From 1D zigzag chain to 1D tubular structure, weak field ligand-dependent assembly of cucurbit[6]uril-based tubular coordination polymer†‡

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The reaction of cucurbit[6]uril with $Cu(NO_3)_2$ and $CuCl_2$, respectively, generates a 1D zigzag chain of $\{[Cu(H_2O)_4(cucurbit[6]uril)]\cdot(NO_3)_2\cdot(H_2O)_8\}_n$ and a 1D tubular structure of $\{[Cu(H_2O)_2(Cl)_2(cucurbit[6]uril)]_{1/3}\cdot(H_2O)_3\}_n$, showing clearly how to control the reversible and mutual interconnections between ligand and metal ion under the guide of coordination chemistry.

Tubular architectures are important materials that attract considerable interest in the fields of nanotechnology, molecular sieves, ion sensors, and fluidic transport systems.[1-2] Inorganic tubular structures, particularly carbon nanotubes, have been the focus of many research efforts, but they could not be assembled with defined structures and sizes. In principle, both organic and inorganic–organic tubular structures could be generated through molecular self-assembly. However, in comparison with many advances achieved in the realm of organic nanotubular ensembles,[3,4] such as the tobacco mosaic virus coat protein,[3] and cyclic D,L-peptides, gramicidin A and its analogues,[3] only a few examples of inorganic–organic coordination tubes have been reported so far.[5,6] The obstacle of assembling inorganic–organic tubular structure is attributed to that formation of such a structure often requires a complementary pair of ligand and metal cation to offer their reversible and mutual interconnection,[6a] but in practice the match is usually difficult to be realized and is influenced by many factors,[7] such as metal ions with different coordination geometry or radius,[8] counter anoins with different coordination ability [9] or bulk,[10] solvent,[11] metal–ligand ratio,[12] and even pH conditions.[13]

Cucurbiturils (Scheme 1), a kind of fascinating macrobicyclic compounds, possess intramolecular cavities that are available for the encapsulation of guests,[14] and have widely been used as synthetic receptors[15] or as building blocks for supramolecular architectures.[16] From the structural viewpoint, cucurbiturils are also ideal modular building units for the assembly of inorganic–organic coordination tubes, because not only terminally linking adjacent cucurbiturils through coordination of metal ions is a known synthetic strategy[6a] to the assembly of such a kind of structure, but also the control over diameter and even length of the tubular structure could be realized by selecting different cucurbiturils and adjusting the ratio of metal to ligand, respectively.

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‡ The first and second authors have the same contribution to this work.
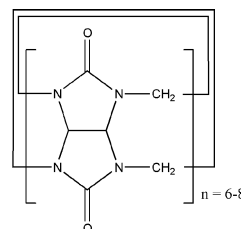
Scheme 1 Molecular structure of cucurbiturils.

However, owing to the weak coordination ability of its carbonyl group, the cucurbituril-based tubular structures assembled so far is either through hydrogen-bonded interaction connecting to the terminal carboxy groups of adjacent cucurbiturils[17] or a pair of Na^+ ions, or Ca^{2+} ions, or Sr^{2+} connected to the terminal carboxyl groups of adjacent cucurbiturils.[18] Although other alkali metal ions, even lanthanide ions were also used to assemble such a kind of tubular structure, more often than not, the end-capped or end-obstructed coordination polymers were obtained.[19] And thus, the assembly of transition metal cucurbituril-based tubular coordination polymer has not succeeded so far.[20]

Because of the difficulty in synthesis, recently, chemist starts to appeal to sulfur-substituted cucurbituril (*i.e.*, the terminal oxygen atom of cucurbituril replaced by sulfur one) to construct such a kind of tubular structure, though the investigation is only limited to theoretical calculation.[21]

Unambiguously, to effectively construct cucurbituril-based co-ordination tube, the key is to enhance the coordination ability of carbonyl group to the metal ion. Based on the theory of coordination chemistry, we know that the separation of metal-bound ligand is closely related to the coordination ability of ligands both at apical and plane positions. A typical example in this aspect is that the copper(II)-water distance in $Cu(HCOO)_2\cdot4H_2O$ is 2.36 Å, while in $CuCl_2\cdot2H_2O$, this distance was shorten to 1.93 Å.[22] Accordingly, if a weak field ligand was selected to coordinate with the metal ion, the coordination ability of the carbonyl group of cucuibutril to the metal ion would be significantly enhanced. Along this line, we chose the copper(II) ion, nitrate and weak field ligand chloride anions, respectively, to construct transition metal cucurbituril-based coordination tube, and report herein the syntheses and structures of one-dimensional chain of $\{[Cu(H_2O)_4(cucurbit[6]uril)]\cdot(NO_3)_2\cdot(H_2O)_8\}_n$ (**1**)[23] and the tubular coordination polymer of $\{[Cu(H_2O)_2(Cl)_2(cucurbit[6]uril)]_{1/3}\cdot(H_2O)_3\}_n$ (**2**),[23] which precisely shows the way of enhancing the coordination ability of the terminal carbonyl group of cucurbituril under the direction of coordination chemistry.§

We firstly start the assembly with copper(II), the nitrate anion and cucurbit[6]uril. Although, in this case, a one-dimensional

chain structure was formed through each copper(II) ion coordinated with two terminal carbonyl groups, respectively, from two adjacent cucurbiturils (Fig. 1). Owing to coordination by water molecules, instead of nitrate anions, the copper(II) ion is, in fact, weakly coordinated by the carbonyl group and exhibits elongated coordination geometry. The bond distances of Cu–O$_{water}$ in plane positions are in the range from 1.931(3) to 1.979(3) Å, much shorter than those of 2.466(3) and 2.543(3) Å, respectively, for Cu–O$_{carbonyl}$ at apical positions, similar to that reported in the Cu-cucurbit[5]uril adduct.[24] Failure of obtaining the copper(II)-cucurbituril complex with the nitrate anions coordinated, we appealed to the weak field ligand, Cl⁻, for the assembly of a cucurbituril-based coordination tube. In order to ensure the coordination of the Cl⁻ anion to copper(II) ion, the reaction was performed in HCl solution (3 mol L⁻¹) so that the concentration of the Cl⁻ anion was kept high enough during the assembly process.
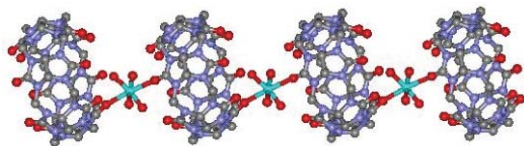

Fig. 1 Ball-and-stick representation showing the 1D structure of **1** viewed along the *a* axis. Hydrogen atoms are omitted for clarity. O = red, C = grey, N = violet and Cu = cyan.

Fig. 2 illustrated the structure of the cucurbituril-based coordination tube. As expected, the coordination of Cl⁻ anion coordinates to copper(II) ion (Cu–Cl = 2.261(3) and 2.278(2) Å) leads to the distance of Cu–O$_{carbonyl}$ (2.341(3) Å) in **2** significantly shorter than that of 2.466(3) and 2.543(3) Å in **1**. The tubular structure of **2** can be viewed as three copper(II) ions linked to six carbonyl groups from two adjacent cucurbiturils with three of them alternately from one cucurbituril and the remaining alternately from adjacent one. It was noted that the tubular structure in **2** is much different from that of [Na₄(cucurbit[6]uril)₂(H₂O)₁₆]Cl₄·6H₂O,[18a] in which, adjacent two cucurbit[6]urils are linked by a pair of Na(I) ions.
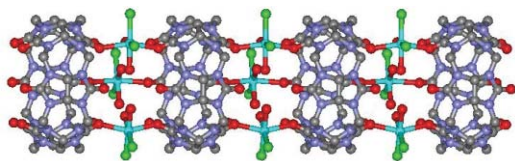

Fig. 2 Ball-and-stick representation showing the tubular structure of **2** viewed along the *a* axis. Hydrogen atoms were omitted for clarity. O = red, C = grey, N = violet, Cu = cyan and Cl = green.

Interestingly, each tubular coordination polymer in **2** is surrounded by three neighbours, stacking into a honeycomb structure with linear and hexagonal channels through weak C–H···Cl hydrogen bonding interaction (H···Cl1 = 2.731 Å, C–H···Cl1 = 158.9°, H···Cl2 = 2.738 Å, C–H···Cl2 = 144.8°) with Cl⁻ from one tubular coordination polymer and the C–H from the "waist" of cucurbituril from the neighbouring tube as shown in Fig. 3. The diameter of the hexagonal channel is above 12 Å obtained from the shortest distance of C···C from the opposite 1D tube. The accessible porosity for the guest molecule calculated through the PLATON program[25] is 1099.8 Å³ mol⁻¹ (31.7%), which is
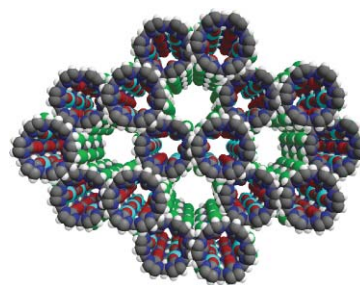

Fig. 3 Space-filling representation showing stack of the tube into a hexagonal channel with a diameter of *ca.* 12 Å viewed along the *c* axis. O = red, C = grey, H = white, N = blue, Cu = cyan and Cl = green. Water and methanol molecules were omitted for clarity.

filled with guest molecules. It is noted that, although the stack arrangement in **2** is very similar to that reported in Rb-cucurbituril coordination polymer,[19b] there is significantly difference between the two structures. In the Rb-cucurbituril coordination polymer, a pair of Rb(I) ions linking with adjacent cucurbiturils is bridged by two water and methanol molecules, respectively, and the channel of Rb-cucurbituril coordination polymer is, in fact, obstructed by the bridges. In **2**, such bridge is prevented and **2** exhibits a discreet coordination tube.

In summary, we have reported the syntheses of a 1D zigzag chain and 1D tubular structure through the reaction of cucurbit[6]uril with Cu(NO₃)₂ and CuCl₂, respectively. Their structural differences indicate that the coordination ability of carbonyl group of cucurbituril to copper(II) ion could effectively be enhanced by selecting proper weak field ligand, revealing clearly how to control the reversible and mutual interconnections between ligand and metal ion under the guide of coordination chemistry.

Acknowledgements

Notes and references

§ **1**: To a water–methanol solution (10 : 1 (v/v)) of Cu(NO₃)₂·3H₂O (0.12 g, 0.50 mmol) was added an aqueous solution of cucurbit[6]uril (0.10 g, 0.1 mmol). After heated for *ca.* 10 min, the mixture was filtered and colourless prismatic crystals of **1** were obtained within 2 d in 50% yield. Elemental analysis for C₃₆H₆₀CuN₂₆O₃₀ (**1**), calcd (%): C 30.84, H 4.28, N 25.99. Found (%): C 30.89, H 4.26, N 25.42. **2**: To a HCl (3 mol L⁻¹) solution (10 mL) was added 0.10 g (0.10 mmol) cucurbit[6]uril. After the cucurbit[6]uril was completely dissolved, a water–methanol solution (10 : 1 (v/v)) of CuCl₂·3H₂O (0.24 g, 1.0 mmol) was added. The mixture was kept at room temperature and greenish claviform crystals of **2** were obtained in about two weeks. Elemental analysis for C₁₂H₂₂.₆₇Cl₂CuN₈O₉ (**2**), calcd (%): C 25.86, H 3.95, N 20.11. Found (%): C 27.91, H 4.53, N 18.28. The difference between the calcd and found in the elemental analysis is attributed to that the part of methanol and water molecules could not be found. Consistently, there are 431.0 Å³ voids accessible for solvents in **2**.

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23 The crystal data of **1** and **2** were collected on a Bruker Apex-2000 diffractometer using graphite monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å) at 173 K. The, measured intensities were reduced to F^2 and corrected for absorption with SADABS.[26] Structural solution and full-matrix least-squares refinement were performed with the SHELXS-97 and SHELXL-97 program package,[27,28] respectively. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of organic ligands were generated geometrically (C–H = 0.96 Å). Hydrogen atoms of water molecules were not considered. Analytical expressions of neutral atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[29] In **2**, one of the chloride anion (Cl$^-$) was dealt with disorder with the occupancy of 0.5 and 0.5, respectively. Crystal data for $C_{36}H_{60}CuN_{26}O_{30}$ (**1**): orthorhombic, space group $P2_12_12_1$, $a = 11.559(2)$, $b = 15.852(3)$, $c = 30.320(5)$ Å, $V = 5555.7(17)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.675$ g cm^{-3}, $M = 1400.64$, $\mu(\text{Mo K}\alpha) = 0.512$ mm^{-1}. $R_1 = 0.0552$ for 9470 reflections with $I > 2\sigma(I)$ ($R_{int} = 0.0290$), and w$R_2 = 0.1454$ for 10 364 reflections and 849 parameters. Crystal data for $C_{12}H_{22.67}Cl_2CuN_8O_9$ (**2**): hexagonal, space group $P6_3/m$, $a = 19.5216(17)$, $c = 10.5282(18)$ Å, $\gamma = 120°$, $V = 3474.7(7)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.599$ g cm^{-3}, $M = 557.49$, $\mu(\text{Mo K}\alpha) = 1.232$ mm^{-1}. $R_1 = 0.0741$ for 1852 reflections with $I > 2\sigma(I)$ ($R_{int} = 0.0169$), and w$R_2 = 0.1951$ for 2051 reflections and 176 parameters.

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