Development of chiral N,N-ditopic metalloligands based on a *Cinchona* alkaloids' backbone for constructing homochiral coordination polymers[†]

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The bimetallic chiral bipyridyl-type metalloligands based on a luminium derivatives of cinchonine, $[R_2Al(\mu-CN)]_2$ (R = Me or Et), in combination with the corresponding ZnR₂ compound as nodes were used for the generation of novel homochiral heterometallic coordination polymers of either zig-zag or helical topology, depending on the character of the R substituent.

Extensive research in the area of chiral coordination polymers arises from the increasing demand for materials for enantioselective catalysis and separation and the interest in fundamental aspects of molecular recognition.¹ The most common approach to build homochiral architectures is the rational combination of chiral multifunctional ligands as linkers and metal ion nodes bearing a specific coordination geometry.^{1,2} However, the engineering of the ligand's features such as size, flexibility, and directionality of binding centres is limited by the difficulty of its synthesis. This is exactly the case of bipyridines as N,N-ditopic organic linkers which are one of the most widely-used building blocks for the synthesis of metal-organic frameworks,3 but their chiral derivatisation has encountered difficulties.⁴ Recently, we are developing a synthetic strategy which focuses on designing new chiral metal complexes based on readily accessible Cinchona alkaloids as effective chiral building blocks (Scheme 1).^{5,6} Initially we used bischelate aluminium complexes, [XAl(CN)₂] (CN = deprotonated cinchonine), as novel chiral N,N-metalloligands I (Scheme 1), and showed their excellent capability as metallotectons for constructing coordination polymers of helical topology and microporous chiral architectures prone



Scheme 1 Strategy for developing novel chiral N,N-ditopic linkers.

to enantioselective sorption.^{5a} Very recently we have revealed that the dinuclear aluminium–cinchonine complexes (the metallotecton **II**) can also effectively utilize their molecular shapes in the generation of the unique chiral nanotubular architectures through non-covalent interactions-driven selfassembly, and the resulting novel flexible microporous materials showed unique structure and gas separation properties.^{5b} Herein, we report primary results on the employment of the type **II** dimeric aluminium complexes with a cinchonine backbone as chiral *N*,*N*-ditopic metalloligands for the generation of homochiral heterometallic coordination polymers with ZnR₂ species as nodes.⁷ We further explore the revealed inherent capabilities of these metallotectons for the construction of helical chains and discuss subtle factors that control the formation of corresponding supramolecular motifs.

Previously, we revealed that the molecular complex $[Me_2Al(\mu-CN)]_2$ (1a) assembles into a non-covalent porous material with the specific arrangement of the pore-defining 1a dimeric units,^{5b} where each 1a molecule points at its neighbour by uncoordinated quinoline nitrogen atoms mimicking a helical coordination polymer with connector elements being removed (Fig. 1). Therefore, one can describe this system as a "virtual helix" composed entirely of the metalloligand 1a species and attempt to insert metal centres between dimeric 1a units in order to obtain the desired polymeric entity—a "real helix" (Fig. 1). Consequently, we carried out a series of reactions combining $[R_2Al(\mu-CN)]_2$ [R = Me (1a), Et (1b)] units with ZnR₂ [R = Me and Et] to test the utilities of $[R_2Al(\mu-CN)]_2$ complexes as metalloligands with specific disposition of peripheral N-donor sites.

The reactions of 1a and 1b with equimolar amount of $ZnMe_2$ or $ZnEt_2$, respectively, in toluene changed immediately colourless solutions to pale yellow and single rod-shaped yellow crystals of the corresponding $1a-ZnMe_2$ (2a) and $1b-ZnEt_2$ (2b) compounds were obtained from the mother solution. The X-ray studies revealed that both products assemble into 1D coordination polymers where the



Fig. 1 From "virtual helix" to "real helix"—an illustration of the concept; the helically arranged $[R_2Al(\mu-CN)]_2$ metallotecton forming a single-stranded helical coordination polymer upon coordination-driven self-assembly with a ZnR_2 node.

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Fig. 2 (a) The two metalloligand molecules of the asymmetric unit of 2a, A (left) and B (right), were shown overlaid on their simplified representation (blue and gold blocks); (b) zig-zag chain topology of the 1D coordination polymer 2a; (c) non-covalent-bonded 2D layers of 2a stacked loosely along the a direction.

metalloligands bridge ZnR_2 connectors. The analysis of their supramolecular structures shows that the methyl derivative **2a** unfolded from the expected "real helix" topology forming a zig-zag-like chain packing motif (Fig. 2 and Fig. S1, ESI†), however, the desired "real helix" entity was obtained as a result of the substrates alteration to the corresponding aluminium and zinc ethyl derivatives (Fig. 3 and Fig. S3, ESI†).

Compound **2a** crystallises in the orthorhombic space group $P2_12_12$ and the asymmetric unit contains two **1a**–ZnMe₂ units



Fig. 3 Graphical representation of the coordination-driven selfassembly of the N,N-ditopic metalloligand 1b and ZnEt₂ leading to the helical coordination polymer 2b (toluene molecules shown as spacefilling models).

connected by one of the two ZnMe₂ connectors (with the average Zn-N distance of 2.292 Å). The two independent molecules of the metalloligand 1a (A and B, see Fig. 2a and Fig. S1, ESI⁺) display basic geometric parameters typical for this type of dialkylaluminium alkoxides,8 however certain values of bond lengths and angles differ in A and B molecules (Table S1, ESI⁺). For instance, the Al-N bond lengths in A are equal to 2.137(9) and 2.146(8) Å, whereas in **B** the corresponding values reach 2.210(9) and 2.242(8) Å (the average intramolecular Al-N distance in 'free' 1a is 2.216 Å).5b More importantly, the difference in relative orientations of quinoline moieties in each of the metalloligand units affects the angularity of the N,Nditopic linker resulting in the discrepancy of the angles 80.2° and 48.6° formed by the links in **A** and **B**, respectively. The former value exceeds significantly the corresponding angle of 49.3° that characterizes free $1a^{5b}$ and indicates the flexible nature of this metalloligand. Both A and B molecular conformations are stabilized by intramolecular C–H $\cdot\cdot\pi$ interactions involving a set of Al-Me and vinyl hydrogen atoms and the quinoline aromatic systems (Fig. S2, ESI[†]).

The crystal structure of 2a extends infinitely along the c direction into a 1D zig-zag-like chain with a translation pitch of 14.50 Å (Fig. 2b and Fig. S1, ESI⁺). The particularly interesting feature of the zig-zag structure is the effective utilization of the complex molecular shape of the metalloligand in the 2a formation which was recognized to be an important factor directing the packing motif (Fig. S1, ESI[†]). Such a close packing arrangement is supported by a C–H··· π interaction involving a quinoline hydrogen atom and the neighbouring quinoline aromatic system of the adjacent ZnMe₂-sharing metalloligand unit (Fig. S2, ESI[†]). The same class of non-covalent interactions also supports molecular shape-driven grouping of single zig-zag strands along b axis into tight 2D layers (Fig. 2c and Fig. S1 and S2, ESI[†]). The latter stack in turn loosely along the *a* direction forming an essentially non-porous crystal architecture (Fig. 2c and Fig. S1, ESI[†]).

In contrast, the coordination-driven self-assembly of 1b and ZnEt₂ moieties afforded the connected single-stranded real helix exhibiting a remarkable architecture in the solid state. Compound 2b crystallises in the orthorhombic space group $P2_12_12_1$ and the asymmetric unit consists of the dimeric ethylaluminium complex 1b with one molecule of ZnEt₂ coordinated through one of the quinoline N-donor sites (with the average intramolecular Al-N distance of 2.203 Å and the Zn-N distance of 2.307 Å) (Fig. 3a and Fig. S3, ESI[†]). The geometric parameters of the metalloligand unit are slightly different than those observed in the crystal structure of 1a (Table S3, ESI[†]).^{5b} Interestingly, the angle between the binding directions of the two free N-basic sites (85.6°) is widened even to a larger extent than the corresponding angle in A in the structure of 2a (80.2°) which further substantiates the flexibility of this type of metalloligands. The extended metalloligand–ZnEt₂ assembly folds into the helical structure with a left-handed M configuration and a pitch of 9.51 Å (Fig. 3b and S3, ESI⁺). As it was observed in the case of 2a, the dimeric molecules utilize their shape (Fig. S3, ESI[†]) in the formation of the helical coordination polymer fitting closely with the support of four independent C–H··· π interactions

linking cooperatively each pair of neighbouring, translationally equivalent metalloligand 1b units (Fig. S4, ESI[†]). From the comparison of 2a and 2b structures one can find another factor that might contribute to the stabilization of the helical structure in 2b which is the significant change in relative orientation of neighbouring quinoline planes connected by ZnEt₂ unit (Fig. S5, ESI[†]). It can be clearly observed that the alteration from ZnMe₂ connector in 2a to ZnEt₂ connector in 2b causes greater steric repulsions between the bulkier Et group and the quinoline moieties and the resulting twist is stabilized by a new set of two cooperative C-H \cdots π interactions (Fig. S4 and S5, ESI[†]). Thus, due to the unique semi-rigid character of the metalloligand 1 even subtle changes in its metal coordination sphere can lead to highly divergent topology of the resulting coordination polymers. It should be emphasized that in the case of flexible dipyridyl organic ligands switching between zig-zag and helical chains was usually effected by more significant modifications such as change of a nodal metal centre or disposition of N-centres in a ditopic linker.9

The crystal structure of **2b** is formed by the parallelly packed helices exhibiting the same M handedness and comprises of a homochiral 3D network with 1D channels filled by toluene molecules (Fig. 3c and Fig. S3, ESI[†]). In line with our earlier studies⁵ we can conclude that the homochirality of the helical chains is induced by both the chiral cinchonine precursor and the mode of metalloligand connection. Assuming that the 1b and **1a** crystal structures are analogous we can compare patterns in crystal architectures of the pure metalloligand 1a and coordination polymer 2b. Basically, the helically arranged dimeric molecules in the structure of 1a were moved closer along the helical axis to the close-fitting positions and connected by the ZnEt₂ species with essential preservation of the **1a** crystal network motif.^{5b} However, this shift in positions ceases with the "tongue-to-groove" pattern that characterizes the crystal structure of 1a and compresses the columns' width (Fig. S6, ESI[†]). It is also accompanied by breaking of the noncovalent bonds (C–H···N and C–H··· π) that previously defined the 2D bilayer motif in the structure of 1a, in place of which a new set of interchain C–H \cdots π interactions has been formed (Fig. S4 and S6, ESI†). Such disassembly of the bilayers can be illustrated as formation of "virtual bilayers" while assembling into the "real helix". Both the compression of the helical column width and the presence of more bulky ethyl groups at aluminium centres in 1b lead to shrinking the free space inside the micropores, ultimately rendering it inaccessible to solvent molecules. Interestingly, a new set of 1D channels filled by toluene molecules have been generated between the helices (Fig. 3c and Fig. S3, ESI⁺), and those molecules are strongly bonded to the pore walls by cooperative C–H··· π interactions (Fig. S4, ESI[†]).

TGA analysis on **2b** revealed that the toluene molecules leave the crystal framework up to ~120 °C (Fig. S7, ESI†). However, the removal of the guests resulted in loss of crystallinity by the solid, and the resulting amorphous material is nonporous as indicated by the PXRD and gas (N₂, H₂) sorption experiments. In conclusion, this work demonstrates that the dinuclear metal-cinchone complexes can effectively act as chiral, semirigid building units, and provide a viable means for constructing novel heterometallic coordination polymers of various topology. We believe that the reported synthetic approach could provide new perspectives on the preparation of complex and robust metallosupramolecular architectures with high nuclearity and desired functionalities.

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