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Formation of a [1 + 1] metallomacrocycle from a heterotritopic ligand containing two terpy and one bipy metal-binding domains

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Reaction of the heterotritopic ligand L, which contains one bipy and two terpy metal-binding domains linked by a flexible spacer with iron(II) chloride results in the formation of a [1 + 1] metallomacrocycle.

Ligands containing multiple bipy or terpy metal-binding domains have been extensively used in the metal-directed assembly of novel supramolecules such as helices, grids, catenanes and knots.[1] Recent studies by several groups[2,3] have shown that ligands containing two tpy domains linked through short, or rigid spacer regions can self-assemble, in the presence of six-coordinate metal ions to form metallomacrocycles. However, the investigation of ligands containing longer, more flexible spacers in metal-directed assembly processes is less common,[4] due to the tendency for formation of polymeric or polydispersed oligomeric species. In this report, we describe the synthesis of such a ligand and the outcome of a metal-directed assembly process.

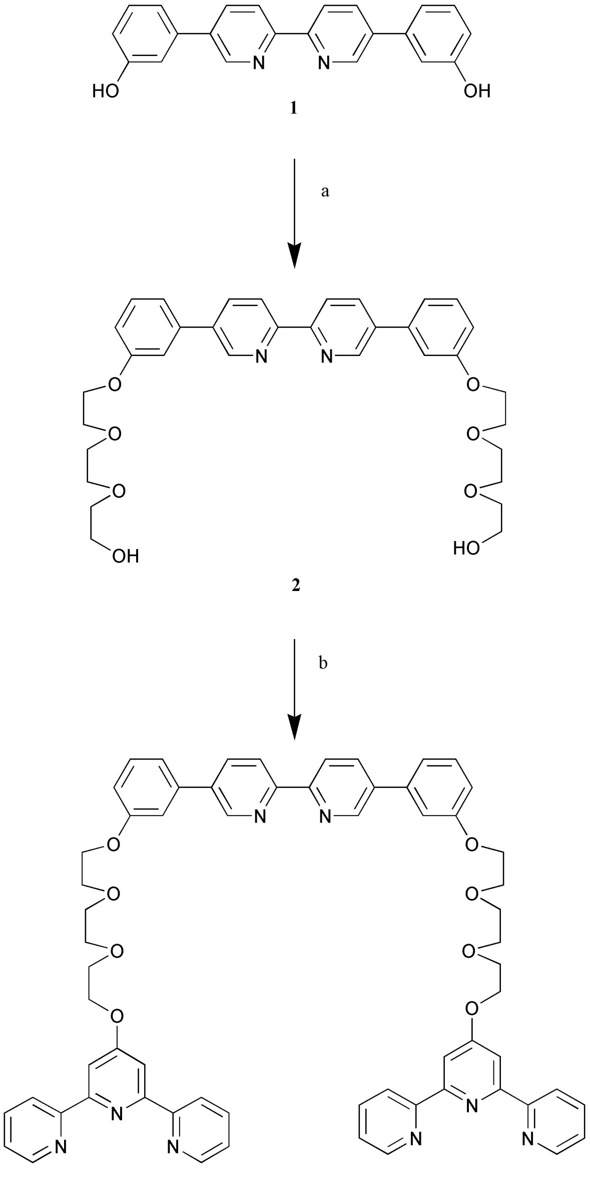
The heterotritopic ligand **L** containing two terpy domains and one bipy domain linked through polyether spacers, **L**† was conveniently prepared in two steps from the 5,5′-disubstituted 2,2′-bipyridine **1**[5] in an overall yield of 56% (Scheme 1). Reaction of **1** with 2-[2-(2-chloroethoxy)ethoxy] ethanol in DMF in the presence of potassium carbonate gave diol **2**† as a waxy yellow solid in 70% yield. This compound was efficiently converted to **L** in 80% yield by reaction with 4′-chloro-2,2′:6′,2″-terpyridine[6] in DMSO in the presence of potassium hydroxide.[7]

The interaction of **L** with iron(II) chloride was investigated. Addition of one molar equivalent of aqueous iron(II) chloride to a solution of **L** in acetonitrile immediately produced a purple solution (λ_{max} = 558 nm), typical of a {Fe(terpy)$_2$} chromophore. Analysis of the solution composition by TLC (silica gel, MeCN-saturated aqueous KNO$_3$–H$_2$O 10:0.5:1.5) after 5 min showed the formation of several purple products, indicating the formation of a library of complexes of different stoichiometries. However, over time several of these components disappeared, and after 24 h TLC analysis showed the presence of a single purple species. Addition of NH$_4$PF$_6$ precipitated a purple solid of composition {Fe**L**(PF$_6$)$_2$}.

The ^{1}H NMR spectrum of a CD$_3$CN solution of the isolated purple complex indicated high symmetry with only single terpy and bipy domains being observed. The aromatic region of the 500 MHz ^{1}H NMR spectrum is shown in Fig. 1 together with the assignments from a COSY experiment and comparison with model compounds. The doublet at δ 8.68 is due to H$_{6A}$ adjacent to the bipy nitrogen atoms and its resonance to low field is characteristic of a non-coordinated bipy domain.[8] The high R_F of the complex (R_F 0.6) also indicates that the product is not a high nuclearity polymer.

The ESMS of the complex in CH$_3$CN exhibited peaks at *m*/*z* 1451 {[Fe**L**][PF$_6$]$_2$ + K}$^+$, 1435 {[Fe**L**][PF$_6$]$_2$ + Na}$^+$, 1141 {[Fe**L**][F]$^+$, and a doubly charged ion at 561 [Fe**L**]$^{2+}$. While these are indicative of a 1:1 ligand:metal stoichiometry, the detection of a low intensity peak at *m*/*z* 2680 corresponding to {Fe$_2$**L**$_2$(PF$_6$)$_3$}$^+$ raised an ambiguity whether this was due to a genuine [2 + 2] species of a cluster ion {(Fe**L**)$_2$(PF$_6$)$_3$}$^+$.

Conformation of the product stoichiometry was obtained through X-ray structural analysis.‡ The complex is a mononuclear [1 + 1] metallomacrocycle (Fig. 2), in which a ring is formed through the coordination of both terpy domains in a single **L** ligand to an iron(II) centre. As predicted from the ^{1}H NMR data, the bipy domain is non-coordinated, with nitrogen atoms N7 and N8 adopting a *transoid* arrangement in the solid



Scheme 1 *Reagents*: (a) 2-[2-(2-chloroethoxy)ethoxy] ethanol, K$_2$CO$_3$, DMF; (b) 4′-chloro-2,2′:6′,2″-terpyridine, KOH, DMSO.

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state. The metal centre is coordinated to both terpy motifs in the expected octahedral environment (selected Fe–N bond distances are shown in the Fig. 2 caption). Additionally, one half of the macrocyclic cavity is occupied by an acetone molecule, whose position is stabilised through weak electrostatic interactions between the hydrogen atoms of C65 and C67 and the oxygen atoms of the spacer linkage (all distances between C65 and C67 and oxygen atoms O1–O4 in the range 3.45–3.75 Å).

Formation of this metallomacrocycle in high yield is very unexpected, as polymeric structures could be formed through either coordination to the bipy motif, or through coordination of each metal centre to binding domains of different ligand molecules. The formation of a single thermodynamic product is in this case remarkable due to the far greater length and flexibility of the spacers in **L** compared to previously published examples of multitopic ligands containing two terpy domains.[2,3]

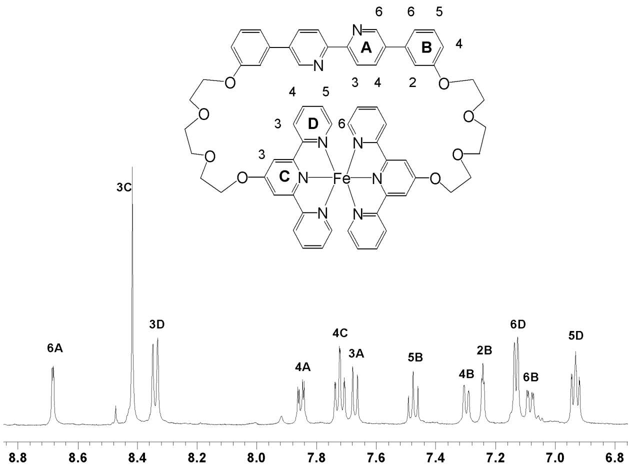

Fig. 1 The aromatic region of the 500 MHz ^{1}H NMR spectrum of a CD_3CN solution of [Fe**L**][PF_6]$_2$ showing the assignments.

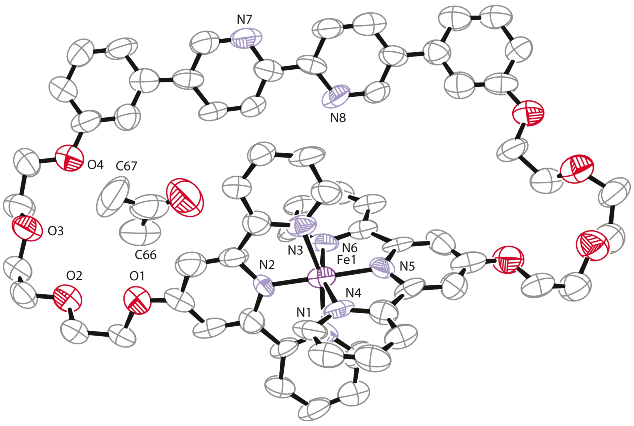

Fig. 2 X-Ray structure of the [1 + 1] metallomacrocycle showing the encapsulated acetone molecule. Hydrogen atoms and counter ions have been omitted. Ellipsoids are drawn at the 50% probability level. Selected Fe–N bond distances (Å): Fe1–N1, 2.014; Fe1–N2, 1.853; Fe1–N3, 1.998; Fe1–N4, 1.998; Fe1–N5, 1.936; Fe1–N6, 2.012.

In conclusion, we have shown that the tritopic ligand **L**, which contains mixed metal-binding domains connected through large flexible spacers, self-assembles to form a thermodynamically stable [1 + 1] metallomacrocycle in the presence of iron(II). Current investigations involve varying the length and flexibility of the spacer regions with a view to regulating the assembly process.

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Notes and references

† *Selected data* for compound **2**: ESMS: *m/z* 627 ([M + Na]$^+$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.92 (d, 2H, H_{6A}), 8.49 (d, 2H, H_{3A}), 8.02 (dd, 2H, H_{4A}), 7.41 (t, 2H, H_{5B}), 7.25 (m, 2H, H_{6B}), 7.23 (m, 2H, H_{2B}), 6.97 (dd, 2H, H_{4B}), 4.23 (t, 4H), 3.91 (t, 4H), 3.75 (m, 12H), 3.63 (t, 4H).

L. ESMS: *m/z* 1089 ([M + Na]$^+$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.88 (d, 2H, H_{6A}), 8.66 (m, 4H, H_{6D}), 8.60 (t, 4H, H_{3D}), 8.45 (d, 2H, H_{3A}), 8.04 (s, 4H, H_{3C}), 7.97 (dd, 2H, H_{4A}), 7.82 (m, 4H, H_{4D}), 7.36 (t, 2H, H_{5B}), 7.31 (m, 4H, H_{5D}), 7.20 (m, 4H, H_{3B}/H_{6B}), 6.95 (dd, 2H, H_{4B}), 4.40 (t, 4H), 4.21 (t, 4H), 3.93 (m, 8H), 3.80 (m, 8H).

‡ X-Ray quality crystals were obtained through diffusion of diethyl ether into an acetone solution of the complex. *Crystal data*: $C_{64}H_{58}F_{12}FeN_8O_8P_2 \cdot C_3H_6O$ (purple prisms), M = 1471.05, monoclinic, space group $P2_1/n$, a = 9.4845(5), b = 20.2873(12), c = 33.9574(18), β = 93.440(3), U = 6522.1(6) Å^3, T = 223(2), Z = 4, μ(Cu-Kα) = 3.184 mm^{-1}. 12903 reflections measured, 7257 unique, 2216 observed with $I > 2\sigma I$, R(obs.) = 0.1027. CCDC reference number 187005. See http://www.rsc.org/suppdata/cc/b2/b205233d/ for crystallographic data in CIF or other electronic format.

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