

1D and 2D metal–organic frameworks functionalized with free pyridyl groups

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Received 15 February 2006; received in revised form 23 March 2006; accepted 24 March 2006

Available online 5 June 2006

Abstract

We show that a molecule constructed from an organic solid-state synthesis, namely, *rctt*-1,3-bis(2-pyridyl)-2,4-bis(4-pyridyl)cyclobutane (ht-2,4'-tpcb) upon reaction with Cu(II) and Zn(II) ions gives one- (1D) and two-dimensional (2D) metal–organic frameworks (MOFs) of composition $[\text{Cu}(\text{hfac})_2(2,4'\text{-tpcb-ht})]_\infty$ (where: hfac = hexafluoroacetylacetonate) (1) and $[\text{Zn}(2,4'\text{-tpcb-ht})_2(\text{H}_2\text{O})_2]_\infty^{2+}$ (2). Each MOF possesses uncoordinated, or free, 2-pyridyl groups that decorate the walls of each extended structure.

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Keywords: Metal–organic framework; Template; Self-assembly; [2+2] Photodimerization

1. Introduction

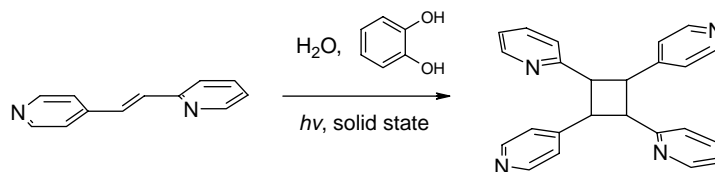
Nature excels at transfer of information via supramolecular forces [1]. For example, the information contained in ribonucleic acid (RNA) is stored in the form of nucleotide bases. The information is transferred to a protein by way of translation, a process involving hydrogen bonds between sets of three nucleotide bases (i.e. codons and anticodons) to give a sequence of amino acids [1]. In the language of Lehn [2], every molecule is considered to contain information, which is stored in the form of the molecular structure and functional groups. These factors then control how a molecule will interact with additional chemical species. In the context of coordination chemistry, ligands are considered to be coded with information (e.g. number, type, positions of coordination sites) that is read by a metal to give an output (i.e. coordination product) [2]. In recent years, we have shown how supramolecular forces can be used to transfer information by directing the formation of covalent bonds [3]. This has been achieved by utilizing molecular templates that facilitate the hydrogen-bonded-directed formation of organic molecules in molecular co-crystals. Moreover, we have shown that the products of such template-directed solid-state syntheses can

be used as ligands in coordination chemistry. The ligands possess sites for metal–ion coordination positioned by the hydrogen bonds used for their construction.

In particular, we have shown that 4-chlororesorcinol can be used to direct the assembly of *trans*-1-(2-pyridyl)-2-(4-pyridyl)ethylene (2,4'-bpe) in the solid state in a geometry suitable for an intermolecular [2+2] photodimerization to give *rctt*-1,2-bis(2-pyridyl)-3,4-bis(4-pyridyl)cyclobutane (2,4'-tpcb-hh) (where: hh = head-to-head) quantitatively and in gram amounts [4]. We have also shown that reaction of 2,4'-tpcb-hh with Cu(II) salts of hexafluoroacetylacetonate (hfac) and NO_3^- anions give a metal–organic polygon [4] and polyhedron, respectively [5]. In this manuscript, we wish to report the isolation of two coordination products of the head-to-tail regioisomer of 2,4'-tpcb, namely *rctt*-1,3-bis(2-pyridyl)-2,4-bis(4-pyridyl)cyclobutane (2,4'-tpcb-ht) (where: ht = head-to-tail) (Scheme 1), a molecule also obtained via a [2+2] photodimerization in the solid state. The solid-state synthesis of 2,4'-tpcb-ht has been achieved in a hydrogen-bonded co-crystal based on catechol [6]. Specifically, we demonstrate that reaction of 2,4'-tpcb-ht with Cu(II) and Zn(II) ions gives one- (1D) and two-dimensional (2D) metal–organic frameworks (MOFs) of composition $[\text{Cu}(\text{hfac})_2(2,4'\text{-tpcb-ht})]_\infty$ (1) and $[\text{Zn}(2,4'\text{-tpcb-ht})_2(\text{H}_2\text{O})_2]_\infty^{2+}$ (2). In contrast to the polygon and polyhedron cited above, these metal–organic assemblies possess uncoordinated, or free, 2-pyridyl groups that, owing to the stereochemistry of the functionalized cyclobutane ring,

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Scheme 1.

decorate the walls of each framework. Our results are proof-of-principle that a molecule constructed in the solid state can be used to introduce free binding sites into the cavities of MOFs. This area of MOF chemistry, which is emerging as a means to develop solids that exhibit unique guest binding and/or catalysis properties, remains mostly unexplored to date [7,8].

2. Experimental

2.1. General

All reagents were purchased from Aldrich Chemical Co., and used as received unless otherwise stated. 2,4'-tpcb-ht was synthesized as reported [6]. 2,4'-tpcb-ht was separated from catechol using an aqueous solution of sodium hydroxide layered over dichloromethane.

2.2. Synthesis of **1**

Methanolic solutions of 2,4'-tpcb-ht (0.025 g, 0.0685 mmol) and Cu(hfac)₂·H₂O (0.068 g, 0.137 mmol) were combined (1:2 ratio; 25 mL methanol total). The resulting green solution was allowed to evaporate slowly over a period of approximately 2 days, after which green rectangular single crystals of **1** were obtained (yield: 0.030 g, 39%).

2.3. Synthesis of **2**

Methanolic solutions of 2,4'-tpcb-ht (0.025 g, 0.0685 mmol) and Zn(NO₃)₂·H₂O (0.014 g, 0.0685 mmol) were combined (1:1 ratio; 25 mL methanol total). A 5 mL aliquot of the resulting colorless solution was layered on top of 10 mL toluene. After a period of approximately 1 week, colorless rectangular single crystals of **2**·2(NO₃)·5(H₂O)·2.5(CH₃OH) were obtained (yield: 0.034 g, 83%).

2.4. X-ray crystallography

Intensity data for **1** and **2** were collected on a Nonius Kappa CCD single-crystal X-ray diffractometer at 190 K using Mo K_α radiation ($\lambda=0.7107$ Å) (Table 1). The structures were solved using direct methods and refined by full-matrix least-squares based on F^2 . The multi-scan method of absorption correction was applied. All non-hydrogen atoms were refined anisotropically and hydrogen atoms bonded to carbon atoms were placed in idealized positions with parameters allowed to ride on the atom to which they were attached. Electron density consistent with highly disordered solvent molecules was located in **2**. The disordered solvent molecules were refined isotropically with,

in some instances, partial site occupancies. All crystallographic calculations were conducted using SHELXL-97 [9], locally implemented on an IBM-compatible, Pentium-based PC.

3. Results

A perspective view of **1** is shown in Fig. 1. The asymmetric unit contains one half of a molecule of 2,4'-tpcb-ht, one half of a copper atom, and a single hfac anion. Each copper atom lies in an octahedral coordination environment, being coordinated to two *trans*-4-pyridyl units [Cu–N distances (Å): Cu–N(1) 2.02(1)] and two chelating hfac anions [Cu–O distances (Å): Cu–O(1) 2.06(4), Cu–O(2) 2.24(1)]. The cyclobutane ligand lies disordered over two positions, with relative occupancies of 0.55 (A) and 0.45 (B). As a consequence of these arrangements, the components of **1** have assembled to form a 1D coordination polymer (metal···metal separation: 14.3 Å) that lies parallel to the *hkl* plane (0 –2 1) (Fig. 1a). In contrast to the 4-pyridyl groups, the 2-pyridyl units do not participate in metal–ion coordination (Fig. 1b). Neighboring chains of **1** pack in a criss-

Table 1
Crystallographic data for **1** and **2**

	1	2
Empirical formula	CuF ₆ O ₂ N ₂ C ₁₂ H ₁₁	ZnO _{15.5} N ₁₀ C _{50.5} H ₆₄
Formula weight	842.1	2300.8
<i>T</i> (K)	190(2)	190(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> -1
<i>a</i> (Å)	16.715(3)	17.630(2)
<i>b</i> (Å)	18.954(4)	18.180(2)
<i>c</i> (Å)	13.364(3)	20.570(2)
α	90.00	73.99(3)
β	126.52(3)	73.87(3)
γ	90.00	62.63(3)
Volume (Å ³)	3403(1)	5538(1)
<i>Z</i>	4	2
<i>D</i> _c (g cm ⁻³)	1.64	1.32
μ (mm ⁻¹)	0.754	0.517
<i>F</i> (000)	1691	2289
Crystal size (mm)	0.04 × 0.07 × 0.14	0.20 × 0.22 × 0.80
θ (°)	2.9–22.5	2.6–22.5
Limiting indices	–17 ≤ <i>h</i> ≤ 17 –20 ≤ <i>k</i> ≤ 20 –14 ≤ <i>l</i> ≤ 10	–18 ≤ <i>h</i> ≤ 18 –19 ≤ <i>k</i> ≤ 19 –22 ≤ <i>k</i> ≤ 22
Reflections collected	8411	27,410
Unique reflections	2232	14,299
Completeness to θ (%)	99.9	98.9
<i>R</i> [<i>I</i> > 2 σ <i>I</i>]	0.077	0.098
<i>wR</i> ₂	0.184	0.270

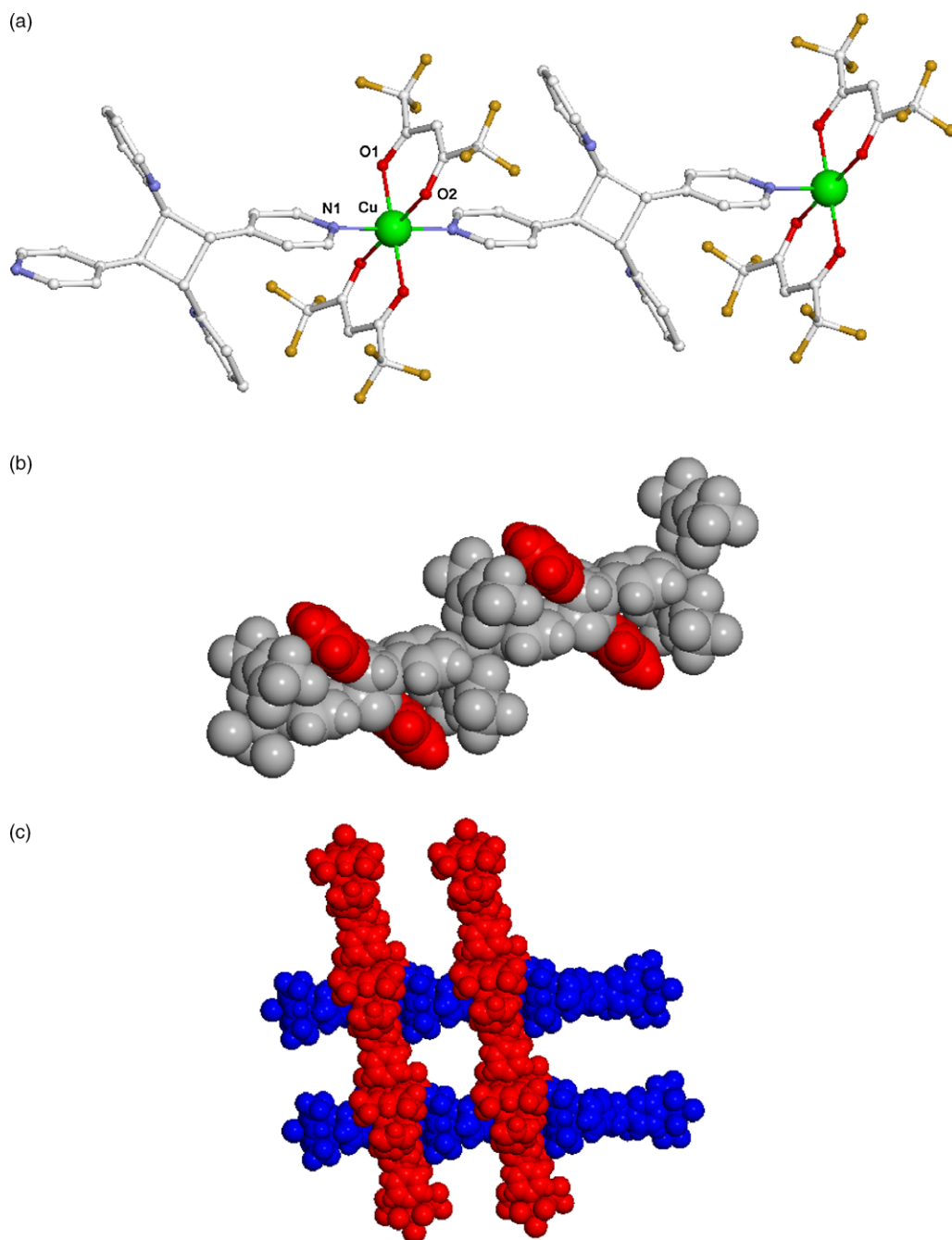


Fig. 1. X-ray crystal structure of **1**: (a) ball-and-stick representation, (b) space-filling model highlighting the free 2-pyridyl groups (red) and, (c) orientation of neighboring 1D strands (red and blue). (For interpretation of the reference to colour in this legend, the reader is referred to the web version of this article).

cross fashion, with the 4-pyridyl groups participating in face-to-face π – π forces (Fig. 1c).

A perspective view of **2** is shown in Fig. 2. The asymmetric unit contains four molecules of 2,4'-tpcb-ht, two zinc atoms, four NO_3^- ions, 14 water molecules, and five methanol molecules. Similar to **1**, each zinc atom lies in an octahedral coordination environment, being coordinated to four 4-pyridyl groups in the equatorial positions [Zn–N distances (Å): Zn(1)···N(1) 2.14(2), Zn(1)···N(2) 2.14(2), Zn(1)···N(3) 2.16(2), Zn(1)···N(4) 2.16(2) and Zn(2)···N(5) 2.12(2), Zn(2)···N(6) 2.13(2), Zn(2)···N(7) 2.15(2), Zn(2)···N(8)

2.16(2)] and two water molecules [Zn–O distance (Å): Zn(1)···O(1) 2.14(2), Zn(1)···O(2) 2.25(2) and Zn(2)···O(3) 2.20(2), Zn(2)···O(4) 2.16(2)] in the apical positions. As a consequence of these arrangements, the components of **2** have assembled, in contrast to **1**, to form a 2D cationic coordination polymer parallel to the hkl plane (1 1 0) (Fig. 2a). The topology of the 2D MOF conforms to a (4,4)-net [10,11] in which the metal ions define 4-connected nodes. Owing to the geometry of the cyclobutane ring, the 2D framework is composed of a grid of rhombus-shaped cavities (metal···metal separations (Å): 13.75, 13.86, 13.92, 13.97; corner angles (°): 96.39, 84.19,

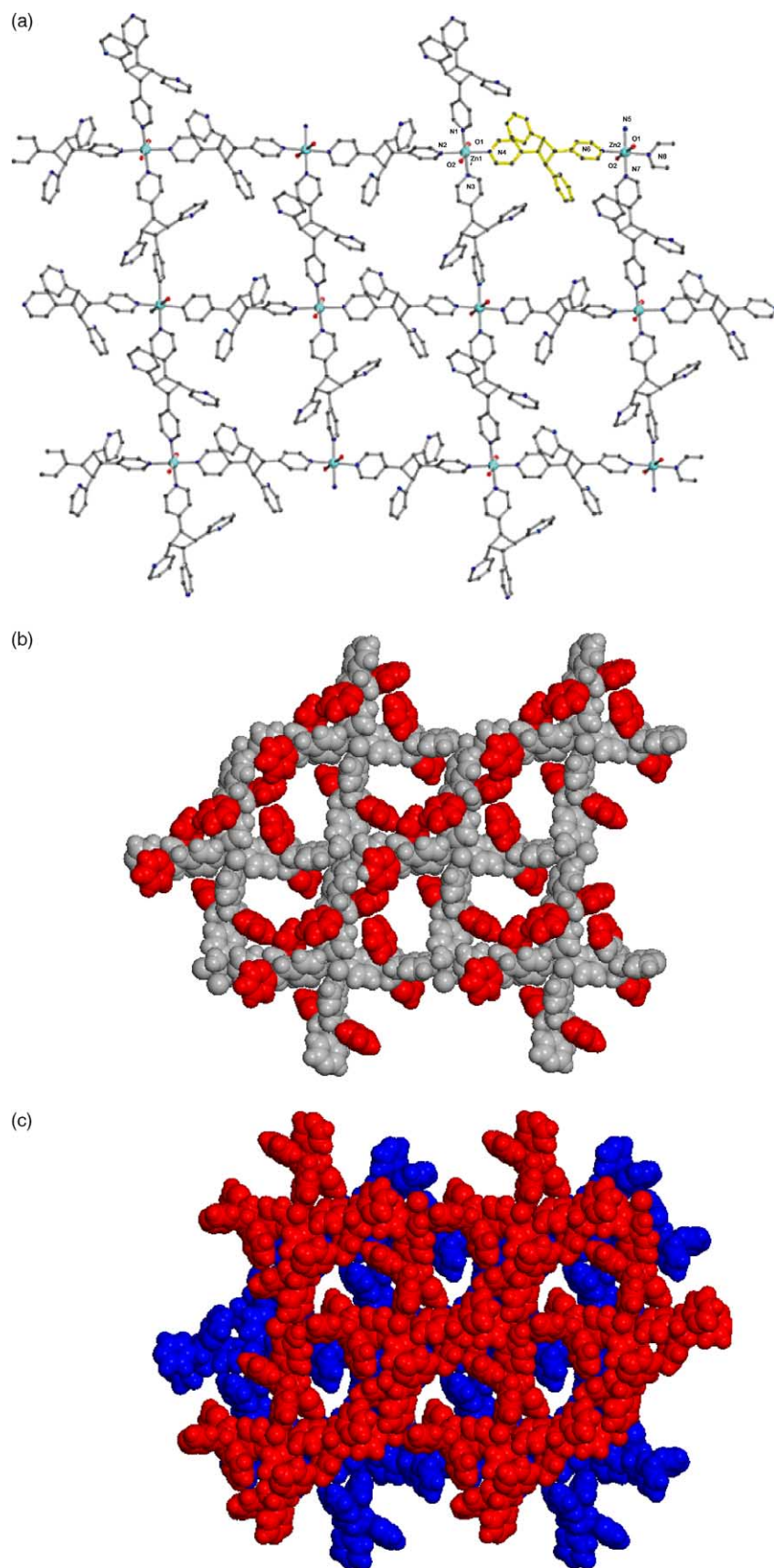


Fig. 2. X-ray crystal structure of **2**: (a) ball-and-stick representation, (b) space-filling model highlighting the free 2-pyridyl groups (red) and, (c) stacking of two layers (red and blue). (For interpretation of the reference to colour in this legend, the reader is referred to the web version of this article).

95.08 and 84.34) that host NO_3^- ions and highly disordered solvent water and methanol molecules as guests. Similar to **1**, the 2-pyridyl groups of **2** do not participate in metal–ion coordination. Instead, the 2-pyridyl groups extend into each rhombus-shaped cavity, one participating in an O–H \cdots N hydrogen bond [O \cdots N distance (Å): O(1) \cdots N(1) 2.82(2)] with an included methanol molecule. The 2-pyridyl groups of **2**, thus, serve to decorate the walls of the 2D framework and interact with included solvent guest species. The grids of **2** pack in an *ABAB*... fashion to form offset stacked layers (metal-to-metal separation: 9.3 Å) along the crystallographic *x*-axis (Fig. 2c). The stacking of the grids gives rise to slit-shaped channels that both run in the plane either along (dimensions: 7 \times 9 Å) or inclined (dimensions: 3 \times 5 Å) to the stacked grids (dimensions: 3 \times 5 Å) and are occupied by the NO_3^- and disordered solvent species.

4. Discussion

The head-to-tail regioisomer of 2,4'-tpcb possesses 4-pyridyl units that, in contrast to the head-to-head isomer, span the diagonal of the 4-membered cyclobutane ring. This stereochemical relationship has enabled 2,4'-tpcb-ht to function as a linear bridge in both **1** and **2**. The length of the bridge (N \cdots N separation: 9.9 Å) is slightly longer than 4,4'-bipyridine (N \cdots N separation: 7.1 Å) and compares favorably to the olefin *trans*-1,2-bis(4-pyridyl)ethylene (N \cdots N separation: 9.4 Å) [7]. The remaining 2-pyridyl groups then serve to decorate the surface of each framework structure. In that way, the cyclobutane ring of 2,4'-tpcb-ht has provided a scaffold from which the 2-pyridyl functionality protrudes into cavities. One of the N-donor atoms of the 2-pyridyl groups functions as a hydrogen bond acceptor site by interacting with a methanol molecule. There has been an upsurge of interest in the design of MOFs with walls lined with such free, or secondary, sites for binding [7,8]. Both 2D and 3D MOFs with free carboxyl, pyridyl, amino, and hydroxyl groups have been reported [8]. Experiments are currently underway to elucidate chemico-physical properties of **1** and **2** and determine the ability of related cyclobutanes obtained from the solid state to decorate the surfaces of additional MOF structures.

5. Conclusion

In conclusion, we have employed a hydrogen-bond-based solid-state organic synthesis to produce a functionalized cyclobutane that functions as a linear bridge of a 1D and 2D MOF structure. The cyclobutane has also served as a scaffold

by allowing the surfaces of the MOFs to be decorated with pyridine functionality. Work is now underway to construct additional MOFs based on 2,4'-tpcb and related molecules obtained from the solid state. We also note that our results demonstrate how regioisomers of a polypyridyl ligand can give different MOFs, where the information used to construct each regioisomer is carried on from the solid-state to the metal-based self-assembly process.

6. Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC-298294 for **1** and CCDC-298295 for **2**.

Acknowledgements

We acknowledge the National Science Foundation (DMR-0133138) for partial support of this work.

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