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# Molecular tectonics: coordination networks based on porphyrins bearing pyridine *N*-oxide groups as coordinating sites†

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The combination of the two positional isomers **1** and **2**, porphyrin backbones bearing two pyridine *N*-oxide groups (PNO), with Zn(II) cations leads to **1**-Zn and **2**-Zn self-complementary tectons which generate in the crystalline phase analogous 1-D zigzag type coordination networks with different metrics. In both cases, only one PNO group bridges the consecutive tecton through coordination to the Zn atom which adopts the square based pyramidal geometry.

## Introduction

Coordination polymers or networks are infinite architectures formed by mutual interconnection between organic moieties bearing coordinating sites and metal cations or metal complexes possessing free coordination sites. Within the molecular tectonics approach,[1–4] both the organic- and metal-containing moieties are considered as tectons or active construction units.

The rational design of coordination polymers in the solid state with predicted connectivity and structure is a subject of current interest because one may combine a large variety of organic and metallic tectons and thus generate an infinite number of periodic molecular architectures which may be of interest for their applications as functional materials.[5–12]

In order to generate coordination networks, also called metalloorganic frameworks (MOF), one must consider a pair composed of the organic and metallic tectons.

Dealing with the organic tecton, let us focus here mainly on the porphyrin core as a backbone. Indeed, porphyrin derivatives have been widely used as tectons for the generation of molecular crystalline solids displaying chemical, physical or catalytic properties.[13] The interest in the porphyrin backbone arises from its robustness (both thermally and chemically), its ability to be metallated by a variety of elements and its possible functionalisation at the β-pyrrolic and/or *meso* positions with a large variety of coordinating groups. Among various functionalised porphyrins reported, derivatives such as **3**, **4** and **6** (see Scheme 1) bearing pyridine groups at the *meso* position as exocyclic coordinating sites have been shown to form several topologically different finite[14–20] or polymeric[21–30] architectures.

Dealing with the metal centre, the $Zn^{2+}$ ion is a particularly well suited cation for the construction of coordination polymers.[31] Indeed, the spherical nature ($d^{10}$ configuration) of the $Zn^{2+}$ cation affords variability in terms of coordination environment and geometry as well as coordination lability. The latter issue (reversibility of binding) is of particular importance for the self-assembly process since it enables the metal ion and ligand pair to rearrange during the building event and thus to generate highly ordered network structures. Another interesting feature associated with the use of a porphyrin core and a Zn(II) cation is related to the fact that such a combination leads to a neutral tecton, thus avoiding the presence of counterions. Indeed, when anions are required, they might play an important role through their coordination to the metal centre and thus modify the connectivity of the network.

Combinations of porphyrins **4–6** as ligands with Zn(II) afford the metalloporphyrins ***X***-Zn (***X*** = **4–6**). These complexes behave as self-complementary tectons and were shown to self-assemble in the solid state into coordination polymers.[21–30,32] The formation of these extended architectures results from the ability of the zinc centre, localised within the porphyrin ring, to increase its coordination number from 4 to 5 (square-pyramidal geometry)[22] or in a few cases from 4 to 6, (octahedral geometry)[30,32] through the coordination of one or two pyridines respectively.

The monopyridyl porphyrin tecton **5**-Zn has been shown to generate a 1-D coordination network in the crystalline phase (Fig. 1).[22] The chain architecture, of the zigzag type, is formed by the interconnection of consecutive **5**-Zn complexes through coordination of the pyridine nitrogen atom of each tecton to the metal centre of the consecutive **5**-Zn unit. The coordination of the peripheral pyridine unit to the Zn(II) takes place at the axial position and leads to a pentacoordinated metal centre adopting the square pyramidal coordination geometry.

Interestingly, the same type of arrangement has been observed with the tetrapyridylporphyrin complex **6**-Zn, in crystals obtained from non-protic solvents.[30] In this case, the tetradentate ligand **6**-Zn also behaves as a monodentate tecton. Indeed only one pyridine unit out of the four available participates in the interconnection of the consecutive units through Zn–pyridine bond formation.

Recently,[32] using **4**-Zn complex as a self-complementary tecton, we have demonstrated the formation of a robust porous crystalline material capable of reversible guest exchange. In this case, the Zn is hexacoordinated and both pyridyl groups are involved in the interconnection of consecutive tectons into a 3-D coordination polymer offering hexagonal channels. The same type of arrangement has also been observed for **6**-Zn in crystals obtained from protic solvents.[30]

Although pyridine is one of the most often used coordinating groups for the formation of coordination networks, recently pyridine *N*-oxide (PNO) has been demonstrated to be another interesting neutral unit for the generation of infinite

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† Dedicated to the memory of A. Rassat.

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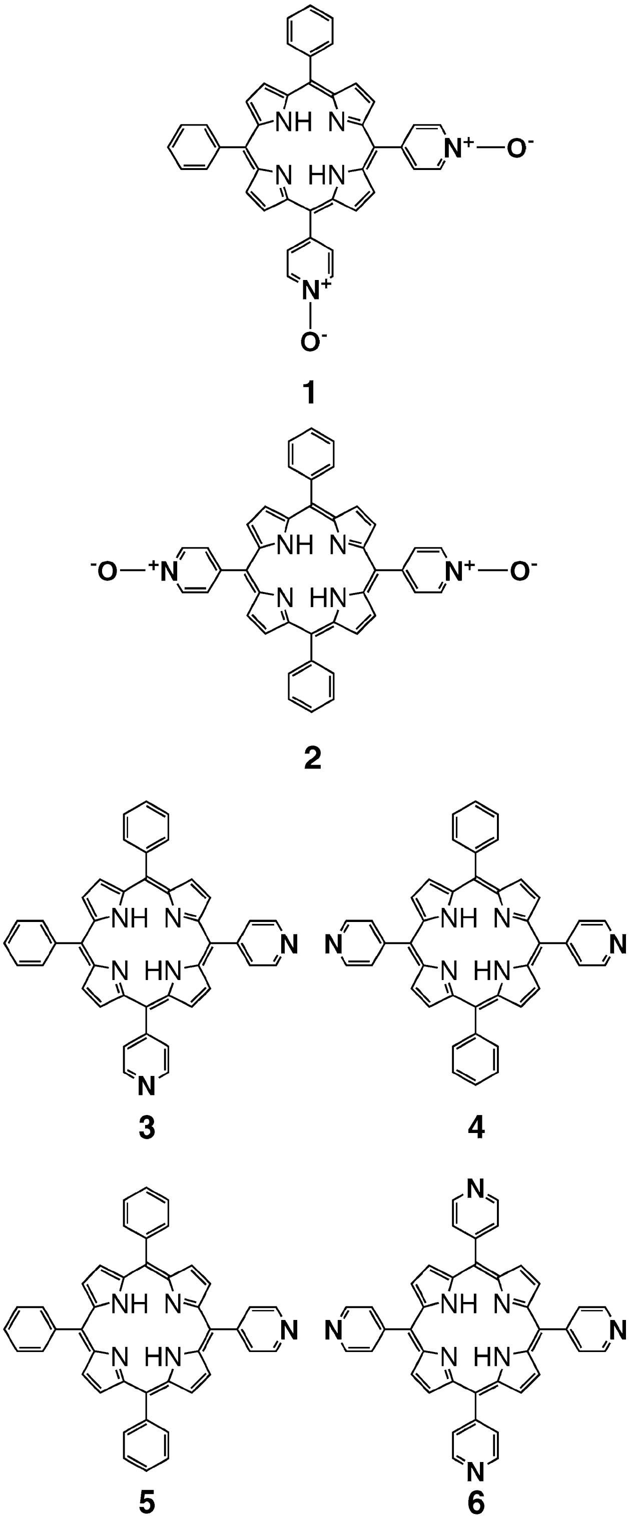

Scheme 1

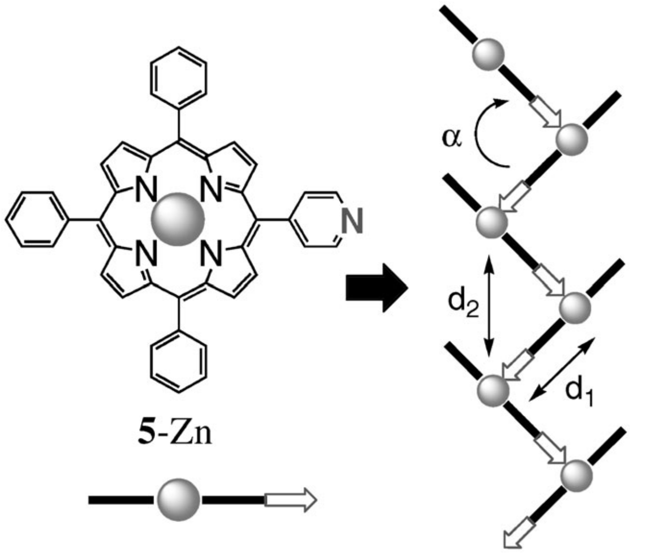

**Fig. 1** Schematic representation of the infinite edge-to-face 1-D network formed by **5**-Zn. The open arrow represents the pyridine nitrogen lone pair.

frameworks.[33,34] In particular, Schröder *et al.* showed that a combination of tectons bearing PNO moieties and lanthanide cations leads to the formation of a variety of coordination networks.[33]

The oxidation of the pyridyl groups to pyridine *N*-oxide leads to a less sterically demanding and more coordinatively flexible coordinating site. Indeed, for the PNO group, the binding takes place through the oxygen, increasing the size of the tecton by *ca.* 1.3 Å for each PNO group with respect to the unoxidised precursor. Furthermore, when compared to pyridine, for which the binding of the metal is linear because of the disposition of the lone pair of nitrogen, in the case of PNO, again due to the orientation of the lone pairs centred on the oxygen atom, the binding of the metal centre occurs in a bent fashion with an M–O–N bond angle of *ca.* 120°.

In the continuation of our exploration of new tectons able to form infinite coordination networks,[3,7] in particular porphyrin based building blocks,[32,35–38] taking into account the above-mentioned features of the PNO group, we combined the latter with the porphyrin core and thus designed the two porphyrin derivatives **1** and **2** as tectons (see Scheme 1). Both **1** and **2** are based on the porphyrin core functionalised at all four *meso* positions by two phenyl and two pyridine *N*-oxide groups. Compounds **1** and **2** are isomers and differ by the location of the PNO groups. Whereas for **1**, the two PNO groups located at the *meso* positions 5 and 10 are in *cis* disposition, for **2**, the two binding sites are in *trans* configuration (PNO groups attached to the *meso* positions 5 and 15). Following the reported procedure, porphyrin derivatives **1** and **2** were obtained upon oxidation by *m*-chloroperbenzoic acid of the corresponding precursors **3** and **4**.[39]

In this contribution, we report on the formation under self-assembly conditions and characterisation in the crystalline phase by X-ray diffraction on single crystals of three coordination polymers based on the self-complementary tectons **1**-Zn, **2**-Zn and **3**-Zn.

Since tectons **1**-Zn and **2**-Zn bear two PNO groups, several relative orientations of the two oxygen lone pairs involved in the binding of the metal centre are possible. In particular, if the lone pair for each PNO group was located in the same plane as the pyridine moiety, one would expect three relative orientations (*syn*, *anti* and mixed) in the case of **1**-Zn, whereas in the case of **2**-Zn, only the *syn* and *anti* conformations of the lone pair are possible (Fig. 2). In marked contrast with the pyridine based precursors **3** and **4**, this angular flexibility adds another dimension to the design possibility.

## Results and discussion

In order to compare the role played by the pyridine and PNO groups in the formation of coordination networks, all three ligands **1–3** were explored. At room temperature, upon slow diffusion of a $CHCl_3$ solution containing ligands **1**, **2** or **3** into a solution of $ZnCl_2$ or $Zn(OAc)_2$ in MeOH, purple crystalline materials were obtained after 5–7 days. Their analysis by single crystal X-ray diffraction revealed that, in the case of **1** and **2**, crystals are composed of **1**-Zn (monoclinic, *C*2/*c*) or **2**-Zn

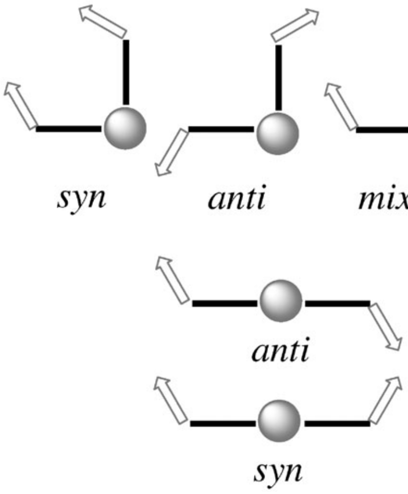

**Fig. 2** Schematic representation of the relative orientation of the oxygen lone pairs (open arrows) of the two PNO groups in **1**-Zn (top) and **2**-Zn (bottom). The sphere represents the Zn atom and the bold lines the porphyrin core bearing the two PNO groups.

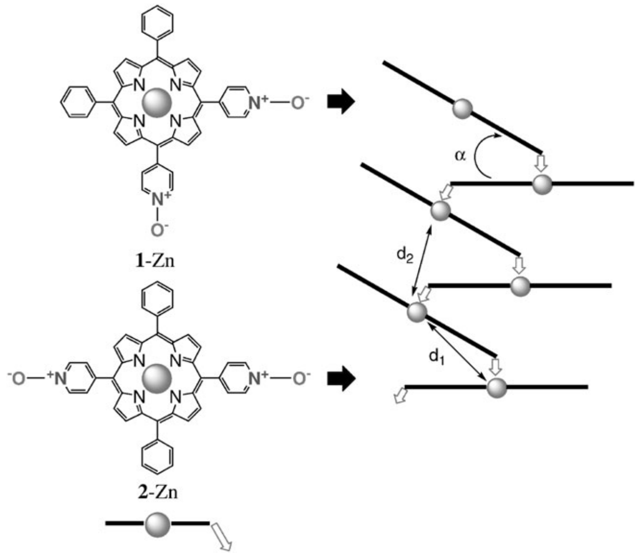

**Fig. 4** Schematic representation of the structures obtained with **1**-Zn and **2**-Zn. Since only one PNO group is engaged in the formation of the network, only one open arrow, representing the lone pair of the oxygen connected to the Zn atom, is presented.

(monoclinic, $P2_1/c$) units and both disordered $H_2O$ and MeOH solvent molecules, whereas in the case of **3**, the crystal contains **3**-Zn (monoclinic, $P2_1/c$) and only MeOH solvent molecules. The three crystalline solids present common structural features. Indeed, **1**-Zn, **2**-Zn and **3**-Zn tectons generate analogous zigzag type coordination networks. The Zn(II) cation is located within the core of the porphyrin and adopts a distorted square pyramidal geometry. The 1-D network structures are formed by the mutual bridging of consecutive units through apical binding of Zn centres by either oxygen atoms belonging to the PNO groups in the case of **1**-Zn and **2**-Zn or a nitrogen atom of the pyridine ring in the case of **3**-Zn.

For the tecton **1**-Zn (Fig. 3), the Zn–N and Zn–O distances are *ca.* 2.05 Å and 2.12 Å respectively. The porphyrin core presents a clear saddle-shape distortion and the Zn is located 0.25 Å out of the porphyrin mean plane (24 atoms) toward the oxygen atom of the PNO group of the consecutive tecton **1**-Zn. Among the two PNO groups of the tecton **1**-Zn, only one is engaged in the coordination of the Zn centre belonging to the consecutive unit (Fig. 4). The other PNO group is disordered over the two *meso* 10 and 20 positions with the same occupancy and hydrogen bonded to a water solvent molecule ($d_{\text{O–O}}$ of *ca.* 2.8 Å). The Zn–N–O angle of 117.80° is close to the expected 120°. All four aromatic moieties connected to the *meso* positions are tilted with respect to the porphyrin mean plane (24 atoms). For the PNO ring participating in the formation of the infinite structure, the tilt angle is 49.24°.

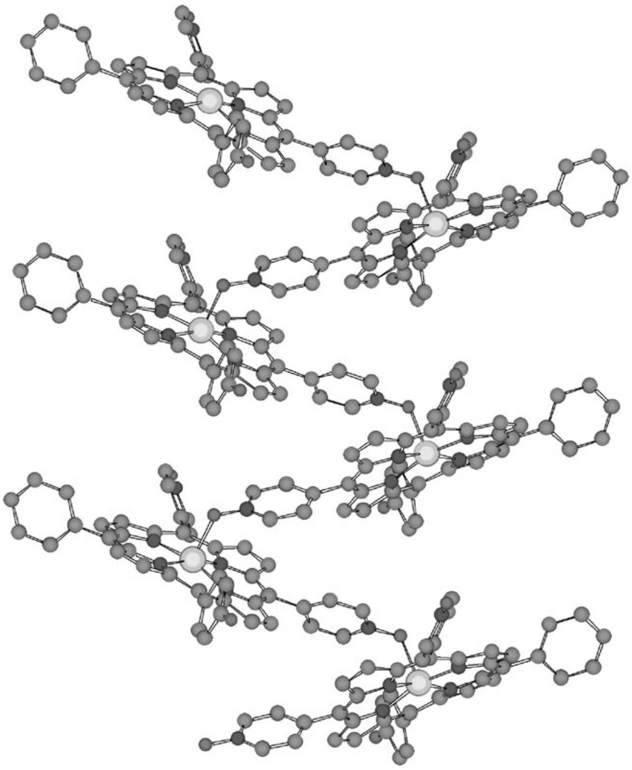

**Fig. 3** A portion of the X-ray structure along the *b* axis showing the formation of zigzag type 1-D coordination network formed by **1**-Zn. For the sake of clarity, H atoms and solvent molecules are not represented. For bond distances and angles see text.

Within a 1-D network, the Zn–Zn distances are 10.34 Å and 9.20 Å for $d_1$ and $d_2$ respectively (Fig. 4). The dihedral angle between two adjacent porphyrins (α) is 53.28° while the angle between three consecutive $Zn^{2+}$ cations is 52.84°. The 1-D networks are packed in a parallel fashion and the empty spaces are filled with solvent molecules.

For the *trans* isomer **2**-Zn (Fig. 5), the same type of arrangement as for **1**-Zn is observed, however, as expected, with slightly different metrics and a different conformation for the porphyrin moiety. Again Zn(II) is pentacoordinated, adopting a distorted square pyramidal geometry with Zn–N and Zn–O distances of *ca.* 2.07 Å and 2.10 Å respectively. The porphyrin core adopts the ruffled conformation with the Zn centre at 0.35 Å out of the porphyrin mean plane (24 atoms) toward the oxygen atom of the PNO group of the consecutive tecton **2**-Zn. Again, among the two PNO groups present on the tecton **2**-Zn, only one is engaged ($d_{\text{NO}} = 1.34$ Å) in the binding of the zinc atom belonging to the consecutive unit, with a Zn–N–O angle of 116.4°. The PNO ring bound to the metal centre is tilted with respect to the porphyrin mean plane (24 atoms) with an angle of 66.63°.

Within a 1-D network, the Zn–Zn distances are 10.23 Å and 10.06 Å for $d_1$ and $d_2$ respectively (Fig. 4). The dihedral angle between two adjacent porphyrins (α) is 71.27° while the angle between three consecutive $Zn^{2+}$ cations is 58.90°. Again, the 1-D networks are packed in a parallel fashion and the empty spaces are filled with solvent molecules.

For the pyridine based tecton **3**-Zn (Fig. 6), the crystal is composed of **3**-Zn and MeOH molecules. No water molecules are present in the crystal. As for the two other cases mentioned above, the Zn atom is located within the porphyrin ring with

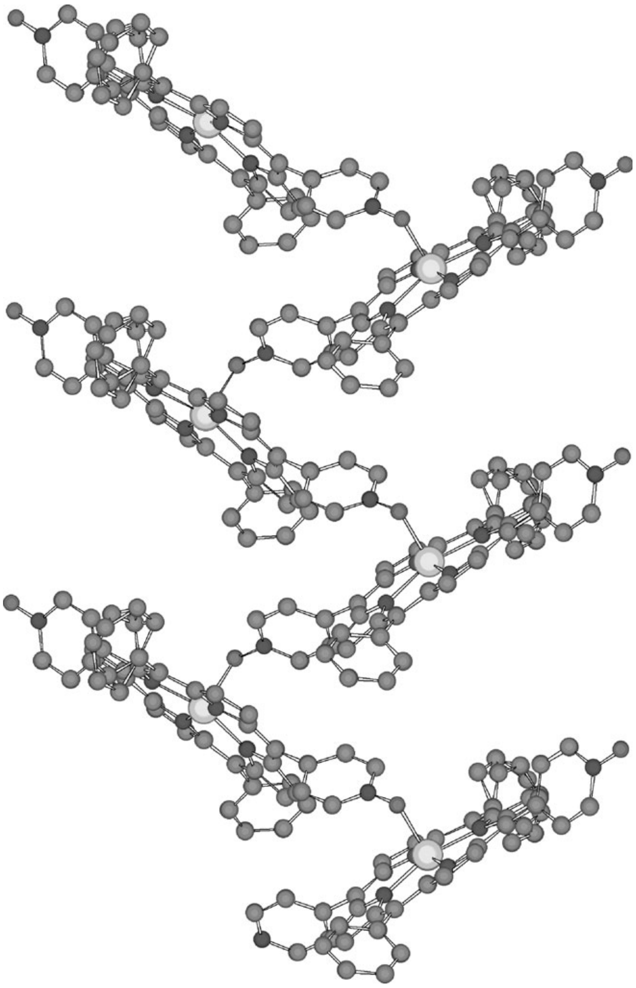

**Fig. 5** A portion of the X-ray structure along the *b* axis showing the formation of zigzag type 1-D coordination network formed by **2**-Zn. One of the two phenyl rings is disordered over two positions. For the sake of clarity, H atoms and solvent molecules are not represented. For bond distances and angles see text.

an average Zn–N distance of *ca.* 2.07 Å. The fifth coordination site around the metal is occupied by the nitrogen atom of the pyridine belonging to the consecutive unit, with a Zn–N distance of *ca.* 2.15 Å. This pyridine unit is almost perpendicular to the mean plane of the porphyrin. In contrast with the **1**-Zn and **2**-Zn cases, the porphyrin remains almost planar. The Zn centre is located 0.33 Å out of the porphyrin mean plane (24 atoms) toward the nitrogen atom of the pyridine group of the consecutive tecton **3**-Zn. Among the two pyridines of the tecton **3**-Zn, only one is engaged in the coordination of the Zn centre belonging to the consecutive unit (Fig. 6). The other pyridine is hydrogen bonded to a MeOH solvent molecule ($d_{\mathrm{N-O}}$ of *ca.* 2.89 Å). All four aromatic moieties connected to the *meso* positions are tilted with respect to the porphyrin mean plane (24 atoms). For the pyridine coordinated to the Zn centre the tilt angle is 61°.

Within a 1-D network, the Zn–Zn distances are 9.81 Å and 13.76 Å for $d_1$ and $d_2$ respectively (Fig. 7). The dihedral angle between two adjacent porphyrins (α) is 77.70° while the angle between three consecutive $\mathrm{Zn}^{2+}$ cations is 89.10°. The 1-D networks are packed in a parallel fashion and the empty spaces are filled with MeOH solvent molecules. The arrangement obtained is almost identical to the one observed with the monopyridyl porphyrin **5**-Zn. The main difference observed is the angle between the porphyrin core and the pyridine ring coordinated to the metal centre. Indeed, in the case of **5**-Zn the angle is *ca.* 80°, whereas in the case of **3**-Zn the angle is *ca.* 89°.

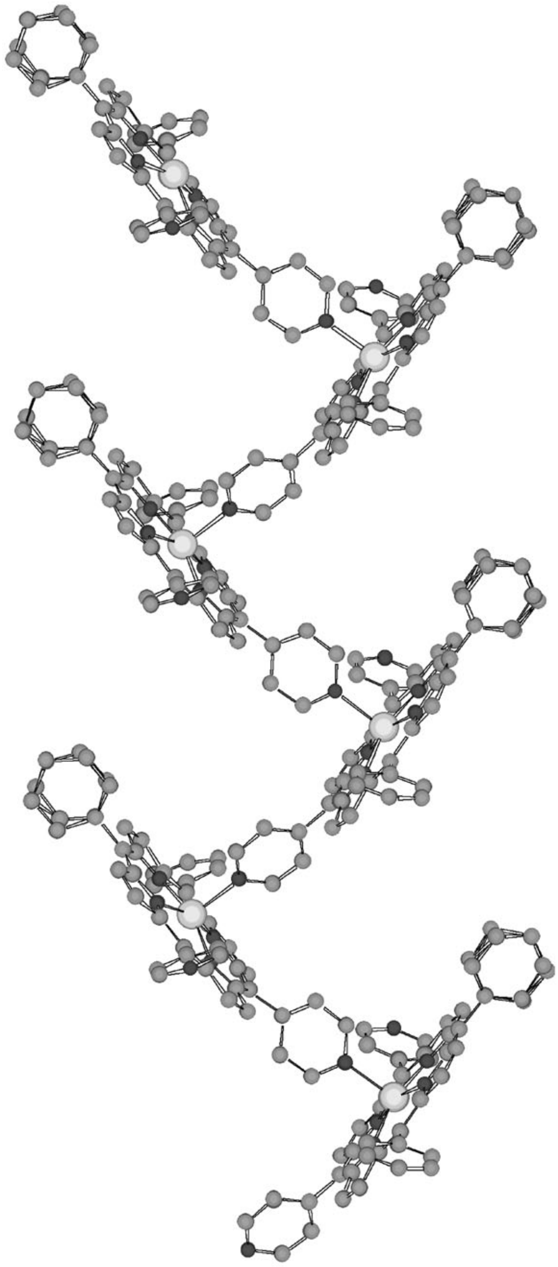

**Fig. 6** A portion of the X-ray structure along the *b* axis showing the formation of a zigzag type 1-D coordination network formed by **3**-Zn. One of the two phenyl rings is disordered over two positions. For the sake of clarity, H atoms and solvent molecules are not represented. For bond distances and angles see text.

In principle, for the self-complementary tectons such as *X*-Zn (*X* = **1–4** and **6**), the connectivity pattern and thus the topology of the network depends on both the coordination number and geometry of the zinc atom and on the denticity of the substituted porphyrin backbone. For both compounds **4**-Zn[32] and **6**-Zn[30], it has been previously shown that, the metal centre is hexacoordinated with octahedral coordination geometry thus leading to a 3-D coordination network. However, whereas **4**-Zn, a bis-monodentate ligand, behaves indeed as a linear bis-monodentate tecton, for **6**-Zn, a tetrakis-monodentate ligand, only two pyridine units out of four available take part in the formation of the 3-D network. Surprisingly, although all three **1**-Zn, **2**-Zn and **3**-Zn are bis-monodentate ligands, under the conditions used (protic solvent), they all behave as self-complementary tectons for which only one PNO or pyridine group participates in the formation of the 1-D network; the remaining site being engaged in a H-bond with a solvent molecule ($H_2O$ for **1**-Zn and **2**-Zn and MeOH for

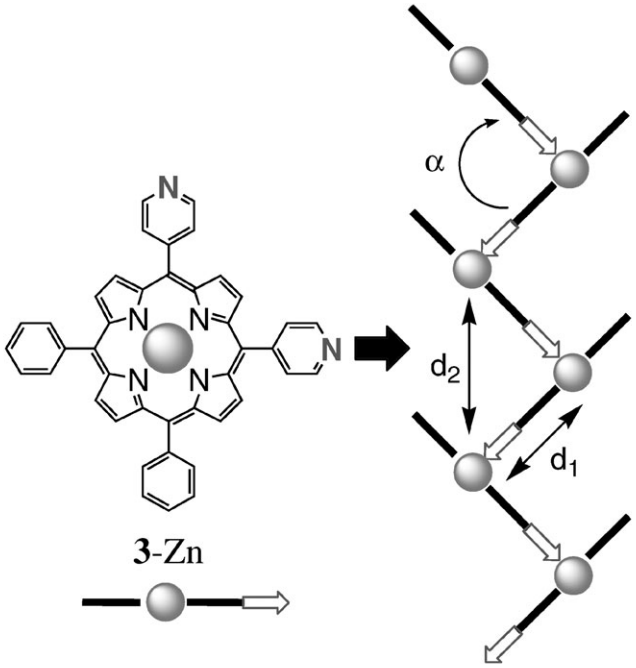

**Fig. 7** Schematic representation of the 1-D network generated by the tecton **3**-Zn. The open arrow represents the pyridine nitrogen lone pair. Since only one pyridine group is engaged in the formation of the network, only one open arrow, representing the lone pair of the nitrogen connected to the Zn atom, is presented.

**3**-Zn). This behaviour has been previously observed for porphyrins bearing a single (**5**-Zn)[22] or four (**6**-Zn)[30] pyridyl units in crystals obtained in protic media. Thus, it appears that, at least for crystals generated in protic solvents, the connectivity between the self-complementary pyridine or PNO bearing tectons *X*-Zn (*X* = **1–3**) is dictated by the pentacoordination taking place on the zinc metal centre.

Interestingly, the comparison of the two 1-D networks obtained for **1**-Zn and **2**-Zn revealed significant differences in the networks' metrics. Indeed, a difference of *ca.* 18° in the dihedral angle between two consecutive porphyrin cores is observed. Consequently, a difference of *ca.* 8° in the angle between three consecutive zinc atoms within the same strand is obtained. Since the two tectons **1**-Zn and **2**-Zn behave in a similar fashion, the observed difference results from the difference in the conformations adopted by the porphyrin cores in **1**-Zn (saddle) and **2**-Zn (ruffled) and from the difference of *ca.* 18° in the dihedral angles between the PNO groups and the mean planes of the porphyrin rings.

## Conclusion

The two positional isomers **1** and **2**, based on a porphyrin backbone bearing two pyridine *N*-oxide groups (PNO), in the presence of a Zn(II) cation lead to tectons **1**-Zn and **2**-Zn. The latter are self-complementary units and thus lead to the formation of analogous 1-D zigzag type coordination networks in the crystalline phase displaying different metrics. For both tectons, only one out of the two PNO groups present takes part in the formation of the 1-D network. The remaining PNO group is H-bonded to a protic solvent molecule present in the crystal. In both cases, for the 1-D network obtained, the connectivity between consecutive tectons is ensured by the coordination of the zinc centre, adopting the square based pyramidal geometry, to the oxygen atom of the PNO group belonging to the consecutive unit. The same type of architecture is obtained with the parent porphyrin **3**.

The combination of ligands **1** and **2** with other metal centres and under different crystallisation conditions is currently under investigation.

## Experimental

The porphyrins **1** and **2** were synthesised according to literature methods[39] by oxidation of the corresponding free base (**3** and **4**) with *m*-chloroperbenzoic acid. Crystals suitable for X-ray analysis were obtained at room temperature by slow diffusion of a solution (2.5 mg in 0.5 ml) of $ZnCl_2$ for **1** and of $Zn(OAc)_2$ for **2** and **3** in MeOH into a solution of the porphyrin in $CHCl_3$ (0.5 mg in 0.5 ml).

Data were collected at 173(2) K on a Bruker SMART CCD Diffractometer equipped with an Oxford Cryosystem liquid $N_2$ device, using graphite-monochromated Mo-Kα ($\lambda$ = 0.71073) radiation. For all structures, diffraction data were corrected for absorption and structural determination was achieved using the APEX (1.022) package. All hydrogen atoms have been calculated except those connected to disordered atoms. CCDC reference numbers 279174–279176.‡

### Crystallographic data for 1-Zn

(**1**-Zn), 1.25 MeOH, 0.25 $H_2O$, $C_{43.25}H_{31.5}N_6O_{3.50}Zn$, $M$ = 756.61, monoclinic, $a$ = 37.961(2), $b$ = 9.2045(5), $c$ = 24.5855(16) Å, $\beta$ = 118.492(4)°, $U$ = 7550.0(8) Å$^3$, space group $C2/c$, $Z$ = 8, $\mu$ = 0.700 mm$^{-1}$, refls measured: 33747, independent reflns: 8669, $R$(int): 0.0869, final $R$ indices [$I > 2\sigma(I)$]: $R_1$ = 8.66, w$R_2$ = 25.46.

### Crystallographic data for 2-Zn

(**2**-Zn), 2MeOH, 0.5 $H_2O$, $C_{176}H_{140}N_{24}O_{18}Zn_4$, $M$ = 3140.60, monoclinic, $a$ = 12.0889(4), $b$ = 10.0599(4), $c$ = 31.2347(11) Å, $\beta$ = 98.449(2)°, $U$ = 3757.3(2) Å$^3$, space group $P2_1/c$, $Z$ = 1, $\mu$ = 0.708 mm$^{-1}$, reflns measured: 39980, independent reflns: 8595, $R$(int) = 0.0935, final $R$ indices [$I > 2\sigma(I)$]: $R_1$ = 7.74, w$R_2$ = 18.80.

### Crystallographic data for 3-Zn

(**3**-Zn) , MeOH, $C_{43}H_{30}N_6OZn$, $M$ = 712.10, monoclinic, $a$ = 11.3493(15), $b$ = 13.7663(17), $c$ = 22.097(4) Å, $\beta$ = 100.786(6)°, $U$ = 3391.4(9) Å$^3$, space group $P2_1/c$, $Z$ = 4, $\mu$ = 0.769 mm$^{-1}$, reflns measured: 34149, independent reflns: 7794, $R$(int) = 0.1238, final $R$ indices [$I > 2\sigma(I)$]: $R_1$ = 6.79, w$R_2$ = 15.73.

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‡ For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511049c

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