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Cite this: DOI: 10.1039/x0xx00000x

A supramolecular assembly ofmethyl-substituted cucurbit[5]uril and its potential applications in selective absorption

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Received 00th January 2014,

Accepted 00th January 2014

DOI: 10.1039/x0xx00000x

A supramolecular assembly of a methyl-substituted cucurbit[5]uril (SPMeQ[5]) derived from 3-α-methyl-glycoluril is formed in the presence of the organic structure-directing agent, hydroquinone (Hyq). The structure-directing effect of Hyq is not only useful in the construction of novel supramolecular assemblies based on cucurbit[n]uril (Q[n]) and organic molecules but it could also enable the preparation of Q[n]-based porous materials for in molecular sieves, and sensors, used in absorption and separation.

Introduction

Porous materials are generally associated with classes of microporous zeolite, mesoporous silica, metal oxides, and macroporous polymers.[1] They have fundamental and diverse applications ranging from structural materials to energy technologies, which in turn have wide uses in catalysis, adsorption, ion-exchange and supramolecular assembly. Designing target structures with specific properties and functionalities is the subject of numerous studies in materials science.[2]According to the IUPAC, porous materials are usually classified according to the diameter of their pores. Thus, they may be distinguished as microporous (<2 nm), mesoporous (2–50 nm) or macroporous (>50 nm).[3]Supramolecular assemblies formed by induction with organic compounds are an emerging extensive class of nanoporous crystalline materials. Their structure is composed of an organic molecule joined by a variety of organic linkers through C–H···π interaction, π···π stacking, ion–dipole interaction, hydrogen bonding and so forth.[4-7]Versatile organic ligands and organic structure-directing agents enable molecular engineering of supramolecular assemblies with various novel structures.[7]

Synthesis of cucurbit[*n*]urils (Q[*n*]s)[8-12] proved the value of these molecules in the field of supramolecular chemistry.[7,13-23]Because of their symmetrical shape, rigid architecture, and hydrophobic cavity, Q[*n*]s are unique among the supramolecular hosts known to date. Supramolecular architectures and functional materials have been found to have an increasingly important role in research into Q[*n*] chemistry. However, Q[*n*]s-based supramolecular assemblies are limited because of the lack of understanding of approaches to synthesize them. These difficulties intrigued a number of researchers who studied them; their investigations achieved some valuable results. Kim and co-workers prepared Q[*n*]-based supramolecular assemblies that not only had novel architectures but also unique gas sorption properties and anisotropic proton conductivity.[24-26] Our group recently synthesized supramolecular assemblies based on Q[*n*]s and substituted cucurbit[*n*]urils (SQ[*n*]s) in the presence of a second species, which was an organic or inorganic structure-directing molecule.[7,17]By adding the structure-directing agent *p*-hyydroxybenzoic acid($HObzCO_2H$),[27]an example of such supramolecular assembly,the porous materialQ[5]-KI-$HObzCO_2H$, was readily prepared by self-assembly. Accessible channels of its structure and significant absorption selectivity for a group of polar volatile organic molecules were clearly observed. Lin and co-workers prepared Q[6]/calixarene supramolecular assemblies by utilizing the hydrophobic–hydrophobic and hydrophilic–hydrophilic interactions to direct their formation. Outer-surface interactions of Q[*n*]s were considered as the driving forces for their formation.[4]

In the present work, a cucurbituril that is partially substituted with methyl and derived from 3-α-methyl-glycoluril (SPMeQ[5]),[28] (Figure 1) was used as a building block to investigate the formation of a supramolecular assembly in the presence of hydroquinone (Hyq). We then prepared stable, accessible channels by crystallization of the supramolecular SPMeQ[5]–Hyq assembly. Results of further experimentation suggest that this porous assembly could be used in selective sorption of volatile alcohols.

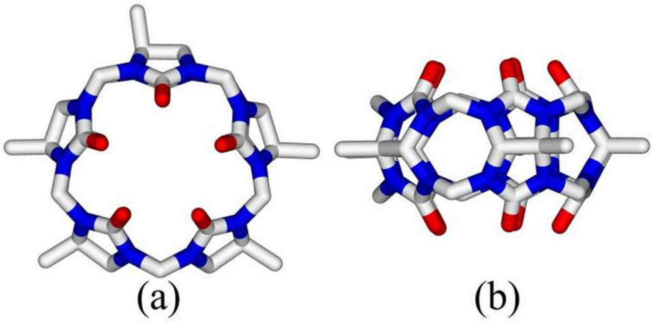

Figure 1 Structure of the methyl-substituted cucurbituril (SPMeQ[5]) (a) top view, (b) side view.

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Results and Discussion

Description of the crystal structures of the compound. Q[*n*]s are well-known for their ability to include various organic molecules into their cavities.Similarly,the portal carbonyl of Q[*n*]s or SQ[*n*]s are also known to coordinate tovarious metal ions Thusouter-surface interaction of Q[*n*]swith various compounds, such as aromatic compounds, inorganic anions, and polyoxometalates could become a new area for research into Q[*n*]-based supramolecular assemblies.[4]

In the present work, we synthesized a typical SPMeQ[5]-based porous supramolecular assemblyby using Hyq as an organic structure-directing agent. It is a typical example in which the outer-surface interaction of SPMeQ[5] with Hyq results in the formation of the assembly.The crystal structure shows that the binding stoichiometry of SPMeQ[5] moleculesto Hyq molecules is 1:2. Figure2a and 2b shows details of the interactions of SPMeQ[5] molecules with Hyq molecules through outer-surface interactions of Q[*n*]s. Each SPMeQ[5] molecule interacts with eight Hyq moleculesin two different ways (Figure 2a), namely:1) C−H···π interactions of substituted methyl groups on the outer surface of SPMeQ[5] molecule with aromatic moieties of Hyq (red dashed lines); and 2) weak hydrogen bonding of bridge methylene groups on the outer surface of SPMeQ[5] with hydroxyl oxygen of Hyq (black dashed lines). In turn, each Hyq molecule can interact with four SPMeQ[5] molecules in two different ways as shown in Figure2b. The distance of hydroxyl oxygen of Hyq with methylene on the outer surface of SPMeQ[5] molecules (O···H−C in black dashed lines) is 3.140 Å and that of aromatic moieties of Hyq with methyl groups on the outer surface of neighboring SPMeQ[5] molecules (red dashed lines) is 3.579 Å. A combination of all of these interactions results in the formation of the novel SPMeQ[5]−Hyq-based porous supramolecular assembly with symmetrical linear channels (7.2 Å Longand4.8Å wide along the *c* axis; Figure 2c and 2d), Large amounts of water molecules fill the channels through a complicated hydrogen-bonding network. Each SPMeQ[5] molecule includes a water molecule (omitted for clarity). Close inspection reveals that the aperture of each channel is composed of four SPMeQ[5] molecule chains which are linked by Hyq molecules through the so called weak hydrogen bonds and by C−H···π outer-surface interactions with Q[*n*]s, The latter interaction links neighboring SPMeQ[5] molecules (Figure 2d).

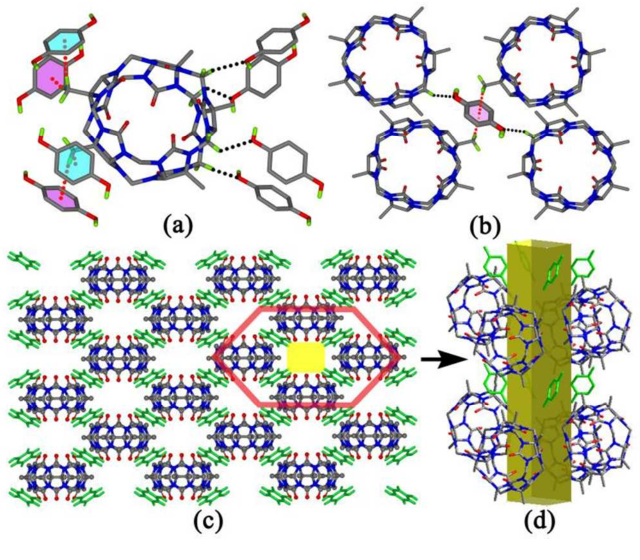

Figure 2 X-ray crystal structures of the hydroquinone (Hyq)-induced, SPMeQ[5]-based porous supramolecular assembly: a) Details of the interactions between a SPMeQ[5] molecule and eight surrounding Hyq molecules,b) Details of interactions between aHyq molecule and four surrounding SPMeQ[5] molecules,c) Overall view of the assembly along the *c* axi, d) A channel composed of SPMeQ[5] molecules and Hyq molecules. Water molecules are omitted for clarity.

Isothermal titration calorimetry (ITC). ITC experiments provided information on the interaction between SPMeQ[5] and Hyq in neutral aqueous solution. In contrast to the experimental condition (0.5 M HCl) for the preparation of the SPMeQ[5]−Hyq supramolecular assembly, ITC provides useful information on the interaction between Hyq and SPMeQ[5]. Results of the experiments indicate a ~0.5 binding stoichiometry, suggesting that each SPMeQ[5] molecule interacts with two Hyq in neutral aqueous solution. In particular, they reveal that 1) interactions between Hyq and SPMeQ[5] in solution are consistent with those in the solid state; and 2) the interaction between SPMeQ[5] and Hyq is an endothermic reaction ($\Delta H>0$). According to the Gibbs formula, $\Delta G = -RT \ln Ka = \Delta H - T\Delta S$where R is the gas constant and T is the absolute temperature. It implies that the term $T\Delta S$ determines the outcomeof the reaction, that is, it is the driving force (Figure 3).

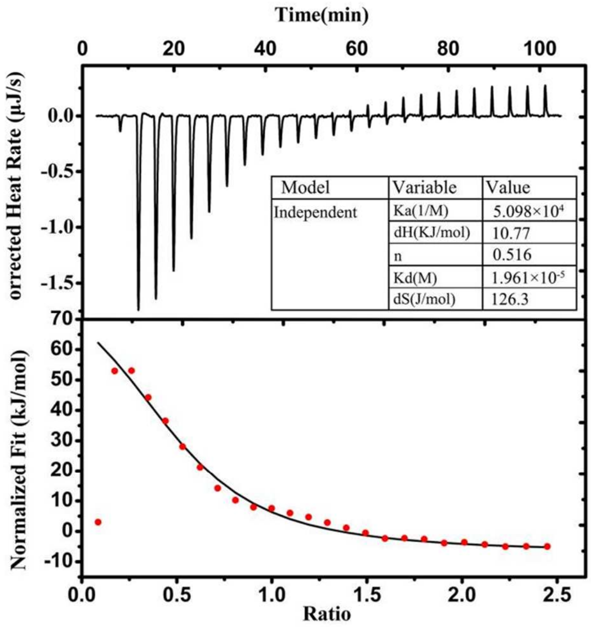

Figure 3Profiles of SPMeQ[5] with hydroquinone obtained by isothermal titration calorimetry at 293.15 K

Sorption properties of the complex. We have described in detail the solid structure of the SPMeQ[5]–Hyq-based porous supramolecular assembly. According to analysis of the single-crystal structure, the channels and molecular cavities of SPMeQ[5] are filled with a large amount of water molecules. Free volumes of the channels and molecular cavities were respectively estimated to be 19.5% and 3.7% of the total crystal volume. Recently, we synthesized porous Q[6]–$[PtCl_6]^{2-}$-based material with linear channels, having diameters of 8.5 Å. We also carried out further research into its potential application in selective sorption.[29]

In the present work,sorption properties of the supramolecular assembly for volatile substances were examined. Isotherms for methanol gas sorption of the material up to 0.88 atm at 298 K were obtained. The BET surface area of the activated assembly, as calculated from the isotherm, is 334.8 m^2/g.This value islarger than that of SPMeQ[5] powder (251.8 m^2/g) (Figure S1). The protruding carbonyl oxygens and hydroxy group of Hyq decorate the inner walls of the channels in the assembly.Therefore, polarity plays a dominant role in the selectivity of the channels toward various volatile substances.Results of the sorption experiments concur with this conclusion.

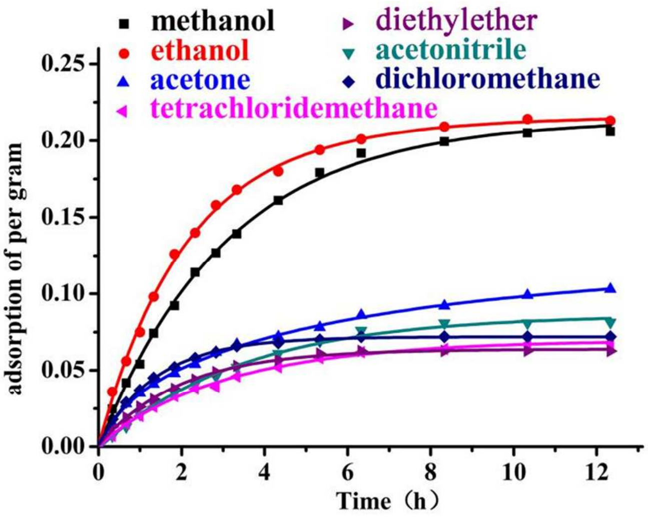

Figure 4Profiles of sorption of (■) methanol,(●) ethanol, (▲) acetone, (▼) acetonitrile, (◄) tetrachloridemethane, (►) diethylether, (◆) dichloridemethane on the SPMeQ[5]–Hyq-based porous supramolecular assembly

Figure 4 shows profiles of sorption of several volatile substances on the assembly. It reveals different sorption capacities for volatiles with different polarities. Sorption capacities for methanol and ethanol were over 20% (wt), whereas the capacity for tetrachloridemethane was only about 6% (wt). Sorption capacities (wt% at 25°C, 0.89 atm) of methanol, ethanol, acetonitrile, acetone, tetrachloridemethane, diethylether, and dichloridemethane were 20.6%, 21.3%, 8.1%, 10.3%, 6.8%, 7.2%, and 6.3%, respectively (Figures S2–8). Comparison of sorption capacities of the assembly with those SPMeQ[5] powder indicates that the latter is not selective toward polar or non-polar volatiles (Figure 4 and Figures S2–8).

The sorption capacity of Q[6]-based or Q[6]/$[PtCl6]^{2-}$-based porous material was compared against that of SPMeQ[5]–Hyq-based porous material under the same conditions.[29] This comparison easily demonstrated that the latter has greater selectivity toward polar or non-polar volatiles,especially alcohols. Meanwhile, lifetime tests on the SPMeQ[5]–Hyq-based porous material and on SPMeQ[5] powder using methanol and ethanol revealed that both are stable, with the SPMeQ[5]–Hyq-based porous material having larger sorption capacity for methanol and ethanol (Figure S9). Results of other analyses on the SPMeQ[5]–Hyq-based porous material, such as PXRD and TG–DSC are shown in Figures S10 and S11. The thermal analysis reveals that the differential scanning calorimetry (DSC) and thermogravimetric (TG) curves of the above mentioned compound are different from the free SPMeQ[5], the free guest hydroquinone (Figure S11a and b). Comparison of the DSC and TG curves indicates that the free SPMeQ[5] shows a relatively simple variation: the first endothermic band ending at ~220°C with a weight loss of ~6.2% corresponding to a fast dehydration, then a large broad endothermic band starting at ~310°C (ending at ~500°C) with a weight loss of ~70% corresponding to a decomposition of SPMeQ[5]; the free guest Hyq shows two endothermic bands which could correspond to sublimation and decomposition of Hyq with peak temperatures at ~180°C and ~260°C, respectively; the compound shows three stages for the weight loss. The first stage was associated with the evaporation of intramolecular and intermolecular moisture, and it take place in the temperature range 30−179 °C with a mass loss of 12.02 wt%. The second stage of the assembly occurred in the 179−325 °C temperature range with a mass loss of 13.15 wt %, which could be the sublimation and decomposition of hydroquinone. The final stage of the assembly occurred beyond 325 °C with the mass loss of 57.66 wt%, which was attributed to the carbonization of the related components.

Conclusion

We synthesized a new type of porous materialsby using an organic inducer and SPMeQ[5] as ligands. We also demonstrated that use of an organic structure-directing agent plays an important role in the synthesis. Driving forces of the structure-directing effect of Hyq could be attributed to the C−H···π interaction and weak hydrogen bonding. More importantly, we demonstrated potential applications of this porous material in selective sorption. Experiments on sorption of volatile organic molecules revealed that this porous material possesses large pore size (~34.6 Å^2) with high BET surface area (334.8 m^2·g^{-1}) and high thermal stability, which may be useful properties for molecular sieves, and sensors, used for absorption and separation.

Experimental Section

Synthesis

Chemicals, such as hydroquinone and hydrochloric acid, were of reagent grade and were used without further purification. SPMeQ[5] was prepared by the procedures reported previously.[25] Elemental analyses were carried out on a EURO EA-3000 elemental analyzer. Aqueous HCl (0.5 mol L^{-1}) was used to prepare crystals of SPMeQ[5]-Hyq. A similar process was used to prepare crystals of related compounds: hydroquinone (91.7 mg, 0.83 mmol) and SPMeQ[5] (150 mg, 0.14 mmol) were dissolved in 20 mL 0.5 mol L^{-1}aqueous HCl solution, The solution stood to allow slow evaporation in air at room temperature. Light brown crystals were obtained from the solution within one week. Anal. Calcd. For$C_{47}H_{74}N_{20}O_{25}$(%): C, 42.79; H, 5.65; N, 21.24. Found: C, 43.62; H, 5.48; N, 21.77.

X-ray crystallography

A suitable single crystal (~0.2 × 0.2 × 0.1 mm^3) was taken up in paraffin oil and mounted on a Bruker SMART Apex II CCD diffractometer equipped with a graphite-monochromated Mo-K_α (λ = 0.71073 Å, μ = 0.828 mm^{-1}) radiation source operating in the ω-scan mode and a nitrogen cold stream (293 K). Data were corrected for Lorentz and polarization effects (SAINT), and semi-empirical absorption corrections based on equivalent reflections were also applied (SADABS). The structure was elucidated by direct methods and refined by the full-matrix least-squares method on F^2 with the SHELXS-97 and SHELXL-97 program packages, respectively.[30-31] All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were introduced at calculated positions, and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. Most of the water molecules in the compounds were omitted using the SQUEEZE option of the PLATON program. The squeezed water molecules is 11 for this compound, respectively. Analytical expressions for neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.Crystal data for compound: $C_{47}H_{74}N_{20}O_{25}$, M = 1319.26, orthorhombic, Pmmn, a= 17.916(13), b= 11.364(8), c= 14.414(11)Å,V = 2935(4) Å^3, Z = 2, T = 293 K, ρ_{calcd} = 1.493 g·cm^{-3}, R1 = 0.1102 (I>2s(I)), wR2 = 0.3736 (all data), GOF = 1.222, CCDC 1031071. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via 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, UK; fax: +44 1223 336033.

Acknowledgements

We acknowledge the support ofthe National Natural Science Foundation of China (No. 21302026 and 21272045), the Natural Science Foundation of the Department of Education of Guizhou Province.

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