



**Exploiting dimensional variability in coordination polymers:
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Journal:	<i>ChemComm</i>
Manuscript ID:	CC-COM-05-2015-004349.R1
Article Type:	Communication
Date Submitted by the Author:	29-Jun-2015
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Journal Name

COMMUNICATION

Exploiting dimensional variability in coordination polymers: solvent promotes reversible conversion between 3D and chiral 1D architectures

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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DMSO promotes dimensional variability driving the formation of Cu-bpy architectures such as a 3D nanoporous network (1) and a 1D chiral polymer (2) self-assembled from achiral building blocks. The same solvent rules a reversible conversion between 1 and 2.

Coordination polymers have attracted increasing interest along the last two decades due to their several functionalities and applications such as sensing, catalysis and gas sorption (just to mention the most studied).¹ The functions of these material are strongly related to their structure. For instance, dimensionality may have strong influence on the framework flexibility and hence on the host-guest properties.² Despite the massive attention devoted by researchers to these compounds, there are still controversial opinions whether a real design in their synthesis can be applied.³ In the context of coordination polymers, the predictability of the final network and dimensionality is an open challenge as a consequence of the complexity of the self-assembly process that involves competing reversible and simultaneous interactions among the metal, the ligand, the counteranion and the solvent. Surely, the solvent has the most ambiguous and unpredictable role. It may influence and regulate the self-assembly mechanism, the crystallization, the network structure and topology and even the final properties of the coordination supramolecular system.^{3c,4} During the self-assembly it can act as ligand, as guest, as structure-directing agent or as gelator, but its influence has been rarely addressed in systematic studies.⁵ In particular, the coordinating ability of solvents can play a crucial role in promoting the network dimensionality, as evidenced by few but significant works.⁶ One of the first reported examples is the Cd(II)-4,4'-dipyridylsulphide system where different coordinating solvents (DMF, CH₃CN, CH₃OH) lead to coordination polymers with 1D, 2D or 3D dimensionality.^{6a} Much rarer are the systems where different dimensionalities are obtained from the same solvent.^{6b} In this context, we studied the

system Cu(II)-4,4'-bipyridine (bpy) in the presence of the coordinating solvent DMSO starting from Cu(ClO₄)₂ as metal source. As already reported, [Cu(bpy)₂(X)]_n systems have been obtained starting from several copper metal salts (often X = BF₄⁻, PF₆⁻ and CF₃SO₃⁻)^{2,7} leading to frameworks with 2D and 3D dimensionality. It has been shown how the 2D [Cu(bpy)₂(CF₃SO₃)_n] framework can be transformed into a hydrogen bond assisted 3D architecture through a solvent (H₂O) mediated process.^{7f} Again, selective solvent dependent routes have been developed to obtain 2D and 3D [Cu(bpy)₂(CF₃SO₃)_n] frameworks. It has been demonstrated that such a different dimensionality has a strong influence on the gas adsorption properties. In this communication, we show that the highly coordinating solvent DMSO can promote a reversible conversion between a 3D network and a chiral 1D Cu-bpy based architecture. Fig. 1 summarizes our results: by adding the bpy ligand to Cu(ClO₄)₂ dissolved in DMSO, we obtained the 3D network {Cu₂(bpy)₄(DMSO)₃(ClO₄)₃·2DMSO}_n (**1**) after slow evaporation of the solvent. At variance, the chiral (M and P) {Cu(bpy)₂(DMSO)₄](ClO₄)₂]_n (**2**) 1D coordination polymer is formed if we add a co-solvent (EtOAc) to the DMSO solution. Moreover, **1** can be redissolved in DMSO and converted in **2**, *viceversa* **2** can be converted in **1** in the same way.

The 3D network **1** was obtained in high yield (ca. 90%) as deep blue single crystals. As determined by single crystal X-ray studies, the compound crystallizes with an orthorhombic *Pbca* cell where *b* and *c* axes have similar length (*b* = 28.4369(4) and *c* = 28.5016(3)). The cell is very close to that reported for the [Cu(bpy)₂(CF₃SO₃)_n] framework that crystallizes with a tetragonal *I*₄/acd space group.^{8,2,7c} The compound contains coordinated and uncoordinated DMSO solvent molecules and ClO₄⁻ anions. The asymmetric unit of **1** is shown in Fig. 2a. Compared to the similar [Cu(bpy)₂(CF₃SO₃)_n] framework,^{7c} which contains one independent Cu(II) ion, the asymmetric unit of **1** contains two independent Cu(II) centres. The equatorial positions of the metal sites are occupied by bpy molecules (Cu-N = 2.01-2.04 Å) in a very similar fashion to the previously reported 2D and 3D Cu-bpy based architectures. The two copper atoms differ in the axial

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† Electronic supplementary information (ESI) available: Syntheses, CD spectra and crystallographic details. CCDC numbers: 1402764–1402766. See DOI: 10.1039/x0xx00000x

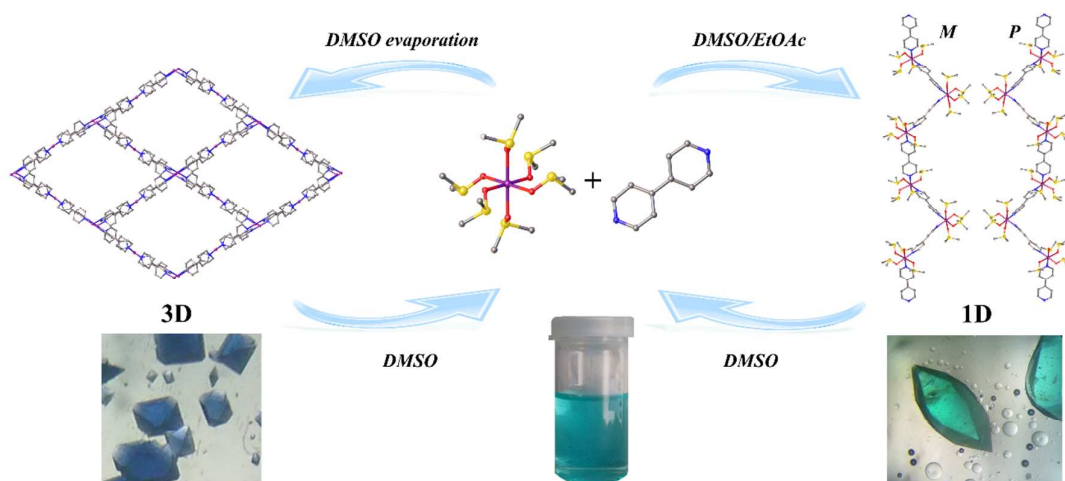


Fig. 1 Reversible control on the dimensionality of the Cu-bpy based coordination polymers **1** and **2** promoted by the coordinating solvent DMSO. Slow evaporation leads to a 3D framework (**1**) while crystallization in presence of a co-solvent gives a conglomerate of enantiomeric pure single crystals (**2**) starting from achiral building blocks. Colour code: Cu, purple; O, red; S, yellow; N, blue; C, grey; H omitted.

positions of their Jahn-Teller distorted octahedral coordination. Cu1 is coordinated by two DMSO molecules, while Cu2 by one solvent molecule and one perchlorate anion. Cu-O distances are similar for the DMSO molecules ($\text{Cu-O}_{\text{DMSO}} = 2.35\text{--}2.47 \text{ \AA}$) and higher for the anion oxygen ($\text{Cu-O}_{\text{ClO}_4} = 2.64 \text{ \AA}$).

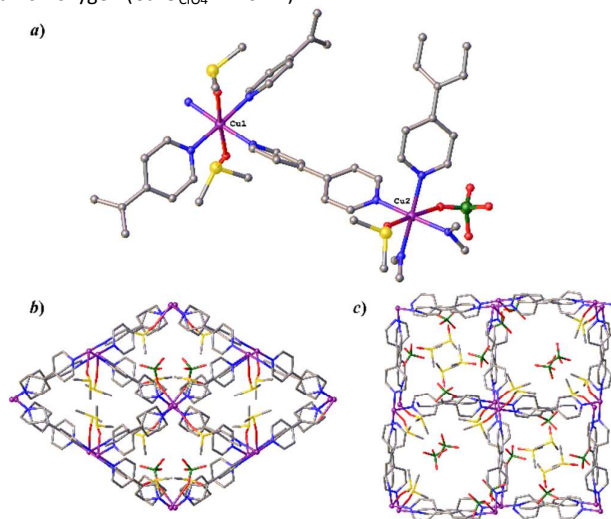


Fig. 2 a) Asymmetric unit in compound **1**, uncoordinated ClO_4^- anions and DMSO molecules omitted. b) Rhomboid channels along the c axis c). Square channels along the a axis. Colour code: Cu, purple; Cl, green; O, red; S, yellow; N, blue; C, grey; H omitted.

Despite the different space group and asymmetric unit, the supramolecular 3D framework is essentially the same described by Ciani *et al.*^{7c} Although in compound **1** the Cu(II) centres are not equivalent like in the tetragonal structure, they act as similar planar-square nodes for the 3D network leading to large rhombic channels along the b and c axes (Fig 2b), and to square channels along the a axis (Fig 2c). In both the 3D networks (**1** and $[\text{Cu}(\text{bpy})_2(\text{CF}_3\text{SO}_3)]_n$ ^{7c}) the axial positions of Cu(II) ions are occupied by solvent molecules and/or anions allocated in the structures voids. Both the 3D frameworks develop along the equatorial planes of the Cu(II) ions through Cu-bpy-Cu fragments. This leads to two

structures with the same topology (4^28^4 – lvt, 2-fold interpenetrated). The edge along the Cu1-bpy-Cu2-bpy-Cu1 chain is 22 \AA *ca.* (rhomboid units delimited by Cu1 centres have edge of 22.07 and 22.08 \AA , while those delimited by Cu2 centres of 22.08 and 22.09 \AA). Along the a axis we observe square channels with Cu1-bpy-Cu2 edges of 11 \AA *ca.* (two slight different Cu1-Cu2 distances, 11.05 and 11.06 \AA , are present). As depicted in Fig. 2c, two different square channels are generated. The first contains the axial coordinated solvent molecules and anions, plus uncoordinated anions. The second contains only uncoordinated anions and DMSO molecules.⁵⁵ If the DMSO solvent is led to complete evaporation, a second kind of light blue single crystals appears as an impurity in the last evaporation stages (yield 1–2 % *ca.*). X-ray analysis reveals a chiral 1D coordination polymer of formula $[\text{Cu}(\text{bpy})_2(\text{DMSO})_4][\text{ClO}_4]_2 \cdot n$ (**2**). Compound **2** can be synthesized in quantitative yield by layering the DMSO solution with a co-solvent (*i. e.* EtOAc).

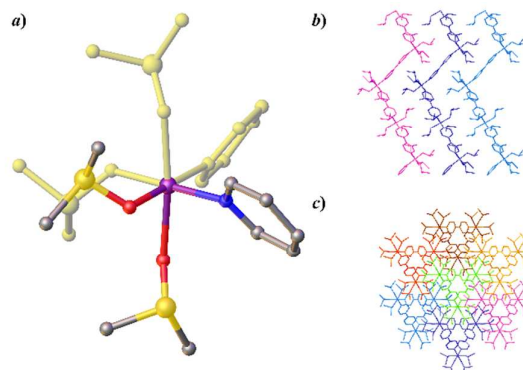


Fig. 3 a) Asymmetric unit in compound **2**, ClO_4^- anions omitted, light yellow: atoms related by symmetry (+y, +x, 1-z). b, c) Packing of compound **2** along a and c axes, respectively. Colour code: Cu, purple; O, red; S, yellow; N, blue; C, grey; H omitted.

The 1D polymer has a helicoidal shape and crystallizes in the trigonal $P3_121$ (**2M**) or $P3_221$ (**2P**) chiral space group. Interestingly, although we start from achiral building blocks, enantiopure single crystals can be obtained by means of spontaneous resolutions. The

bulk product is a conglomerate, as evidenced by Circular Dichroism (CD) spectroscopy that shows a silent CD signal (ESI). Trials to control the handedness during the crystallization were carried on by introducing a chiral inducing agent to achieve a bulk homochiral product, but also in this case a conglomerate was obtained. The asymmetric unit of **2** is shown in Fig. 3a. The metal centre has a Jahn-Teller distorted octahedral coordination. The equatorial positions are occupied by two symmetry related DMSO oxygen atoms and two symmetry related bpy nitrogen atoms (Cu-O = 2.01 Å, Cu-N = 2.02 Å). The axial sites are occupied by two symmetry related solvent molecules (Cu-O = 2.33 Å). The edge Cu-bpy-Cu is 11 Å *ca.*, this length is in perfect agreement with results found for compound **1**. The chain grows as a threefold helix along the *c* axis with a 23 Å *ca.* pitch.

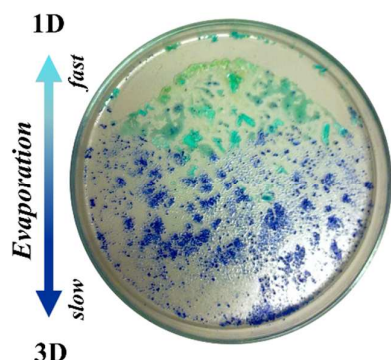


Fig. 4 Crystallization of compounds **1** and **2** by complete DMSO evaporation on a Petri dish lying on an inclined plane. In the area where the evaporation is slower crystallization of **1** occurs, on the contrary, a faster evaporation promotes the formation of **2**.

As stated above, both compounds **1** and **2** can be easily redissolved in DMSO and converted each other by changing the crystallization conditions. DMSO evaporation leads to **1**, while crystallization from a DMSO/EtOAc solution leads to **2**. Hence, the same coordinating solvent (DMSO) drives the dimensionality of these Cu-bpy architectures through the molecular (0D) $\{Cu(DMSO)_6\}^{2+}$ complex generated in solution. Moreover, we found that also the solvent evaporation rate can affect the final product. In particular, faster evaporation seems to promote the formation of compound **2**. On the contrary, slower evaporation promotes the formation of framework **1**. This can be shown by placing a Petri dish containing a $Cu(ClO_4)_2$ and a bpy DMSO solution on an inclined plane. In the area with less solvent (hence faster evaporation) we observed the formation of **2**, while in the area with more solvent (slower evaporation) the formation of **1**, Fig. 4.

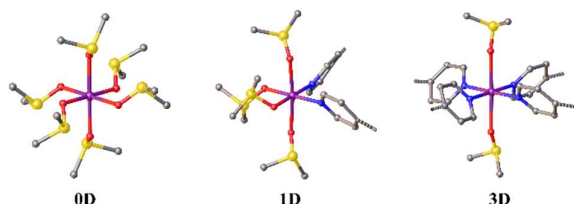


Fig. 5 Local coordination of the Cu(II) centre, DMSO blocks a lower numbers of coordination sites moving from the species in solution (0D), to compound **2** (1D) and to compound **1** (3D). Colour code: Cu, purple; O, red; S, yellow; N, blue; C, grey; H omitted.

In solution, DMSO and bpy molecules establish a series of dynamic equilibria to coordinate the metal centre during the self-assembly process of coordination polymers.^{§§§} DMSO promotes the formation of compounds **1** or **2** and the dimensional variability by blocking a different number of coordinative sites as depicted in Fig. 5. This allows to selectively and reversibly obtain a 3D nanoporous network and a 1D chiral polymer. Notably, the 1D chiral architecture is obtained from achiral building blocks and it displays spontaneous resolution during the crystallization leading to a racemic mixture of enantiomeric pure single crystals.

This work was supported by the Italian MIUR through FIRB RBAP114AMK "RINAME". M. R. thanks the University of Padova for a "Senior Research" fellowship and for a "Young Scholar" grant. Authors thank Dr. Marco Crisma of ICB-CNR and Dr. Jacopo Tassarolo of the University of Padova for helpful discussions.

Notes and references

§ The orthorhombic *Pbca* space group is a subgroup (general, no maximal) of the tetragonal *I4₁/acd* space group. The orthorhombic *Ibca* space group is the intermediate one.

§§ In the $[Cu(bpy)_2(CF_3SO_3)]_n$ framework reported by Ciani *et al.*^{7c} these channels have been described like hydrophilic and hydrophobic since they contain H_2O and CH_2Cl_2 molecules, respectively.

§§§ The presence of water in these equilibria cannot be ignored.

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