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Trifluoromethanesulfonate Anion-linked Supramolecular Frameworks of Cucurbit[5]uril and Cucurbit[7]uril

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Two crystals based on cucurbit[5]uril and cucurbit[7]uril, $C_{30}H_{30}N_{20}O_{10}\cdot 2CF_3SO_3H\cdot 7.25H_2O$ (**1**) and $C_{42}H_{42}N_{28}O_{14}\cdot CF_3SO_3H\cdot 8H_2O$ (**2**) have been synthesized in trifluoromethanesulfonic acid and structurally determined by single-crystal X-ray diffraction analyses. These two crystal structures demonstrated that the highly-ordered trifluoromethanesulfonate anions play essential roles in the formation of three-dimensional supramolecular frameworks with 1D elliptical channels or circular channels.

Exploring novel supramolecular architectures by using a variety of noncovalent interactions such as hydrogen bonds, coordination bonds, π–π interactions, and electrostatic interactions has aroused increasing research interests.[1] For organic assembling units, macrocyclic host molecules are advantageous. Due to the properties of high-symmetry and rigidity, highly regular molecular architectures tend to form. Subsequently, extended pores and channels can be created from stacking of the macrocyclic units. Therefore, more sophisticated framework structures with the intrinsic cavity of macrocycle itself could be designed and synthesized.[2]

Amongst known macrocyclic hosts, cucurbit[*n*]urils (CB[*n*], $n = 5$–10) are cyclic oligomers of glycoluril with a confined cavity that displays outstanding properties.[3] A vast number of cucurbituril assembly structures have been prepared through metal-ion linkage[4] or polypseudorotaxane.[5] Especially some efforts have been focused on design and synthesis of metal-organic frameworks using cucurbiturils as ligands to coordinate with metal ions, for instance, alkali, alkaline-earth, and lanthanide ions. Except metal-ion linkage and polypseudorotaxane, anion linkage has been far less comprehensively investigated.

For cucurbituril homologs, cucurbit[5]uril (CB[5]) and cucurbit[7]uril (CB[7]) can considerably dissolve in dilute solution of some inorganic acids, such as HCl[6] and H_2SO_4.[7] However, in the crystal structures thereby formed, anions are usually omitted for being disordered. Meanwhile no metal-free CB-assembly structures containing anions from organic acids have been structurally characterized so far, apart from a CB[6]-based polyrotaxane network containing Ag^+ and $CF_3SO_3^-$.[8] Herein by using trifluoromethanesulfonic acid, two novel crystal structures based on CB[5] and CB[7] are reported, where trifluoromethanesulfonate anions can participate in supramolecular frameworks in highly-ordered fashions and play essential roles in linking CB units together.

The X-ray crystal structure of **1**[9,10] reveals that each CB[5] molecule links directly with two CB[5] neighbors through C–H···O hydrogen bonds (H21A–O5, 2.637 Å), and indirectly with six CB[5] neighbors through trifluoromethanesulfonate anions acting as hydrogen bond acceptors (Figure 1b) among which four CB[5] neighbors are linked through C–H···O hydrogen bonds (aver. 2.604 Å) and two remaining CB[5] neighbors are linked through C–H···F hydrogen bonds (H25B–F2, 2.592 Å). The shortest distance between trifluoromethanesulfonate anions is 6.125 Å (taking the sulfur atom as reference). On the other hand, CB[5] molecules interact with each other indirectly through water molecules or hydronium ions to stack into 1D supramolecular chains[11] along the *a* axis. Figure 1a reveals that interactions between two neighboring CB[5] molecules are from one portal carbonyl-oxygen atom (O1, O4, and O6) to water molecules (O6W, O8W, and O7W), then interlinking with the adjacent portal oxygens (O2W and O1W). The H-bonding distances are 2.749 (O1–O6W), 2.911 (O6W–O2W), 2.958 (O4–O8W), 2.842 (O8W–O1W), 2.769 (O6–O7W), and 2.861 Å (O7W–O1W), respectively. As shown in Figure 1c, 1D supramolecular chains (along *a* axis) knitted by hydrogen bonds amongst CB[5] molecules and trifluoromethanesulfonate anions are extended in three dimensions to form supramolecular framework with elliptical channels.

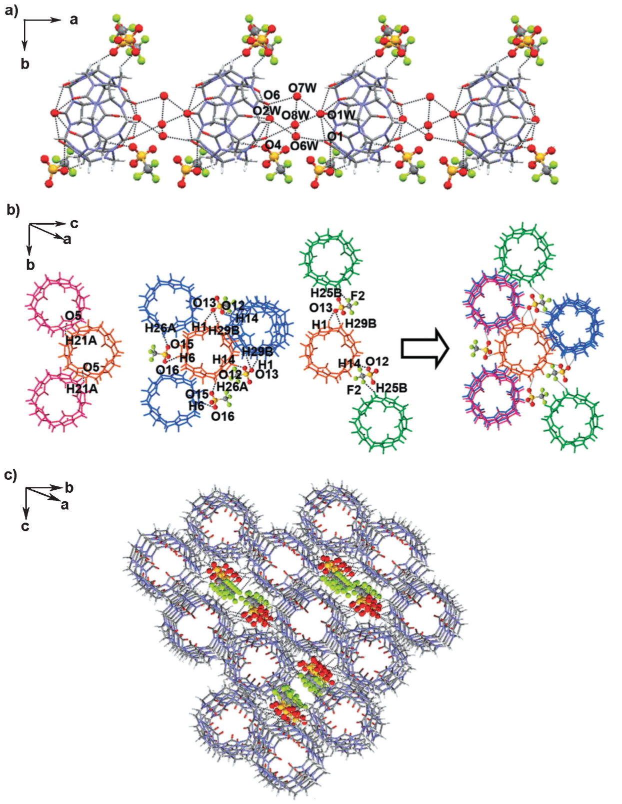

Figure 1. X-ray crystal structure of **1**. a) 1D supramolecular chain of CB[5]. b) Geometry of eight nearest neighbors linked to one center CB[5] molecule. Color codes of CB[5] molecules: center CB[5] molecule, orange; interacting directly with center CB[5] molecule by hydrogen bonds, purple; interacting with center CB[5] molecule through trifluoromethanesulfonate anions, especially, linked by H···O bond: blue, linked by H···F bond: green. c) Infinite 3D structure. Some water molecules are omitted for clarity.

The X-ray crystal structure of **2**[9,10] is remarkably different from that of **1** although they were both crystallized in the presence of

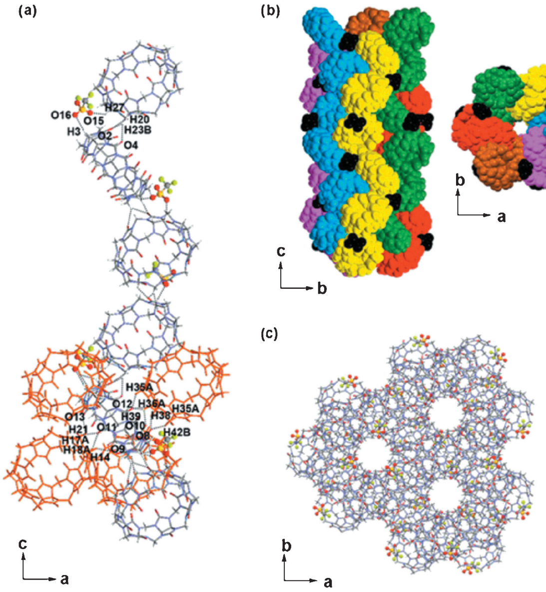

Figure 2. X-ray crystal structure of **2**. a) Helix generated by CB[7] units and trifluoromethanesulfonate anions alternately (Orange: CB[7] neighbors interacted directly to each CB[7] molecule on the helix by C–H···O hydrogen bonds). b) 1D channel formed by six helixes. Each color represents one helix. c) 3D framework with 1D channels.

trifluoromethanesulfonic acid. CB[7] is inclined to form hydrogel in dilute inorganic acids[7] which is unique from other CB homologs as Kim reported. Few investigations on supramolecular frameworks of CB[7] have been carried out so far. In this work, a novel assembly structure of CB[7] was readily obtained by addition of trifluoromethanesulfonic acid. Along the *c* axis, CB[7] molecules are arranged in a 1D helix (Figure 2b) with trifluoromethanesulfonate anions linking every two adjacent CB[7] units by hydrogen bonds (H27–O15, 2.461 Å and H3–O16, 2.615 Å), which are reinforced by C–H···O bonds (H20–O2, 2.546 Å; H23B–O2, 2.495 Å; and H23B–O4, 2.672 Å) between side CH or CH_2 groups of one CB[7] molecule and its neighboring CB[7]'s portal-oxygen atoms. The shortest distance between trifluoromethanesulfonate anions is 8.588 Å (taking the sulfur atom as reference). At the same time, each CB[7] molecule on 1D helix interacts directly with four other CB[7] molecules out of the helix through C–H···O hydrogen bonds in a distorted square-planar geometry (Figure 2a). The lengths of the hydrogen bonds are 2.638 (H17A–O13), 2.382 (H21–O11), 2.365 (H18A–O11), 2.381 (H14–O9), 2.661 (H35A–O12), 2.316 (H36A–O12), 2.490 (H39–O12), 2.329 (H39–O10), 2.332 (H38–O8), and 2.477 Å (H42B–O8), respectively. Such multiple hydrogen-bond interactions render the formation of supramolecular framework with 1D channels by hexagonal arrangement in three dimensions. On the *ab* plane, it can be observed that the 1D channel has an aperture with a diameter of approximately 8 Å (Figure 2c).

In this paper, we have described two novel supramolecular frameworks based on CB[5] and CB[7] where trifluoromethanesulfonate anions are highly ordered and play essential roles. Trifluoromethanesulfonate anions act as hydrogen-bond acceptors and side CH or CH_2 groups of CB act as hydrogen-bond donors. These hydrogen-bond interactions result in the formation of three-dimensional framework structures with 1D elliptical channels or circular channels, in concert with other well known multiple noncovalent interactions, including direct C–H···O hydrogen bonds between CB units,[12] hydrogen bonds between CB units and water molecules or hydronium ions which balance the negative charges on the anions.[11] For the first time, the roles of anion linkers in the construction of these supramolecular architectures have been fully demonstrated. Such organic crystals with 1D channels can be potentially useful in applications as organic zeolites.[13] The solvent-accessible free volumes of crystal **1** and **2** are estimated to be 22.9 and 36.7% of the total crystal volumes, respectively. Systematic studies of other anions to construct supramolecular architectures are ongoing in our laboratory and will be reported soon.

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10 Crystallographic data for **1**: $C_{30}H_{30}N_{20}O_{10}\cdot 2CF_3SO_3H\cdot 7.25H_2O$, fw 1261.50, orthorhombic, $P2_12_12_1$, $a = 12.322(2)$ Å, $b = 15.457(3)$ Å, $c = 27.114(5)$ Å, $V = 5164.2(16)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.620\ \mathrm{g\,cm^{-3}}$, $T = 293(2)$ K, $\mu = 0.226\ \mathrm{mm^{-1}}$, unique reflns = 9117, obsd reflns = 6954, $R_1 = 0.0825$ $(I > 2\sigma(I))$, $wR_2 = 0.2232$, GOF = 1.031. Crystallographic data for **2**: $C_{42}H_{42}N_{28}O_{14}\cdot CF_3SO_3H\cdot 8H_2O$, fw 1457.24, $R\bar{3}$, $a = 32.3851(9)$ Å, $b = 32.3851(9)$ Å, $c = 36.135(2)$ Å, $V = 32821(2)$ Å^3, $Z = 18$, $D_{\mathrm{calcd}} = 1.326\ \mathrm{g\,cm^{-3}}$, $T = 185(2)$ K, $\mu = 0.141\ \mathrm{mm^{-1}}$, unique reflns = 12899, obsd reflns = 6775, $R_1 = 0.0931$ $(I > 2\sigma(I))$, $wR_2 = 0.2645$, GOF = 1.009. Crystallographic data for the structures reported have been deposited with the Cambridge Crystallographic Data Centre as reference Nos. CCDC-760652 and -760653. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44 1223 336033.

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