

Short communication

Syntheses, crystal structures and properties of self-assembly supramolecular compound based on cucurbit[6]uril

Guoshuai Zhang^a, Yuekun Zhang^a, Weibo Ren^a, Jinpeng Liu^a, Mei Liu^{a,b,*}^a School of Chemistry and Life Science, Changchun University of Technology, Changchun, Jilin 130012, China^b Advanced Institute of materials Science, Changchun University Of Technology, Changchun 130012, China

ARTICLE INFO

Article history:

Received 28 July 2016

Received in revised form 20 September 2016

Accepted 1 October 2016

Available online 6 October 2016

Keywords:

Cucurbit[6]uril

Solvothermal

Supramolecular interactions

Sensing property

ABSTRACT

A new cucurbit [6]uril based compound $\{[\text{Cd}_2\text{Cl}_2(\text{INA})_2(\text{HCOO})_2(\text{H}_2\text{O})_2](\text{CB}[6]) \cdot 2(\text{HCOOH}) \cdot 5\text{H}_2\text{O}\}(\text{CCUT-101})$ was synthesized by the solvothermal reaction of cadmium chloride, cucurbit[6]uril (CB[6]), and isonicotinic acid (HINA). X-ray diffraction analysis indicated that coordination of INA^- with the Cd^{2+} resulted in the formation of some one-dimensional wave-like chains, which connected with CB[6] by $\pi \cdots \pi$ stacking and hydrogen bonding, and further extended to a 2D layer. The luminescence behaviors and sensing properties of **CCUT-101** in different solvents were carried out.

© 2016 Elsevier B.V. All rights reserved.

Nowadays, coordination polymers have attracted increasing research interest due to their potential applications in sensors, catalysis, molecular separation, storage, photoluminescence, and so on [1,2]. Cucurbit[*n*]urils (CB[*n*]s), a kind of macrocyclic hosts, features a pumpkin-like shape with two identical carbonyl fringed portal and a characteristic rigid hydrophobic cavity, have attracted wide research interest in supramolecular chemistry and coordination chemistry [3–11]. It has been revealed that the outer surface of CB[*n*]s could provide a balance of various supramolecular driving forces, such as C—H \cdots π interactions, $\pi \cdots \pi$ stacking, and hydrogen-bonding, which could generate some remarkable CB[*n*]-based supramolecular architectures and functional materials [11–15]. Recently, Tao and co-workers summarized the function of the electrostatically positive outer surface of CB[*n*]s [16], in particular the interactions of the outer surface of CB[*n*]s with aromatic compounds via $\pi \cdots \pi$ and/or C—H \cdots π interactions, which could present not only novel structural features but also potential applications in catalysis, sensing, and polymer materials [17]. For instance, a novel pH-triggered hydrogel exhibiting guest-induced stimuli-responsive behavior were demonstrated by Kim and co-workers, the driving force for gelation could be attributed to the strong hydrogen-bonding interactions between CB[7] portals and hydronium ions, as well as between CB[7] molecules. Recently, a series of CB[*n*]-based supramolecular assemblies were obtained using different construction strategies in Kim's group, in particular the interactions of the outer surface of CB[*n*]s with aromatic compounds via C—H \cdots π and/or $\pi \cdots \pi$ interactions [18–22]. Later, Sun's

group successfully obtained two novel three-dimensional (3D) supramolecular assemblies with CB[*n*], which were constructed via the outer-surface interactions of CB[*n*]s with the polyaromatic compound 4,4',4''-benzene-1,3,5-triyl-tribenzoate as a structure-directing agent [23]. Therefore, understanding these weak interactions is paramount in designing and synthesizing new crystalline architectures and materials. In this work, combination of all of these supramolecular interactions, we selected CB[6] as basic building blocks, the isonicotinic acid (HINA) as a structure-directing agent (Fig. 1), and obtained a CB[6]-based supramolecular assemblies in $\text{H}_2\text{O}/\text{DMF}$ solutions under solvothermal condition.

CCUT-101 crystallizes in a monoclinic system with space group $C2/c$. Single-crystal X-ray diffraction analysis revealed that Cd^{2+} ions are seven-coordinated by five oxygen atoms from one INA^- ligand, one ethanoic acid (can be assigned to the decomposition of DMF) in a bidentate mode (Cd–O: 2.29–2.46 Å), one water molecule, one N atom from another INA^- connector (Cd–N: 2.331 Å), and one coordinated chloride ion from CdCl_2 (Cd–Cl: 2.534 Å) (Fig. 2a). Each Cd^{2+} ion linked by one INA^- ligand and formed some 1D wave-like chains. CB[6]s molecules are sandwiched by these 1D chains through supramolecular interactions (Fig. 2c, d) and further formed 2D layers (Fig. 2b). A close inspection reveals that the chains catch the CB[6]s molecules through interactions between the outer surface of CB[6]s, including (1) $\pi \cdots \pi$ stacking interactions (average distance 3.936 Å) between the pyridine ring of INA^- ligands and rings of CB[6]s (Fig. 2c), (2) C—H \cdots π interactions between electronegative INA^- and the methylene groups on the outer surface of CB[6]s (Fig. 2d). (3) hydrogen-bonding interactions between the portal carbonyl oxygen atoms of CB[6]s and the cooperative H_2O and Cl^- (Fig. 2d). Thus, the combination of these interactions

* Corresponding author at: School of Chemistry and Life Science, Changchun University of Technology, Changchun, Jilin 130012, China.

E-mail address: liumei@ccut.edu.cn (M. Liu).

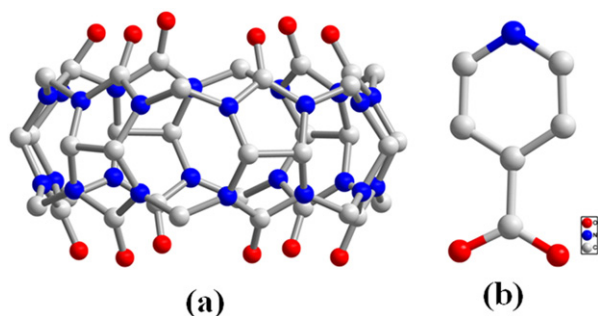


Fig. 1. The structure of CB[6] (a) and INA^- (b).

resulted in the formation of the novel CB[6]-based 2D supramolecular assembly.

The purity of the as-synthesized **CCUT-101** was confirmed by the agreements between simulated and experimental PXRD patterns (Fig. 3a). TG-DSC of compound **CCUT-101** exhibits two-step weight loss in

the range of room temperature to 735 °C (Fig. 3b). The weight loss from room temperature to 205 °C can be assigned to the release of all the lattice solvent molecules (5 water molecules for **CCUT-101**, calc. 4.0%; found: 4.1%). The second step ranging from 205–735 °C can be attributed to the gradual decomposition of the organic components in **CCUT-101**.

The emission spectra of **CCUT-101** in powder form were investigated at room temperature under certain excitation maximum. Compared with that of related carboxylate ligands, emission spectra of **CCUT-101** are slightly red-shifted 32 nm, which may be ascribed to the cooperative effects of intraligand emission and ligand-to-metal charge transfer (LMCT) and the intermolecular interactions (such as $\pi\cdots\pi$ stacking and hydrogen bonding) between the molecules in the solid state (Fig. 4) [24].

To explore the potential application of **CCUT-101** for the sensing of solvents, we investigate the sensitization ability of **CCUT-101** toward different solvents. The samples were dispersed in trichloromethane (CHCl_3), ethyl acetate (EtOAc), ether (Et_2O), ethanol (EtOH), methanol (MeOH), *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF),

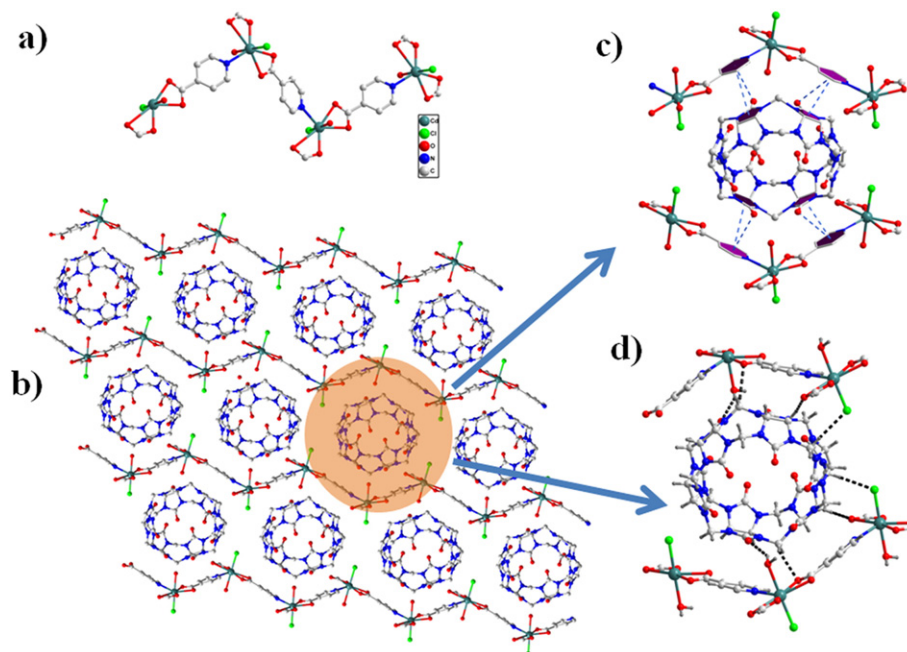


Fig. 2. X-ray crystal structure of **CCUT-101**: The coordination environment of Cd atoms in **CCUT-101** (a). The supramolecular stacking between CB[6]s and the adjacent chains (b), hydrogen atoms, free solvate water and methanoic acid molecules are omitted for clarity. Outer-surface interactions of CB[6]s with the coordinated water molecules, chloride ions and INA^- (c, d), dashed lines: hydrogen bonds, $\text{C-H}\cdots\pi$ or $\pi\cdots\pi$ interactions.

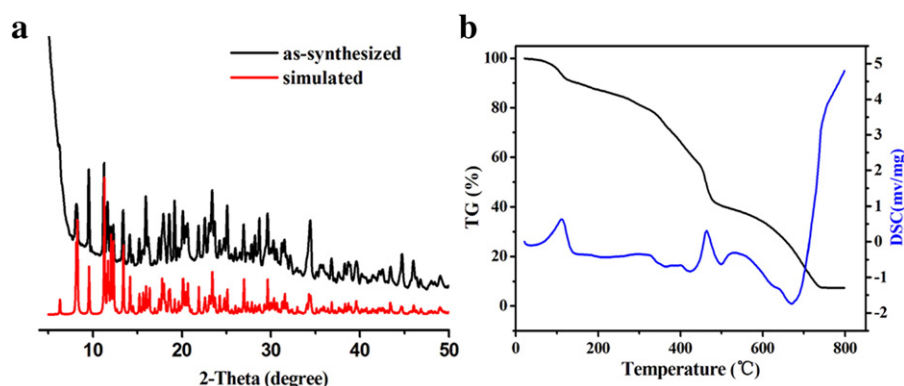


Fig. 3. PXRD patterns for **CCUT-101** and simulated spectra of **CCUT-101** from single crystal data (a). TG-DSC curves for as-synthesized compound **CCUT-101** (b).

Download English Version:

<https://daneshyari.com/en/article/5151370>

Download Persian Version:

<https://daneshyari.com/article/5151370>

[Daneshyari.com](https://daneshyari.com)