Neutral highly branched metallomacromolecules: incorporation of a (2,2′:6′,2″-terpyridine)ruthenium(II) complex without external counterions

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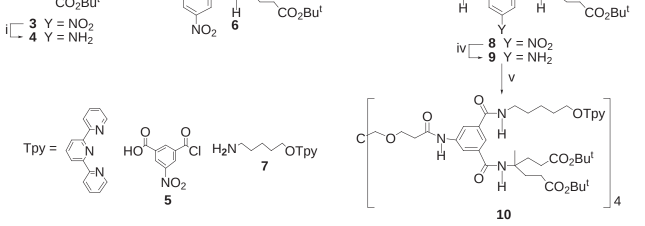
Neutral dendritic metallomacromolecules possessing four bis-terpyridine Ru^{II} linking sites with internal counter ions have been prepared and their electrochemical properties have been studied.

The assembly of highly branched metallomacromolecules has been reported, and they have been shown to possess interesting magnetic, electronic, electrochemical, photooptical and catalytic properties.[1] To the best of our knowledge, these assemblies all utilize external counter ions, *e.g.* Cl^-, BF_4^-, PF_6^-. We herein report the construction of two tiers of overall neutral, dendritic metallomacromolecules, **1** and **2**, which incorporate (2,2′:6′,2″-terpyridine)ruthenium(II) ([< Ru >]) complexes with internally counter balanced charges. The use of four [< Ru >] linkages generated a supramolecular construct of precise description, based on the structural analysis of its components, and the eight internal carboxylate ions balance the charges of these Ru^{II} centers.

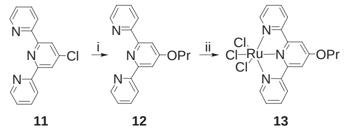
The core construct **10** was prepared from $EtNO_2$ with 2 equiv. of *tert*-butyl acrylate in liquid NH_3 affording (95%) di-*tert*-butyl 4-nitro-4-methylheptane-1,7-dioate **3**, which was converted (96%) to amine **4** by Raney Nickel reduction (Scheme 1).[2] Treatment of **4** with nitroisophthalic acid monochloride **5**[3] gave (58%) monocarboxylic acid **6**. Subsequent DCC coupling[4] of **6** with 5-aminopentyl 4′-(2,2′:6′,2″-terpyridinyl) ether[5] **7** generated **8** (92%), which was reduced[6] with 10% Pd-C and ammonium formate to afford the desired monomer **9** (90%). Treatment of **9** (4 equiv.) with a tetraacyl chloride core in the presence of Et_3N gave **10** (67%) possessing eight easily hydrolyzed *tert*-butyl ester moieties. All components were characterized by ^1H NMR, ^{13}C NMR, IR and elemental analyses, and ESI-MS.

4′-Chloro-2,2′:6′,2″-terpyridine **11**[7] was heated with PrOH and powdered KOH in DMSO[5] to give (93%) propyl 4′-(2,2′:6′,2″-terpyridinyl) ether **12**, which was refluxed with $RuCl_3{\cdot}3H_2O$ in EtOH to afford (89%) the unbranched **13** (Scheme 2). The surface branching, amine **15**[8] was coupled with 4-[4′-oxa-(2,2′:6′,2″-terpyridinyl)]butanoic acid[5] **16** to afford **17** (86%), which was similarly transformed (84%) with $RuCl_3{\cdot}3H_2O$ to give appendage **18** (Scheme 3). Both **13** and **18** were used without further purification due to their extremely low solubility in most organic solvents; fortunately, their purity was confirmed by elemental analyses and the analyses of the resultant assemblies.

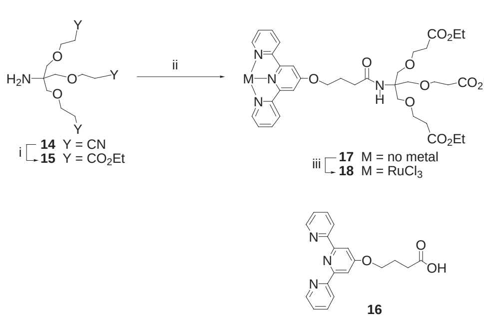
Core **10** (1 equiv.) was refluxed with 4 equiv. of either **13** or **18** in EtOH in the presence of 4-ethylmorpholine, as reducing agent, to assemble **19** (93%) or **21** (96%), respectively (Scheme 4). Although **13** and **18** possessed limited initial solubility, they dissolved upon addition of the reducing agent to give the characteristic deep-red color of the [< Ru >] complex. After



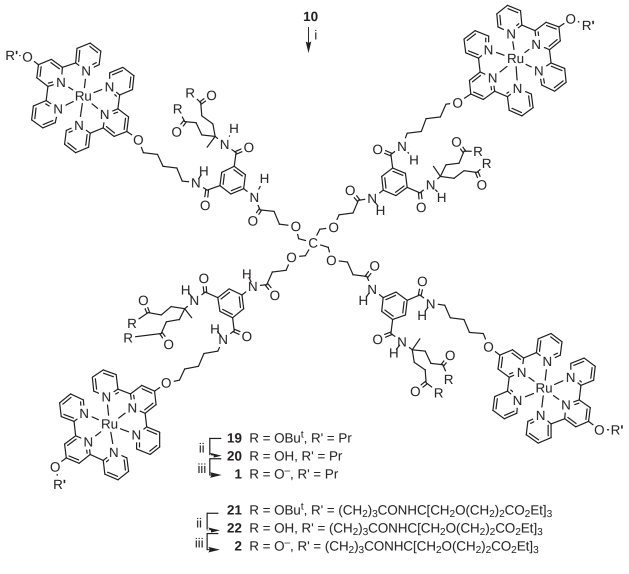
Scheme 1 *Reagents and conditions*: i, Raney nickel, H_2, 4 atm., 12 h, 25 °C; ii, **5**, Et_3N, THF, 12 h, −5 °C; iii, **7**, DCC, 1-HOBT, DMF, 24 h, 25 °C; vi, 10% Pd on C, HCO_2NH_4, MeOH, 30 min, 50 °C; v, Et_3N, $C[CH_2OCH_2CH_2COCl]_4$, THF, 12 h, 25 °C.



Scheme 2 *Reagents and conditions*: i, PrOH, KOH, DMSO, 24 h, 60 °C; ii, $RuCl_3{\cdot}3H_2O$, Et_3OH, 4 h, reflux.



Scheme 3 *Reagents and conditions*: i, HCl, EtOH, 6 h, reflux; ii, **16**, DCC, 1-HOBT, DMF, 24 h, 25 °C; iii, $RuCl_3{\cdot}3H_2O$, EtOH, 6 h, reflux.



Scheme 4 *Reagents and conditions*: i, **13** (→**19**) or **18** (→**21**) (4 equiv.), 4-ethylmorpholine, EtOH, 6 h, reflux; ii, HCO_2H, 6 h, 25 °C; iii, KOH, H_2O–MeOH, dialysis, 24 h, 25 °C.

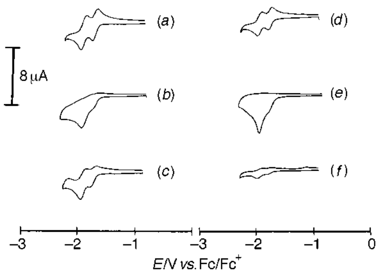


Fig. 1 CV responses for 1.0 mM solutions of (*a*) **21**, (*b*) **22**, (*c*) **2**, (*d*) **19**, (*e*) **20**, and (*f*) **1** (the smaller current observed was due to the limited solubility of **1** that presented in DMF) in Et_4NBF_4 (0.1 M) in DMF at 25 °C; scan rate 200 mV s^{-1}.

dialysis, the desired constructs were supported by the significant downfield shift (^{13}C NMR) of all terpyridine carbons. The *tert*-butyl groups were removed from **19** or **21** by treatment with formic acid,[9] affording complexes **20** (98%) or **22** (97%), respectively. The characteristic downfield shift of ^{13}C NMR ($\Delta\delta$ = 4 ppm) of the carbonyl carbon supports the transformation; the retention of the external alkyl ester moieties was evidenced by the presence of the ethyl signals. Final neutral complexes **1** (92%) or **2** (97%) were formed by addition of a slight excess of KOH into a H_2O–MeOH solution of **20** or **22**. After dialysis, the desired neutral complexes **1** and **2** were analyzed (0.00% of Cl), and only one downfield shift ($\Delta\delta$ = 3.4 ppm for **1** and 4.2 ppm for **2**) for the internal acid carbonyl carbon supports the formation of the carboxylate carbon centers. The UV–VIS spectra of the macromolecules possessing the four [< Ru >] linkages are analogous to related systems.[5,10] All the intermediate molecules and final complexes exhibit correct molecular weights. MALDI-TOF mass spectra of **19** and **21** exhibited low sensitivity and broad signals with all attempted matrices.

Electrochemical experiments with these metallodendrimers gave further insight to their electrocatalytic potential. Fig. 1(*a*) shows the two reversible waves that characterize the cathodic CV response of the two terpyridine ligands of **21**[11]. After internal deprotection of the *tert*-butyl groups, the presence of the carboxylic acid moieties in **22** results in a merging of the two redox waves and the virtual disappearance of the corresponding anodic signal [Fig. 1(*b*)]. Based on previous studies of the electrochemical reduction of pyridine and its derivatives,[12] the observed irreversibility is due to an electrochemical–chemical reaction in which a proton from the vicinal carboxylic acid group quenches the aromatic anion radical resulting in a probable 1,4-reduction of one of the pyridine rings of each terpyridine ligand. This explanation is further supported by CV experiments with neutral dendrimer **2**; as seen in Fig. 1(*c*), the lack of neighboring acidic protons, readily available in **22**, results in the recovery of the typical ‘two wave’ reversible response of the terpyridine ligands.

CV experiments on the first tier dendrimer series **19**, **20** and **1** showed similar voltammetric responses to those discussed above. By careful inspection of Table 1, however, the second tier assemblies **21** and **2** show slightly larger ΔE_p values than those corresponding to the first tier series **19** and **1**. This observation is in perfect agreement with previous reports[13] and has been attributed to the slower electron transfer kinetics that characterizes molecules featuring bulkier dendritic structures around their electroactive sites.

Table 1 CV data for **1**, **2**, **19**–**22**

Compound	Terpyridines $E_{1/2}$/V (ΔE_p/V)^a	 $E_{1/2}$/V (ΔE_p/V)^a	Ru^{III}/Ru^{II} $E_{1/2}$/V (ΔE_p/V)^a
19	−1.945 (0.082)	−1.759 (0.068)	0.627 (0.073)
20	I^b	I^b	0.629 (0.057)
1	−1.950 (0.072)	−1.788 (0.077)	0.624 (0.059)
21	−1.950 (0.086)	−1.751 (0.088)	0.640 (0.100)
22	I^c	I^c	0.627 (0.097)
2	−1.935 (0.102)	−1.767 (0.106)	0.634 (0.089)

^{a} *E*/V *vs.* Fe/Fe$^+$. Same conditions as those described in Fig. 1. ^{b} Irreversible cathodic peak at −1.945 V. ^{c} Irreversible cathodic peak at −1.968 V.

In summary, we have constructed $[<\mathrm{Ru}>]_4$ dendrimers possessing an overall neutral charge. The loss of external counterions in these metallomacromolecules had a marginal effect on their spectra, as well as stability and physical properties. However, the solubilities of these neutral species decreased in polar solvents, such as MeOH and H_2O. Complexes **19–22** are all slightly soluble in H_2O, whereas, **1** and **2** are insoluble in H_2O. The neutral metallodendrimers have internally balanced carboxylates, which are weaker counter ions than most others like Cl^-, NO_3^- and PF_6^-. Thus, addition of inorganic salts to these neutral species allows convenient interchange between external counter ions. Notably, **1** and **2** are not soluble in DMF, but quickly go into solution upon addition of salts like BF_4^- or PF_6^-. Another important aspect is that these neutral metallomacromolecules were more easily ionized (*i.e.* lower laser power) and gave stronger signals in MALDI-TOF mass spectrometry in comparison to the *tert*-butyl and acid metallodendrimers possessing external Cl^- or PF_6^- counter ions. The observed intramolecular proton transfer during the redox process stands to give insight into the potential chemistry within such macromolecular constructs.

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Notes and references

† All new compounds exhibited satisfactory spectral, elemental and mass data.

‡ *Selected data* for **1**: $C_{233}H_{240}N_{36}O_{40}Ru_4$; *M* = 4589.0; mp > 230 °C (decomp.); Found: C, 60.61; H, 5.45; N, 10.23; Cl, 0.00; requires: C, 60.98; H, 5.27; N, 10.99; Cl, 0.00%; *m/z* (MALDI-TOF, IAA matrix) 4590 [M + H$^+$].

For **2**: $C_{313}H_{372}N_{40}O_{80}Ru_4$; *M* = 6378.9; mp > 210 °C (decomp.); Found: C, 58.49; H, 5.86; N, 8.71; Cl, 0.00; requires: C, 58.94; H, 5.88; N, 8.78; Cl, 0.00%; *m/z* (MALDI-TOF, IAA matrix) 6381 [M + H$^+$].

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