

Five-component assembly of molecular loops†

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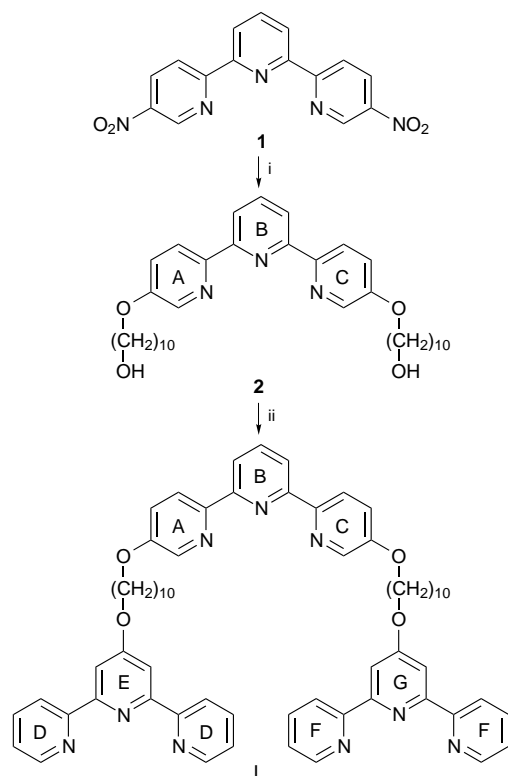
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The new tritopic ligand L contains three 2,2':6',2''-terpyridine (tpy) metal-binding domains and reacts with iron(II) salts to form a species of stoichiometry [Fe₃L₂]⁶⁺ which adopts a doubly looped (bow tie) structure.

Ligands containing multiple oligopyridine or 1,10-phenanthroline metal-binding domains are widely used in the metal-directed assembly of topologically and structurally novel supramolecules such as multiple helices, knots, boxes, grids and catenanes.¹ The majority of systems investigated to date have rigid or short flexible spacers between the metal-binding domains in order to limit the possibilities in conformational space. Here, we discuss the effect of introducing long flexible spacers.

Our target was molecule L which contains three 2,2':6',2''-terpyridine (tpy) metal-binding domains separated by a O(CH₂)₁₀O spacer. This was prepared in two steps from 5,5''-dinitro-2,2':6',2''-terpyridine **1** in 38% overall yield (Scheme 1). The reaction of **1** with an excess of decane-1,10-diol in Me₂SO in the presence of KOH gave **2** as a white solid in 50% yield.‡ Subsequent reaction of **1** with 2 equiv. of 4'-chloro-2,2':6',2''-terpyridine³ under the same reaction conditions gave L as a white crystalline solid‡ in 75% isolated yield. The free ligand L is highly symmetrical and the ¹H NMR



Scheme 1 Reagents: i, KOH, HO(CH₂)₁₀OH, Me₂SO; ii, 4'-chloro-2,2':6',2''-terpyridine, KOH, Me₂SO

spectrum clearly shows that rings A and C are equivalent, as are rings D and F, and rings E and G.

Ligand L contains three terdentate metal-binding domains and is expected to interact with six-coordinate metal centres. Whilst polymeric structures might be expected from an uncontrolled assembly process, the coding within the metal and ligand might be sufficient to lead to M₃L₂ species in which the 18 donors of two ligands are satisfied by three six-coordinate centres. A number of discrete M₃L₂ molecular species might be expected, including non-cyclic helical, catenated or looped structures (Fig. 1). Surprisingly, the reaction of L with 3 equiv. of FeCl₂·4H₂O in MeOH–CHCl₃ gave a single purple product which was obtained as the PF₆⁻ salt in 77% yield after recrystallisation from MeCN–thf–H₂O.

The stoichiometry [Fe₃L₂][PF₆]₆ was confirmed by microanalysis and the FAB mass spectrum exhibited peaks at *m/z* 2972 {Fe₃–L₂(PF₆)₅} and 2827 {Fe₃L₂(PF₆)₄}. The doubly looped structure is easily distinguished from double helical and

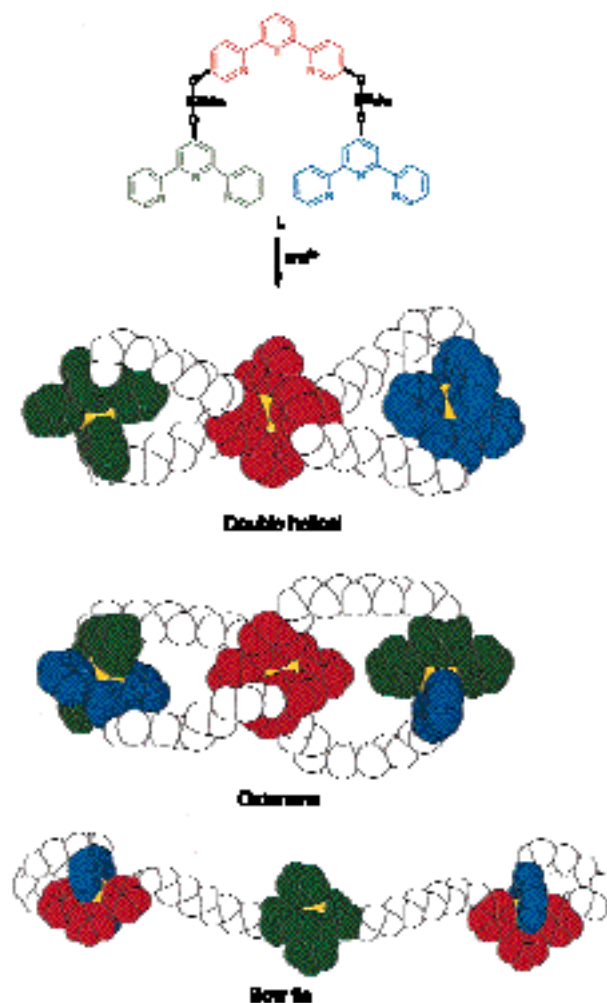


Fig. 1 Possible consequences of the formation of 3:2 complexes with L

catenated structures on the basis of molecular symmetry. In the catenane and the double helix the two 4'-substituted tpy rings (green and blue) of each ligand are equivalent. This means that rings D and F are equivalent, as are rings E and G. Furthermore, the central (red) 5,5''-disubstituted tpy unit is symmetrical with rings A and C being equivalent. In contrast, the bow tie (double looped) structure is unique with the green and blue ligands being non-equivalent and rings A and C of the central red tpy unit also being non-equivalent. The 500 MHz ^1H NMR spectrum of a CD_3CN solution of $[\text{Fe}_3\text{L}_2][\text{PF}_6]_6$ is shown in Fig. 2 together with the assignments that follow from a COSY experiment and from comparison with model compounds. The simplest feature of note is the observation of two equal intensity signals for $\text{H}^{6\text{A}}$ and $\text{H}^{6\text{C}}$. This asymmetry of the central tpy unit is only possible in the doubly looped structure. The remaining assignments fully confirm the asymmetry that is only compatible with the looped structure.

The non-equivalence of the iron(ii) centres is also seen in the differential pulse voltammogram of an acetonitrile solution of $[\text{Fe}_3\text{L}_2][\text{PF}_6]_6$ which exhibits a two-electron iron(ii)/(iii) process at +0.64 V (terminal metal centres) and a single electron

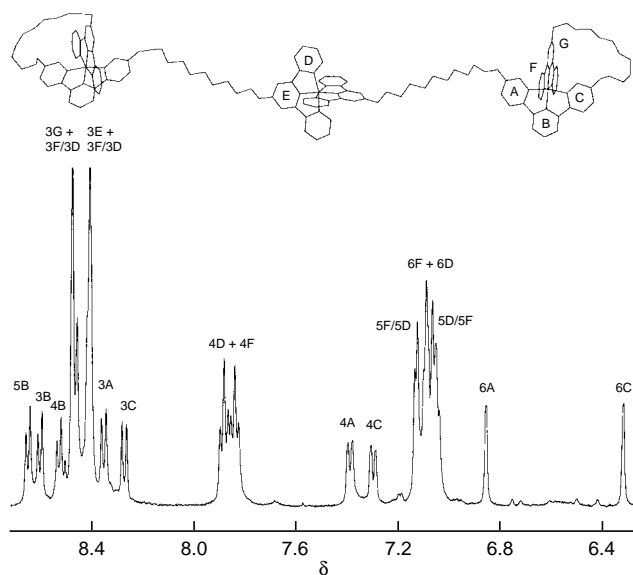


Fig. 2 The aromatic region of the 500 MHz ^1H NMR spectrum of a CD_3CN solution of the looped complex $[\text{Fe}_3\text{L}_2][\text{PF}_6]_6$ showing the assignments

process at +0.75 V corresponding to the central iron centre (all potentials quoted against internal ferrocene–ferrocenium couple). These potentials correspond well to the model compounds $[\text{FeL}^1_2][\text{PF}_6]_2$ ($\text{L}^1 = 4'$ -ethoxy-2,2':6',2''-terpyridine, +0.60 V) and $[\text{FeL}^2_2][\text{PF}_6]_2$ ($\text{L}^2 = 5,5''$ -bis(n - $\text{C}_{10}\text{H}_{21}\text{O}$)-2,2':6',2''-terpyridine, +0.73 V).

In conclusion, we have shown that the tritopic ligand L forms a doubly looped structure upon coordination to iron(ii). Although singly looped structures have been described previously⁴ we believe this to be the first example of such a five-component assembly of a doubly looped system. We are currently investigating the effects of varying the chain length and the metal centres.

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Footnotes

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† This ChemComm is also available in enhanced multi-media format *via* the World Wide Web: <http://chemistry.rsc.org/rsc/ccencha.htm>

‡ All new compounds were fully characterised. Some pertinent details are presented below. **L**: mp 205 °C. MS: m/z 1040 (M^+). ^1H NMR (CDCl_3): δ 8.70 (4H, dd, $\text{H}^{6\text{D}}$), 8.53 (2 H, d, $\text{H}^{3\text{A}}$), 8.41 (4 H, d, $\text{H}^{3\text{D}}$), 8.35 (2 H, d, $\text{H}^{6\text{A}}$), 8.26 (2 H, d, $\text{H}^{3\text{B}}$), 8.00 (4 H, s, $\text{H}^{3\text{E}}$), 7.88 (1 H, t, $\text{H}^{4\text{B}}$), 7.85 (4 H, dd, $\text{H}^{1\text{D}}$), 7.32 (6 H, dd + dd, $\text{H}^{4\text{A}}$ + $\text{H}^{5\text{D}}$), 4.22 (4 H, t, $4'$ -tpyOCH₂), 4.06 (4 H, t, $5'$ -tpyOCH₂), 1.2–1.7 (32 H, m).

2: mp 125–132 °C. MS: m/z 578 (M^+). ^1H NMR (CDCl_3): δ 8.52 (2 H, d, $\text{H}^{3\text{A}}$), 8.35 (2 H, d, $\text{H}^{6\text{A}}$), 8.27 (2 H, d, $\text{H}^{3\text{B}}$), 7.87 (1 H, t, $\text{H}^{4\text{B}}$), 7.32 (2 H, dd, $\text{H}^{4\text{A}}$), 4.07 (4H, t, tpyOCH₂), 3.63 (4 H, t, CH₂OH), 1.83 (4 H, qnt, tpyOCH₂CH₂), 1.2–1.6 (28 H, m).

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