Temperature-dependent supramolecular stereoisomerism in porous copper coordination networks based on a designed carboxylate ligand

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Two novel temperature-controlled supramolecular stereoisomers of porous copper coordination networks have been synthesized and characterized.

There is a growing interest in the study of supramolecular isomerism in crystal engineering.[1] Supramolecular isomerism often results from the existence of several different building units with little or no difference in formation energy, making it difficult to accurately predict final structures. The study of supramolecular isomerism is not only important in producing novel materials with interesting properties but may also be helpful in developing a fundamental understanding of the factors influencing crystal growth.[2]

Although many coordination polymers have been reported as supramolecular isomers, a substantial number of them are based on the co-existence of different guest molecules.[1a,3] It would be more suitable to categorize these structures as pseudo-polymorphs, rather than true isomers.

Supramolecular isomers include structural isomers,[1a,3b] in which atom connectivities differ, and stereoisomers, in which atom connectivities don't change from isomer to isomer. The latter encompasses diastereomers[1b] (including *cis–trans* and conformational isomers) and enantiomers.[4]

The study of supramolecular stereoisomerism is important due to the potential of generating chiral coordination polymers based on achiral ligands. However, the study of stereoisomerism in a coordination network is still rare.[5]

In order to study supramolecular stereoisomerism systematically, we have designed a new tetra-carboxylate ligand, namely, the tetra-anion of *N*,*N*,*N*′,*N*′-tetrakis(4-carboxyphenyl)-1,4-phenylenediamine (TCPPDA) (Fig. 1). TCPPDA has many desirable characteristics, including three stereoisomers (a pair of enantiomers and a diastereomer). The first is a C_{2h} isomer with three phenyl rings oriented as left- and right-handed propellers around the two N atoms. There exists a plane of symmetry through the central phenyl ring, reflecting one N-centred propeller onto the other. The pair of enantiomers possess D_2 point group symmetry. In one case, the two N-centred propellers are all right handed (${}^{\delta}D_2$), while in the other case the direction of the N-centred propellers are inverted (${}^{\lambda}D_2$). The conversion of the isomer from C_{2h} to D_2 will take place if the direction of one propeller is inverted by rotating two *N*-carboxyphenyl bonds on one side. The interconversion of the ${}^{\delta}D_2$ and ${}^{\lambda}D_2$ isomers can be achieved by the inversion of both propellers, rotating all four *N*-carboxyphenyl bonds. The energy barrier for the inversion of a propeller should be low enough that TCPPDA should exist in all three forms at room temperature. However, in a coordination network, there is a chance that one of the three isomers will be favoured over the others. Due to the non-planarity of the TCPPDA, non-interweaving, porous coordination networks will most likely form.

In this communication, we report temperature-controlled supramolecular stereoisomerism in porous copper coordination networks $Cu_2(D_2\text{-TCPPDA})(H_2O)_2\cdot 2DMSO\cdot 6H_2O$ (**1**) and $Cu_2(C_{2h}\text{-TCPPDA})(H_2O)_2\cdot 2DMSO\cdot 6H_2O$ (**2**), possessing PtS and NbO net topologies, respectively.

The novel TCPPDA ligand was synthesized in two steps through an amination reaction.[6] Solvothermal reactions of $Cu(NO_3)_2\cdot 2.5H_2O$ and $H_4TCPPDA$ in DMSO at 120 and 115 °C result in the formation of yellow crystals of **1** and burgundy crystals of **2**,† respectively. Both compounds were suitable for X-ray diffraction studies.‡ Complexes **1** and **2** have the same formula, $Cu_2(TCPPDA)(H_2O)_2\cdot 2DMSO\cdot 6H_2O$, and include the well-known Cu_2 paddlewheel secondary building unit (SBU) (Fig. 2c) connected by the TCPPDA ligand. In **1**, both ${}^{\lambda}D_2$ and

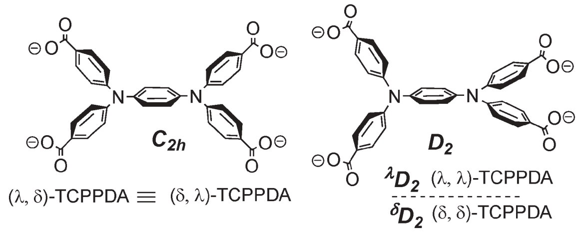

Fig. 1 The designed carboxylate ligand: The tetra-anions of *N*,*N*,*N*′,*N*′-tetrakis(4-carboxyphenyl)-1,4-phenylenediamine (TCPPDA).

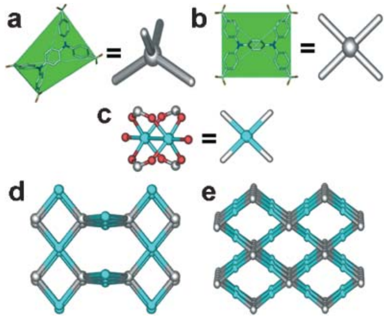

Fig. 2 View of (a) the approximate tetrahedral conformation of D_2-TCPPDA, (b) the near square-planar conformation of C_{2h}-TCPPDA, (c) the paddlewheel SBU as a square-planar node, and the resulting (d) PtS net and (e) NbO net. (Colour scheme: aqua, Cu; red, O; and grey, C.).

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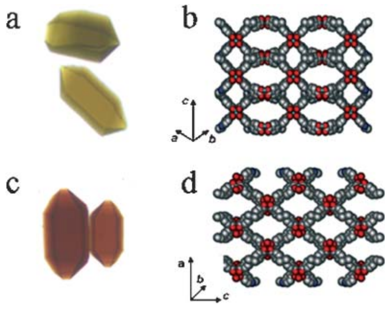

Fig. 3 (a) Photograph of single crystals of **1**. (b) 3D porous framework of **1** possessing PtS net topology. (c) Photograph of single crystals of **2**. (d) 3D porous framework of **2** possessing NbO net topology.

$^{\delta}D_2$ are found in a racemic combination, but in **2**, only the C_{2h} isomer exists. The D_2-TCPPDA can be simplified to a 4-connected tetrahedral node (Fig. 2a), and the C_{2h}-TCPPDA can be viewed as a 4-connected square-planar node (Fig. 2b).

Heating a mixture of H_4TCPPDA and $Cu(NO_3)_2{\cdot}2.5H_2O$ in DMSO to 120 °C for 24 h gave the yellow crystalline product **1** in 60% of yield (Fig. 3a). X-ray diffraction reveals that **1** adopts the orthorhombic *Cccm* space group and the 3D topology of a PtS net (Fig. 2d). The dicopper unit is axially coordinated by two water molecules and is surrounded by four carboxylate groups from four different ligands. Each TCPPDA ligand connects four SBUs, giving rise to a porous 3D framework in which DMSO and water solvates reside (Fig. 3b). The channels are 9.439 × 14.418 Å along the a-axis, 12.739 × 15.256 Å along the c-axis, and 10.847 × 23.594 Å along [111]. All of the TCPPDA ligands in **1** have D_2 symmetry, and thus are chiral. Since the ratio of $^{\delta}D_2$ to $^{\lambda}D_2$ TCPPDA is 1 : 1, the coordination network is racemic overall. The four carboxylate groups of the D_2-TCPPDA ligand are not located in one plane. If two carboxylate carbon atoms and a nitrogen atom on each end form two planes, the dihedral angle is 66° (Fig. 2a). The PtS net topology is the "default" structure of a square-planar SBU reticulated with a tetrahedral connector.[7] The structure is non-interpenetrating with a total potential solvent-accessible volume of 79.7%, calculated using the PLATON program[8] after guest and axial ligand removal.

When the same reaction was carried out under lower temperatures, burgundy crystals of **2** were obtained (Fig. 3c). Complex **2** crystallizes in the orthorhombic space group *Imma* and is the supramolecular stereoisomer of **1**. However, all of the TCPPDA ligands in **2** have C_{2h} symmetry. In each C_{2h}-TCPPDA, the four carboxylate groups lie approximately in one plane (Fig. 2b). Thus, each square-planar paddlewheel SBU links four C_{2h}-TCPPDA, and each ligand connects four paddlewheel SBUs, giving rise to a 3D porous network with the topology of an NbO net (Fig. 2e). The rhombic channels are 19.866 × 19.866 Å along the b-axis, in which DMSO and water solvates reside. After the removal of guests and axial ligands, the total calculated solvent-accessible volume (79.1%) is slightly smaller than that of **1**.

Complexes **1** and **2** possess similar thermal stabilities. TGA shows a weight loss from 50 to 350 °C, with a weight loss of 28.80% from 50 to 200 °C corresponding to six waters, two DMSO solvates and possibly two axially-coordinated water molecules (calc. 29.6%). There is no weight loss from 200 to 300 °C and both complexes decompose from 300 to 600 °C.

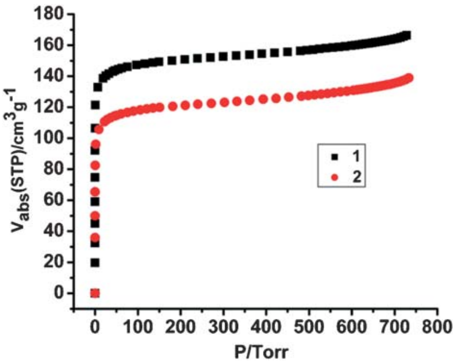

Fig. 4 Nitrogen adsorption isotherms for **1** and **2** measured volumetrically at 77 K.

The gas sorption behaviour of **1** and **2** was measured to determine whether the two isomers can retain their porosity after guest removal. The as-synthesized samples of **1** and **2** were exchanged with methanol to remove DMSO and water solvates, then dried under vacuum overnight. N_2 sorption at 77 K (Fig. 4) showed that complexes **1** and **2** possess type-I isotherms with Langmuir surface areas of 626.72 and 504.22 $m^2\ g^{-1}$, respectively.[9] The hydrogen storage capabilities (14 mg g^{-1} for **1** and 12 mg g^{-1} for **2**) of both compounds (Fig. 5) are comparable to reported values.[10] The difference in hydrogen storage capacities of the two isomers is attributed to the variation of porosity, consistent with structures and calculated potential solvent-accessible volumes.

The research presented herein has shown that stereoisomers that are interconvertible by bond rotation with a very small energy barrier, otherwise not separable at room temperature due to similar isomer stabilities, can be stabilized and isolated in pure form in a coordination network. Interestingly, the formations of complexes **1** and **2** are separated by only 5 °C in reaction temperature. To the best of our knowledge, this is the first example of temperature-dependent supramolecular stereoisomerism.

Recently, Kitagawa and co-workers also reported a case of temperature-dependent supramolecular isomerism based on the variation of coordination modes.[11] However, this can be classified as structural isomerism because the atom connectivity changes from one isomer to the other.

A possible explanation for the remarkable temperature-dependent behaviour in this report can be traced to the interconversion of the D_2 and C_{2h} isomers of TCPPDA. At

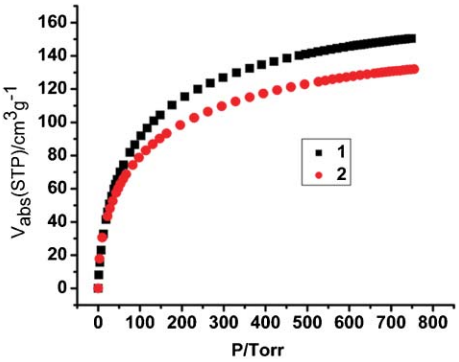

Fig. 5 Hydrogen adsorption isotherm for **1** and **2** measured volumetrically at 77 K.

temperatures lower than 115 °C, C_{2h} may dominate during the assembly of **2**. When the temperature is raised to 120 °C, conversion of the C_{2h} to D_2 may be facilitated. The inversion of the δ propeller of the C_{2h} isomer will lead to the $^{\lambda}D_2$ isomer, and the change in direction of the λ propeller in the C_{2h} isomer yields the $^{\delta}D_2$ isomer. Since there is an equal chance of inversion in either propeller of a C_{2h} isomer, a racemic mixture forms at 120 °C. The C_{2h}-TCPPDA leads to the formation of an NbO type net, and the D_2-TCPPDA gives rise to a PtS type topology.

Attempts to transform complex **2** to complex **1** at temperatures higher than 115 °C were unsuccessful. Evidently, the inversion of an N-centred propeller in a lattice takes a lot more energy than is required in a solution. Rearrangement may also include the cleavage of all metal–ligand bonds. This is quite different from the reported transformation of a metal–organic framework from the NbO to PtS net.[12]

In using the TCPPDA ligand, we have also synthesized supramolecular enantiomers in which the ligand is in either the $^{\delta}D_2$ form or the $^{\lambda}D_2$ form. These results will soon be submitted for publication.

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Notes and references

† *Synthesis of* **1**: A mixture of $Cu(NO_3)_2{\cdot}2.5H_2O$ (0.01 g, 4.3 × 10^{-4} mol) and H_4TCPPDA (0.005 g, 8.5 × 10^{-6} mol) in 1.5 mL DMSO was sealed in a Pyrex tube under vacuum. The tube was heated to 120 °C for 24 h and cooled to room temperature at a rate of 0.1 °C min^{-1}. The resulting yellow crystals were washed with DMSO to give **1** (0.0052 g). Yield: 60%. Elemental analysis calc. (%) for **1**: C, 45.10; H, 4.78; N, 2.77. Found: C, 44.83; H, 4.30; N, 2.76. *Synthesis of* **2**: A mixture of $Cu(NO_3)_2{\cdot}2.5H_2O$ (0.01 g, 4.3 × 10^{-4} mol) and H_4TCPPDA (0.005 g, 8.5 × 10^{-6} mol) in 1.5 mL DMSO was sealed in a Pyrex tube under vacuum. The tube was heated to 115 °C for 24 h and cooled to room temperature at a rate of 0.1 °C min^{-1}. The resulting burgundy crystals were washed with DMSO to give **2** (0.0028 g). Yield: 33%.

‡ *Crystal data for* **1**: $C_{34}H_{24}Cu_2N_2O_{10}$, M = 747.63, orthorhombic, space group *Cccm*, a = 15.2563(12), b = 28.288(2), c = 23.5937(18) Å, V = 10182.2(14) $Å^3$, Z = 4, D_c = 0.488 g cm^{-3}, μ = 0.437 mm^{-1}, $F(000)$ = 1520, 29155 reflections measured, 4802 unique (R_{int} = 0.0791) which were used in all calculations. Final residuals (for 113 parameters) were $R1$ = 0.0474, $wR2$ = 0.1205. CCDC 269580. *Crystal data for* **2**: $C_{34}H_{24}Cu_2N_2O_{10}$, M = 747.63, orthorhombic, space group *Imma*, a = 23.712(4), b = 27.877(4), c = 15.376(2) Å, V = 10164(3) $Å^3$, Z = 4, D_c = 0.489 g cm^{-3}, μ = 0.438 mm^{-1}, $F(000)$ = 1520, 31430 reflections measured, 5511 unique (R_{int} = 0.0541) which were used in all calculations. Final residuals (for 113 parameters) were $R1$ = 0.0547, $wR2$ = 0.1443. CCDC 269581. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b505664k

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