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Short communication

Study on a new cyclodextrin based metal–organic framework with chiral helices

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ABSTRACT

Staring from β-cyclodextrins and Na salts, a new metal–organic framework with chiral helices, $(C_{42}O_{35}H_{70})_2(NaOH)_4\cdot H_2O$ (CD-MOF-**1**), has been successfully synthesized. X-ray diffraction analysis reveals that CD-MOF-**1** exhibits a 3D framework with left-handed helical channels running through the structure created by the ligation of Na ions to the primary and secondary faces of the β-cyclodextrins rings. Additionally, inclusion properties of CD-MOF-**1** were also studied, and the result shows that the inclusion rate using CD-MOF-**1** as inclusion materials is higher than that of β-cyclodextrins, which is expected to become a new type of green crystal material from edible natural products.

Supramolecular chemistry has been used to understand the intermolecular interactions of molecular packing and to design new solid materials with desired physical and chemical properties [1], especially, the study of metal–organic frameworks (MOFs) [2]. Considerable efforts have been devoted to extending the structural library of MOFs. During the construction of MOFs, transition metal centers and organic struts derived from non-renewable petrochemical feedstocks are often chosen because they possess well-known coordination behaviors with each other. Compared to these cases, the investigation and development of MOFs constructed by nature product (such as cyclodextrin, porphine, amino acids) are relatively rare [3]. As a special class of carbohydrates, β-cyclodextrin (β-CD) (shown in Fig. 1) consists of seven α-1,4-linked D-glucopyranosyl repeating units and displays the –OCCO-binding motif on both their primary and secondary faces auguring well in forming extended structures with metal cations [4]. These characteristics of CDs can merge into MOFs with alkali metals to contribute the natural porous materials (named as CD-MOFs) [5]. More importantly, CD-MOFs can be crystallized from water or ethanol, which are inexpensive and "green" in the sense that they can be synthesized from renewable sources that are themselves derived from water, CO_2, and nontoxic metal salts. So the syntheses of MOFs based on nature product remain an attractive research topic.

The challenge in preparing CD-MOFs lies in the inherent asymmetry of CD and the interaction between metal ions with carboxylate oxygen atoms owing to large differences in electronegativity, so it is uneasy to predict and control the coordination geometry of CD-MOFs. Furthermore, the study on MOFs with helix is of particular interest and a challenging area, because not only living organisms utilize helices to store and transmit genetic information, but also these helical compounds have important applications in optical devices and asymmetric catalysis [6]. Although many CD-MOFs (α-, β- and γ-CD) have been reported, only one CD-MOF with left-handed helical channel was reported until recently [7], in which six-member cyclic variant of CD (α-CD) coordinated by rubidium ions formed porous, infinitely long left-handed helical channels. As a continuation of the synthesis of CD-MOFs, herein, using seven-member cyclic variant of CD (β-CD) and alkali metal ($Na_2C_2O_4$), we reported a new β-CD based MOF, $(C_{42}O_{35}H_{70})_2(NaOH)_4\cdot H_2O$, termed CD-MOF-**1**, which represents the first example of β-CD based MOF with the left-handed helical structure.

The new CD-MOF-**1** is obtained by solvothermal method from the reaction of β-CD (0.25 mol), $Na_2C_2O_4$ (1 mol) and 10 mL CH_3OH/H_2O (8/2, *v*/*v*) [8]. Single-crystal X-ray analysis [9] reveals that the asymmetric unit of CD-MOF-**1** is composed of two β-CD molecules, four Na cations, four OH^- ion and one lattice waters (Fig. 2a). The β-CD molecule adopts five-coordination mode linking with three Na1 cations and two Na2 cations via a-, c-, d-, e- and g-glucopyranosyl (Fig. 2b). In turn, two crystallographically Na cations adopt different coordination modes, namely, Na1 which is six coordinated by O10 (C6), O30 (C6), O26 (ring), O25 (C6), O32 (C2), and O33 (C3) from three β-CD molecules (Fig. 2c) and Na2 which is two coordinated by O27 (C3) and O12 (C2) from two β-CD molecules (Fig. 2d). The bond distances are listed in Table 1.

One fascinating feature is that the CD-MOF-**1** exhibits a 3D framework with left-handed helical channels running through the structure created by the ligation of Na ions to the primary and secondary faces of the β-CD rings. Firstly, through Na1 cations, each β-CD molecule

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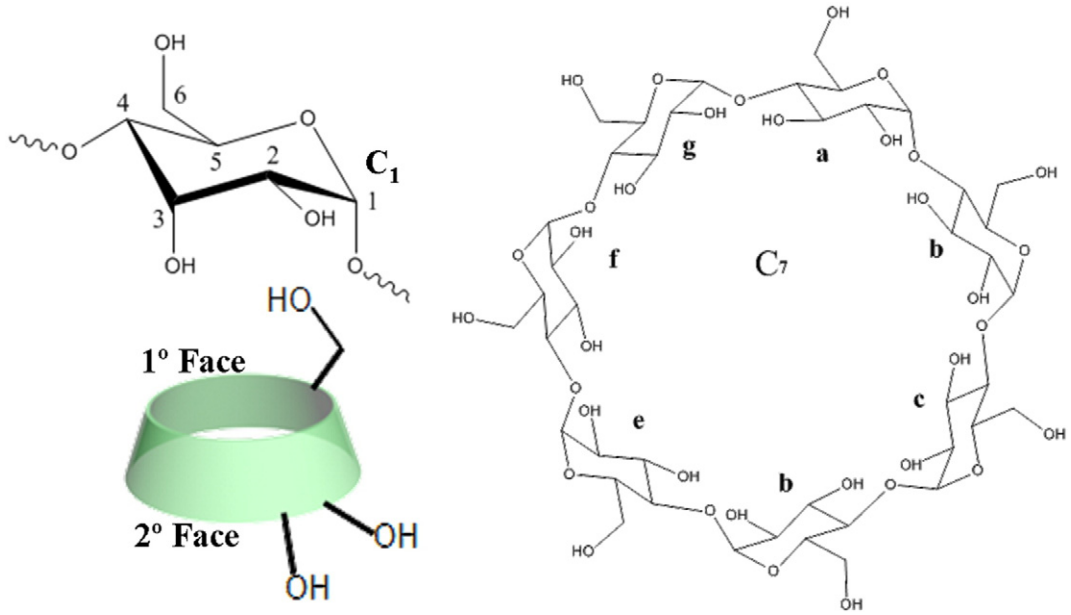

Fig. 1. Structure formulas of the asymmetric (C_1) α-1,4-linked D-glucopyranosyl residues and β-cyclodextrin (β-CD) with its C_7 symmetry. The seven C_6 hydroxy (OH) groups and the seven glycosidic ring oxygen atoms constitute the primary (1°) face of β-CD molecules, and the 14 C_2 and C_3 OH groups constitute the secondary (2°) face.

using its 2,3-OH group from a- and d-glucopyranosyl links with adjacent β-CD using its 6-OH and 2,3-OH groups from e- and c-glucopyranosyl forming 1D chains along *a* axis. Secondly, the adjacent 1D chains are fused together via Na2–O12 obtaining 1D double chains with double channel and left-handed helical structure shown in Fig. 3a and b. More specifically, β-CD molecules with Na1 and Na2 atoms form left-handed helical chains (β-CD–Na1-β-CD–Na2-β-CD–Na1) with a pitch of 10.353 Å (Fig. 3a and c), which is consistent with the unit length of *a* axis (a = 10.353(5) Å). Finally, each left-handed helical chain is surrounded by four same channels via Na1–O10 (primary face 6-OH) forming the 3D CD-MOFs (Fig. 4). Note that CD-MOF **1** is the first example of β-CD based MOF with the left-handed helical structure.

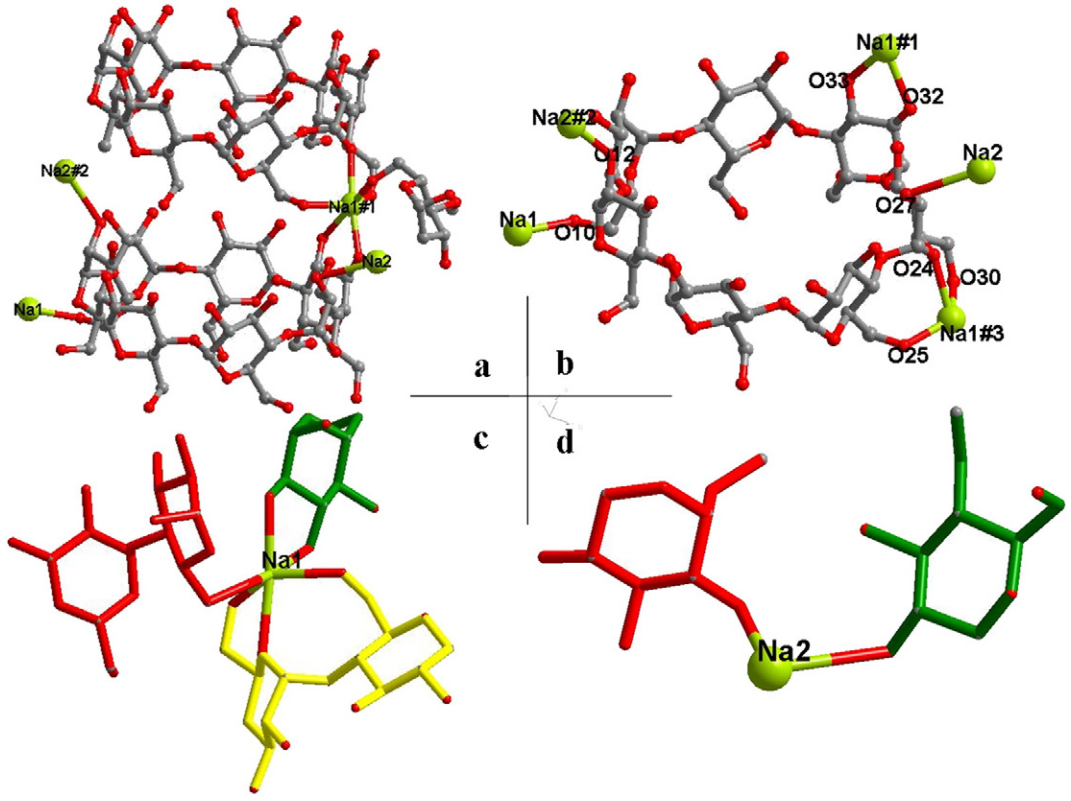

Fig. 2. Ball and stick representation of the asymmetric of CD-MOF (a); the coordination environment of β-CD molecules (b), Na1 cation (c) and Na2 cation (d) (symmetry code: #1: −0.5 − x, −y, 0.5 + z; #2: −0.5 + x, −0.5 − y, 1 − z; #3: 0.5 − x, −y, 0.5 + z).