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Molecular tectonics: homochiral 3D cuboid coordination networks based on enantiomerically pure organic tectons and ZnSiF<sub>6</sub><sup>†</sup>

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Upon combining enantiomerically pure bis-monodentate organic tectons with ZnSiF<sub>6</sub>, homochiral 3D cuboid architectures displaying chiral channels are formed.

Coordination polymers<sup>1</sup> or Metal–Organic Frameworks (MOFs) are promising solid materials for separation, storage, catalysis and sensing, for example.<sup>2</sup> It is interesting to note that the majority of the reported examples are achiral. Although chiral architectures are of interest for chiral separation or enantio- or stereo-selective transformations, only a small number of chiral coordination polymers have been reported.<sup>3</sup> The design of coordination polymers may be achieved using concepts developed in molecular tectonics.<sup>4</sup> Indeed, such hybrid periodic architectures in the crystalline phase may be obtained under self-assembly conditions upon combinations of organic and metallic tectons.<sup>5</sup>

Here we report the design and structural characterisation of three new enantiomerically pure chiral coordination polymers based on combinations of enantiomerically pure asymmetric organic tectons with  $\text{ZnSiF}_6$  (Fig. 1).

ZnSiF<sub>6</sub> is an interesting salt because in the presence of bismonodentate organic tectons bearing N donor atoms, it forms an infinite pillar through mutual bridging between SiF<sub>6</sub><sup>2-</sup> anions and Zn<sup>2+</sup> cations with a Zn–Zn distance of *ca.* 7.5 Å.<sup>6</sup> Interestingly, the cation adopts a distorted Oh geometry with the two apical positions occupied by two F atoms belonging to two consecutive SiF<sub>6</sub><sup>2-</sup> anions. The remaining four coordination sites occupying the square base of the octahedron serve as connecting nodes leading thus to a variety of architectures depending on the nature of the organic tecton.<sup>7</sup> One may exploit this particular arrangement for the design of chiral 3D networks by combining ZnSiF<sub>6</sub> with chiral organic tectons (Fig. 1).

The design of the 3D cuboid chiral networks is based on combinations of enantiomerically pure tectons 1–3 with



**Fig. 1** Schematic representations of 3D cuboid coordination networks (a and b) and their square bases (c and d) composed of non-symmetric bismonodentate chiral tectons and  $ZnSiF_{6-}$  + and - indicate clockwise and anticlockwise orientation of the organic tectons.

ZnSiF<sub>6</sub> (Scheme 1). Tectons 1–3 are similar chiral bismonodentate units differing in the nature of their chiral group. Tectons 1 (R,R isomer) and 2 (S,S isomer) differ in both handedness of chiral centres and their distance to the O-phenyl moiety *i.e.* insertion of a methylene unit between the O atoms and the chiral centre



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in 2. Tecton 3 (R,R isomer) bears an extra OH group located on the chiral centre. It is worth noting that, by construction, the chiral fragments should be oriented towards the channels.

All three tectons, owing to the location of the two chiral centres at positions 2 and 5 and the pyridyl units at positions 1 and 4, are non-symmetric units. Consequently, upon bridging two consecutive  $Zn^{2+}$  cations they may adopt clockwise (Fig. 1c) or anticlockwise (Fig. 1d) relative orientation. Thus, for the 3D cuboid architecture, many possibilities may be encountered. Two of the most symmetrical ones are schematically presented in Fig. 1a and b.

Tectons 1-3 were synthesized in good yields starting from commercially available enantiomerically pure alcohols 4, 6 and 8 (Scheme 1). The activation of alcohols 4 and 6, achieved at RT in CH<sub>2</sub>Cl<sub>2</sub> by treatment with *p*-TsCl in the presence of Et<sub>3</sub>N and a catalytic amount of DMAP, afforded compounds 5 and 7 in 79 and 98% yields respectively. For compound 8, owing to the presence of both primary and secondary OH groups, the activation process using 1 equiv. of p-TsCl at -20 °C yielded, in addition to the desired compound 9 (50%), the di-tosylated by-product which was removed using column chromatography. The OH protected 10 was obtained at RT in 98% yield by reacting 9 with DHP in the presence of a catalytic amount of PPTS in CH2Cl2. The dibromo intermediates 11 and 12 were obtained in 86 and 84% yields, respectively, upon condensation of 2,5-dibromohydroquinone with 5 or 7 in the presence of Cs<sub>2</sub>CO<sub>3</sub> in DMF at 100 °C. Compound 13 was prepared in 60% yield by reaction of 2,5-dibromohydroquinone with 10 followed by a deprotection step using HCl in MeOH. Finally, tectons 1, 2 and 3 were obtained in 75, 74 and 75% yields, respectively, by a Pd(PPh<sub>3</sub>)<sub>4</sub> catalyzed Suzuki coupling reaction between 11, 12 or 13 and 4-pyridylboronic acid under anaerobic conditions.

In addition to classical characterization in solution, the structures of all three enantiomerically pure tectons **1–3** were studied in the solid state using X-ray diffraction on single crystals. Colorless crystals of **1** and **2** were obtained upon slow diffusion of *n*-pentane vapors into a CHCl<sub>3</sub> solution of **1** or **2**. Yellowish crystals of **3** were obtained upon slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub>–MeOH solution of **3**. As expected, all three tectons crystallized in a chiral space group ( $P2_12_12_1$ ,  $P_1$  and  $P2_1$  for **1**, **2** and **3** respectively) (see ESI<sup>†</sup> for crystallographic tables). The pyridyl units are tilted with respect to the central phenyl group by *ca.* 49.67° and 48.20° for **1**, 39.58° and 43.66° for **2** and 39.14° and 35.46° for **3**. In all three cases, no solvent molecules are present in the crystal. The length of the tectons *i.e.* the distance between the two N atoms is around **11.4** Å for **1–3** (Fig. 2).

Upon slow diffusion through a buffered layer of DMSO of an EtOH solution of  $ZnSiF_6 \cdot xH_2O$  into a  $CHCl_3$  solution of the organic tecton **1**, **2** or **3**, colorless crystalline materials were obtained after a few days (see ESI<sup>†</sup>). For all three combinations, structural studies



Fig. 2 X-ray structures of tectons 1–3. H atoms are omitted for clarity. For bond distances and angles, see text.

were performed using X-ray diffraction on single crystals (see crystallographic tables in ESI<sup>†</sup>). In all three cases, the crystal (space group *P*4 for 1·ZnSiF<sub>6</sub> and 3·ZnSiF<sub>6</sub> and *I*4 for 2·ZnSiF<sub>6</sub>) is composed of the organic tecton,  $Zn^{2+}$  cation,  $SiF_6^{2-}$  anion and solvent molecules (3, 2 and 1 CHCl<sub>3</sub> molecules for 1, 2 and 3 respectively).

The alkyl chains in  $1 \cdot \text{ZnSiF}_6$  and  $2 \cdot \text{ZnSiF}_6$  were found to be disordered over two positions. Owing to the large disorder of CHCl<sub>3</sub> solvent molecules located within the channels, the data were processed using the Squeeze command. Unfortunately, all three crystalline materials were found to be rather unstable and upon removal of the solvents molecules they irreversibly collapsed within a few seconds. Consequently, no PXRD studies could be carried out.

In all cases, a 3D cuboid architecture is formed. The latter may be described as follows: the  $Zn^{2+}$  cation behaving as an octahedral node is surrounded by a 4N2F set of atoms. The interconnection of consecutive cations through the four corners of the square base of the octahedron by four pyridyl moieties belonging to four enantiomerically pure organic tectons **1**, **2** or **3** leads to the formation of a 2D square grid type arrangement in the *ab* plane (Zn–N distance in the range 2.12–2.15 Å). Within the sheet, the Zn–Zn distance is in the 15.58–15.62 Å range (Fig. 3a, 4a and 5a). The pyridyl units are tilted with respect to the phenyl group by *ca.* 48.7° and 51.1° for **1**, 52.9° and 56.6° for **2**, 50.2° and 48.4° for **3**. As stated above, owing to the non-symmetric nature of tectons **1–3**, within the square grid, among many relative orientation possibilities, in all three cases, the organic tectons adopt either clockwise (Fig. 1c) or anticlockwise dispositions (Fig. 1d).

To reach the cuboid type architecture, in all three cases the consecutive square grid type arrangements are further interconnected along the *c* axis by  $\text{SiF}_6^{2-}$  dianions through Zn–F bonds located at the apical positions of the octahedral nodes (distance in the 2.10–2.14 Å range). Along the third dimension, the distance between consecutive Zn<sup>2+</sup> cations is in the 7.55–7.65 Å range (Fig. 3b, 4b and 5b).

Alternatively, the 3D architecture may be described as the interconnection of consecutive pillars, formed upon bridging of



**Fig. 3** Views along the *c* (a, c and d) and *a* (b) axes of a portion of the X-ray structure of the cuboid architecture formed by combining tecton **1** with  $ZnSIF_6$ . The view along the *c* axis (a) clearly shows that in consecutive planes, tectons **1** are either anticlockwise (c) or clockwise (d) oriented.



**Fig. 4** Views along the *c* (a, c and d) and *a* (b) axes of a portion of the X-ray structure of the cuboid architecture formed by combining tecton **2** with ZnSiF<sub>6</sub>. The view along the *c* axis (a) clearly shows that in consecutive planes, tecton **2** adopts the same anticlockwise orientation (c and d).



**Fig. 5** Views along the *c* (a, c and d) and *a* (b) axes of a portion of the X-ray structure of the cuboid architecture formed by combining the tecton **3** with  $ZnSiF_6$ . The view along the *c* axis (a) clearly shows that in consecutive planes, tecton **3** adopts anticlockwise (c) and clockwise (d) orientations.

consecutive hexa-coordinated  $Zn^{2+}$  cations adopting an octahedral coordination geometry by  $SiF_6^{2-}$  anions, by four organic tectons 1, 2 or 3.

For the cuboid architectures, whereas for  $1 \cdot \text{ZnSiF}_6$  (Fig. 3c and d) and  $3 \cdot \text{ZnSiF}_6$  (Fig. 5c and d) within the consecutive *ab* planes along the *c* axis, the organic tectons 1 or 3 are clockwise and anticlockwise oriented, in the case of  $2 \cdot \text{ZnSiF}_6$  (Fig. 4c and d) they are only anticlockwise disposed.

Finally, it is worth noting that whereas for  $1 \cdot \text{ZnSiF}_6$  and  $2 \cdot \text{ZnSiF}_6$ the chiral pores are hydrophobic, in the case of  $3 \cdot \text{ZnSiF}_6$  they are hydrophilic owing to the convergent orientation of the OH groups.

In conclusion, considering the pillar formed upon bridging of  $Zn^{2+}$  cations by SiF<sub>6</sub><sup>2–</sup> anions as an infinite tecton, using enantiomerically pure bis-monodentate organic tectons a series of homochiral 3D cuboid architectures were designed and generated. Owing to the localisation of the chiral centres, the porous crystals display chiral channels occupied by solvent molecules. With the aim of forming robust crystalline materials, the replacement of  $Zn(\pi)$  by  $Co(\pi)$  or  $Cu(\pi)$  and of Si(rv) by Ti(rv) or Sn(rv) is currently under investigation.

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