Metallomicellanols: Incorporation of Ruthenium(II)–2,2′ : 6′,2″-Terpyridine Triads into Cascade Polymers

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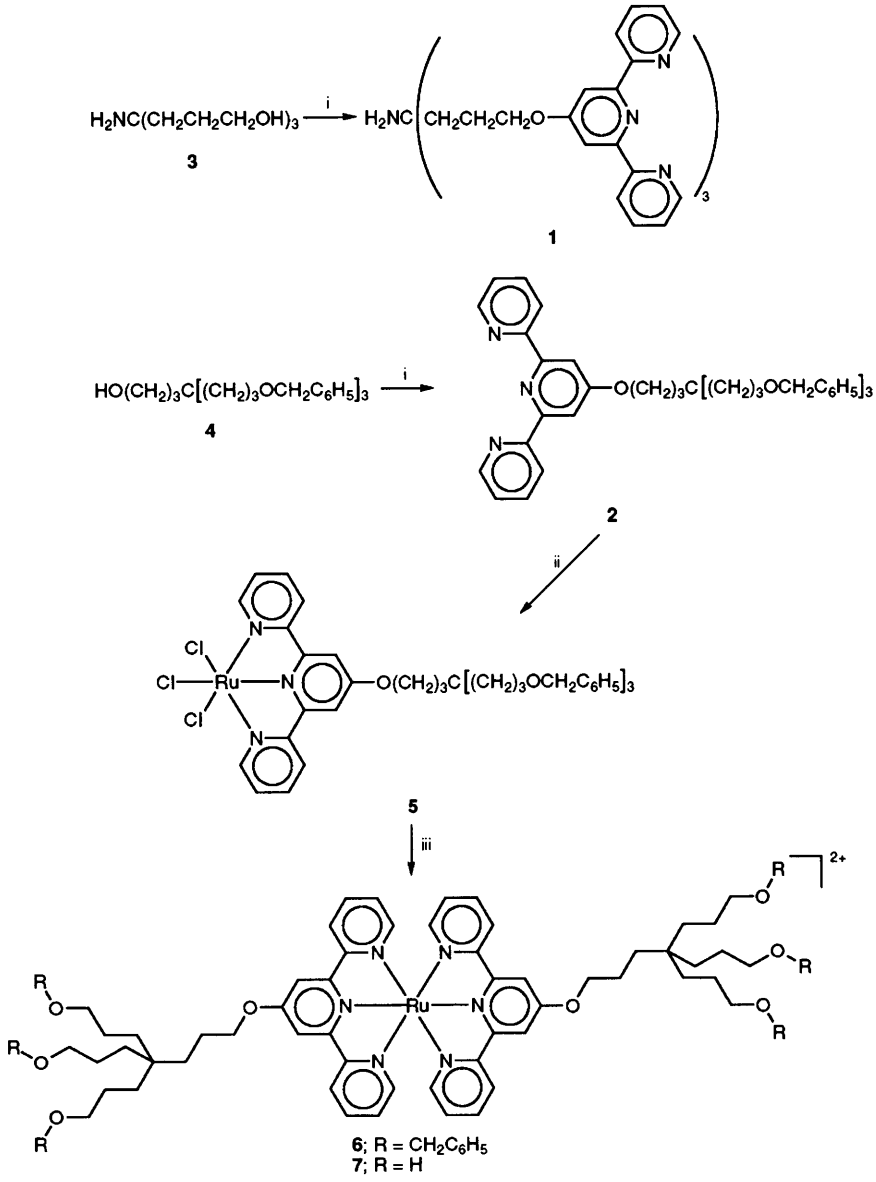
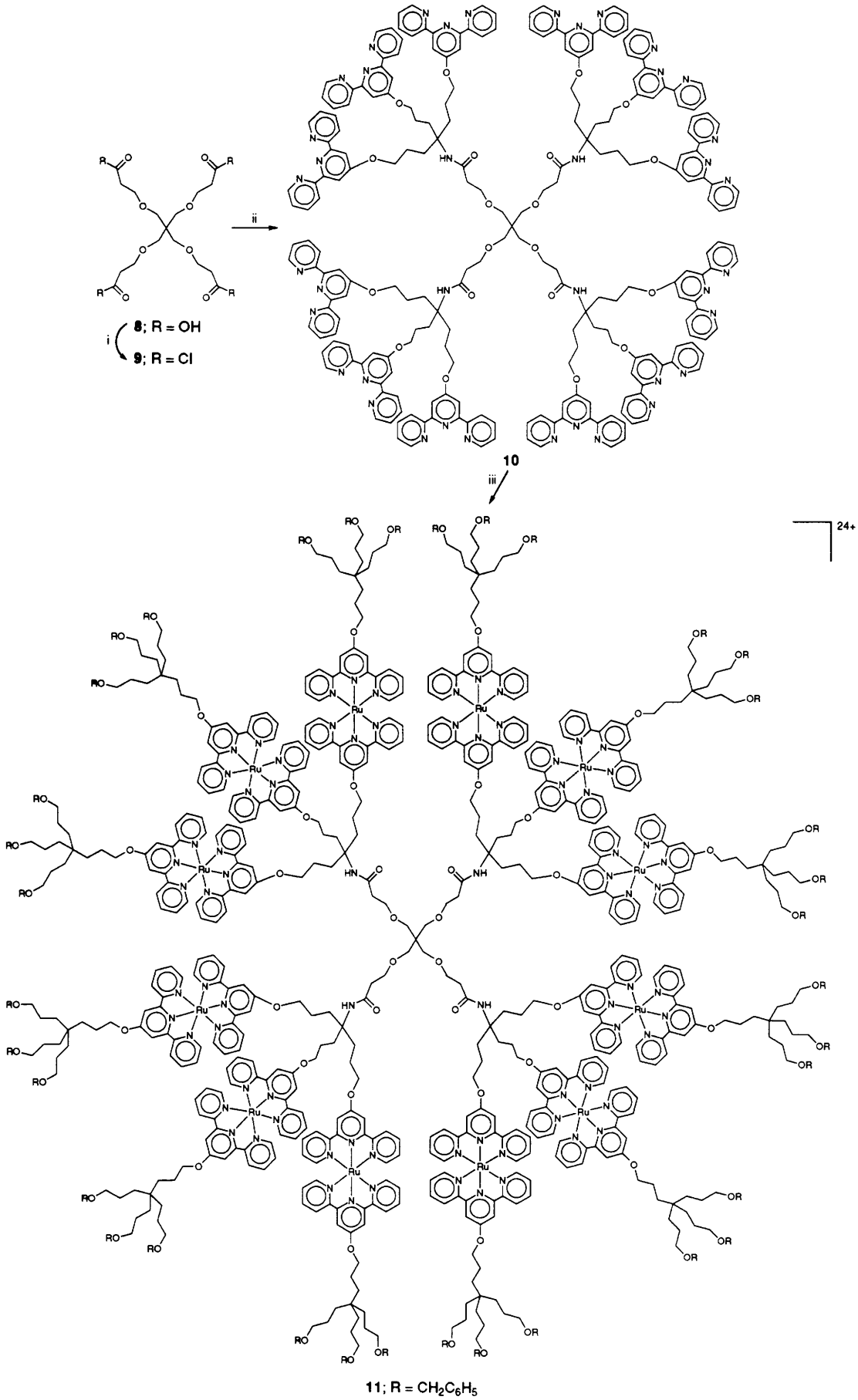
Facile alkoxylation of 4′-chloro-2,2′ : 6′,2″-terpyridine with the mono- and tri-hydroxylic cascade (dendritic) building blocks, 4-(3-hydroxypropyl)-4-(3-benzyloxypropyl)-1,7-bis(benzyloxy)heptane **4** and 4-amino-4-(3-hydroxypropyl)heptane-1,7-diol **3**, has allowed the synthesis of a dodecaruthenium macromolecule **11** employing ligand–metal–ligand connectivity.

The construction of most cascade macromolecules has relied on heteroatom connectivity[1] with several notable exceptions.[2] Thus, in our quest of new supramolecular systems, we have created a new family of multifunctional molecules possessing a predetermined spherical morphology which utilizes an octahedral or pseudooctahedral ruthenium(II) metal centre coordinated to two different orthogonal 2,2′ : 6′,2″-terpyridines (tpy) [Ru^{II}(Ytpy)(Xtpy)][3] to build the arms of the cascade polymer. Such technology permits the placement of multiple, heteroleptic metal complexes at predetermined



Scheme 1 *Reagents and conditions*: i, Cltpy, KOH, DMSO, 60 °C, 20 h; ii, $RuCl_3 \cdot 3H_2O$, absolute EtOH, reflux, 20 h; iii, *N*-ethylmorpholine, MeOH, reflux, 2 h



Scheme 2 *Reagents and conditions*: i, $SOCl_2$, CH_2Cl_2, 45 °C, 13 h; ii, Et_3N, **1** (4 equiv.), 25 °C, 3 days; iii, *N*-ethylmorpholine, **5** (15 equiv.), MeOH, reflux, 1.5 h

internal sites within the hydrophilic-surfaced Micellane framework.[4]

The key building blocks, amine **1**† and tpy **2**,† were prepared by the treatment of triol[5] **3** and alcohol[2] **4**, respectively, with 4′-chloro-2,2′:6′,2″-terpyridine (Cltpy)[6] in the presence of solid KOH in anhydrous dimethyl sulfoxide (DMSO) (Scheme 1). The ^{13}C NMR spectra for **1** and **2** show the expected shift of the peak for the 4′-carbon from δ 146.1 to 167.1 denoting the successful formation of the ethereal bond. The addition of 1 equiv. of **2** with $RuCl_3 \cdot 3H_2O$ in boiling ethanol gave (72%) the orange microcrystalline, paramagnetic complex **5**, which was used without further purification owing to its limited solubility. In order to test the facility of the coupling procedure, this ruthenium(III) complex **5** was treated with 1 equiv. of ligand **2** in boiling methanol and *N*-ethylmorpholine, as the reducing agent, then after a brief period of reflux, the solution was filtered hot and an excess of NH_4PF_6 was added to give the homoleptic complex **6**.† Although the NMR data for **6** fit with the general ranges previously delineated, the downfield shift (Δ +0.32 ppm comparative to ligand **2**; ^1H NMR) for the CH_2Otpy protons was greater than anticipated, whereas the upfield shift (Δ −1.41 ppm) for 6-H was at the upper range. As noted the delicate balance of positive charge upon coordination, juxtaposition of pyridine rings and unknown anisotropic effects caused by the metal centre, limit assignment predictability. Upon removal of the benzyl protecting groups, this red, microcrystalline complex is the precursor to the corresponding two-directional arborol **7**.

The carboxylic acid **8**, core for the construction of a four-directional cascade series,[7] was transformed by careful treatment with redistilled $SOCl_2$ in CH_2Cl_2 to the corresponding acyl chloride **9**, which, without further purification, was dissolved in anhydrous CH_2Cl_2 containing an excess of Et_3N and carefully added to 4 equiv. of amine **1** to afford (73%) the dodeca(tpy) **10**,† as a white solid. The ^{13}C NMR spectrum of **10** confirmed the amidation by the presence of peaks attributed to both components and the observation of the expected downfield shift (from δ 52.2 to 58.0) of the signal assigned to newly introduced quaternary carbon moiety (CONH*C*). Treatment of **10** with 15 equiv. of complex **5** generated (76%) the red crystalline dodecaruthenium heteroleptic complex **11**.† The symmetry and simplified spectral data for **11** support the assigned structure. The ^{13}C NMR spectrum was most useful structure verification due to significant broadening of signals in the ^1H NMR spectrum. Peak broadening was observed for the carbon resonances also, however it was not as pronounced. Characteristic absorptions (^{13}C NMR) evidencing cascade complex formation include δ 22.9 (CH_2CH_2Otpy^{ext}), 23.5 ($CH_2CH_2OCH_2C_6H_5$), 25.5 (CH_2CH_2Otpy^{int}), 32.5 ($CH_2CH_2CH_2O^{ext}$) and 36.6 (*C*-quat.^{ext}).

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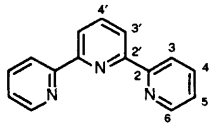
† All new compounds gave consistent spectral and analytical data. ^1H and ^{13}C NMR data were obtained on a Brüker 360 MHz AMX NMR spectrometer using $CDCl_3$ as the solvent and $SiMe_4$ as the reference (^1H NMR); Superscripts ext and int refer to external and internal moieties, respectively. *Selected NMR data* for new compounds: **1** ^1H NMR δ 1.66, 1.92 (2 m, $CH_2CH_2CH_2O$, 12 H), 2.59 (s, NH_2, 2 H), 4.28 (t, CH_2O, *J* 6.1 Hz, 6 H), 7.28 (t, 5-H, *J* 4.3 Hz, 6 H), 7.80 (t, 4-H, *J* 6.1 Hz, 6 H), 8.01 (s, 3-H, 6 H), 8.58 (d, 3-H, *J* 7.9 Hz, 6 H), 8.67 (d, 6-H, *J* 4.0 Hz, 6 H); ^{13}C NMR δ 23.4 (CH_2CH_2O), 36.3 ($CHCH_2CH_2O$), 52.9 (H_2NC), 68.4 (CH_2O), 107.4 (C-5), 121.3 (C-4), 123.7 (C-3), 136.6 (C-3′), 149.0 (C-6), 156.2 (C-2), 157.0 (C-2′), 167.1 (C-4′); **2** ^1H NMR δ 1.10–1.85 [m, $C(CH_2CH_2)_4$, 16 H], 3.41 (t, $CH_2OCH_2C_6H_5$, *J* 6.5 Hz, 6 H), 4.16 (t, CH_2Otpy, *J* 6.1 Hz, 2 H), 4.48 (s, $CH_2C_6H_5$, 6 H), 7.32 (m, C_6H_5, 5-H, 17 H), 7.83 (t, 4-H, *J* 7.9 Hz, 2 H), 8.01 (s, 3′-H, 2 H), 8.59 (d, 3-H, *J* 7.9 Hz, 2 H), 8.67 (d, 6-H, *J* 4.0 Hz, 2 H); ^{13}C NMR δ 23.0 (CH_2CH_2Otpy), 23.6 ($CH_2CH_2OCH_2C_6H_5$), 32.6 [$C(CH_2)_4$], 36.6 (C-quat.), 68.9 (CH_2Otpy), 71.2 ($CH_2OCH_2C_6H_5$), 72.9 ($CH_2C_6H_5$), 107.5 (C-5), 121.4 (C-4), 123.8 (C-3), 136.8 (C-3′), 148.9 (C-6), 156.1 (C-2), 157.0 (C-2′), 167.3 (C-4′), 127.4, 127.6, 128.3, 138.7 (C_6H_5); **6** ^1H NMR δ 1.20–1.95 [m $C(CH_2CH_2)_4$, 32 H], 3.46 (t, $CH_2OCH_2C_6H_5$, *J* 6.1 Hz, 12 H), 4.48 (br s, $CH_2C_6H_5$, CH_2Otpy, 16 H), 7.03 (t, 5-H, *J* 7.6 Hz, 4 H), 7.26 (m, C_6H_5, 6-H, 34 H), 7.61 (t, 4-H, *J* 7.6 Hz, 4 H), 8.07 (s, 3′-H, 4 H), 8.20 (d, 3-H, *J* 7.9 Hz, 4 H); ^{13}C NMR δ 22.8 (CH_2CH_2Otpy), 23.5 ($CH_2CH_2OCH_2C_6H_5$), 32.3 [$CH_2(CH_2)_2$Otpy], 32.5 [$C(CH_2)_3$], 36.5 (C-quat.), 70.8 (CH_2Otpy), 71.2 ($CH_2OCH_2C_6H_5$), 72.8 ($CH_2C_6H_5$), 110.8 (C-5), 124.1 (C-4), 127.6 (C-3), 137.5 (C-3′), 151.8 (C-6), 155.7 (C-2), 157.8 (C-2′), 166.0 (C-4′), 127.3, 127.5, 128.2, 138.5 (C_6H_5); **10** ^1H NMR δ 0.80–2.50 [m, CH_2CONH, $C(CH_2CH_2)_3$, 56 H], 2.95–4.25 (m, CH_2OCH_2, CH_2Otpy, NH, 44 H), 7.00–8.80 (m, tpy-H, 120 H); ^{13}C NMR δ 23.3 (CH_2CH_2Otpy), 35.5 ($CH_2CH_2CH_2O$), 37.5 (CH_2CONH), 45.5 [$C(CH_2O)_4$], 58.0 (HNC-quat.), 68.2, 68.0 (CH_2OCH_2), 68.1 (CH_2Otpy), 107.4 (C-5), 121.2 (C-4), 123.7 (C-3), 136.6 (C-3′), 148.9 (C-6), 156.1 (C-2), 156.9 (C-2′), 167.0 (C-4′), 171.0 (C=O); **11** ^1H NMR δ 1.10–2.80 [m, CH_2CONH, $HNC(CH_2CH_2)_3$, $C(CH_2CH_2)_4$, 248 H], 3.47 [br s, $CH_2OCH_2C_6H_5$, $C(CH_2OCH_2)$, 88 H], 4.49 (br s, NH, $CH_2C_6H_5$, CH_2Otpy, 124 H), 6.70–8.65 (m, tpy-H, C_6H_5, 420 H); ^{13}C NMR δ 22.9 (CH_2CH_2Otpy^{ext}), 23.5 ($CH_2CH_2OCH_2C_6H_5$), 25.5 (CH_2CH_2Otpy^{int}), 32.2 ($CH_2CH_2CH_2O^{ext}$), 36.6 (C-quat.^{ext}), 67.9 (CH_2Otpy^{int}), 70.9 (CH_2Otpy^{ext}), 71.2 ($CH_2OCH_2C_6H_5$), 72.8 ($CH_2C_6H_5$), 110.7, 111.7 (C-5), 123.9, 124.5 (C-4), 127.4 (C-3), 137.3 (C-3′), 151.5, 152.4 (C-6) 155.7, 155.9 (C-2), 157.7, 158.4 (C-2′), 166.1, 166.7 (C-4′), 127.4, 127.6, 128.3, 138.6 (C_6H_5). Terpyridine spectral assignments were based on the following numbering scheme.



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