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Metal–Organic Nanotubes

Self-Assembled Arrays of Single-Walled Metal–Organic Nanotubes**

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Many recent advances in the field of metal–organic framework (MOF) materials have been reported, not only from the standpoint of the potential applications, ranging from gas storage to catalysis and drug delivery, but also because of their intriguing architectures and framework topologies.[1,2] Conceptually, endless structures can be produced by assembling judiciously selected molecular building blocks.[2] Just as the notable saying in crystal engineering goes “the limits are mainly in our imagination”,[2a] any conceivable MOF might be obtained in the future, although it is all currently imagination. Since the first discovery of carbon nanotubes (CNTs) by Iijima in 1991,[3] discrete hollow tubular structures such as various CNTs and other synthetic nanotubes (SNTs) prepared from inorganic, organic, or biological precursors have been successfully developed, because they possess useful functionalities and can serve as molecular capillaries, sieves, and biological models.[4–6] In theory, the curling-up or rolling-up mechanism of topology transformations from 2D flat sheets to 1D hollow tubes is achievable.[4d] Thanks to effective design and synthesis strategies, many porous MOFs with various interesting network topologies have been reported over the past decade.[2] Compared with the focus on CNTs and SNTs, it is surprising that significantly less effort has been directed to the preparation of metal–organic nanotubes (MONTs).[7–9] In particular, discrete MONT structures are extremely rare to date.[9]

As part of our ongoing efforts in the design and synthesis of functional crystalline materials,[2f,8d,10] we wish to report herein on a unique type of MOF of $[\{[\mathrm{Cd(apab)_2(H_2O)}]_3(\mathrm{MOH})\cdot\mathrm{G}\}_n]$ (MAS-21–23, $\mathrm{M^I = Cs^I, K^I, Na^I}$, respectively; for MAS-22, $\mathrm{G = 18\,H_2O\cdot 6\,C_2H_5OH\cdot 3\,C_4H_8O}$; apab = 4-amino-3-[(pyridin-4-ylmethylene)amino]benzoate; MAS = materials of Academia Sinica), all of which consist of a large single-walled metal–organic nanotube of $[\{\mathrm{Cd(apab)_2(H_2O)}\}_{3n}]$ (MONT-A1) with an exterior wall diameter of up to 3.2 nm and an interior channel diameter of 1.4 nm. These MONTs are held together by alkaline cations to form 3D nanotubular supramolecular arrays (Figure 1). To the best of our knowledge, a single-walled MONT with such a large diameter is unprecedented.[9]

Compounds MAS-21–23 were synthesized by reaction of cadmium perchlorate, 4-amino-3-[(pyridin-4-ylmethylene)amino]benzoic acid (Hapab), and MOH ($\mathrm{M^I = Cs^I, K^I}$, and $\mathrm{Na^I}$, respectively) in an EtOH/THF/H_2O solvent diffusion system at 4 °C through a single-step, self-organization process (Scheme 1). The appropriate choice of an organic ligand with specific functional groups and geometry is a major factor in achieving these large nanotube-based structures. The multifunctional Schiff base ligand of Hapab was designed deliberately and possesses a bending angle of 120° between the pyridyl and carboxylate groups. Unlike similar banana-shaped organic linkers, the use of the apab scaffold favors the formation of a tubular structure, rather than a spherical network.[11]

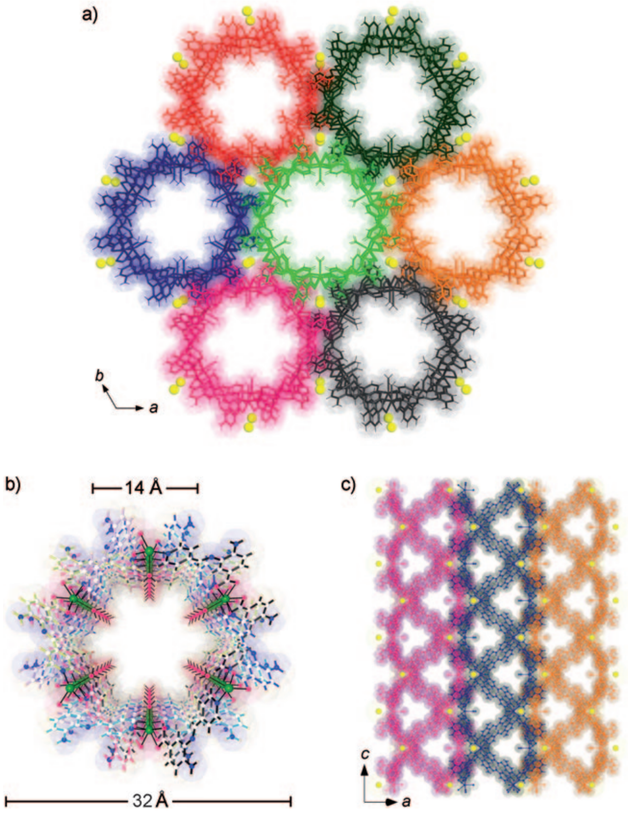

Figure 1. a) Assembly of MONTs-A1, which are held together by potassium cations in MAS-22; K yellow. b) Top view of MONT-A1; Cd green, C white, O pink, N blue, H tan. c) Side view of (a).

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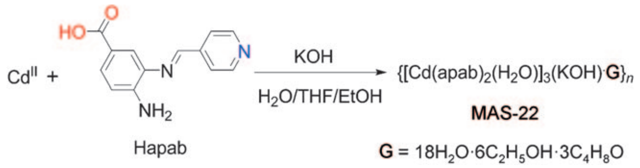

Scheme 1. Synthesis of MAS-22 by a one-step self-organization process.

Single-crystal X-ray diffraction analyses revealed that MAS-21–23 are all isomorphous and crystallize in the trigonal space group $P\bar{3}1c$.[12] Therefore, only the structure of MAS-22 is discussed in detail. The asymmetric unit of MAS-22 consists of one half of the Cd^{II} center, one apab ligand, one third of the K^{I} center, and one coordinated water molecule; other disordered anions and guest molecules are not crystallographically well-defined. Analysis of the local symmetry of the metal cations showed that the Cd^{II} center resides on a special position (site occupancy factor (SOF) = 0.5) containing a twofold axis of rotation, and the K^{I} center resides on the other special symmetry site (SOF = 1/3) containing a threefold axis of rotation and other perpendicular twofold axes of rotation. Each Cd^{II} center is bound to one water molecule and two pyridyl nitrogen atoms, four carboxylate oxygen atoms in a heptacoordinate manner. Each K^{I} center is octahedrally bound to six carboxylate oxygen atoms of the six separate apab ligands (Figure S1 in the Supporting Information).

The most intriguing feature of MAS-22 is that there is a large single-walled metal–organic nanotube formed from a four-connected pseudo-square-planar Cd^{II} node and an angular bidentate organic linker of the apab ligand (Figure 2a). The top view of the open-ended, hollow nanotube indicates that it is an undulated hexanuclear $\{Cd_6(apab)_{12}(H_2O)_6\}$ metallamacrocycle with a very large 72-membered ring (72MR) consisting of six Cd^{II} atoms and six apab ligands (6 Cd, 48 C, 12 N, and 6 O) with S_6 symmetry (Figure 2b). Every alternating Cd center is coplanar, and each cadmium–cadmium separation, bridged by the apab ligand, is 13.45(2) Å. It is noteworthy that the MONT has a large cross section with an exterior wall diameter of 3.2 nm, and an interior channel diameter of 1.4 nm (calculated from the van der Waals radii of the relevant atoms; Figure 1c).

To illustrate the unique structure of MONT-A1, each Cd center, which is connected to four apab ligands, is represented by a distorted square four-connected node, and the apab linker is simplified by an angular bar with a bending angle close to 120° (Figure 2c). In Figure 2d,e, the unusual skeleton of MONT-A1 with the only topology having all equivalent links and four-connected pseudo-square-planar nodes is apparent. This cylinder topology is potentially of great interest, but has been not addressed previously.[9,13]

Conceptually, when a selected 2D layer is rolled up and its adjacent edges glued appropriately, an open-ended hollow tube with variable diameter will be generated.[6] Certainly, MONT-A1 can be regarded as a nanotube that is folded from a (4,4)-topology sheet (Figure 3a).[9a,b] In general, the manner in which the graphene sheet are wrapped is represented by a pair of indices (n,m).[4a] Analogous to the three types of single-walled CNTs, it is interesting to see how the (4,4)-square layer is rolled up to make the nanotubes. Thus, the index of MONT-A1 is defined as (6,6). Its tube axis is along a direction diagonal to the (4,4)-square layer (Figure 3c). The tube is not chiral and can be depicted as hexastranded helices consisting of three right-handed and three left-handed helical chains with a 6_1-screw axis and a 6_5-screw axis, respectively. The Cd–Cd translation per helix turn is 63.17 Å ($3\times c$). Interestingly, as shown in Figure 3a, this huge and magnificent column-shaped nanostructure of MONT-A1 resembles a rolled-up dragon column, which can be found in Chinese palaces and temples. (Rolled-up dragons are a type of ancient Chinese totem representing nobleness and authority; see Figure 3b.)

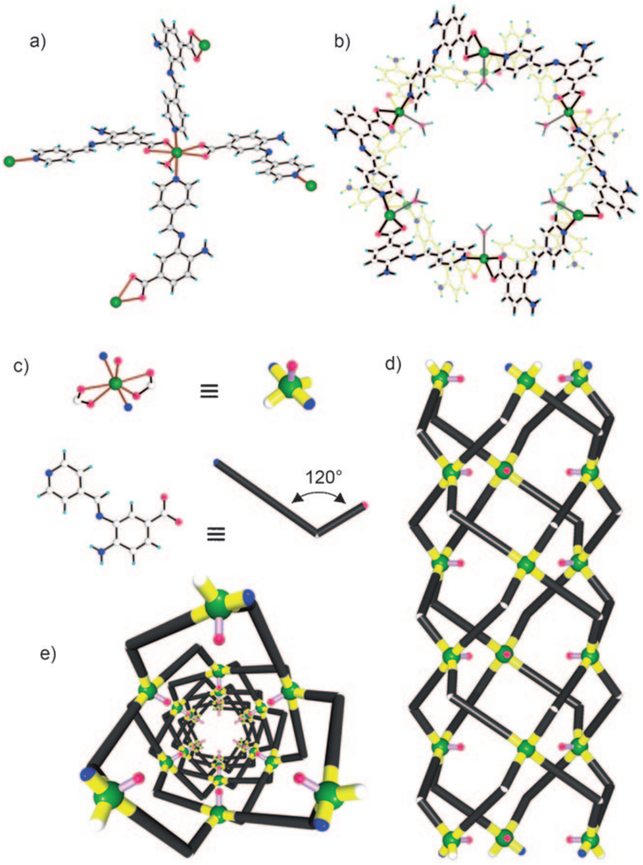

Figure 2. Structures of MONT-A1 in MAS-22: a) A four-connected pseudo-square-planar cadmium center. b) The cross section of the nanotube showing 72-MR with S_6 symmetry. c) Simplified view of a four-connected cadmium center and the angular apab ligand. d) Side view and e) top view of the simplified nanotube structure. Cd green, C white, O pink, N blue, H aqua.

The large nanotubes are all held together by potassium ions and are closely packed in a hexagonal manner to form a 3D framework (Figure 3d). As shown in Figure 1c, this array of MONTs in MAS-22 is analogous to a packet of densely packed straws. An analysis using the PLATON[14] software tool indicates that the extra-framework volumes per unit cell for MAS-21, -22, and -23 are approximately 63, 61, and 59%, respectively. These large free spaces within the frameworks cause the structures to be highly porous and have low

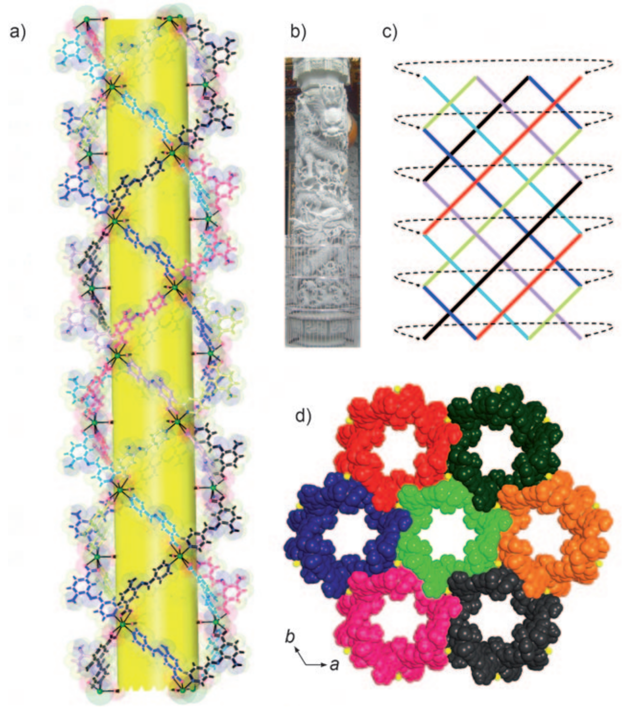

Figure 3. a) Ball-and-stick representation of the MONT-A1 with helical strands individually colored. b) A curling-up dragon column. c) Topology relationship between a (4,4)-layer and the nanotube (colors are the same as in (a)). d) Packing array of the nanotubes (nanotubes individually colored).

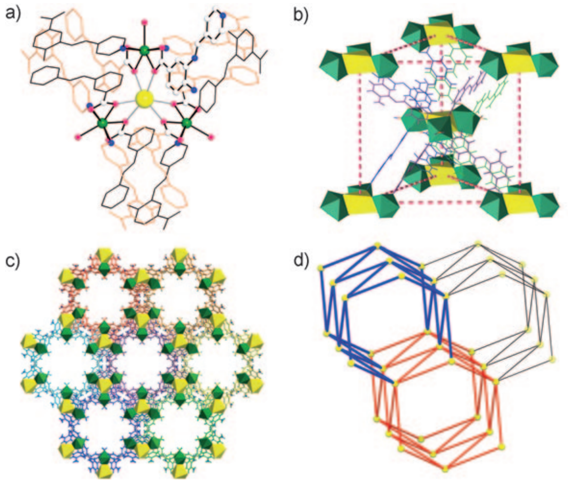

Figure 4. a) Coordination environment of the $\{KO_6Cd_3\}$ cluster. b) The six-connected trigonal prismatic building units of the $\{KO_6Cd_3\}$ cluster. c) Top view of the MAS-22 framework. d) The $4^9.6^6$-acs net.

calculated densities (in the absence of all guests) of 0.72, 0.75, and 0.81 $g\,cm^{-3}$, respectively. A side view of the framework reveals other triangular channel openings with effective dimensions of 9×9 Å along the *a* and *b* axes (Figure 1c). The overall array contains a 3D intersecting channel system and large open windows. This structure is likely to be a major factor in the unusually high instability of these three frameworks upon the loss of guest moieties. Nitrogen sorption studies reflect this structural characteristic (Figure S12 in the Supporting Information).

Interpenetration is currently a major barrier to the design and synthesis of low-density MOFs.[2b,15] Interestingly, MAS-21–23 are all non-interpenetrating, despite the large 3D intersecting channel systems within the frameworks, mainly because the large single-wall MONTs are tightly held together by alkaline cations. Thus, this is likely to be an effective strategy for creating non-interpenetrated frameworks through direct discrete tube-to-tube adherence, because interpenetration is truly forbidden in such cases (Figure 3d).

Further analysis of the frameworks reveals the MONT-based structure as a suitable candidate. In considering the weaker supramolecular interactions between the K^+ center and carboxylate oxygen atoms (K–O 2.644(1) Å), the K^+ center is surrounded by six carboxylate oxygen atoms of six separate apab ligands in an octahedral manner. Thus, a six-connected tetranuclear supramolecular cluster with the formula $\{KO_6Cd_3\}$ is formed (Figure 4a,b). Each $\{KO_6Cd_3\}$ cluster serves as a trigonal prismatic building block that is linked by 12 separate ditopic apab ligands (Figure 4b,c). The double antiparallel apab ligands serve as linkers to bridge to two $\{KO_6Cd_3\}$ clusters. The overall array of the framework results in a rare $4^9.6^6$-acs topology, a high-symmetry uninodal six-connected semiregular net (Figure 4d).[16,17]

In conclusion, we have prepared a new type of MOF consisting of a large single-walled metal–organic nanotube (MONT). These large MONTs are held together by alkaline cations, in an analogous way to a packet of densely packed straws, leading to unique supramolecular nanotubular arrays. Our innovative results highlight an important research topic and provide vision for the development of discrete metal–organic nanotube-based materials that have been largely unexplored. We believe that this type of MONT should be isolated and will have great potential in the future. Further research is currently underway.

Experimental Section

MAS-22: A solution of $Cd(ClO_4)_2{\cdot}4H_2O$ (0.10 mmol) in C_2H_5OH (5 mL) was carefully layered on top of a bilayer solution comprised of a solution of KOH (0.25 mmol) and 4-amino-3-[(pyridin-4-ylmethylene)amino]benzoic acid (Hapab, 0.20 mmol) in H_2O (7 mL) on the bottom and a blank buffer solvent of THF (8 mL) on the top. *Caution: perchlorate salts are potentially explosive and should be handled with care.* The system was allowed to stand at 4 °C for 4 weeks, after which time deep orange hexagonal crystals had formed in 18% yield (based on Cd^{II}). The solid product was washed with deionized water and ethanol, and only slightly dried in air prior to elemental analysis. Elemental analysis (%) for $C_{102}H_{163}Cd_3KN_{18}O_{43}$: calcd C 45.28, H 6.07, N 9.32; found C 45.71, H 6.31, N 9.96. The formula $\{[Cd(apab)_2(H_2O)]_3(KOH)\}{\cdot}18H_2O{\cdot}6C_2H_5OH{\cdot}3C_4H_8O$ was assigned by elemental microanalysis, thermogravimetric analysis, IR spectroscopy, and single-crystal X-ray diffraction studies. MAS-21 and -23 were also synthesized under similar reaction conditions using the same molar ratios of reactants, except that CsOH or NaOH were used instead.

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[12] Crystal structure data for MAS-22: $C_{78}H_{67}Cd_3KN_{18}O_{16}$ [{[Cd-(apab)$_2$(H$_2$O)]$_3$(KOH)}$_n$], $M_r = 1888.80$, trigonal, $P\bar{3}1c$, $a = b = 21.3676(4)$ Å, $c = 21.056(1)$ Å, $V = 8325.6(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 0.753\ g\,cm^{-3}$, $\mu = 0.442\ mm^{-1}$, λ (Mo$_{K\alpha}$) = 0.71073 Å, $F(000) = 1904$, $T = 293(2)$ K. Final R indices: $R_1 = 0.0366$, $wR_2 = 0.1074$ for 3667 reflections [$I > 2\sigma(I)$]; $R_1 = 0.0478$, $wR_2 = 0.1112$ for 4926 independent reflections (all data) and 185 parameters, $GOF = 1.101$. The contribution of the disordered area to the overall intensity data was eliminated using the SQUEEZE method in PLATON. The hydroxide anion was disordered and added in the formula only to show a charge balance. CCDC 736746 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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