

COMMUNICATION

2D → 2D Parallel interpenetration of (4,4) sheets constructed from a ditopic bis(4,2':6',4''-terpyridine)

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Edwin C. Constable,^a Catherine E. Housecroft,^{*a} Srboj Vujovic^a and Jennifer A. Zampese^aReceived 00th January 2012,
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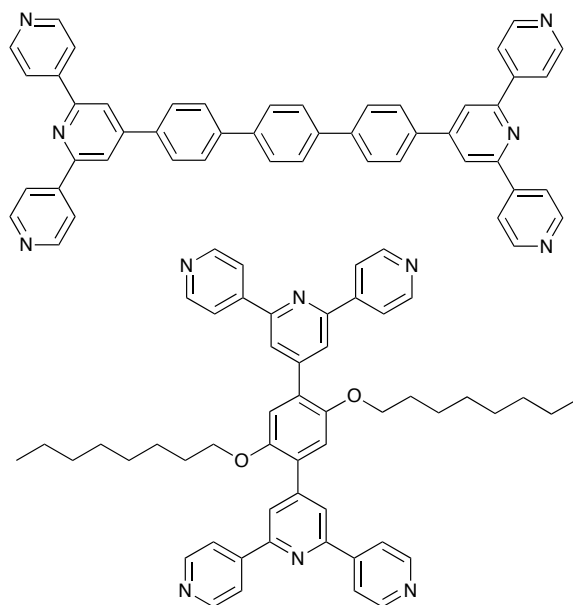
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The ditopic ligand 1,4-bis(*n*-octyloxy)-2,5-bis(4,2':6',4''-terpyridin-4'-yl)benzene reacts with ZnCl₂ to give 2-dimensional (4,4) nets with a corrugated topology facilitating interpenetration in a 2D → 2D parallel manner.

The coordination chemistry of 4,2':6',4''-terpyridines has blossomed¹ in the 15 years since the report of the first coordination polymer containing the parent 4,2':6',4''-tpy ligand.² To date, no examples are known in which the central pyridine ring is coordinated and the remaining divergent donor set lends itself to the assembly of 1-dimensional coordination polymers or metallomacrocycles.¹ The incorporation of diphenylphosphino,³ carboxylato,^{4,5,6,7,8,9,10,11,12,13} or pyridyl^{13,14,15,16,17,18,19,20} functionalities into the scaffold leads to the assembly of molecular capsules and networks. Multitopic ligands incorporating multiple 2,2':6',2''-terpyridine domains²¹ have significantly expanded the diversity of structures accessible with the cheating 2,2':6',2''-tpy unit and have led to a wide range of architectures. Outside the patent literature, reports of multidomain 4,2':6',4''-tpy ligands are remarkably sparse,^{22,23,24} although Yoshida *et al.* have investigated the coordination behaviour of 1,3-di((4,2':6',4''-terpyridin-4'-yl)benzene which forms a triply interpenetrating network with cobalt(II).²³ Here we describe the synthesis of the ditopic ligand **1** (Scheme 1) and its reaction with zinc(II) chloride to give a coordination network consisting of (4,4) sheets engaging in 2D → 2D parallel interpenetration.

Although initial synthesis of a ditopic ligand containing a 4,4''-(1,1':4',1''-triphenylene) spacer connecting the 4'-positions of two 4,2':6',4''-tpy domains was successful,[†] the product (Scheme 1) was poorly soluble in common organic solvents. We therefore decided to introduce solubilizing alkyl chains. Following the one pot method of Wang and Hanan²⁵, the reaction of two equivalents of 4-acetylpyridine with 2,5-bis(octyloxy)benzene-1,4-dicarbaldehyde in EtOH in the presence of NH₃ lead to the formation of pale yellow **1** in 30% yield

after recrystallization from EtOH/CHCl₃.[†] The base peak at *m/z* 797.9 in the electrospray mass spectrum (MeOH) of **1** was assigned to [M + H]⁺. Solution ¹H and ¹³C NMR spectra of **1**[†] were assigned by COSY, HMQC and HMBC methods and confirmed the presence of a single, C₂-symmetric 4,2':6',4''-tpy environment. A singlet at δ 7.16 ppm was assigned to the proton of the phenylene spacer; resonances in the alkyl region confirmed the presence of the octyloxy chains. The absorption spectrum of **1** exhibits intense, high energy bands arising from spin-allowed π* ← π and π* ← n transitions which tail into the visible (Fig. S1[†]). A crystal of X-ray quality was selected from the bulk sample and the structure of **1** is shown in Fig. 1.



Scheme 1. Structures of ditopic ligand with 4,4''-(1,1':4',1''-triphenylene) spacer and of ligand **1**.

Compound **1** crystallizes²⁶ in the space group $P2_1/c$ with half the molecule in the asymmetric unit; the second half is generated by an inversion centre. The phenylene ring is twisted 46.3° with respect to the plane of the pyridine ring to which it is bonded, thereby minimizing H...H contacts between the rings. The 4,2':6',4''-tpy unit is close to planar (angles between the rings containing N1/N2 and N2/N3 = 12.3 and 3.9°), concomitant with efficient π -stacking of 4,2':6',4''-tpy units in adjacent molecules. The N2/N3 pyridine rings exhibit face-to-face contacts with the N2ⁱⁱ/N3ⁱⁱ pair of rings (separation of planes = 3.44 Å, centroid...centroid separations = 3.59 Å; symmetry code ii = $1-x, -1-y, 1-z$). The stacking is restricted to pairs of 4,2':6',4''-tpy domains, with each pair being sandwiched between a pair of alkoxy chains which adopt extended conformations (Fig. 2).

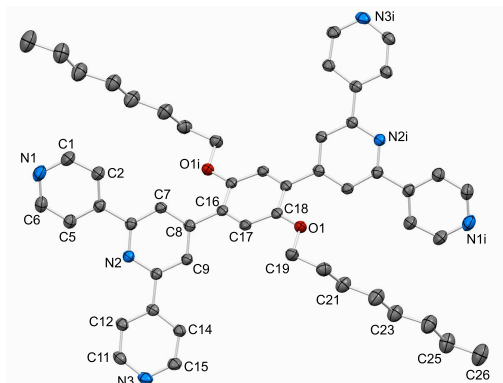


Fig. 1. ORTEP diagram of **1** with ellipsoids plotted at 50% probability level; H atoms omitted for clarity. Symmetry code i = $1-x, -y, 1-z$. Selected bond parameters: O1–C18 = $1.3684(16)$, O1–C19 = $1.4390(16)$, C8–C16 = $1.4852(17)$, range N–C = $1.335(2)$ to $1.3455(17)$ Å; C18–O1–C19 = $118.70(10)$, C1–N1–C5 = $115.64(12)$, C10–N2–C6 = $118.13(11)$, C15–N3–C11 = $115.75(12)^\circ$.

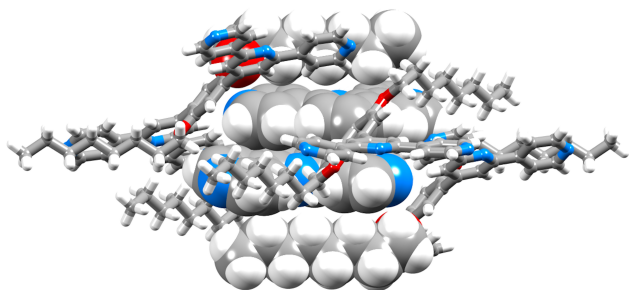


Fig. 2. Alkoxy/tpy/tpy/alkoxy stacking motif in the crystal lattice of **1**.

Ligand **1** is potentially a 4-connecting node and could lead to a multiplicity of discrete and network structures upon interaction with metal ions, including two-dimensional (4,4) sheets and diamantoid (6,3) three dimensional structures.²⁷ We have previously shown that tetrahedral ZnX_2 units ($M = F, Cl, Br$ or I) act as topologically linear two-connecting linkers to assemble 4,2':6',4''-tpy ligands into complex architectures.¹ Layering of chloroform and methanol solutions of, respectively, **1** and $ZnCl_2$ (ratio of equivalents of **1** : $ZnCl_2 = 1 : 2$) resulted in the formation of yellow crystals of a complex that analysed as $[Zn_2Cl_4(\mathbf{1})]^+$. Structural determination²⁸ of the complex confirmed the formation of $\{[Zn_2Cl_4(\mathbf{1})] \cdot 4H_2O\}_n$ in which each molecule of **1** binds zinc(II) only through the outer pyridine donors (Fig. S2[†]). Non-coordination of the central pyridine ring is typical of 4,2':6',4''-tpy and

its derivatives.¹ $\{[Zn_2Cl_4(\mathbf{1})] \cdot 4H_2O\}_n$ crystallizes in the $C2/c$ space group with half the ligand and one $ZnCl_2$ unit in the asymmetric unit. The octyloxy chain is disordered and has been modelled with each of the last five C atoms of the chain in two sites of fractional occupancies of 0.46 and 0.54. Residual electron density in the lattice was modelled as partial occupancy water molecules. The conformation of **1** in $\{[Zn_2Cl_4(\mathbf{1})] \cdot 4H_2O\}_n$ is close to that in the free ligand (Fig. S3[†]); angles between the planes of adjacent pyridine rings are 16.7 and 2.1° , and between the central pyridine and phenyl rings is 49.1° . As expected, each ligand acts as a 4-connecting node with tetrahedral zinc(II) centres as linkers. The primary unit that assembles is a metallomacrocyclic (Fig. 3) which contains four zinc(II) ions and four **1** ligands. Metal centres 1 and 2 and metal centres 3 and 4 are each bridged by single 4,2':6',4''-tpy domains whereas centres 2 and 3 and 4 and 1 are linked by two nitrogen donors from each of the 4,2':6',4''-tpy domains of a single ligand. As a consequence of the different bonding modes of the ligands, the metallomacrocyclic is non-planar. Interconnection of these metallomacrocyclics produces a (4,4) sheet lying in the bc -plane, and Fig. 4a depicts part of one sheet. A view of the same sheet down the c -axis (Fig. 4b) illustrates its corrugated topology, with the extended alkoxy chains threaded through the middle of the sheet.

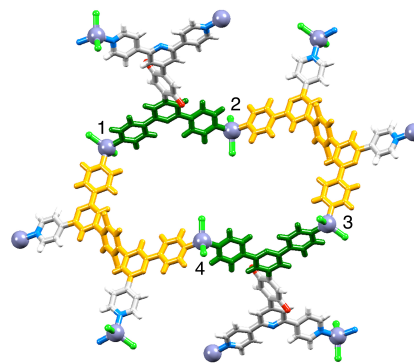
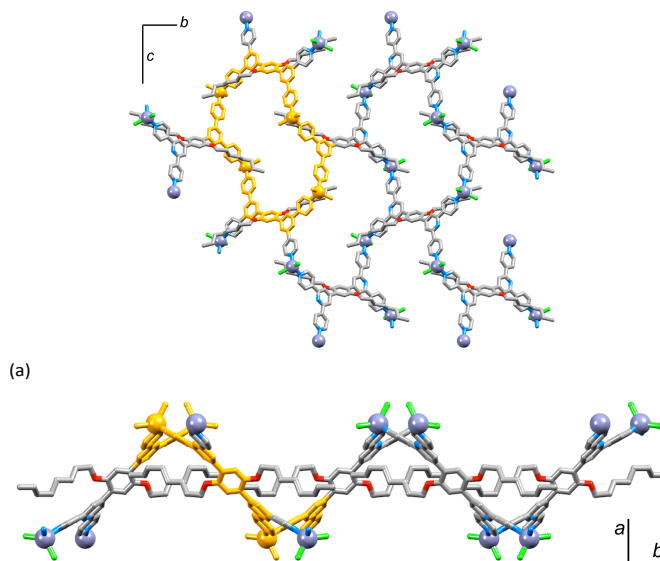


Fig. 3. One macrocyclic unit in $\{[Zn_2Cl_4(\mathbf{1})] \cdot 4H_2O\}_n$, emphasizing the two different bridging modes of **1** (see text). Alkyl chains omitted for clarity.



(b)

Fig. 4 (a) Part of one (4,4) sheet in $\{[\text{Zn}_2\text{Cl}_4(\mathbf{1})] \cdot 4\text{H}_2\text{O}\}_n$, with one macrocyclic unit highlighted in orange; view down the a axis. (b) The same sheet viewed down the c -axis. Hydrogen atoms are omitted.

The corrugated form of each sheet allows two such sheets to interpenetrate,²⁹ in a 2D \rightarrow 2D parallel manner^{30,31} to optimize packing (Figs. 5 and 6). Zinc dichloride units protrude from the top and bottom of the resultant layer and are accommodated in the V-shaped cavities (Fig. 5) of the adjacent layer. Interactions between layers involve offset face-to-face stacking of 4,2':6',4''-tpy units at a separation of 3.59 Å. Within each layer, there are no face-to-face stacking interactions between aromatic rings, and each octyloxy chain is sandwiched between a pair of 4,2':6',4''-tpy units. This suggests that the presence of the alkyl chains on $\mathbf{1}$ may have a significant influence on the assembly of the network, and we are now investigating analogous systems with shorter alkoxy functionalities.

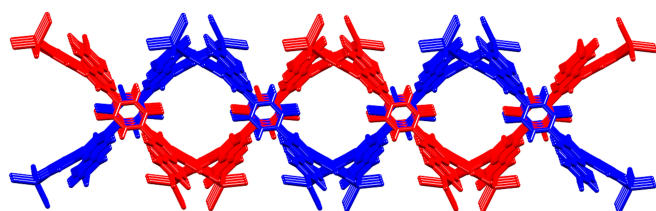


Fig. 5. View down the c -axis showing 2D \rightarrow 2D parallel interpenetration of sheets in one layer of the lattice in $\{[\text{Zn}_2\text{Cl}_4(\mathbf{1})] \cdot 4\text{H}_2\text{O}\}_n$. Alkyl chains have been deleted for clarity.

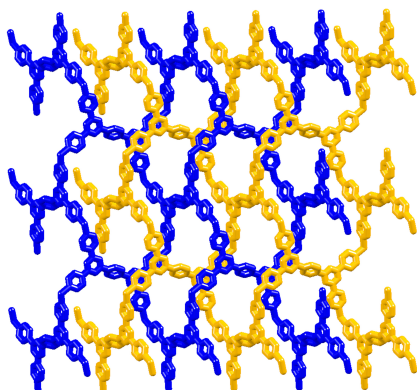


Fig. 6. View down the a -axis showing interpenetration of two sheets in one layer of the lattice in $\{[\text{Zn}_2\text{Cl}_4(\mathbf{1})] \cdot 4\text{H}_2\text{O}\}_n$. Alkyl chains have been deleted for clarity.

Conclusions

We have described the synthesis and characterization of a ditopic 4,2':6',4''-tpy ligand, $\mathbf{1}$, bearing solubilizing alkyl chains, and have demonstrated its use in the assembly of a coordination network. The ligand acts as a 4-connecting node with ZnCl_2 units as linkers in $\{[\text{Zn}_2\text{Cl}_4(\mathbf{1})] \cdot 4\text{H}_2\text{O}\}_n$. The complex assembles in (4,4) nets with a corrugated topology allowing interpenetration in a 2D \rightarrow 2D parallel manner. The octyloxy chains incorporated into the phenylene spacer in $\mathbf{1}$ adopt an extended conformation and are sandwiched between

pairs of 4,2':6',4''-tpy domains, suggesting that the length of the chain may assist in directing the assembly of the interpenetrated sheets.

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Notes and references

^a Department of Chemistry, University of Basel, Spitalstrasse 51, CH4056 Basel, Switzerland. Fax: +41 61 267 1018; Tel: +41 61 267 1008; E-mail: catherine.housecroft@unibas.ch

[†] Electronic Supplementary Information (ESI) available: Synthetic and general crystallographic details: Fig. S1. Absorption spectrum of $\mathbf{1}$; Fig. S2. Structure of the 4-connecting node in $\{[\text{Zn}_2\text{Cl}_4(\mathbf{1})] \cdot 4\text{H}_2\text{O}\}_n$; Fig. S3. Overlay of the ligand conformations in $\mathbf{1}$ and the complex. See DOI: 10.1039/c000000x/

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