A 3D chiral nanoporous coordination framework consisting of homochiral nanotubes assembled from octuple helices†

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A 3D chiral nanoporous coordination framework consisting of homochiral nanotubes assembled from octuple helices with a 19.4 Å by 22.4 Å aperture is formed by the parallel alignment of eight infinite helical chains.

Interest in nanotubular structures is fuelled by the discovery of carbon nanotubes[1] and their concomitant utility in ion exchange, molecular sieves, sensors, and fluidic transport systems.[2] Inorganic nanotubes have experienced revolutionary evolvement from pure carbon to non-carbon elements (*e.g.* B, N, Si) over the past decade.[3] Organic nanotubes, self-assembled from cyclic oligomers such as peptides, ureas, or carbohydrates, have also undergone exciting progress.[4] In contrast to the rapid developments in the fields of inorganic and organic nanotubes, the development of coordination framework-based nanotubes is still in its infancy.[5] On the other hand, the increasing demand for materials for enantioselective catalysis and separation, and the importance of chirality in biological processes have stimulated extensive research in the area of chiral coordination polymers.[6] Although chirality and porosity play important roles in chemistry and biology, it is still challenging to design a crystalline material combining both properties,[7] as evident from two critical reviews by Davis, and Veciana *et al.*[8] Chiral nanotubes, being one type of chiral porous materials, combine the character of uniform, fixed internal diameters arising from nanotubes, with the functionality associated with chirality. Such chiral materials contain pores in the size range of 1.0–2.0 nm and are likely to open up new application possibilities in chirotechnology and nanotechnology.

One straightforward strategy to generate chiral nanotubes is to construct helical chains that have proved to be ideal candidates for hierarchical assembly into nanotubular architectures.[5a,5b,9] In the known nanotubular coordination polymers, the only two examples that have chirality must be mentioned here: a nanometre-scale chiral tubule formed from the helical assembly of alternating *p*-sulfonatocalix[4]arenes and lanthanide ions,[5a] and an interlocked chiral nanotube assembled from quintuple helices, reported by Lin *et al.*[5b] Our group has recently reported a chiral 3D interlocked array originating from nine homochiral nanotubes;[10] however, the absence of guest species in chiral nanotubes finally results in a dense framework. To overcome this problem, we borrow ideas from the methodology used in the preparation of zeolite-type materials, where extra-large-pore frameworks have been prepared in the presence of large organic amines which yield smaller ammonium ions owing to the hydrolysis of amines.[11] *N*,*N*′-Dimethylacetamide (DMA) is able to undergo decarbonylation under solvothermal conditions to produce the dimethylamine cation, hence templating the formation of open frameworks.[12] Choosing it as the solvent, herein we report an unprecedented 3D chiral nanoporous framework built from the covalent linkage of homochiral nanotubes made up of octuple helices.

Crystals of $[(CH_3)_2NH_2][Cd(bpdc)_{1.5}]\cdot 2DMA$ (**1**), where bpdc is 4,4′-biphenyldicarboxylate, were obtained by heating a mixture of $Cd(NO_3)_2\cdot 4H_2O$, H_2bpdc, and L-leucine in DMA at 140 °C for 2 days.‡ The phase purity of the bulk products was confirmed from powder X-ray diffraction. A single-crystal X-ray diffraction study revealed§ that **1** crystallizes in the chiral hexagonal space group $P6_122$ (number 178) and consists of a chiral anionic $[Cd(bpdc)_{1.5}]^-$ framework. Charge neutrality is achieved by the protonated dimethylamine cation. Each asymmetric unit contains two crystallographically independent Cd^{2+} ions with identical coordination environments. Each Cd^{2+} ion lies on a twofold axis and is coordinated by two pairs of chelating oxygen atoms (Cd–O 2.282(2)–2.471(3) Å) and two bridging oxygen atoms from four bpdc ligands (Cd–O 2.254(2) and 2.300(2) Å) to complete a distorted octahedral geometry (see ESI†). Two types of bpdc ligands exist in **1**: $bpdc^A$ contains two chelating carboxylate groups, whereas $bpdc^B$, located on another twofold axis, contains four bridging carboxylate groups (see ESI†). Crystallographically unique Cd^{2+} ions are alternately bridged by long $bpdc^A$ spacers to form an infinite helical chain running along the *c* axis (Fig. 1). The right-handed helix is generated around the crystallographic 6_1 axis with a helical pitch of 63.68 Å, which is fourfold the *c*-axis length. To the best of our knowledge, it represents the longest helical pitch presently known. Notably, on the turning of the helix, the angle between the planes defined by two C–O–Cd–O–C chelate rings at one metal center is 123.92°, and this leads to the helix coiling along the winding axis in a hexagonal cross-section (see ESI†). Most exciting, however, is the fact that eight homochiral helical chains associate in parallel to form the wall of a hexagonal nanotube (Fig. 1). The opening of the hexagonal nanotube is about 19.4 Å by 22.4 Å which is near to the pore size of mesopores, and is comparable to the largest neutral molecular hexagons characterized by single-crystal X-ray diffraction methods.[13] Prior to this work, nanotubular architectures have usually been formed either

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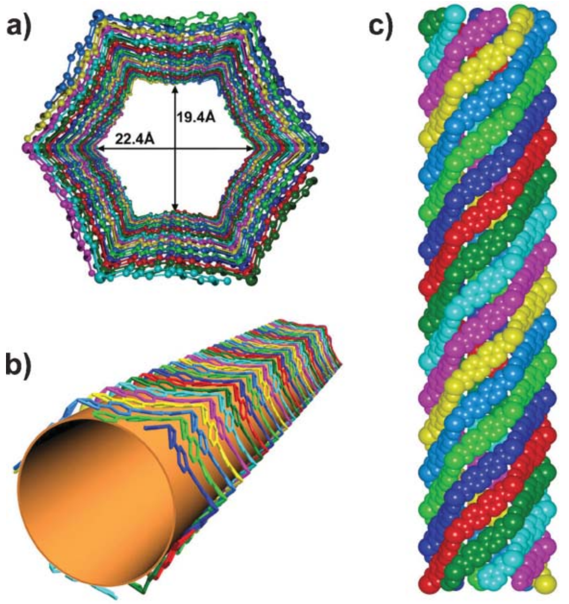

Fig. 1 (a) Parallel association of eight helices into a chiral nanotube with a 19.4 Å by 22.4 Å free aperture. (b) Perspective view of a chiral nanotube. (c) A space-filling representation of octuple helices, highlighting the extra-long pitch.

by association of metallocycles *via* judiciously designed multidentate ligands[5c–e,14] or by a single-stranded helix,[5a,9,10] even though serendipitous motifs sometimes can be found.[15] We are aware of only one exceptional case in which a tetragonal nanotube is formed due to parallel alignment of five infinite helical chains.[5b] Therefore, the chiral nanotube assembled from eightfold helices reported herein represents by far the highest degree of association of 1D motifs. It is supposed that the extra-long helical pitch is a key factor in the formation of this striking motif resembling the single-wall carbon nanotube.

As mentioned above, the cadmium ions have an affinity for a six-coordinate environment, four of which are occupied by bpdc^{A} ligands in the nanotube; therefore the remaining two provide additional binding sites. As shown in Fig. 2, each hexagonal nanotube serves as a tertiary building unit[16] and is further linked to six adjacent nanotubes in the other two directions *via* bpdc^{B} ligands to generate a 3D chiral framework. This is the first observation of homochiral nanotubes being linked through covalent bonds. Interestingly, two types of channels exist in the 3D network along the *c* axis which are occupied by highly disordered counter ions and DMA guest molecules: one is formed by octuple helices, the other is generated by interlinking of the hexagonal nanotubes, the cross-section of which is best described as an equilateral triangle with a side length of 7.1 Å. Calculations with PLATON[17] show that the effective volume for the inclusion is 5097.4 Å^3 per unit cell, which is 51.8% of the crystal volume. It should be noted that the walls of both the hexagonal and the trigonal channels (see ESI†) are enwrapped by large numbers of biphenyl groups. Although numerous achiral porous metal–organic frameworks with extremely high surface areas have been reported based on clever synthetic strategies,[18] chiral porous coordination frameworks are still extremely rare.[19] The most significant character of **1** is the utilization of chiral nanotubes to construct 3D covalent chiral porous frameworks, thereby combining the common features of chirality, porosity, and nanotubes.

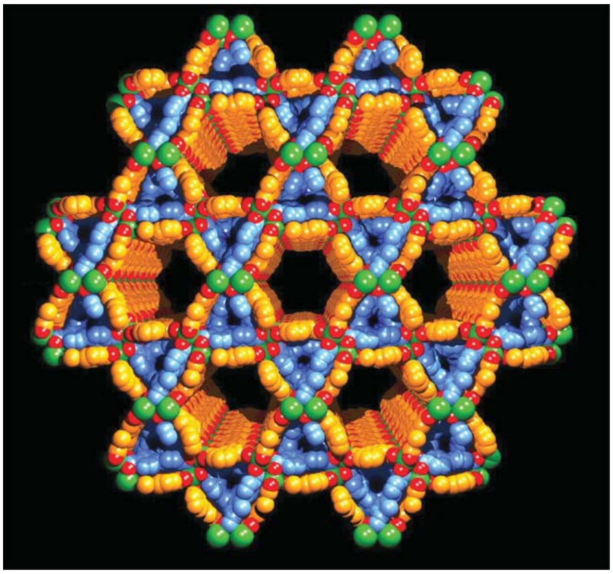

Fig. 2 A space-filling diagram showing two types of channels. Here hexagonal and trigonal channels are displayed in yellow and blue.

Encouraged by the single-crystal X-ray diffraction result, which reveals large free spaces within the framework, we carried out powder X-ray diffraction (PXRD) experiments to investigate the stability of compound **1** upon removal of guest molecules according to thermogravimetric (TG) analysis. The TG curve (see ESI†) shows a weight loss of 24.95% from 110 to 200 °C, corresponding to the release of DMA guest molecules (expected 25.14%). No weight loss was observed between 200 and 300 °C, suggesting that no chemical decomposition occurred between the desolvating and ligand-releasing temperatures. These results prove that DMA guest molecules can be easily removed. Upon heating the as-synthesized material at 120 °C *in vacuo* for 12 h, **1** experienced 24.76% weight loss consistent with the removal of two guest DMA molecules per formula unit. The powder pattern of the evacuated solids (Fig. 3c) is similar to that of the pristine solids (Fig. 3b), which indicates that the open structure is maintained even after removal of guest molecules. A further adsorption study was carried out on the evacuated solid after soaking it in DMA for 2 h. The PXRD pattern (Fig. 3d) shows that the peak positions and their intensities are coincident to those observed for the as-synthesized solids, which confirms the reversibility of the inclusion process. For the anionic nanotunnel, attempts have also been made to exchange [(CH$_3$)$_2$NH$_2$]$^+$ with inorganic cations such as Na$^+$ or K$^+$. Unfortunately they failed, most likely due to the strong hydrogen bonding interactions between [(CH$_3$)$_2$NH$_2$]$^+$ cations and the host framework.

In conclusion, we have successfully constructed a 3D chiral nanoporous metal–organic framework based on the covalent linkage of 1D chiral nanotubes. The unusual features observed in **1** (unique chiral nanotube motif, anionic nanotunnel, network chirality) make it a rare case of the handful of chiral porous compounds and a useful model for exploring the sorption, inclusion and catalytic properties of porous metal–organic

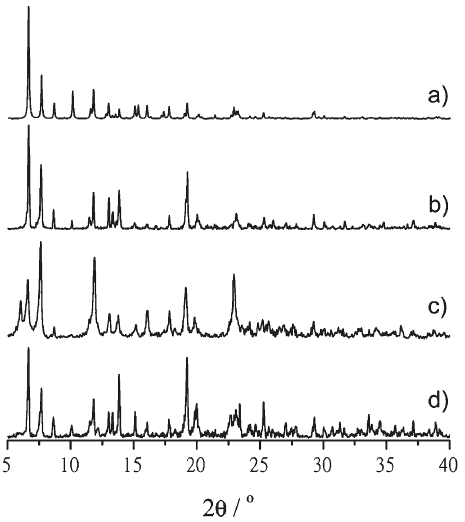

Fig. 3 PXRD patterns for **1**: (a) simulated from single-crystal X-ray diffraction data, (b) as-synthesized solids, (c) after removal of guest solvent molecules, and (d) after re-adsorption of solvent molecules.

frameworks. Further studies for its applications in enantioselective separations and catalyses are in progress.

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Notes and references

‡ Synthesis: a DMA solution (5 mL) containing $Cd(NO_3)_2·4H_2O$ (92 mg, 0.3 mmol), H_2bpdc (60 mg, 0.25 mmol), and L-leucine (59 mg, 0.45 mmol) in a Teflon-lined steel bomb was heated at 140 °C for 2 days. Colorless rod-shaped crystals were collected, washed with Et_2O, and dried at room temperature (yield: 133 mg, 64% based on Cd). Elemental analysis (%) calcd for **1**: C 53.72, H 5.53, N 6.06; found: C 53.63, H 5.38, N 6.25. D-Leucine or other amino acids, such as D-proline or L-proline, could also be used instead of L-leucine, and the fact that neither were included in the product suggested that they played a subtle role in adjusting crystallization of the product, in that no crystals suitable for single-crystal X-ray diffraction could be obtained without them.

§ Crystal data for **1**: $C_{31}H_{38}CdN_3O_8$: $M_r = 693.04$, hexagonal, space group $P6_122$, $a = 26.712(4)$, $b = 26.712(4)$, $c = 15.919(3)$ Å, $\alpha = \beta = 90$, $\gamma = 120°$, $V = 9837(3)$ Å^3, $Z = 12$, $\rho_{calcd} = 1.404$ g cm^{-3}, $T = 133(2)$ K, $S = 1.047$, Flack parameter = −0.01(3), $R1 = 0.0384$ and $wR2 = 0.798$ for 9677 independent reflections [$I > 2\sigma(I)$]. CCDC 653346. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b711405b

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