

# Metal-directed assembly of a conformationally restricted metallomacrocyclic

Hoi Shan Chow, Edwin C. Constable,\* Catherine E. Housecroft and Markus Neuburger

Department of Chemistry, University of Basel, Spitalstrasse 51, CH 4056 Basel, Switzerland.

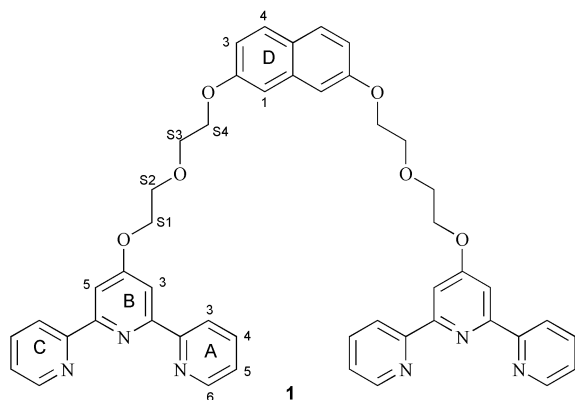
E-mail: edwin.constable@unibas.ch; Fax: +41 61 267 1005; Tel: +41 61 267 1001

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A new ditopic ligand based upon a 2,7-disubstituted naphthalene bearing two terpy-terminated bis(ethyleneoxy) substituents has been prepared and shown to give a conformationally locked [1 + 1] macrocycle upon reaction with iron(II) salts.

Metal-directed self-assembly allows the synthesis of a range of novel supramolecular species.<sup>1</sup> Metallomacrocycles are constructed by the metal-directed cyclisation of compounds bearing two pendant metal-binding domains. The stoichiometry of the reaction may be controlled by the rigidity and length of the spacer group between the metal-binding domains and a range of  $[n + n]$  complexes of generic formula  $[M_{2n}L_n]^{(m \times n)+}$  have been prepared. We<sup>2</sup> and others<sup>3</sup> have shown that ligands bearing two terpy metal-binding domains may be cyclised with labile first row transition metal salts to give [1 + 1], [2 + 2], [3 + 3] or [4 + 4] metallomacrocycles, depending upon the nature of the spacer. In this Communication we report the unusual behaviour of a new homoditopic ligand.



Ligand **1** has a relatively short spacer attaching the terpy metal-binding domains to a planar aromatic naphthalene core. Modelling indicated that a [1 + 1] complex with first row transition metal ions would be significantly strained and we anticipated the formation of a [2 + 2] metallomacrocyclic. Compound **1**† was prepared in 33% overall yield from 2,7-dihydroxynaphthalene in two steps; reaction of  $\text{ClCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$  with 2,7-dihydroxynaphthalene in DMF gave the diol-functionalised compound 2,7-bis[2-(2-hydroxyethoxy)ethoxy]naphthalene which was converted to **1** by reaction with 4'-chloro-2,2':6',2''-terpyridine and KOH in DMSO. The compound had the expected spectroscopic properties; the assignment of the methylene resonances in the <sup>1</sup>H NMR spectrum of **1** was made using NOESY methods; H<sup>3B</sup> and H<sup>1D</sup> showed strong cross-peaks to H<sup>S1</sup> and H<sup>S4</sup> respectively.

The reaction of **1** with  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  in MeOH resulted in the formation of a purple solution typical of an  $\{\text{Fe}(\text{terpy})_2\}^{2+}$  chromophore. TLC analysis of the solution in a variety of solvent systems indicated only one iron complex to be present and precipitation with  $\text{NH}_4\text{PF}_6$  gave  $\{\text{Fe}(\text{1})\}_n[\text{PF}_6]_{2n}$  as a deep purple microcrystalline material in quantitative yield.‡ The ESMS of an MeCN solution of this solid only exhibited peaks that

could be assigned to a 1 : 1  $[\text{Fe}(\text{1})][\text{PF}_6]_2$  species ( $\{\text{Fe}(\text{1})[\text{PF}_6]\}^+$ ,  $m/z$  999.2;  $\{\text{Fe}(\text{1})\text{F}\}^+$ ,  $m/z$  873.3;  $[\text{Fe}(\text{1})]^{2+}$ ,  $m/z$  427.2). The <sup>1</sup>H NMR spectrum of a CD<sub>3</sub>CN solution of the iron complex exhibited a number of unusual features. The spectrum showed two sets of signals assigned to coordinated terminal rings of the terpy, two H<sup>3</sup> signals from the terpy central ring and two sets of signals from the methylene groups of the spacer, in each case in a 1 : 1 ratio. However, the naphthalene gave rise to only three signals with the resonances assigned to H<sup>1D</sup> being unusually highly shielded ( $\delta$  4.86). The ratios of the peaks were constant for different samples of the complex and the data suggest that either the two terpy domains are chemically and magnetically non-equivalent or that each terpy is no longer symmetrical about the central ring. The COSY spectrum showed protons H<sup>3B</sup> and H<sup>5B</sup> to be coupled ( $J = 2.0$  Hz) establishing a structure in which the two terminal rings of each terpy are non-equivalent. In addition the H<sup>3B</sup> and H<sup>5B</sup> protons show NOE cross peaks in the NOESY spectrum to H<sup>3A</sup> and H<sup>3C</sup> respectively allowing the complete assignment presented in the footnote. The large differences in chemical shifts between the A and C rings are notable as is the upfield shifting of H<sup>1D</sup>. The resonances for ring C are very similar to those for  $[\text{Fe}(\text{terpy})_2]^{2+}$  ( $\Delta\delta$  H<sup>6C</sup> +0.29, H<sup>5C</sup> -0.04, H<sup>4C</sup> -0.04, H<sup>3C</sup> -0.09, H<sup>3B</sup>,  $\Delta\delta = \delta([\text{Fe}(\text{1})][\text{PF}_6]_2) - \delta([\text{Fe}(\text{terpy})_2][\text{PF}_6]_2)$  whereas those from the A ring are all significantly shielded ( $\Delta\delta$  H<sup>6A</sup> -0.41, H<sup>5A</sup> -0.54, H<sup>4A</sup> -0.57, H<sup>3A</sup> -0.28). The A ring is thus creating the binding cleft for the spacer. The methylene protons of the spacer appear as eight partially overlapping resonances. This <sup>13</sup>C NMR spectrum exhibits only four resonances for the spacer and <sup>1</sup>H-<sup>13</sup>C correlation established pairwise relationship of the eight proton resonances to the carbons. The eight methylene protons thus arise from a diastereotopic pair at each carbon.

On the basis of the above observations we propose a conformationally restricted [1 + 1] complex in which the naphthalene is locked into a cleft between the two terpy ligands. The short spacer means that the naphthalene is locked on one side of the complex such that the terpy terminal rings are non-equivalent. The resultant structure is chiral (see Fig. 1) with the two

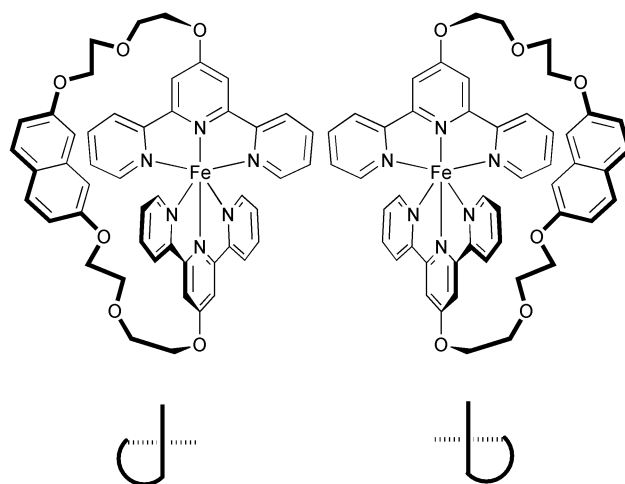
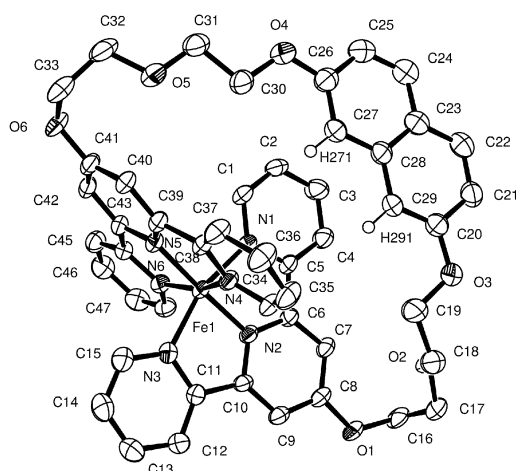


Fig. 1 The two enantiomers of  $[\text{Fe}(\text{1})]^{2+}$  and a cartoon representation.



**Fig. 2** Solid state structure of one of the two enantiomeric  $[\text{Fe}(\mathbf{1})]^{2+}$  cations present in the lattice of  $[\text{Fe}(\mathbf{1})][\text{PF}_6]_2$  showing the numbering scheme adopted; hydrogen atoms with the exception of  $\text{H}^{1\text{D}}$  of the naphthalene have been omitted. Selected bond lengths (Å) and angles ( $^\circ$ ): Fe1–N1 1.962(3), Fe1–N2 1.876(3), Fe1–N3 1.970(3), Fe1–N4 1.970(3), Fe1–N5 1.874(3), Fe1–N6 1.961(3); N1–Fe1–N2 80.9(1), N1–Fe1–N3 161.9(1), N2–Fe1–N3 81.0(1), N1–Fe1–N4 92.8(1), N2–Fe1–N4 96.7(1), N3–Fe1–N4 90.2(1), N1–Fe1–N5 97.5(1), N2–Fe1–N5 177.0(1), N3–Fe1–N5 100.6(1), N4–Fe1–N5 80.9(1), N1–Fe1–N6 89.9(1), N2–Fe1–N6 101.4(1), N3–Fe1–N6 92.7(1), N4–Fe1–N6 161.9(1), N5–Fe1–N6 81.0(1).

enantiomers being interconverted only by dissociation of a terpy or a high energy process involving the spacer loop passing over a terpy ligand. The asymmetry in the  $^1\text{H}$  NMR spectrum indicates that the interconversion is slow on the NMR time-scale. This explains both the asymmetry within the terpy ligands and the diastereotopic methylene groups. The unusual chemical shift of the naphthalene  $\text{H}^{1\text{D}}$  protons is seen to arise as these are oriented towards the metal and lie in the shielding anisotropic region above a pyridine ring. Modelling showed two equivalent local minima with the naphthalene  $\pi$ -stacked with one of the two chemically equivalent C rings. The observed symmetry in the NMR spectra is compatible with a rapid interconversion between these two conformations but no interconversion between enantiomers. We are currently investigating the dynamic processes in these systems and will report these results in a future manuscript.<sup>5</sup>

In order to confirm the formation of the  $[1 + 1]$  structure we have determined the solid state crystal structure of  $[\text{Fe}(\mathbf{1})][\text{PF}_6]_2 \cdot (\text{C}_2\text{H}_5\text{OC}_2\text{H}_5) \cdot 0.5\text{MeCN}$ § obtained by the diffusion of diethyl ether vapour into a MeCN solution. One of the two enantiomeric  $[\text{Fe}(\mathbf{1})]^{2+}$  cations present in the lattice is presented in Fig. 2. Bond lengths and angles within the coordination

sphere of the iron and the terpy ligands are typical. There are no significant short contacts between the  $\text{PF}_6^-$  anions, the solvent molecules and the cations. The spacer and naphthalene lie snugly in the cleft between two terpy terminal rings as predicted. The naphthalene is  $\pi$ -stacked with a terpy terminal ring corresponding to the local minima discussed above with a least squares interplane angle of  $5.9^\circ$  and an interplanar separation of 3.6 Å. The naphthalene  $\text{N}^{1\text{D}}$  protons (H271 and H291) lie directly above the non-stacked terpy C ring and 3.7 Å above the least squares plane.

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## Notes and references

† **1**:  $m/z$  (EI-MS): 799,  $\{\mathbf{1H}\}^+$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.67 (ddd, 4H,  $\text{H}^{6\text{A}}$ ), 8.60 (dt, 4H,  $\text{H}^{3\text{A/C}}$ ), 8.05 (s, 4H,  $\text{H}^{3\text{B/B}}$ ), 7.83 (td, 4H,  $\text{H}^{4\text{A/C}}$ ), 7.60 (d, 2H,  $\text{H}^{4\text{D}}$ ), 7.31 (ddd, 4H,  $\text{H}^{5\text{A/C}}$ ), 7.02 (s, 2H,  $\text{H}^{1\text{D}}$ ), 7.01 (dd, 2H,  $\text{H}^{3\text{D}}$ ), 4.44 (t, 4H,  $\text{H}^{5\text{1}}$ ), 4.25 (dd, 4H,  $\text{H}^{8\text{4}}$ ), 4.02 (m, 8H,  $\text{H}^{2\text{S2/S3}}$ ).

‡  $[\text{Fe}(\mathbf{1})][\text{PF}_6]_2$ :  $m/z$  (ES-MS): 999.2  $\{[\text{Fe}(\mathbf{1})][\text{PF}_6]\}^+$ , 873.3  $\{[\text{Fe}(\mathbf{1})\text{F}]\}^+$ , 427.2  $[\text{Fe}(\mathbf{1})]^{2+}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  = 8.82 (d, 2H,  $\text{H}^{3\text{B}}$ ), 8.41 (d, 2H,  $\text{H}^{5\text{B}}$ ), 8.37 (d, 2H,  $\text{H}^{3\text{C}}$ ), 8.18 (d, 2H,  $\text{H}^{3\text{A}}$ ), 7.84 (td, 2H,  $\text{H}^{4\text{C}}$ ), 7.54 (d, 2H,  $\text{H}^{4\text{D}}$ ), 7.35 (d, 2H,  $\text{H}^{6\text{C}}$ ), 7.31 (td, 2H,  $\text{H}^{4\text{A}}$ ), 7.02 (ddd, 2H,  $\text{H}^{5\text{C}}$ ), 6.85 (dd, 2H,  $\text{H}^{3\text{D}}$ ), 6.65 (d, 2H,  $\text{H}^{6\text{A}}$ ), 6.52 (ddd, 2H,  $\text{H}^{5\text{A}}$ ), 4.86 (d, 2H,  $\text{H}^{1\text{D}}$ ), 5.38 (m, 2H,  $\text{H}^{5\text{1a}}$ ), 4.67 (dt, 2H,  $\text{H}^{5\text{1b}}$ ), 4.13 (m, 4H,  $\text{H}^{2\text{a/S2a}}$ ), 4.07 (m, 2H,  $\text{H}^{5\text{3a}}$ ), 3.80 (m, 6H,  $\text{H}^{3\text{b/S4a/S4b}}$ ).

§ Crystal data for  $[\text{Fe}(\mathbf{1})][\text{PF}_6]_2 \cdot (\text{C}_2\text{H}_5\text{OC}_2\text{H}_5) \cdot 0.5\text{MeCN}$ ,  $\text{C}_{52}\text{H}_{50}\text{F}_{12}\text{FeN}_6\text{O}_6\text{P}_2$ ,  $M = 1222.8$ , triclinic, space group  $P-1$ ,  $a = 11.424(1)$ ,  $b = 13.635(2)$ ,  $c = 18.271(2)$  Å,  $\alpha = 75.402(9)$ ,  $\beta = 87.442(9)$ ,  $\gamma = 78.327(11)^\circ$ ,  $U = 2697.2$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.506$  Mg m<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 0.438$  mm<sup>-1</sup>,  $T = 173$  K, 67536 (12329 independent) reflections collected on an Enraf Nonius Kappa CCD instrument. Refinement of 7800 reflections (820 parameters) with  $I > 3.0\sigma(I)$  converged at final  $R1 = 0.0610$ ,  $wR2 = 0.0665$ . CCDC reference number 220368. See <http://www.rsc.org/suppdata/dt/b3/b313972g/> for crystallographic data in CIF or other electronic format.

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