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Synthesis and structure of new carbohydrate metal–organic frameworks and inclusion complexes

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ABSTRACT

Two new metal–organic framework compounds based on natural β-cyclodextrin molecules (β-CD) and alkali metals (Na^+/K^+) were synthesized and characterized by elemental analyses, IR, XPRD and ^{1}HNMR. Single-crystal X-ray diffraction analysis reveals that compounds **1** and **2** possess the bowl-like pore and the “8” type double channels configuration. Due to the [blow + channel] double configuration, 5-Fluorouracil (5-FU) and Quercetin inclusion complexes of compound **1** are studied, and the results show that the two kinds of drug with different structure and size can be included into the compound at the same time, which is expected to become a new type of multi-functional green crystalline solid material.

1. Introduction

Green chemistry has become a central issue in both academic and industrial research in 21st century, involving organic synthesis, material chemistry and biochemistry. The metal–organic frameworks (MOFs), a new class of crystalline solid materials consisting of metal ions and organic ligands, are being evaluated for diverse potential applications, such as gas adsorption [1–8], storage of clean gas fuels [9,10], separations [11–13], and drug delivery [14–16]. However, the vast majority of MOFs reported to date are composed of organic subunits derived from non-renewable petrochemical feedstocks and transition metals. Once these MOFs are applied to the industrialization, some urgent problems may appear as follow: 1) High costs make it difficult to large-scale applications in the industry; 2) Pollution control during the synthesis; 3) Non-renewable ingredients. Therefore, it is necessary that the preparing MOFs from natural products derive environmentally benign, clean synthetic procedures, and renewable materials.

As a special class of carbohydrates [17,18], cyclodextrin (CD) consists of six, seven or eight α-1,4-linked D-glucopyranosyl repeating units and displays the –OCCO- binding motif on both their primary and secondary faces auguring well for forming extended structures with Group IA and IIA metal. These characteristics of CDs can merge into metal–organic frameworks (named as CD-MOFs) with alkali metals as organic candidates to contribute the natural porous materials [19–23]. More importantly, CD-MOFs are inexpensive and “green” in the sense, because they can be synthesized from renewable sources that are themselves derived from water, CO_2, and nontoxic metal salts. On the other hand, the host–guest complexes of CDs have been studied extensively over a long period depending on their natural flexible porosities, and such complexes are used in the pharmaceutical and food industries [24–26]. Although many CD-MOFs assembled form α-, β-, and γ- CD were reported, and their structures exhibit the barrel, the cage, the independent double CD and three-leaf oar, and so on, but the 2D bowl-like structure was rarely reported.

On the basis of the above considerations, to seek the green natural porous material, and to isolate the suitable crystals of CD-MOF with different structure, herein, we report the unprecedented and rapid formation of a well-defined porous materials constituted by natural β-cyclodextrin (β-CD) molecules and alkali metals (Na^+/K^+) *via* a pollution-free method. Our success owes to the C7 symmetric of β-CD with causing the asymmetric coordinating mode with alkali metals. Due to the interesting [blow + channel] double configuration of CD-MOF, the drug (5-FU and Quercetin) inclusion complexes of CD-MOFs are studied (shown in Scheme 1).

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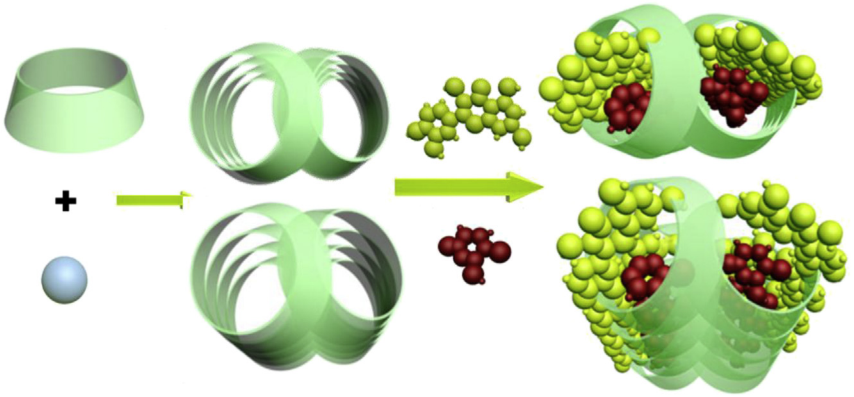

Scheme 1. Schematic representation of CD-MOF with double configuration and the drug inclusion complexes of CD-MOFs.

2. Experimental section

2.1. General information

All reagents were purchased commercially and used with further purification. Elemental analyses (C and H) were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer. The IR spectra were obtained on an Alpha Centaurt FT/IR spectrometer with KBr pallet in the 400–4000 cm^{-1} region. Chromatography work was performed using the HPLC-1100 system (Agilent, CA, USA). Thermal Analysis DSC-Q100 differential scanning calorimeter was performed on a Thermal Analysis Ltd Co, USA. The X-ray powder diffraction (XRPD) patterns were obtained with a Rigaku D/max 2500 V PC diffractometer with Cu-Kα radiation, the scanning rate is 4°/s, 2θ ranging from 5 to 40°. The ^{1}HNMR spectra obtained on a Bruker AV400 instrument with deuterate dimethyl sulphoxide (DMSO) as solvent.

2.2. Synthesis

2.2.1. Synthesis of NaOH ($C_{42}H_{70}O_{35}$)·9H_2O (Na-CD-MOF)

β-Cyclodextrin (1.135 g, 1 mmol) and NaOH (0.32 g, 8 mmol) were dissolved in deionized H_2O (15 ml) and C_2H_5OH (5 ml), and the resulting solution was stirred for 1 h. The solution was filtered through PTFE membrane. After two week, colorless crystals were isolated, washed with C_2H_5OH, and dried at room temperature. Yield: *ca.* 76%. Elemental analysis (%) calcd. for Na($C_{42}H_{70}O_{35}$)·OH·9H_2O: C 37.69, H 6.71; found: C 37.59; H 6.75.

2.2.2. Synthesis of KOH ($C_{42}H_{70}O_{35}$)·9H_2O (K-CD-MOF)

β-Cyclodextrin (1.135 g, 1 mmol) and KOH (0.448 g, 8 mmol) were dissolved in deionized H_2O (15 ml) and C_2H_5OH (5 ml), and the resulting solution was stirred for 1 h. The solution was filtered through PTFE membrane. After two week, colorless crystals were isolated, washed with EtOH, and dried at room temperature. Yield: *ca.* 74%. Elemental analysis (%) calcd. for K($C_{42}H_{70}O_{35}$)·OH·9H_2O: C 37.27, H 6.58; found: C 37.24; H 6.61.

2.3. Preparation of drug-CD-MOF inclusion complexes

Drug-CD-MOF inclusion complexes were prepared by grinding method at room temperature. In brief, 5-FU, Quercetin and CD-MOF were accurately weighted at a molar ration of 1:1:1, respectively. The result compounds were grinded with absolute alcohol as wetter. After grinding for 1 h, the products were rinsed 3 times by using certain amount of absolute alcohol. The inclusion complexes were desiccated at 60 °C until constant weight was obtained.

2.4. X-ray single crystal diffraction analysis

Structural measurements for Na/K-CD-MOF were performed on a Rigaku RAXIS RAPID IP diffractometer with Mo-Kα monochromatic radiation ($\lambda = 0.71069$ Å) at 293 K. The structures were solved by the directed methods and refined by full matrix least-squares on F^2 using the SHELXTL crystallographic software package [27]. All non-hydrogen atoms in **1** and **2** were refined anisotropically. The positions of hydrogen atoms on carbon atoms were calculated theoretically. The crystal data for **1** and **2** are summarized in Table 1. Since the metrical parameters associated with these structures are unexceptional, full listings of bond lengths and angles for the M sites and for the CD are given in the supplementary tables only. Crystallographic data for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC Number 1041731 for **1** and 1041782 for **2**.

3. Results and discussion

3.1. Crystal structures of compounds *1* and *2*

Single crystal X-ray diffraction analysis reveals that compounds **1** and **2** are isostructural, and each consists of one β-CD, one Na$^+$ ion for **1** and one K$^+$ ion for **2** and nine lattice waters and one OH$^-$ ion (Fig. 1a). Here, the structure of compound **1** is discussed as an example. There is a crystallographically independent Na$^+$ ion, which is six-coordinated by six oxygen atoms from four contiguous CD molecules, namely, four secondary hydroxyls, one primary hydroxyl and one ring oxygen atom. The Na–O bond distances are in range of 2.730 Å–2.985 Å (Fig. 1b). The β-CD adopts four coordinated mode linking with four Na ions *via* a-, b- and D-glucopyranosyl (Fig. 1c). . To the best of our knowledge, the coordinated mode of CD has never been found in the other CD based compound.

The prominent structure feature of compound **1** is the presence of the bowl-like pore (size ca.6.0 × 5.8 Å) *via* "T" arrangements of β-CDs and the "8" type double channels (size ca.5.6 × 5.4 Å), which can be understood from Fig. 2. Two adjacent β-CDs link with Na ions forming the "T" shape structure with unique bowl-like pore, in which one β-CD uses its 2, 3–OH groups from *a*- and D-glucopyranosyl and another uses its 6-OH and 2, 3-OH groups from *b*- and D-glucopyranosyl (Fig. 2a). Furthermore, these "T" shape structure units array along the *b*-axis forming the "8" type double channels (Fig. 2b). Note that such an unusual coordination mode has not been found in CD chemistry hitherto. Finally, each of the double channels units held together along the *a*-axis *via* interactions of Na–O leading to the formation of 2D layers in *ab* plans (Fig. 3). The solvent-accessible volume of the unit cell is estimated, (PLATON