

Metallomicellanol: Incorporation of Ruthenium(II)–2,2':6',2''-Terpyridine Triads into Cascade Polymers

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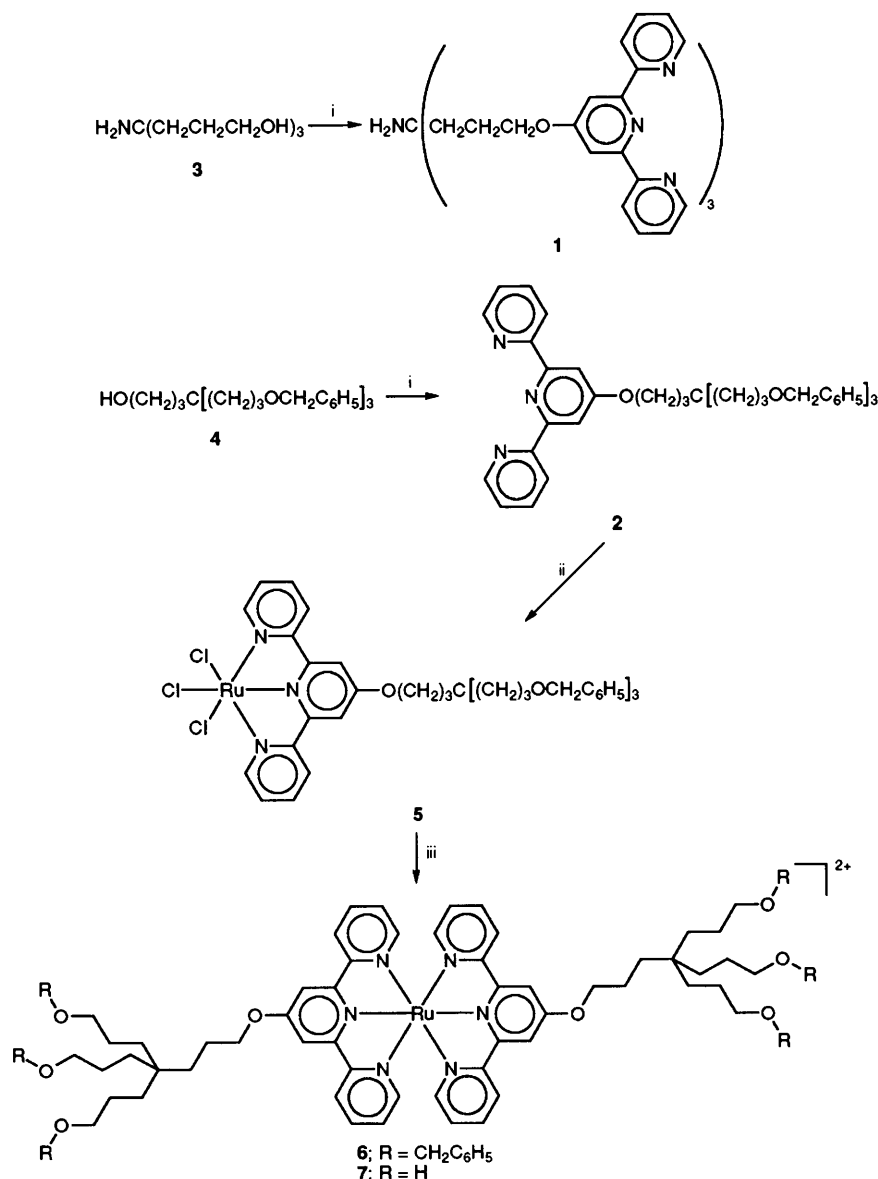
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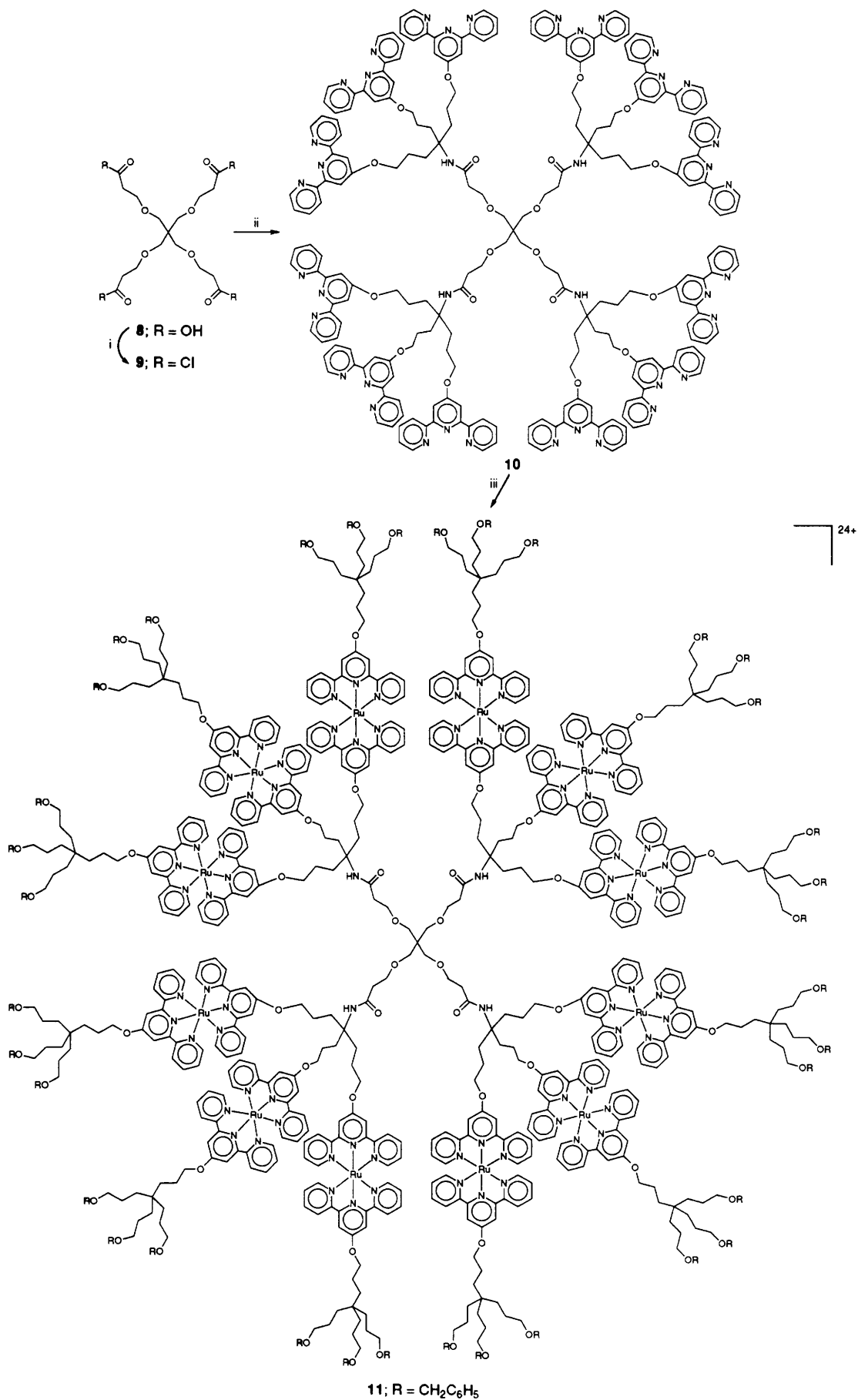
Facile alkoxylation of 4'-chloro-2,2':6',2''-terpyridine with the mono- and tri-hydroxylic cascade (dendritic) building blocks, 4-(3-hydroxypropyl)-4-(3-benzyloxypropyl)-1,7-bis(benzyloxy)heptane **4** and 4-amino-4-(3-hydroxypropyl)heptane-1,7-diol **3**, has allowed the synthesis of a dodecaruthenium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

The construction of most cascade macromolecules has relied on heteroatom connectivity¹ 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, RuCl₃·3H₂O, 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 triol⁵ **3** and alcohol² **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 ¹³C 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 RuCl₃·3H₂O 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

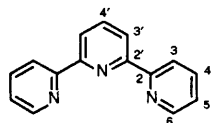
reflux, the solution was filtered hot and an excess of NH₄PF₆ was added to give the homoleptic complex **6**.[†] Although the NMR data for **6** fit with the general ranges previously delineated, the downfield shift (Δ +0.32 ppm comparative to ligand **2**; ¹H NMR) for the CH₂Otpy protons was greater 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 SOCl₂ in CH₂Cl₂ to the corresponding acyl chloride **9**, which, without further purification, was dissolved in anhydrous CH₂Cl₂ containing an excess of Et₃N and carefully added to 4 equiv. of amine **1** to afford (73%) the dodeca(tpy) **10**,[†] as a white solid. The ¹³C 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 (CONHC). 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 ¹³C 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 (¹³C NMR) evidencing cascade complex formation include δ 22.9 (CH₂CH₂Otpy^{ext}), 23.5 (CH₂CH₂OCH₂C₆H₅), 25.5 (CH₂CH₂Otpy^{int}), 32.5 (CH₂CH₂CH₂O^{ext}) and 36.6 (C-quar.^{ext}).

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[†] All new compounds gave consistent spectral and analytical data. ¹H and ¹³C NMR data were obtained on a Bruker 360 MHz AMX NMR spectrometer using CDCl₃ as the solvent and SiMe₄ 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, CH₂CH₂CH₂O, 12 H), 2.59 (s, NH₂, 2 H), 4.28 (t, CH₂O, *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); ¹³C NMR δ 23.4 (CH₂CH₂O), 36.3 (CHCH₂CH₂O), 52.9 (H₂NC), 68.4 (CH₂O), 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(CH₂CH₂)₄, 16 H], 3.41 (t, CH₂OCH₂C₆H₅, *J* 6.5 Hz, 6 H), 4.16 (t, CH₂Otpy, *J* 6.1 Hz, 2 H), 4.48 (s, CH₂C₆H₅, 6 H), 7.32 (m, C₆H₅, 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); ¹³C NMR δ 23.0 (CH₂CH₂Otpy), 23.6 (CH₂CH₂OCH₂C₆H₅), 32.6 [C(CH₂)₄], 36.6 (C-quar.), 68.9 (CH₂Otpy), 71.2 (CH₂OCH₂C₆H₅), 72.9 (CH₂C₆H₅), 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 (C₆H₅); **6** ¹H NMR δ 1.20–1.95 [m C(CH₂CH₂)₄, 32 H], 3.46 (t, CH₂OCH₂C₆H₅, *J* 6.1 Hz, 12 H), 4.48 (br s, CH₂C₆H₅, CH₂Otpy, 16 H), 7.03 (t, 5-H, *J* 7.6 Hz, 4 H), 7.26 (m, C₆H₅, 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); ¹³C NMR δ 22.8 (CH₂CH₂Otpy), 23.5 (CH₂CH₂OCH₂C₆H₅), 32.3 [CH₂(CH₂)₂Otpy], 32.5 [C(CH₂)₃], 36.5 (C-quar.), 70.8 (CH₂Otpy), 71.2 (CH₂OCH₂C₆H₅), 72.8 (CH₂C₆H₅), 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 (C₆H₅); **10** ¹H NMR δ 0.80–2.50 [m, CH₂CONH, C(CH₂CH₂)₃, 56 H], 2.95–4.25 (m, CH₂OCH₂, CH₂Otpy, NH, 44 H), 7.00–8.80 (m, tpy-H, 120 H); ¹³C NMR δ 23.3 (CH₂CH₂Otpy), 35.5 (CH₂CH₂CH₂O), 37.5 (CH₂CONH), 45.5 [C(CH₂O)₄], 58.0 (HNC-quar.), 68.2, 68.0 (CH₂OCH₂), 68.1 (CH₂Otpy), 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, CH₂CONH, HNC(CH₂CH₂)₃, C(CH₂CH₂)₄, 248 H], 3.47 [br s, CH₂OCH₂C₆H₅, C(CH₂OCH₂), 88 H], 4.49 (br s, NH, CH₂C₆H₅, CH₂Otpy, 124 H), 6.70–8.65 (m, tpy-H, C₆H₅, 420 H); ¹³C NMR δ 22.9 (CH₂CH₂Otpy^{ext}), 23.5 (CH₂CH₂OCH₂C₆H₅), 25.5 (CH₂CH₂Otpy^{int}), 32.2 (CH₂CH₂CH₂O^{ext}), 36.6 (C-quar.^{ext}), 67.9 (CH₂Otpy^{int}), 70.9 (CH₂Otpy^{ext}), 71.2 (CH₂OCH₂C₆H₅), 72.8 (CH₂C₆H₅), 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 (C₆H₅). Terpyridine spectral assignments were based on the following numbering scheme.



References

- G. R. Newkome and C. N. Moorefield, in *Advances in Dendritic Macromolecules*, ed. G. R. Newkome, JAI Press, Greenwich, Connecticut, 1993, in the press.
- G. R. Newkome, C. N. Moorefield, G. R. Baker, R. K. Behera and A. L. Johnson, *Angew. Chem.*, 1991, **103**, 1205; *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1176.
- E. C. Constable, A. M. W. Cargill Thompson, D. A. Tocher and M. A. N. Daniels, *New J. Chem.*, 1992, **16**, 855; E. C. Constable and A. M. W. Cargill Thompson, *J. Chem. Soc., Dalton Trans.*, 1992, 3467.
- Metallocellanoic acids: G. R. Newkome and C. N. Moorefield, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, 1993, **34**, 75.
- G. R. Newkome, C. N. Moorefield and K. J. Theriot, *J. Org. Chem.*, 1988, **53**, 5552; M. Broussard, B. Juma, F. R. Fronczek, S. F. Watkins, G. R. Newkome and C. N. Moorefield, *Acta Crystallogr., Sect. C*, 1991, **47**, 1245.
- E. C. Constable and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1990, 1405.
- G. R. Newkome and X. Lin, *Macromolecules* 1991, **24**, 1443.