Orthogonal packing of enantiomerically pure helical silver coordination networks

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The combination of the chiral tecton 3 based on the (*R*)-6,6′-dibromo-1,1’-binaphthyl moiety bearing two isonicotinoyl groups with AgX (X = BF_4^-, $CF_3SO_3^-$, PF_6^-) leads to the formation of enantiomerically pure helical strands with orthogonal packing in the rare space group *I*2$_1$3.

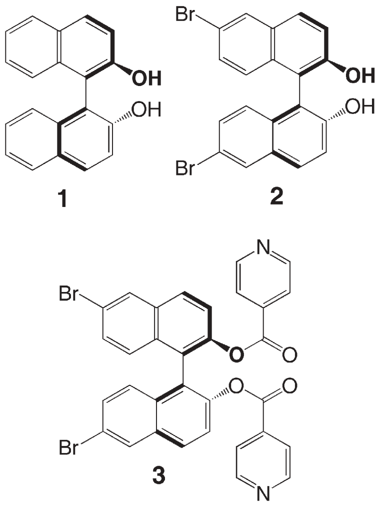
Coordination networks[1,2] in the crystalline phase are periodic infinite metallo-organic architectures assembled through coordination bonds between organic tectons[3,4] bearing divergently oriented coordinating groups and metal centres offering at least two free and divergently-oriented coordination sites.[5] Although for combinations of rigid organic tectons and metal complexes displaying unique and geometrically well-defined sets of free coordination sites, one may predict the connectivity pattern and thus the dimensionality of the network (1-, 2- or 3-D), in the majority of cases based on flexible tectons and/or metal centres offering several possibilities in terms of coordination number and geometry, the prediction of the final architecture still remains a challenge. This is particularly true for the packing of 1- and 2-D networks. The understanding of parameters controlling the formation of coordination networks requires the systematic design of new tectons bearing a variety of coordination sites arranged in different geometries. We[2,3,6] and others[7] have been involved in such a task for some time now. In particular, we have designed many tectons based on rigid or flexible backbones bearing pyridine derivatives as coordinating sites and studied their ability to form 1-, 2- and 3-D coordination networks.[6] Concerning 1-D networks, not only is the design of helical networks a topic of interest but the control of the helicity, both in terms of pitch and orientation, is also an important issue. Although several examples of helical coordination networks have been reported, the majority of described cases deals with racemic mixtures[8] and only few enantiomerically pure helical architectures have been published. In this context, a second point of interest is the understanding of the packing of 1-D networks in general and of helical assemblies in particular. Along these lines, we have reported examples of enantiomerically pure single-[9] and triple-stranded[10] helical coordination networks using an enantiomerically pure backbone based on isomannide bearing two pyridine groups as well as single- and double-stranded helical architectures as racemic mixtures.[11]

Regarding the control of helicity, the 1,1′-binaphthyl backbone is another interesting chiral unit. The formation of helical structures, in particular tubular arrangements based on the use of the 1,1′-binaphthyl derivatives and metal centres has been demonstrated by Lin *et al.*[12]

Here we report the design of the tecton **3** (Scheme 1), based on the (*R*)-6,6′-dibromo-1,1′-binaphthyl unit bearing two pyridyl groups, its ability to form enantiomerically pure 1-D helical coordination networks in the presence of three different silver salts and the orthogonal packing mode of the 1-D networks (cubic system, space group *I*2$_1$3).

The design of the organic tecton **3** is based on the enantiopure (*R*)-6,6′-dibromo-1,1′-binaphthyl backbone bearing two isonicotinoyl groups. An ester group ensures the junction between the two moieties. The synthesis† of **3** is straightforward and based on the esterification of 6,6′-dibromo-1,1′-binaphthol **2**, obtained by bromination of the commercially-available enantiomerically pure binaphthol **1**,[13] by isonicotinoyl chloride in dry THF and in the presence of Et_3N at 25 °C for 48 h (Scheme 1). An example of a discrete heterodimeric platinum complex based on an analogue of **3** lacking the two bromine atoms has been described.[14] The formation of homo- and heterochiral coordination networks based on the use of the analogues of **3** with amide junctions instead of an ester group has been reported recently.[15]

The connecting metal cation, Ag^+ was chosen because of the labile nature of the silver–pyridine bond. Since the tecton **3** is neutral in nature, in order to illustrate the role of the anion associated with cation, three different silver salts [$Ag(BF_4)$, $Ag(CF_3SO_3)$ and $Ag(PF_6)$] were used. Upon slow diffusion at room temperature of an EtOH solution (2 mL) containing 6 mg of either $Ag(BF_4)$, $Ag(CF_3SO_3)$ or $Ag(PF_6)$ into a $CHCl_3$ solution



Scheme 1

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(0.5 mL) of **3** (5 mg), colourless air stable crystals were obtained after *ca.* two days and were investigated by X-ray diffraction on single crystals.‡ The structural study revealed similar connectivity, identical crystalline systems and space groups for all three cases. However, owing to the poor diffraction power of crystals, large enough crystals were obtained only in the case of $AgBF_4$ and consequently, only for that case was the quality of the structural study acceptable and therefore reported here. For the other two cases, although the cationic network could be analysed, the anions and solvent molecules could not be localised.

The crystals (cubic system, space group $I2_13$) are composed of the tecton **3**, silver cation, tetrafluoroborate anion, chloroform and water molecules $[(H_2O–Ag–\mathbf{3})_3(BF_4)_3\cdot 2CHCl_3]$. As expected, the mutual interconnection between the organic tectons **3** and Ag^+ cations leads to the formation of an enantiomerically pure helical strand (Fig. 1). The helical architecture is not cylindrical but rather of the ovaloid type. The unique *P* handedness of the helical arrangement results from the predefined stereochemistry of the (*R*)-6,6′-dibromo-1,1′-binaphthyl moiety. For the organic moiety **3**, the two pyridine units connected to the 1,1′-binaphthyl backbone through ester junctions ($d_{C–O}$ = 1.35 Å and $d_{C=O}$ = 1.20 Å), are twisted and divergently-oriented because of steric effects between the two naphthyl units. The pitch (24.14 Å) of the helix is composed of two metals and two tectons **3**. The Ag^+ cation, although disordered over two positions, adopts a distorted trigonal geometry with two pyridine nitrogen atoms ($d_{Ag–N}$ = 2.15–2.16 Å) and one water molecule ($d_{Ag–O}$ = 2.56 Å) that is also found to be disordered. The O–Ag–N angles vary between 98.4° and 105° and the N–Ag–N angle is 149.4°.

Interestingly, the found packing mode of the helical 1-D coordination networks is rather rare. Indeed, the single stranded helical chains are packed in the cubic crystallographic system (in space group $I2_13$) with each near-neighbour helical rod arranged in an orthogonal disposition to one another (Fig. 2).

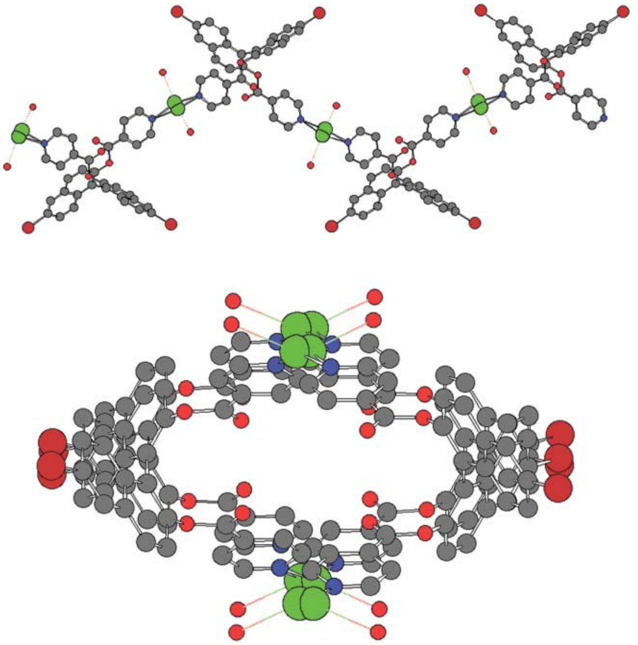

Fig. 1 A portion [perpendicular (top) and along (bottom)] of the structure of the 1-D helical network obtained upon combining the tecton **3** with Ag^+ cations. H atoms, anions and solvent molecules are not represented for the sake of clarity. For bond distances and angles see text.

This type of packing, described by O'Keeffe and Andersson in 1977,[16] for cylindrical rods (Fig. 2, bottom) is rather rare and, to the best of our knowledge, no example of such packing has been reported for 1-D coordination networks. Indeed, a search in the CCDC database reveals only eight examples of crystals belonging to the space group $I2_13$.[17] Among all structures reported, three deal with organic salts (BUZFUX, HEDGAY, SIPCID), four with discrete species (GIRPIG, HAZMUQ, QOZQAX, YETMEP) and one with a 3-D coordination network (IKOQII). Examples of closely related organisation in liquid crystalline phases have been also reported.[18]

A possible explanation for this type of packing may relate to the fact that this type of packing generates cavities within the crystal, which are occupied here by BF_4^- anions and $CHCl_3$ solvent molecules. Furthermore, although no specific hydrogen bonds could be observed between the anions and cationic helical networks, π–π type stacking interactions were found between the

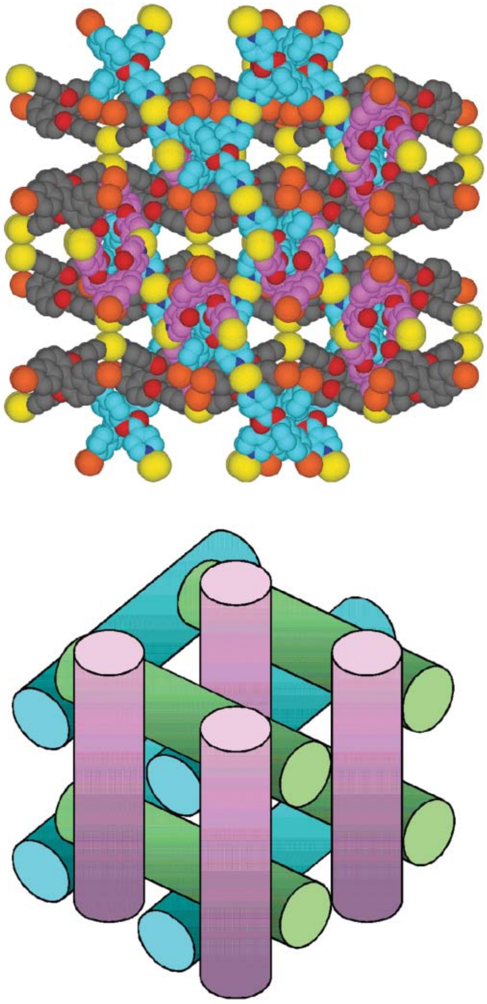

Fig. 2 A portion of the packed structure of the 1-D helical network formed between the tecton **3** and Ag^+ cations (top) and a schematic representation using cylindrical rods (bottom). The rods have been differentiated by colours for better representation. H atoms, anions and solvent molecules are not represented for the sake of clarity.

binaphthyl units and pyridine groups belonging to adjacent helical strands (C–C distance varying between 3.31 and 3.48 Å).

In conclusion, upon combining the chiral organic tecton **3** derived from the (*R*)-1,1′-binaphthyl backbone with three silver salts, the formation of similar enantiomerically pure helical coordination networks was demonstrated. In all three cases, the orthogonal packing of the helical strands occurs in the cubic crystalline system in the extremely rare space group $I2_13$. The generation of other coordination networks using the tecton **3** and other metal cations is currently under investigation.

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Notes and references

† To a degassed solution of (*R*)-6,6′-dibromo-1,1′-binaphthol **2** (0.25 g, 0.5 mmol) in dry THF (20 ml), the hydrochloride salt of isonicotinoyl chloride (0.3 g, 1.6 mmol) was added and the mixture was stirred at room temperature for 15 min. Et_3N (2 ml) was added to the mixture and stirring was further continued for two days. After evaporation to dryness, a saturated aqueous solution of Na_2CO_3 (40 ml) was added to the residue and the mixture extracted with CH_2Cl_2 (3 × 30 ml). The organic solvent was removed and the residue purified by column chromatography [SiO_2, CH_2Cl_2–(0–3%) MeOH] affording the pure compound **3** as slightly yellowish solid in 76% yield (0.25 g). Mp 104 °C, ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm): 8.34 (d, J = 1.6 Hz, 4H), 8.10 (s, 2H), 7.92 (d, J = 8.9 Hz, 2H), 7.53 (d, J = 8.9 Hz, 2H), 7.43 (m, 6H), 7.17 (d, J = 8.9 Hz, 2H); ^{13}C-NMR (50 MHz, $CDCl_3$, 25 °C): δ (ppm): 163.23, 150.57, 146.70, 135.91, 132.73, 131.52, 130.78, 130.29, 129.35, 127.45, 123.16, 122.72, 122.46, 120.54. Anal. calc. for $C_{32}H_{18}Br_2N_2O_4$: C 58.74, H 2.77, N 4.28, found: C 58.85, H 2.95, N 4.41%.

‡ Colourless crystals: $[(C_{32}H_{20}AgBr_2N_2O_5)_3(BF_4)_3\cdot 2CHCl_3]$, $M = 2839.74$, cubic, $a = 23.8747(6)$ Å, $b = 23.8747(6)$ Å, $c = 23.8747(6)$ Å, $\alpha = \beta = \gamma = 90°$. $U = 13608.6(6)$ Å^3, $Z = 4$, space group $I2_13$, $D_c = 1.386$ Mg m^{-3}, $\mu = 2.374$ mm^{-1}, 16542 data with $I > 2\sigma(I)$, $R = 0.1012$, w$R = 0.1012$. 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. 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 604237. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605166a

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