

Short communication

A new cucurbit[6]uril based supramolecular assembly for sensing small organic solvents and rapid adsorption of Reactive Blue 19 Dye

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ABSTRACT

A new cucurbit[6]uril based supramolecular assembly $[\text{Cd}_2(\text{SIP})_2(\text{H}_2\text{O})_8 \cdot \text{CB}[6] \cdot 4\text{H}_2\text{O}]^{2-}$ (**1**) was successfully synthesized by the solvothermal reaction. X-ray diffraction analysis revealed that the outer surface interactions of CB[6] can be the driving forces in the formation of such novel CB[6]-based supramolecular assembly. Interestingly, it was shown potential application for the luminescence sensing of small organic solvent molecules. Furthermore, it can also absorb Reactive Blue 19 Dye (RB19) fast.

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Cucurbit[*n*]urils (abbreviated as CB[*n*], *n* = 5–8), a new generation of host, have attracted a great deal of attention in recent years due to their specific structures. These pumpkin-shaped macrocyclic host molecules have a characteristic rigid hydrophobic cavity accessible through two open polar portals lined with carbonyl groups [1]. They readily form various host-guest inclusion complexes or coordinate with metal ions to form various supramolecular assemblies and frameworks [2–5], which have potential applications in adsorption, sensors, catalysis, molecular separation, molecular switches, drug delivery systems, and so on [6–9]. For example, they have been used for removal of dyes from textile waste water as novel high-efficiency absorbents [10–12]. Kim and co-workers constructed a series of interesting polyrotaxanes and molecular necklaces [13]. Interestingly, recent study revealed that the use of a third species as a structure inducer in CB[*n*]-metal systems (such as inorganic anions and aromatic molecules), can result in the formation of various CB[*n*]-based coordination polymers and supramolecular assemblies, whose structural novelties and properties exceed those of assemblies obtained in the absence of such agents [14–16]. Weak noncovalent interactions derived from the outer surface of CB[*n*], such as C–H···π interactions, π···π stacking, hydrogen-bonding and ion-dipole interactions, which could generate some remarkable CB[*n*]-based supramolecular architectures and functional materials [17–20].

Recently, the function of the electrostatically positive outer surface of CB[*n*]s were summarized by Tao's group [21], in particular the interactions of the outer surface of CB[*n*]s with aromatic compounds via π···π and/or C–H···π interactions [22–24]. Subsequently, two novel three-dimensional (3D) supramolecular assemblies with CB[*n*] were synthesized by Sun's group. The polyaromatic compound 4,4',4''-benzene-1,3,5-triyl tribenzoic acid was employed as a "structure inducer" [25]. With these in mind, we use cadmium (II) as central ion, 5-sulfoisophthalic acid sodium salt (NaH₂SIP) as a "structure inducer", and successfully synthesized a supramolecular assembly $[\text{Cd}_2(\text{SIP})_2(\text{H}_2\text{O})_8 \cdot \text{CB}[6] \cdot 4\text{H}_2\text{O}]^{2-}$ (compound **1**) under solvothermal condition. The chemical structures of SIP³⁻ and CB[6] were shown in Fig. 1.

Compound **1** crystallizes in a triclinic system with space group P-1. Single-crystal X-ray diffraction analysis revealed that all the Cd (II) ions are six-coordinated by four H₂O molecules, and two carboxyl oxygen atoms from two SIP³⁻ ligands. Two Cd (II) ions linked by two SIP³⁻ ligands and featured with isolated squares (Fig. 2a). Each CB[6] molecules are sandwiched by two isolated squares through the π···π stacking interactions between the aromatic ring of SIP³⁻ ligands and carbonyl groups of CB[6] (Fig. 2b), and C–H···π interactions between aromatic ring of SIP³⁻ ligands and the methylene groups on the outer surface of CB[6]s (Fig. 2b). CB[6] molecules connected with the Cd (II) complex anion and neighbouring CB[6] through the hydrogen bond (between the portal carbonyl oxygen atoms and the coordinated H₂O molecules) and the unusual hydrogen bond (between the portal carbonyl oxygen atoms and the methine groups on the outer surface of the neighbouring CB[6] molecules) (Fig. 2c). Thus, the combination of these noncovalent

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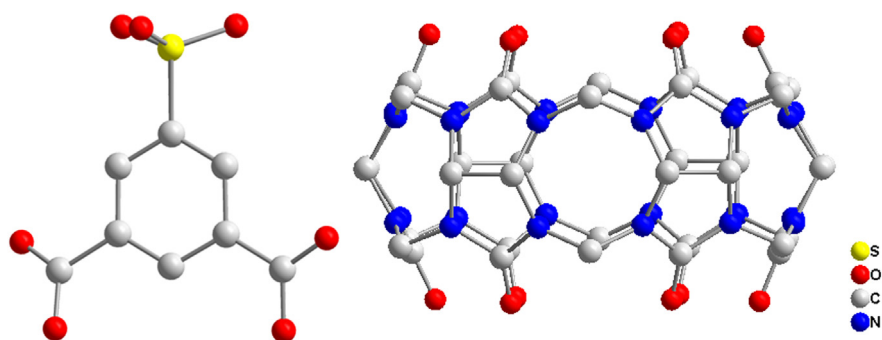


Fig. 1. Chemical structures of SIP³⁻ and CB[6].

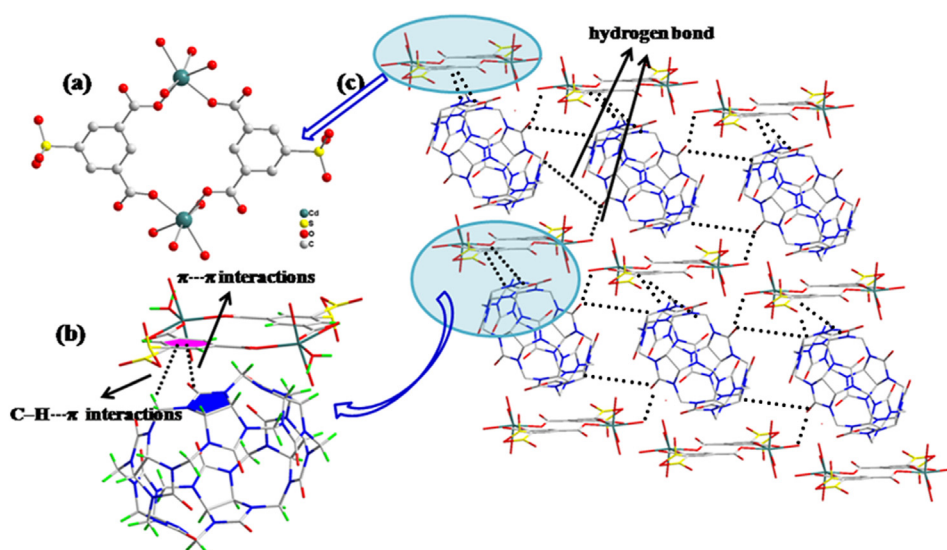


Fig. 2. (a) The coordination environment of Cd (II) ions in **1**; (b) Outer-surface interactions of CB[6]s with the Cd (II) complex anion. (c) X-ray crystal structure of compound **1**. Hydrogen atoms, free solvate water are omitted for clarity. Dash lines: partial C–H... π interactions, π ... π interactions and hydrogen bonds.

interactions resulted in the formation of the novel CB[6]-based 3D supramolecular assembly (Fig. 3).

To explore the potential application of **1** for the sensing of small organic solvent molecules, the samples were dispersed in different solvent emulsions (CH₃OH, CHCl₃, THF, aether and acetone), and their luminescence effect were investigated. Fig. 4 reveals that the photoluminescence spectra are largely rest on the solvent molecules, especially for acetone, which exhibit the most significant quenching effects relative to other dispersants. Furthermore, we also found some changes of emission spectra (red shift or blue shift, Fig. 4 inset), which may be assigned to the solvatochromism, the solvent polarity and the interaction of the solute and solvent plays an important role [26]. Such solvent dependent luminescence properties may be used for the sensing of small organic solvent molecules.

To further explain the reason for the significant quenching effects of acetone, the absorption spectra of CH₃OH, CHCl₃, THF, aether and acetone were investigated respectively in n-hexane, the emission spectra of **1** has a large area overlap with the absorption spectrum of acetone (Fig. S1). As is well-known, if the emission band of the fluorophore has an effective overlap with the absorption band of the analyte, the energy transfer can occur from fluorophore to non-emissive analyte [27]. Therefore, the reason of acetone presented significant quenching effects for **1** can be attribute to energy transfer process.

In consideration of the electrostatically properties of **1** as mentioned above, its adsorption properties toward the typical organic dye Reactive Blue 19 (RB19) was carried out. The chemical structure of RB19 was shown in Fig. 5 (left). The adsorption experiments results revealed

that **1** exhibit good adsorption property toward RB19. As shown in Fig. 5 (right), with the increased time, the solution colour of RB19 nearly disappeared after 20 min, the adsorption phenomenon distinctly shown

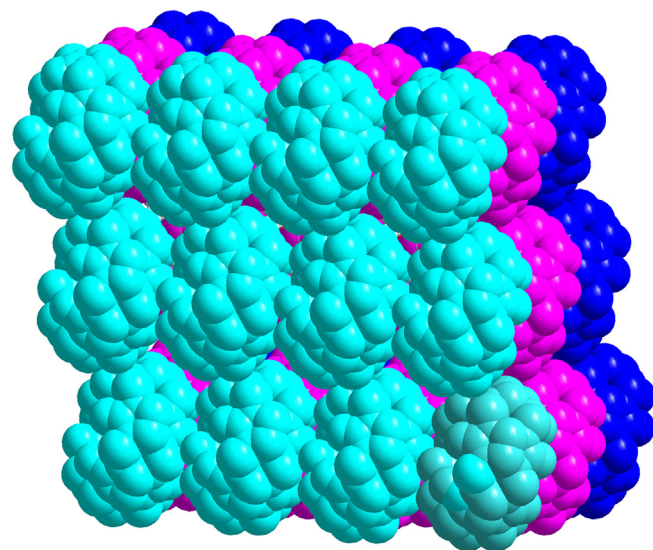


Fig. 3. Space-filled view of the 3D supramolecular assembly of CB[6] units of **1**. Cd (II) complex anion, Hydrogen atoms and free solvate water are omitted for clarity.

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