

Reversible single-crystal-to-single-crystal guest exchange in a 3-D coordination network based on a zinc porphyrin

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A self-complementary tecton based on a zinc porphyrin core bearing two pyridines at the opposite *meso* positions leads to the formation of a 3-D coordination network in the crystalline phase which offers channels which are filled with solvent molecules; reversible exchange of the guest molecules has been proven to take place in a single-crystal-to-single-crystal type transformation demonstrating the robustness of the coordination framework.

The generation of robust porous crystalline materials with controlled pore size is still a challenge.¹ The increasing interest in this type of solid material is due to possible applications such as specific sorption, gas storage and separation, ion exchange and catalysis that such architectures may offer.

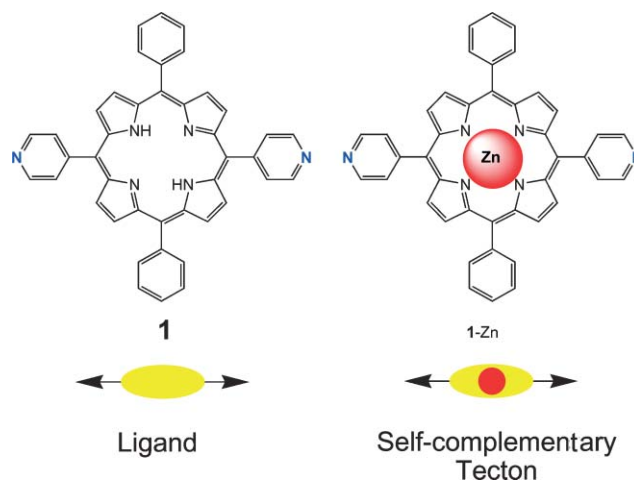
One of the major difficulties associated with porous crystalline solids is the loss of structural integrity upon removal of included guest molecules. A further key issue is to clearly demonstrate that the guest removal and/or exchange takes place by a single-crystal-to-single-crystal transformation.²

Here we report on the formation of robust porous crystals formed by a self-complementary metallaporphyrin based tecton and their ability to undergo single-crystal-to-single-crystal reversible guest exchange.

The porphyrin core is an interesting unit for the design of new tectons. Indeed, one may introduce at the β -pyrrolic or/and *meso* positions a variety of functional groups and recognition sites. In particular, for the generation of coordination networks in the crystalline phase, *i.e.* periodic infinite hybrid metallo-organic architectures based on mutual interconnection of organic and metallic units, one may functionalize the porphyrin core with additional coordinating sites.³

We have previously demonstrated the formation of infinite coordination networks⁴ using atropisomers of *meso* substituted porphyrins⁵ as coordinating tectons.

Following our approach⁶ dealing with the design of coordination networks, we considered the metallaporphyrin **1-Zn** as a self-complementary tecton since it contains both a metal centre capable of further coordination and two pyridines as extra coordinating sites (Scheme). The design of the ligand **1** (5,15-di(4-pyridyl)-10,20-diphenylporphyrin) is based on the porphyrin core bearing two pyridines as extra coordination sites at the 5 and 15 *meso* positions. Thus, compound **1**, prepared according to reported procedure,⁷ is a hexadentate ligand offering four convergent N atoms within the core of the porphyrin ring and two oppositely oriented pyridines.



Scheme 1

In order to transform the ligand **1** into a tecton, the porphyrin derivative was metallated upon treatment with $\text{Zn}(\text{OAc})_2$ affording thus the neutral metallaporphyrin based tecton **1-Zn**. As the metal, Zn^{2+} was chosen because it leads to a neutral unit thus avoiding the occupation of pores by counter ions. Furthermore, although $\text{Zn}(\text{II})$ in a porphyrin environment usually adopts pentacoordination with square-pyramidal geometry, examples of hexacoordinate complexes have been reported.⁸ This strategy has been also previously used for the design of coordination networks based on a porphyrin derivative bearing four pyridine units.^{9,10}

Upon slow diffusion at room temperature of a solution of **1** (0.5 mg) in CHCl_3 (0.5 ml) into a solution of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (2.5 mg) in MeOH or EtOH (0.5 ml), purple mono-crystalline material is obtained after *ca.* 7 days. In both cases, the isomorphous crystals (Rhombohedral, $Z = 9$, space group $R\bar{3}$) are composed of **1-Zn** units and solvent molecules which were found to be disordered.[†]

In both cases, the self-complementary tecton **1-Zn** leads to the formation of a 3-D hexagonal network resulting from the interconnection of the tectons through Zn-N atoms belonging to two adjacent pyridine units (Fig. 1A and B). The porphyrin core of **1-Zn** is planar with almost no out of plane deformation and the Zn atom is located almost at the centre of the ring composed of four N atoms belonging to pyrrolic units (Zn-N distances of *ca.* 2.06 Å and NZnN angles ranging from *ca.* 89° to 91° (*cis*) and 180° (*trans*)). The coordination sphere around zinc is composed of 6 N atoms with the two pyridines in apical positions (Zn-N distance of *ca.* 2.35 Å). The geometry around the metal centre is a distorted octahedron. Indeed, the two apical pyridines are not perpendicular

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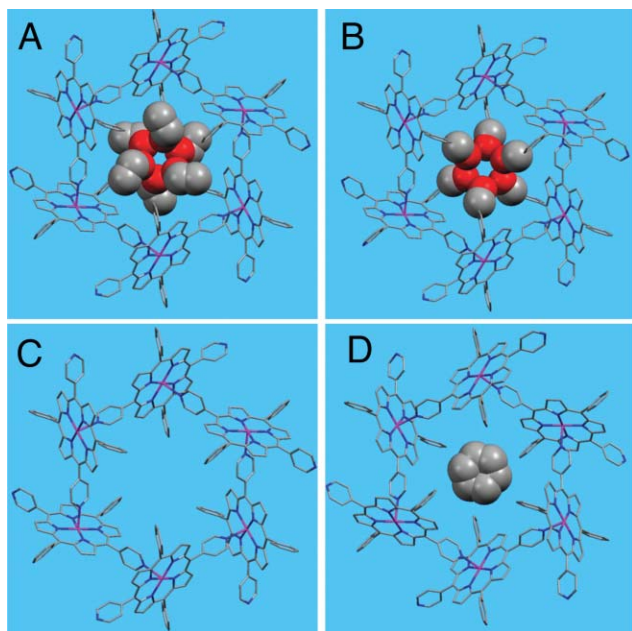


Fig. 1 Portions of structures of **1-Zn·EtOH** (A), **1-Zn·MeOH** (B), **1-Zn** (C) and **1-Zn·cyclohexane** (D) obtained by X-ray diffraction on single-crystals. For the sake of clarity, H atoms are not represented.

to the mean plane (24 atoms) of the porphyrin but tilted by *ca.* 69.9°. The generation of the 3-D hexagonal network results from this deformation. The voids, hexagonal channels, thus generated are filled with disordered MeOH or EtOH molecules with occupancy of 1/3 per **1-Zn** unit. No specific interactions with the framework were spotted. The same type of structure has been reported for the tetrapyrroline analogue of **1** combined with zinc(II),⁹ Co(II) or Mn(II).¹⁰ However, for both cases, no detailed study on the guest exchange process has been reported.

The treatment under vacuum at room temperature for 24 hours of crystals of **1-Zn·X** (X = MeOH or EtOH) afforded crystalline solids which were studied by XRD. The two crystals were identical and only composed of **1-Zn** demonstrating thus a single-crystal-to-single-crystal transformation. The robust empty framework (Fig. 1C) presents almost identical structural features† as the parent solvates (Fig. 1A and 1B). Interestingly, upon exposure of the empty framework to vapours of MeOH or EtOH, the parent structures could be regenerated. This was again demonstrated by XRD studies on a single crystal (Fig. 2). Furthermore, upon sinking the crystal corresponding to the empty framework into cyclohexane, again a single-crystal-to-single-crystal transformation was observed and the resulting crystal corresponded to the inclusion of cyclohexane within hexagonal channels of the framework (Fig. 1D). The reverse process leading to the empty framework was also demonstrated by vacuum treatment of cyclohexane solvates at 50 °C for 1 week.

Finally, it was again demonstrated by XRD studies that the guest exchange may be achieved in solution through a single-crystal-to-single-crystal transformation. Indeed, suspension of **1-Zn·X** (X = MeOH or EtOH) crystals in cyclohexane affords in both cases the cyclohexane inclusion crystalline solid.

In conclusion, a complementary metallatecton based on the zinc porphyrin core bearing two additional pyridines has been designed and prepared. This unit self-assembles into a robust 3-D porous

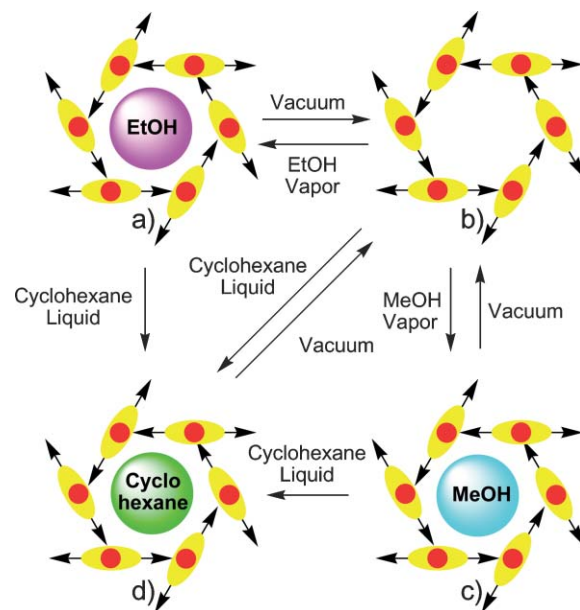


Fig. 2 Schematic representation of the guest exchange taking place on a single crystal demonstrating the conservation of structural integrity of the framework (for conditions see text).

network. The structural integrity of both the empty and solvent inclusion frameworks is maintained. Guest exchange between different solvates and the empty framework takes place both in solution and through the vapour phase *via* single-crystal-to-single-crystal transformations.

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Notes and references

† (Purple, 173(2) K), Rhombohedral, $Z = 9$, space group $R\bar{3}$, (**1-Zn**·0.33 EtOH)_n: $C_{42}H_{26}N_6Zn \cdot 0.33$ EtOH, $M = 695.74$, $a = b = 33.0866(4)$, $c = 9.4360(2)$ Å, $U = 8945.9(2)$ Å³, $D_c = 1.159$ g cm⁻³, Mo-K α , $\mu = 0.653$ mm⁻¹, 4560 independent data with $I > 2\sigma(I)$, $R = 0.0622$, $R_w = 0.2286$. (**1-Zn**·0.33 MeOH)_n: $C_{42}H_{26}N_6Zn \cdot 0.33$ MeOH, $M = 690.97$, $a = b = 32.9114(13)$, $c = 9.4246(5)$ Å, $U = 8840.7(7)$ Å³, $D_c = 1.166$ g cm⁻³, Mo-K α , $\mu = 0.661$ mm⁻¹, 4642 independent data with $I > 2\sigma(I)$, $R = 0.0503$, $R_w = 0.1696$. (**1-Zn**·0.33 cyclohexane)_n: $C_{42}H_{26}N_6Zn \cdot 0.33$ cyclohexane, $M = 706.10$, $a = b = 33.0583(7)$, $c = 9.3302(5)$ Å, $U = 8830.4(5)$ Å³, $D_c = 1.192$ g cm⁻³, Mo-K α , $\mu = 0.662$ mm⁻¹, 4499 independent data with $I > 2\sigma(I)$, $R = 0.0479$, $R_w = 0.1044$. (**1-Zn**)_n: $C_{42}H_{26}N_6Zn$, $M = 680.06$, $a = b = 33.0734(5)$, $c = 9.2921(4)$ Å, $U = 8802.4(4)$ Å³, $D_c = 1.155$ g cm⁻³, Mo-K α , $\mu = 0.662$ mm⁻¹, 4478 independent data with $I > 2\sigma(I)$, $R = 0.0344$, $R_w = 0.0843$. Data were collected on a Bruker SMART CCD diffractometer and structural determination was achieved using the SHELXS-97. For all three structures containing solvent molecules, the occupancy has been fixed in order to obtain the best fit with the largest residual peaks. All hydrogen atoms have been calculated except those of the solvent molecules. CCDC 270779–270782. See <http://dx.doi.org/10.1039/b508135c> for crystallographic data in CIF or other electronic format.

- S. Kitagawa, *Angew. Chem., Int. Ed.*, 2004, **43**, 2434; G. Ferey, C. Mellot-Draznieks, C. Serre and F. Millange, *Acc. Chem. Res.*, 2005, **38**, 218; K. T. Holman, A. M. Pivovar, J. A. Swift and M. D. Ward, *Acc. Chem. Res.*, 2001, **34**, 107; M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keefe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior and M. J. Rosseinsky, *Acc. Chem. Res.*, 2005, **38**, 273.
- S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148; G. J. Halder and C. J. Kepert,

- J. Am. Chem. Soc.*, 2005, **127**, 7891; H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276; B. Rather and M. J. Zaworotko, *Chem. Commun.*, 2003, 830; E. Y. Lee and M. P. Suh, *Angew. Chem., Int. Ed.*, 2004, **43**, 2798; K. Takaoka, M. Kawano, M. Tominaga and M. Fujita, *Angew. Chem., Int. Ed.*, 2005, **44**, 2151; S. Takamizawa, E. Nakata and T. Saito, *Angew. Chem., Int. Ed.*, 2004, **43**, 1368.
- 3 B. F. Abrahams, B. F. Hoskins, D. M. Michail and R. Robson, *Nature*, 1994, **369**, 727; K. S. Suslick, P. Bhurappa, J.-H. Chou, M. E. Kosal, S. Nakagaki, D. W. Smithenry and S. R. Wilson, *Acc. Chem. Res.*, 2005, **38**, 283; I. Goldberg, *Chem. Commun.*, 2005, 1243; L. Pan, S. Kelly, X. Huang and J. Li, *Chem. Commun.*, 2002, 2334; L. Pan, X. Huang, H.-L. N. Phan, T. J. Emge, J. Li and X. Wang, *Inorg. Chem.*, 2004, **43**, 6878; L. Carlucci, G. Ciani, D. M. Proserpio and F. Porta, *CrystEngComm*, 2005, **7**, 78.
- 4 B. Zimmer, M. Hutin, V. Bulach, M. W. Hosseini, A. De Cian and N. Kyritsakas, *New J. Chem.*, 2002, **26**, 1532; B. Zimmer, V. Bulach, M. W. Hosseini, A. De Cian and N. Kyritsakas, *Eur. J. Inorg. Chem.*, 2002, 3079–3082.
- 5 C. Drexler, M. W. Hosseini, J.-M. Planeix, G. Stupka, A. De Cian and J. Fischer, *Chem. Commun.*, 1998, 689; B. Zimmer, V. Bulach, C. Drexler, S. Erhardt, M. W. Hosseini and A. De Cian, *New J. Chem.*, 2002, **26**, 43.
- 6 M. W. Hosseini, *Acc. Chem. Res.*, 2005, **38**, 313; M. W. Hosseini, *CrystEngComm*, 2004, **6**, 318; M. W. Hosseini, *Coord. Chem. Rev.*, 2003, **240**, 157.
- 7 G. G. Meng, R. J. Brian and K. A. Skov, *Can. J. Chem.*, 1994, **72**, 2447.
- 8 J. K. M. Sanders, N. Bampos, Z. Clyde-Watson, S. L. Darling, J. C. Hawley, H.-J. Kim, C. C. Mak and S. J. Webb, *The Porphyrin Handbook*, Academic Press, New York, Eds. K. M. Kadish, K. M. Smith, R. Guillard, 2000, Vol. 3, p. 1.
- 9 H. Krupitsky, Z. Stein and I. Goldberg, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1994, **18**, 177.
- 10 K.-J. Lin, *Angew. Chem.*, 1999, **38**, 2730.