

Spirometallo dendrimers: terpyridine-based intramacromolecular cyclization upon complexation

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The first examples of metallo dendritic spiranes have been obtained via incorporation of single terpyridine units within each dendritic quadrant.

Dendrimers are of special interest in macromolecular chemistry due to interesting utilitarian properties resulting from their well-defined parameters.¹ In particular, the highly branched metallo dendrimers² have been investigated for their magnetic, electronic, photooptical, and catalytic properties.³ Herein, we report the construction of new dendrons containing 2,2':6',2''-terpyridine units, their assembly into dendrimers, and subsequent intramacromolecular metalocyclization resulting in the corresponding bis-terpyridine Ru(II) complexes {-(Ru)-}. Similar architectures have been crafted using transition metal coordination at the spirane junction for investigation as molecular motors⁴ and muscles.⁵

Synthesis of the 1st generation dendron **3** was achieved by treatment of 1-amino-4'-*O*-terpyridinylpentane⁶ with 1 equivalent of acryloyl chloride (Et₃N, THF) to give the corresponding acrylamido analogue, which after Michael addition with CH₃NO₂ (Triton B) afforded the nitro-terpyridine as confirmed (¹³C NMR) by the appearance of a new peak for primary CNO₂ at 74.5 ppm. Treatment of this precursor with a slight excess of *tert*-butyl acrylate (Triton B, CHCl₃, 25 °C, 24 h) gave the nitro functionalized dendron, which was supported by the appearance of the chemical shift for CNO₂ at 92.3 ppm, followed by reduction with Raney-Ni (EtOH, 40 °C) to afford the corresponding desired amine **3**. Characterization included an upfield chemical shift (¹³C NMR) for the C^{4'} from 92.3 to 52.3 ppm; the molecular peak *m/z* 677.82 [M + H⁺] (calcd *m/z* 677.87 [M + H⁺]) in ESI-MS further supported the assignment.

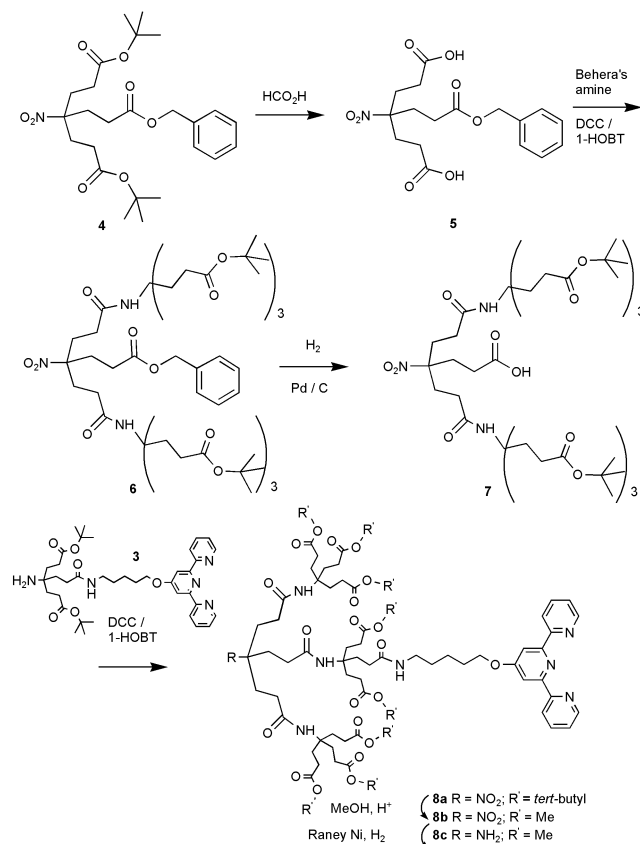
The larger dendron **8** (Scheme 1) was obtained starting with the addition of benzyl acrylate to CH₃NO₂ [di(isopropyl)ethylamine] to afford the initial benzyl γ -nitrobutanoate, which was then treated with *tert*-butyl acrylate (Triton B, THF, 25 °C, 16 h) to afford the 2:1 functionally differentiated triester **4**. The structure was confirmed by the appearance of a chemical shift (¹³C NMR) for the C^{4'} at 91.9 ppm and the molecular ion peak at *m/z* 480.43 [M + H⁺] (calcd *m/z* 480.58 [M + H⁺], ESI-MS). Hydrolysis of *tert*-butyl groups (HCO₂H, 25 °C, 24 h) afforded the corresponding diacid **5** supported by disappearance (¹³C NMR) of *tert*-butyl peaks and appearance of a signal for the acid carbonyl group (C=O) at 173.3 ppm. Treatment of **5** with Behera's amine^{7,8} (DCC, DMF, 25 °C, 24 h) gave the bisamide **6** supported by the downfield shift (¹³C NMR) of the signal at 52.9 to 57.4 ppm attributed to the C^{4'}NHCO moiety. Monoacid **7** was then obtained by hydrogenolysis (Pd/C, MeOH, 25 °C, 24 h) and was confirmed (¹³C NMR) by the disappearance of benzyl absorption and the formation of a new peak at 174.0 ppm corresponding to the new CO₂H group and the molecular peak at *m/z* 1073.35 [M + H⁺] (calcd *m/z* 1073.33 [M + H⁺]) in ESI-MS.

Reaction of hexaester **7** with amine **3** (DCC, DMF, 25 °C, 24 h) gave the nitro *tert*-butyl ester **8a** as confirmed by the formation of a new peak at 170.5 ppm for the new amide carbon. Failure to reduce (Raney-Ni, EtOH) the nitro moiety in **8a** prompted its transesterification (cat. H₂SO₄, MeOH, 60 °C, 24 h). The corresponding methyl ester **8b** was subsequently

identified by the presence of a new methyl peak at 51.5 ppm, as well as the complete disappearance of *tert*-butyl markers. Reduction of the nitro moiety (Raney-Ni, EtOH, 120 psi, 40 °C, 48 h) gave the desired amine **8c**, which is supported (¹³C NMR) by the chemical shift for C^{4'} from 92.9 to 53.6 ppm, confirming the desired C^{4'}NO₂ to C^{4'}NH₂ transformation and the molecular peak (MALDI-TOF⁹) at *m/z* 1386.27 [M + Na⁺] (calcd *m/z* 1386.54 [M + Na⁺]).

First and 2nd generation dendrimers were accessed via treatment of dendrons **3** and **8c**, respectively, with 6,6-bis(carboxy-2-oxabutyl)-4,8-dioxaundecane-1,11-dicarboxylic acid¹⁰ (DCC, DMF, 25 °C, 72 h). Their spectra (¹³C NMR) exhibited the expected downfield shift [52.3 (**3**) and 53.5 ppm (**8c**) to 57.0 (G1) and 56.9 ppm (G2)] for the signals assigned to the new C^{4'}NHCO corroborating amidation and the peaks (MALDI-TOF) at *m/z* 3077.14 [M + Na⁺] (calcd 3077.72 [M + Na⁺]) for G1 and *m/z* 5829.17 [M + Na⁺] (calcd 5829.51 [M + Na⁺]) for G2.

Treatment of each generation with two equivalents of RuCl₃·3H₂O (EtOH, *N*-ethylmorpholine) followed by addition of excess NH₄PF₆ afforded, after chromatography, the bis-Ru(II) spirometallo dendrimers **1a** (41%) and **2** (47%), respectively (Fig. 1). The absence of any free terpyridine moiety, the observed downfield shift of all terpyridine carbons as well as



Scheme 1

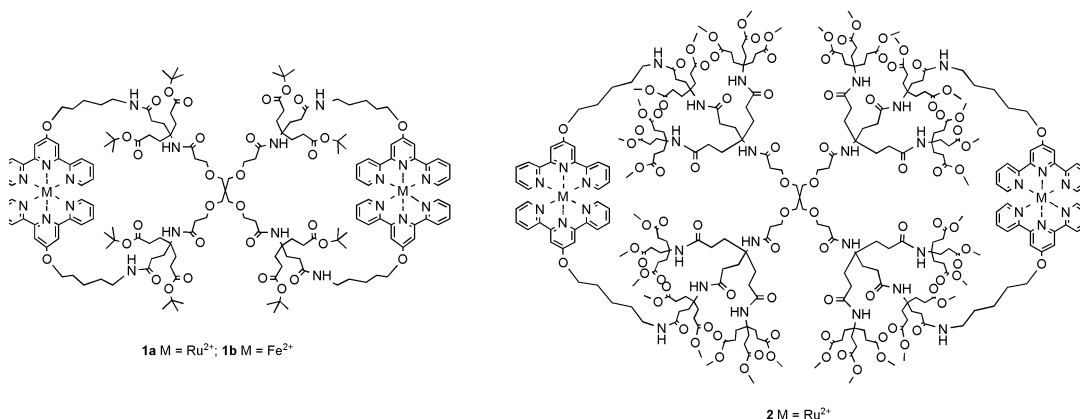


Fig. 1 Bis-Ru(II) spiro metallo dendrimers **1a** and **2**.

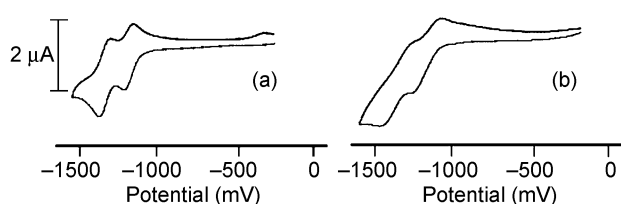


Fig. 2 CV response of 0.1 mM solutions of the spiro metallo dendrimers. (a) **1a** and (b) **2** (0.1 M Et₄N⁺TFB⁻, DMSO, 25 °C; scan rate 200 mV s⁻¹).

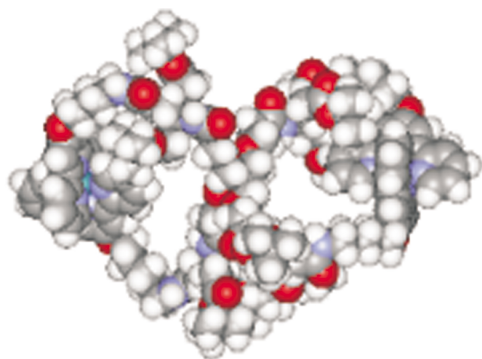


Fig. 3 Space-filling representation of the minimized structure of the spiro metallo dendrimer **1**.

the assignable, symmetric ¹³C NMR spectra and MALDI-TOF mass spectra (molecular peaks at m/z 3691 [M - PF₆]⁺ for **1a** and m/z 3186 [M - 2PF₆]²⁺ for **2**) supported the assigned intramolecular-based structures. Four major absorption bands (λ_{\max} ; 242, 267, 306, 486 nm) were observed for these [-<Ru>-] connected metallo dendrimers; the molar absorptivities (ϵ) of the complexes **1a** and **2** have similar values and are indicative of two molecular assemblies possessing the same number of [-<Ru>-] moieties. Notably, the molar absorptivities $\epsilon = 3.55 \times 10^4$ and 3.45×10^4 dm³ mol⁻¹ cm⁻¹ for **1a** and **2** ($\lambda_{\max} = 486$ nm) are *ca.* two times as strong as Constable's mono Ru(II) complex.¹¹

The cyclic voltammograms of both **1a** (a) and **2** (b) (Fig. 2) were similar and exhibited two quasi-reversible waves at negative potentials corresponding to redox processes on two electroactive terpyridine groups.¹²

Molecular modelling (Fig. 3) of the spiro dendrimer **1** revealed an open structure. The metal to metal distance is estimated to be 25.76 Å and center carbon to metal distance to be 13.38 Å. The overall longest distance is about 34.5 Å.

Additional supporting evidence of the facile intramolecular cyclization was obtained by reacting the 1st tier tetra terpyridyl dendrimer with two equivalents of FeCl₂·4H₂O to give (92%) the pure, corresponding Fe-spiro dendrimer **1b** (MALDI-TOF m/z 3301.2 for [M + 4Cl]; calcd 3301.4). The higher yield presumably results from not having to reduce the Fe(II) rather than the complexation, reduction, and cyclization for Ru(III).

In summary, these examples of macromolecular ring closures are anticipated to provide entrance to dendrimer-based molecular devices *via* the incorporation of differing metals, ligands, and metal oxidation states.

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