357 [M^++K]; found: 5355.

Outside octa(*tert*-butyl ester) tetra-Ru^{II}-metallodendrimer (21): Tetrakisterpyridine core **17** (115 mg, 42.3 μmol) and 4-ethylmorpholine (6 drops) were added to a suspension of four equivalents of **9** (169 mg, 180 μ mmol) in MeOH (10 mL). The workup followed exactly that of **17** affording the complex **21** (210 mg, 82%) as a red solid. ^{1}H NMR (CD_3OD): $\delta = 1.43$ (s, 72H; C(CH_3)$_3$), 1.44 (m, 16H; CH_2CH$_2$OH, CH_2CH$_2$CH$_2$Otpy), 1.75 (m, 24H; CH_2CH$_2$CH_2CH$_2$Otpy, tpyOCH$_2$CH_2), 2.05 (m, 48H; C$^{4'}$CH_2CH$_2$CO$_2$, C$^{4'}$CH_2CH$_2$CONH, CH_2CH$_2$CH$_2$OH), 2.34 (m, 56H; CH_2CONH, C$^{4'}$CH$_2$CH_2CO$_2$, C$^{4'}$CH$_2$CH_2CONH), 3.33 (s, 16H; C$^{4'}$CH_2OCH$_2$, CONHCH_2), 3.58 (m, 16H; C$^{4'}$CH$_2$OCH_2, CH_2OH), 3.64 (s, 24H; CH_3), 4.66 (brs, 16H; CH_2Otpy), 7.30 (dd, $J = 5.0$ Hz, 16H; tpy$H_{5,5''}$), 7.56 (d, $J = 7.5$ Hz, 16H; tpy$H_{6,6''}$), 8.01 (dd, 16H; tpy$H_{4,4''}$), 8.68 (s, 16H; tpy$H_{3',5'}$), 8.81 ppm (d, $J = 4.2$ Hz, 16H; tpy$H_{3,3''}$); ^{13}C NMR (CD_3OD): $\delta = 24.4$ (NHCH$_2$CH$_2$CH_2), 25.9 (CH_2CH$_2$OH), 27.3 (tpyOCH$_2$CH_2), 28.3 (C(CH_3)$_3$), 29.1 (CH_2CO$_2$), 29.6 (C$^{4'}$CH$_2$CH$_2$CONH), 30.0 (CH_2CH$_2$Otpy), 30.8 (CH_2CH$_2$CO$_2$), 31.4 (OCH$_2$CH$_2$CH_2CONH), 31.8 (CONHCH$_2$CH_2), 33.4 (C$^{4'}$CH$_2$CH_2CONH), 35.7 (CH_2CH$_2$CH$_2$OH), 38.2 (OCH$_2$CH_2CONH), 40.2 (CONHCH_2), 46.5 (C$^{4'}$), 52.2 (CO$_2$CH_3), 58.6, 58.9 (CONHC), 62.9 (CH_2OH), 68.8 (OCH$_2$CH$_2$CONH), 70.4 (CCH$_2$O), 71.3 (tpyOCH_2), 81.4 (C(CH$_3$)$_3$), 112.4 (tpy$C_{5,5''}$), 125.8 (tpy$C_{4,4''}$), 128.8 (tpy$C_{3,3''}$), 139.0 (tpy$C_{3',5'}$), 153.3 (tpy$C_{6,6''}$), 157.7 (tpy$C_{2,2''}$), 159.8 (tpy$C_{2',6'}$), 167.4, 167.7 (tpy$C_{4'}$), 173.3 (CONH), 174.5 (CO$_2$C(CH$_3$)), 174.5 (CONH), 175.3 (CONH), 175.3 ppm (CO$_2$CH$_3$); MALDI-TOF: a broad signal at correct formula mass; the precise MS analyses were conducted on the corresponding free acid **22** and subsequent carboxylate **23**.

Outside octaacid tetra-Ru^{II}-metallodendrimer (22): A solution of **21** (120 mg, 19.8 μmol) in HCO_2H (20 mL) was stirred for 12 h at 25 °C; then the formic acid was removed in vacuo. The workup exactly followed that of **19** to afford the complex **22** (105 mg, 99%) as a red solid. ^{1}H NMR (CD_3OD): $\delta = 1.30$ (m, 8H; CH_2CH$_2$CH$_2$Otpy), 1.75 (m, 24H; CH_2CH$_2$CH_2CH$_2$Otpy, tpyOCH$_2$CH_2), 1.83 (m, 8H; CH_2CH$_2$OH), 2.10 (m, 48H; C$^{4'}$CH_2CH$_2$CO$_2$, C$^{4'}$CH_2CH$_2$CONH, CH_2CH$_2$CH$_2$OH), 2.35 (m, 56H; CH_2CONH, C$^{4'}$CH$_2$CH_2CO$_2$, C$^{4'}$CH$_2$CH_2CONH), 3.33 (s, 8H; C$^{4'}$CH_2OCH$_2$), 3.37 (s, 8H; CONHCH_2), 3.59 (m, 16H; C$^{4'}$CH$_2$OCH_2, CH_2OH), 3.63 (s, 24H; CH_3), 4.66 (brs, 16H; CH_2Otpy), 7.28 (dd, $J =$ 5.0 Hz, 16H; tpy$H_{5,5''}$), 7.56 (d, $J = 7.5$ Hz, 16H; tpy$H_{6,6''}$), 8.00 (dd, $J =$ 7.9 Hz, 16H; tpy$H_{4,4''}$), 8.67 (s, 16H; tpy$H_{3',5'}$), 8.78 (d, $J = 4.2$ Hz, 16H; tpy$H_{3,3''}$); ^{13}C NMR (CD_3OD): $\delta = 23.5$ (NHCH$_2$CH$_2$CH_2), 24.4 (CH_2CH$_2$OH), 25.8 (tpyOCH$_2$CH_2), 29.2 (CH_2CO$_2$), 29.6 (C$^{4'}$CH$_2$CH$_2$CONH), 30.0 (CH_2CH$_2$Otpy), 30.5 (CH_2CH$_2$CO$_2$), 31.3 (OCH$_2$CH$_2$CH_2CONH), 31.6 (CONHCH$_2$CH_2), 33.3 (CH_2CH$_2$CH$_2$OH, C$^{4'}$CH$_2$CH_2CONH), 38.3 (OCH$_2$CH_2CONH), 40.3 (CONHCH_2), 46.5 (C$^{4'}$), 52.3 (CO$_2$CH_3), 58.7, 58.8 (CONHC), 65.0 (CH_2OH), 68.8 (OCH$_2$CH$_2$CONH), 70.5 (CCH$_2$O), 71.4 (tpyOCH_2), 112.4 (tpy$C_{5,5''}$), 125.9 (tpy$C_{4,4''}$), 128.8 (tpy$C_{3,3''}$), 139.0 (tpy$C_{3',5'}$), 153.4 (tpy$C_{6,6''}$), 157.8 (tpy$C_{2,2''}$), 159.8 (tpy$C_{2',6'}$), 167.4, 167.7 (tpy$C_{4'}$), 173.4 (CONH), 174.5 (CONH), 175.2 (CONH), 175.3 (CO$_2$CH$_3$), 177.0 ppm (CO$_2$H); MALDI-TOF: m/z calcd: 5575 [M^+ – Cl]; found: 5573.

Neutral (outside octacarboxylate) tetra-Ru^{II}-metallodendrimer (23): To a solution of acid dendrimer **22** (54.4 mg, 10.2 μmol) in MeOH and H_2O, was added KOH (573 μg, 10.2 μmol) in H_2O (20 mL). The workup exactly followed that of **19** to give the desired neutral metallodendrimer **23** (50.1 mg, 87%) as a red solid: ^{1}H NMR (CD_3OD): $\delta = 1.29$ (m, 8H; CH_2CH$_2$CH$_2$Otpy), 1.72 (m, 24H; CH_2CH$_2$CH_2CH$_2$Otpy, tpyOCH$_2$CH_2), 1.83 (m, 8H; CH_2CH$_2$OH), 2.06 (m, 48H; C$^{4'}$CH_2CH$_2$CO$_2$, C$^{4'}$CH_2CH$_2$CONH, CH_2CH$_2$CH$_2$OH), 2.34 (m, 56H; CH_2CONH, C$^{4'}$CH$_2$CH_2CO$_2$, C$^{4'}$CH$_2$CH_2CONH), 3.31 (s, 8H; C$^{4'}$CH_2OCH$_2$), 3.35 (s, 8H; CONHCH_2), 3.60 (m, 16H; C$^{4'}$CH$_2$OCH_2, CH_2OH), 3.61 (s, 24H; CH_3), 4.62 (brs, 16H; CH_2Otpy), 7.27 (dd, 16H; $J = 5.0$ Hz, tpy$H_{5,5''}$), 7.52 (d, $J = 7.5$ Hz, 16H; tpy$H_{6,6''}$), 7.98 (dd, $J = 7.9$ Hz, 8H; tpy$H_{4,4''}$), 8.64 (s, 16H; tpy$H_{3',5'}$), 8.75 ppm (dd, $J = 4.2$ Hz, 16H; tpy$H_{3,3''}$); ^{13}C NMR (CD_3OD): $\delta = 24.5$ (NHCH$_2$CH$_2$CH_2), 25.8 (CH_2CH$_2$OH), 27.8 (tpyOCH$_2$CH_2), 29.2 (CH_2CO$_2$), 29.7 (C$^{4'}$CH$_2$CH$_2$CONH), 30.2 (CH$_2$CH$_2$OPy), 30.5 (CH$_2$CH$_2$CO$_2$), 31.4 (OCH$_2$CH$_2$CH$_2$CONH), 32.4 (CONHCH$_2$CH_2), 33.6 (CH$_2$CH$_2$CH$_2$OH), 35.7 (C$^{4'}$CH$_2$CH$_2$CONH), 38.2 (OCH$_2$CH$_2$CONH), 40.3 (CONHCH$_2$), 46.5 (C$^{4'}$), 52.3 (CO$_2$CH$_3$), 58.7, 59.4 (CONHC), 63.3 (CH$_2$OH), 68.9 (OCH$_2$CH$_2$CONH), 70.6 (CCH$_2$O), 71.3 (tpyOCH$_2$), 112.4 (tpy$C_{5,5''}$), 125.9 (tpy$C_{4,4''}$), 128.8 (tpy$C_{3,3''}$), 139.1 (tpy$C_{3',5'}$), 153.4 (tpy$C_{6,6''}$), 157.8 (tpy$C_{2,2''}$), 159.9 (tpy$C_{2',6'}$), 167.7 (tpy$C_{4'}$), 173.9 (CONH), 174.1 (CONH), 175.4 (CONH), 175.4 (CO$_2$CH$_3$), 180.5 ppm (CO$_2^-$); MALDI-TOF: m/z calcd: 5357 [M^++K]; found: 5355.

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