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### Unexpected helicity control and helix inversion: homochiral helical nanotubes consisting of an achiral ligand<sup>†</sup>

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The ligand tppda has been designed and synthesized as molecular leverage for helicity control when reacted with  $Cd^{2+}$  ions. The guests MeOH or DMF preferentially stabilize the P-helical isomer, while the guest  $H_2O$  causes a helix inversion to give the M-helical isomer as the major isomer without any chiral auxiliary.

Since the discovery of carbon nanotubes (CNTs) in 1991,<sup>1</sup> discrete tubular structures have experienced a revolutionary development from inorganic to organic nanotubes.<sup>2,3</sup> Among all synthetic nanotubes, metal-organic nanotubes (MONTs) could be the most potent materials possessing functional activity since these types of compounds contain both metal ions and organic ligands as functional groups.<sup>3</sup> However, the development of MONTs is still behind in comparison with other synthetic nanotubes, probably due to the largely unpredictable assembly structure.<sup>4,5</sup>

1D coordination helices have been proved to be ideal candidates for the hierarchical assembly of nanotubular structures,<sup>6</sup> in which opposite binding sites in special angular ligands could induce the formation of helical structures when alternately linked by metal ions. Generally, such helical structures generate the alternative **P** and **M** columns or layers with  $\Delta$  or  $\Lambda$  mirror enantiomers, giving racemic crystals if achiral ligands are employed in the constructs. Chiral compounds are usually obtained either by the use of chiral ligands or chiral auxiliaries, or by the spontaneous resolution upon crystallization without any chiral auxiliary. The former approach typically yields enantiopure samples,<sup>7</sup> while the latter method usually

generates conglomerates.<sup>8</sup> A conglomerate is a mechanical and racemic mixture of chiral crystals, in which enantiopure crystals are formed in a chiral space group.<sup>9</sup> However, the phenomenon of achiral components resolving to yield chiral crystals is relatively rare compared to the analogous process with chiral components or auxiliaries.<sup>8c,10</sup> Since the formation of enantiopure crystals is not predictable, to the best of our knowledge, there have been no reports of the two types of enantiopure helical tubular single crystals (**P** and **M** columns) selectively crystallized without any chiral auxiliary.

2,2'-Dipyridylamine is a high-performance unit combining flexibility and a strong chelation ability for transition metal ions.<sup>11</sup> It can be anticipated that introducing angular ditopic dipyridylamine derivatives should enhance the possibility of forming a helix by linking appropriate transition-metal ions. In this study, a series of achiral ditopic ligands with a 120° angle have been designed and synthesized in order to create a novel helix system (Scheme 1). Two periodically ordered homochiral six-fold helical tubes of  $[Cd(tppda)(NO_3)_2]_n$ .solvent (solvent = 0.5*n*MeOH or *n*DMF for **P** helix; solvent = *x*H<sub>2</sub>O for **M** helix) with **P** and **M** columns have been obtained under different reaction conditions (see ESI<sup>†</sup>). They consist of a large single walled MONT of  $[Cd(tppda)(NO_3)_2]_n$  with an exterior wall diameter of up to 2.2 nm and an interior channel diameter of 0.75 nm.



 $\label{eq:scheme1} \begin{array}{l} \mbox{Scheme1} & \mbox{Scheme1}$ 

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Anhui University of Traditional Chinese Medicine, Hefei 230038, P. R. China † Electronic supplementary information (ESI) available: Experimental procedures, structural figures, PRXD, as well as crystallographic data. CCDC 712881, 712882, 712884 and 712885. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc43898h

Yellowish dodecahedral crystals of  $[Cd(tppda)(NO_3)_2]_n$  solvent (1-P) (solvent = nDMF for 1-P-a and 0.5nMeOH for 1-P-b) were obtained from an organic solution containing tppda and  $Cd(NO_3)_2$ :4H<sub>2</sub>O in a 1:1 molar ratio by slow diffusion of ether vapour, or from a MeOH solution by the solvothermal method. Single crystal X-ray diffraction analyses revealed that 1-P crystallized in the chiral hexagonal space group P6(1)22. Each  $Cd^{2+}$ ion is coordinated by two oxygen atoms from a pair of NO<sub>3</sub><sup>-</sup> anions and four bridging nitrogen atoms from two dpa groups of different tppda ligands, forming a distorted octahedral geometry (Fig. 1a). The crystallographically equivalent Cd<sup>2+</sup> ions are bridged by tppda spacers to form an infinite helical chain along the c axis. The Cd(1) atom lies on a crystallographic two-fold axis and atoms N(4) and C(13)-H(13) of the tppda ligand lie on another two-fold axis. The right-handed helix is constructed around the crystallographic 6(1) axis with a pitch of ~21 Å, which is stabilized by alternating  $\pi \cdots \pi$  stacking interactions of pyridyl groups from ligands in the intra-helix (Fig. 1b and c). The most intriguing feature of 1-P is the formation of a large single-walled chiral MONT, which is constructed from a six-connected Cd<sup>2+</sup> node and an angular organic linker tppda (Fig. 2). The top view of the open-ended hollow nanotube indicates that the undulated hexanuclear  $\{Cd_6(tppda)_6(NO_3)_{12}\}$ metallamacrocycle forms a very large 60-membered ring consisting of six Cd<sup>2+</sup> atoms and six tppda ligands (6Cd, 24C and 30N). Each Cd–Cd separation of  $\sim$  9.2 Å is bridged by the tppda ligand. We have previously investigated the Cu<sup>+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup> complexes of tppda, which are potential luminescent and molecular recognition materials.11 These complexes exhibit chain arrangements based on M-X-M bridging modes (X = Cl, Br, I, SCN).



**Fig. 1** (a) Single crystal X-ray structure of the helix chain formed by  $Cd^{2+}$  ions and tppda in **1-P**, showing the coordination of the  $Cd^{2+}$  cation; (b and c) two face-to-face  $\pi \cdots \pi$  stacking interactions in the helix chain (**1-P-a**:  $d_{centroid-centroid}$  a = b = 3.7413(1) Å and dihedral angle  $a = b = 13.56^{\circ}$ ; **1-P-b**: $d_{centroid-centroid}$  a = b = 3.8623(1) Å and dihedral angle  $a = b = 14.87^{\circ}$ ). Cd: green, C: gray, O: red, N: blue. Hydrogen atoms are omitted for clarity.



**Fig. 2** (a) Coordination mode of tppda in **1-P** and **1-M**; (b) top view of **1-P** and **1-M**; (c) intertwist of right-helix into a chiral nanotube in **1-P** (Cd: green, C: gray, O: red, N: blue); (d) left-helix structure of **1-M** (crystal structure can not be fully resolved).

Evidently, the non-bridging anion  $NO_3^-$  plays an auxiliary role in the helical tubular assemblies of **1-P**.

The helical nanotubes are held together by alternating  $\pi \cdots \pi$ stacking (d = 3.55 - 3.65 Å) interactions between the helical columns to form 3D arrays. In this structure, the adjacent helical columns align in parallel directions and interweave the central pyridine rings of the dpa groups in a one-over/one-under fashion (see ESI<sup>†</sup>). This construction generates a gearwheel-type role, in which each center helix is in contact with six neighboring helices of the same handedness via  $\pi$ -stacking interactions. This gearwheel-type role defines a homochiral supramolecular affinity,<sup>8c</sup> which constrains a handedness of helical columns under the internal pressure of a multiscrew-fastening selforganization. Such a homodromous gearwheel-type arrangement along a helical hypersurface is more stable than a heterodromous one using  $\pi$ -stacking interactions, which may constitute the driving force of the homochiral crystal phase cohesion. As a result, there are preferential and extended homochiral interactions between neighboring chiral columns, and the chirality would be able to extend to higher dimensionalities and hence, spontaneous resolution would be more likely to occur. In 1-P, the chirally discriminative interactions arise from the coordination bonds and  $\pi \cdots \pi$  stacking interactions, which are substantially strong, selective, and directional.

The overall crystallization effect is a constitutional self-sorting process in which a unique enantiopure single crystal of **1-P** forms. The chiral amplification experiment was performed by randomly collecting 10 crystals/samples from two distinct crystallization experiments based on single crystal XRD analysis. The results demonstrate a handedness preference towards **P**-crystals: CEE = 100%. In order to measure the overall chirality of the complex,



**Fig. 3** (a) Optic image of complex **1-P**; (b) optic image of complex **1-M**; (c) X-ray powder diffraction of **1-P** and **1-M**; (d) solid-state CD spectra of **1-P** (black) and **1-M** (red) diluted with a KBr matrix.

the solid-state CD was measured on a bulk crystalline KBr pellet (Fig. 3). The result shows a positive peak at 425 nm, which proves the presence of the **1-P** structure. Although these data can not completely rule out the possibility of **M**-helix enantiomers based on the analysis on a limited number of crystals, the results in this work indicate that the **P** structure is at least dominant in the  $[Cd(tppda)(NO_3)_2]_n$  crystal.

Interestingly, single crystals of only M chirality were obtained when the crystallization was performed in water using the hydrothermal method. A single crystal X-ray diffraction study revealed that the crystallographic parameters of 1-M are similar to those of 1-P, although the crystal structure of 1-M can not be fully resolved due to the quality of the crystal itself, even at low temperature. The chiral amplification process was also verified on 10 crystals/samples randomly collected from two distinct crystallization experiments. The solid-state CD spectrum of a bulk crystalline sample of 1-M exhibited a negative peak at 415 nm, which demonstrates the handedness preference towards M-crystals (CEE = 100%). The formation of 1-M may relate to a thermodynamically driven coordination behaviour change of the octahedral Cd<sup>2+</sup> ions under high temperature and pressure in water solution.<sup>8c</sup> This thermodynamic equilibrium results in the inter-exchange of enantiomers (from P to M), which is further resolved to one chiral single crystal, continuously crystallizing out of the equilibrating solution.<sup>12</sup>

It is of interest to investigate whether the modification of angular ligands could generate different supramolecular chiral packings. The ligands were modified at the X and Y positions (Scheme 1) in order to obtain alterable and functional "active sites" in the cavity of helical-tubes. However, the syntheses of helical complexes failed with the ligands **bpab**, **bpafb**, and **bpap** using the same synthetic method as for 1. These results indicate the important role of the N atom at the X position, which could be the potential H-bond acceptor for the spontaneous assembly of the helical structure. In contrast, such interactions could not be formed with a CH group at the X position and the two dpa groups largely separated due to high steric hindrance (ESI<sup>†</sup>).<sup>11b</sup> Thus, these building blocks can not achieve spontaneous assembly of the helix structure with metal ions.

In conclusion, this work demonstrates that the construction of helical-structures are highly dependent on the presence of a N atom on the X site of the ligand and the flexibility of the "dpa-arm" spacers. The chiral tubes in single crystals result from the self-assembly of achiral components. The homochirality in the crystalline state is promoted by the constitutional chiral affinity of supramolecular helices of the same handedness, interacting *via* their van der Waals hypersurfaces. The internal robustness of the helical columns is mainly responsible for the transmission of the supramolecular homochiral order. The coordination modes of Cd-tppda depend on the reaction solvent in this system. The present results provide knowledge on the rational design of helical nanotubes.

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