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Guest-binding properties of functionally porous crystal based on metal complex of *p*-*tert*-butylthiacalix[6]arene

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Abstract—A potassium salt of *p*-*tert*-butylthiacalix[6]arene shows highly-extensive coordination nature to give rise to zeolitic crystal which has huge cavity with the widest span of ca. 19 Å and is capable of crystalline phase guest-addition and -removal.

Construction of porous organic solids relies mainly on arrangements of organic molecules into extensive networks via such intermolecular interactions as hydrogen bonding and metal coordination to generate cavities for guest inclusion.[1] Many efforts along this line have afforded various crystals or amorphous solids[2] which have guest-binding and/or catalytic[3] properties. In most cases, the organic molecules having divergent functional groups are preferred as ligands rather than calixarenes[4] whose convergent ones would mainly be suitable for host–guest complexation restricted. Thus, there are limited numbers of calixarene-based crystals consisting of metal-coordinated polymers or huge cyclic array.[5] In comparison with calixarenes, thiacalixarenes[6] as a counterpart seem to be preferable for infinite intermolecular interaction in the crystalline state because of their bridging sulfur moieties which may be capable of extensive metal coordinations. However, to our best knowledge, there are little examples that have shown possible advantages of the bridging sulfur atoms of thiacalixarenes for construction of highly extended structures.[7] We wish to report here that *p*-*tert*-butylthiacalix[6]arene (**1**·6H, host, Fig. 1a) forms functionally-porous crystal with potassium cations via cooperation of extensive S···K···(O,S) intermolecular metal coordination and hydrophobic interaction of *tert*-Bu moieties.

Treatment of **1**·6H[8] with KH in THF, followed by recrystallization from the methanol solution,[9] affords an adduct $[K_4(\mathbf{1}\cdot 2H)]\cdot 14MeOH\cdot 2H_2O$ as pale-yellow crystals (triclinic, space group $P\bar{1}$).[10] In the crystal, one tetra-anionic host (**1**·2H) binds four potassium cations at the distances ranging from 2.64 to 3.39 Å (Fig. 1b). Incorporated guest molecules can be categorized as either inner guests or outer ones: former means three methanols in a groove consisting of three phenol units of the host; latter means five guest molecules (four methanols and one water) outside the groove (Fig. 1b). Combined with those on a reverse face of the host, the numbers of the guests are in total 6 and 10 per host, for inner and outer guests, respectively.

Complementary and continuous S···K···(O,S) coordinations between neighboring molecules along the *a* axis, with an intermolecular S···K distance of 3.32 Å, afford a doubly-linked ladder-like polymeric 1D chain having lateral branches of *tert*-Bu groups with an axial clearance of l_{Bu} = ca. 11.2 Å (Fig. 2a). Interchain hydrophobic interactions of these branches along the *c* axis with a chain-to-chain distance of l_c = ca. 16.6 Å give rise to a molecular sheet involving huge cavities. Each cavity is surrounded with four potassium ions, two grooves, and four *tert*-Bu groups; thus total 6 inner guests and 10 outer guests fill up a cavity having the widest span of l_w = ca. 19 Å (Fig. 2a). The molecular sheets in parallel with the *ac* plane are layered in a staggered manner along the *b* axis with the sheet-to-sheet distance of ca. 13.4 Å. Consequently the cavities in layered sheets form continuous channels with a bottleneck of l_{bo} = ca. 7.2 Å (Fig. 2b).

Keywords: crystal structure; calixarenes; porous crystal; guest binding; metal complex.

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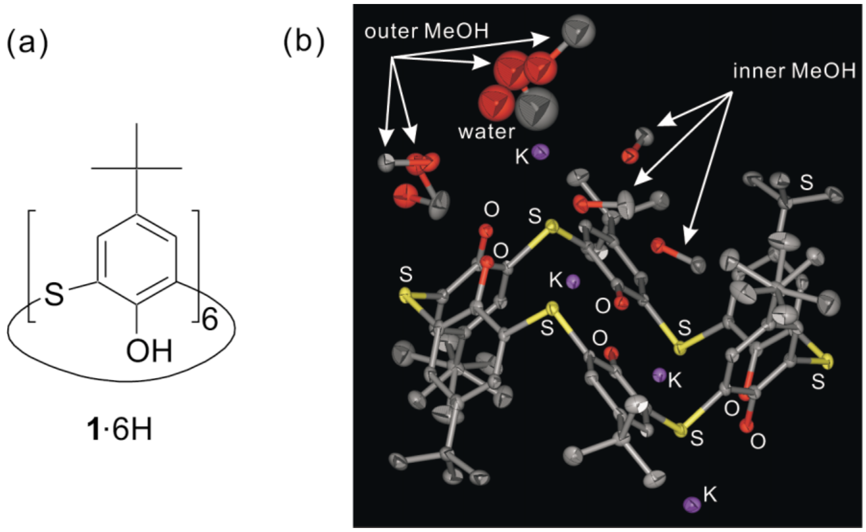

Figure 1. (a) Structural formula of **1**·6H. (b) Crystal structure of $[K_4(\mathbf{1}\cdot 2H)]\cdot 14MeOH\cdot 2H_2O$. All the hydrogen atoms and half of the guest molecules are omitted for clarity.

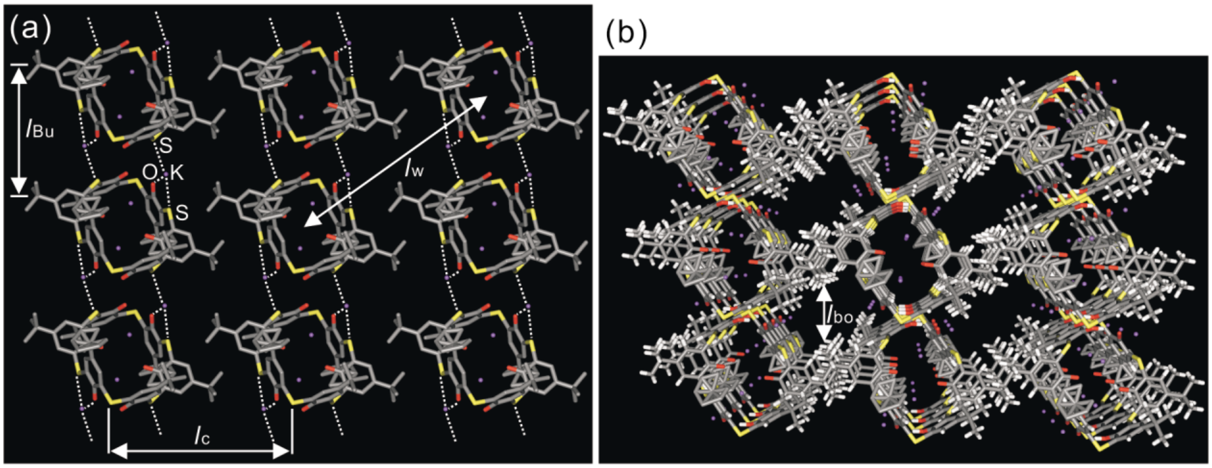

Figure 2. (a) Structure of a molecular sheet in parallel with the *ac* plane. (b) Perspective view of the channels along the *b* axis.

Because of this zeolitic crystal structure, single crystal of adduct $[K_4(\mathbf{1}\cdot 2H)]\cdot 14MeOH\cdot 2H_2O$ immediately loses the methanols with concomitant loss of its single crystallinity to give methanol-free apohost $[K_4(\mathbf{1}\cdot 2H)]\cdot nH_2O$, exposed to air at room temperature (a term 'apohost' means a host without included guest). The apohost is a microcrystalline material with collapsed cavities as evidenced by its PXRD pattern (Fig. 3a) and small specific surface area A_{BET} = ca. 27 m^2/g obtained by an adsorption isotherm for N_2 at 77 K (Supplementary material). It is noteworthy that despite of this condensed nature, the apohost is capable of crystalline phase guest-addition and -removal. Binding isotherms for gaseous guests with apohost are shown in Figure 3b, where molar ratio of guest bound to apohost used are plotted against guest pressure at 25°C for the adsorption. On adsorption of methanol as an original guest within the saturation vapor pressure (P_s = 114 Torr), eventually, more than 10 methanols per a host are adsorbed stepwise into apohost. Not only methanol but also other guests such as benzene and ethyl acetate can also be bound under similar conditions; guest/host stoichiometries at 90% of the saturation vapor pressure of each guest are ca. 5 for benzene and ca. 6 for ethyl acetate, respectively. Any regenerated adduct rapidly loses incorporated guests upon exposure to the atmosphere to afford original apohost as evidenced by PXRD pattern (Fig. 3a). Thus, the apohost can be used repeatedly. As might be expected, guest-free microcrystal of **1**·6H as a corresponding reference having a quite small specific surface area (ca. 4 m^2/g) can hardly bind any guest (Fig. 3b). During the methanol adsorption, the apohost may restore an original crystal structure of $[K_4(\mathbf{1}\cdot 2H)]\cdot 14MeOH\cdot 2H_2O$ as suggested by following two items: (1) The guest/host stoichiometry not less than 10 near the saturation vapor pressure is almost comparable to that of the original adduct; (2) The stepwise adsorption isotherm for methanol having three plateaus as shown in Figure 3b with the guest/host stoichiometries of 2, 6, and more than 10 seems to indicate the step-by-step binding of the inner and outer guests. Unfortunately, PXRD pattern of the regener-

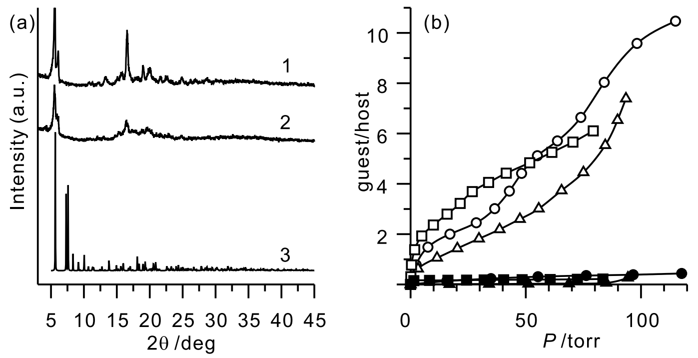

Figure 3. (a) PXRD patterns for apohost obtained from the single crystal of $[K_4(\mathbf{1}\cdot 2H)]\cdot 14MeOH\cdot 2H_2O$ (1), for apohost obtained from regenerated methanol adduct by desorption of the guests (2), or calculated from the crystal structure of $[K_4(\mathbf{1}\cdot 2H)]\cdot 14MeOH\cdot 2H_2O$ (3). (b) Binding isotherms for gaseous guests at 25°C with apohost as $[K_4(\mathbf{1}\cdot 2H)]\cdot 2H_2O$ (○, methanol; △, benzene; □, ethyl acetate) or guest-free microcrystal of **1**·6H (●, methanol; ■, benzene; ▲, ethyl acetate).

ated methanol adduct, for comparison with a calculated pattern from the original crystal structure (Fig. 3a), has not been obtained because of significantly volatile nature of incorporated methanols during the measurements.

The present work thus suggests a potential utility of the bridging sulfur moieties of thiacalixarene for construction of extensively-coordinated structures in the crystalline state. The sulfur-bridged cyclic hexamer **1**·6H drastically differs from a methylene-bridged counterpart *p-tert*-butylcalix[6]arene in that a former can bind as much as four potassium cations at once, while a latter usually forms the complexes with not more than two alkali metal ions.[11] The obtained highly-coordinated crystal may be regarded as intermediate between pure organic crystals involving porosity based on phase transition[12] upon guest binding and metal-coordinated ones possessing permanent or genuine porosity.

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9. Adduct $[K_4(\mathbf{1}\cdot 2H)]\cdot 14MeOH\cdot 2H_2O$: Compound **1**·6H (1.00 g, 0.92 mmol) and KH (0.37 g, 9.2 mmol) in THF (100 mL) was stirred at room temperature for 1 hr. After quenching excess KH with methanol (20 mL), all the solvents were removed in vacuo. The resulting solid material was dissolved in methanol (100 mL) and the remaining insoluble matter was filtered out. The clear solution thus obtained was allowed to stand for 12 h to afford pale-yellow crystals of the adduct: IR (KBr): ν 3530, 3388 (O–H), 2960 (C–H), 1447 (C=C), 1256 (C–O) cm^{-1}; ^1H NMR (300 MHz, CH_3OD, 25°C, TMS): δ 7.20 (br s, 12H; Ar*H*), 1.14 (br s, 54H; $C(CH_3)_3$); FAB MS for $[K_4(\mathbf{1}\cdot 2H)]$: calcd 1233, found 1233; elemental analysis for $[K_4(\mathbf{1}\cdot 2H)]\cdot 6H_2O$: calcd: C 53.70, H 6.01; found: C 53.98, H 6.14.
10. Crystal data: $C_{74}H_{128}O_{22}S_6K_4$, $M=1718.57$, pale yellow, crystal dimensions 0.20×0.20×0.20 mm, triclinic, space group $P\bar{1}$ (No. 2), $a=11.1821(2)$, $b=13.439(1)$, $c=16.581(1)$ Å, $\alpha=108.149(2)$, $\beta=91.478(4)$, $\gamma=107.227(3)°$, $V=2242.3(2)$ Å^3, $Z=1$, Mo Kα radiation ($\lambda=0.71069$ Å), $D_{calcd}=1.273$ g cm^{-3}, $T=103$ K, μ(Mo Kα)$=4.03$ cm^{-1}, Rigaku RAXIS RAPID imaging plate diffractometer, 19642 measured reflections, 9891 unique reflections ($R_{int}=0.073$), 6048 observed reflections ($I>3.00\sigma(I)$), 553 parameters, $R=0.083$, $wR=0.123$, refined against $|F|$,

GOF = 1.49. Crystallographic data for this crystal has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 192468. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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