# Porous Organic–Inorganic Assemblies Constructed from Keggin Polyoxometalate Anions and Calix[4]arene–Na+ Complexes: Structures and Guest-Sorption Profiles**

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The rational design of crystalline solids by self-organization of multiple molecular components is one of the interesting subjects in supramolecular chemistry, as it allows a defined spatial arrangement of the components and the formation of a diverse range of three-dimensional structures with unique functions.[1] In particular, the combination of organic compounds and inorganic metal clusters is interesting owing to their inherently different natures and possible synergetic effects in the crystal lattice. Polyoxometalates, anionic early transition metal oxide clusters, are attractive inorganic building blocks because of their discrete structures and notable acid/base, redox, and photochemical properties, which lead to a vast range of applications.[2,3] Herein we report two porous hybrids assembled from a Keggin polyoxotungstate sodium salt ($Na_3PW_{12}O_{40}$) and calix[4]arene derivatives (**1**, **2**) by host–guest interaction between the

1: R^1 = *t*Bu, R^2 = CH_2CO_2Et
2: R^1 = R^2 = H
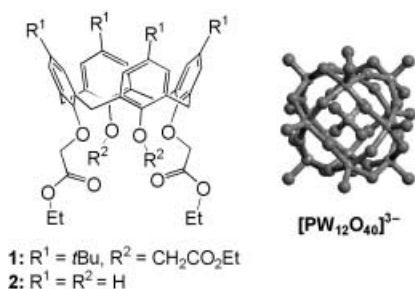
$[PW_{12}O_{40}]^{3-}$

organic hosts and the sodium ion.[4] We also demonstrate the guest-sorption capabilities of these porous materials.

Solutions of **1** in $CHCl_3$ and $Na_3PW_{12}O_{40}$ in MeOH were mixed and allowed to stand at room temperature to give

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single crystals of the 3:1 assembly [**1**-Na]$_3$[$PW_{12}O_{40}$] (**3**). X-ray crystallographic studies revealed the formation of an infinite ionic crystal with a cubic crystal system, which contained a head-to-tail columnar array of the **1**-Na+ complexes as a fundamental component. As shown in Figure 1 a, the columns
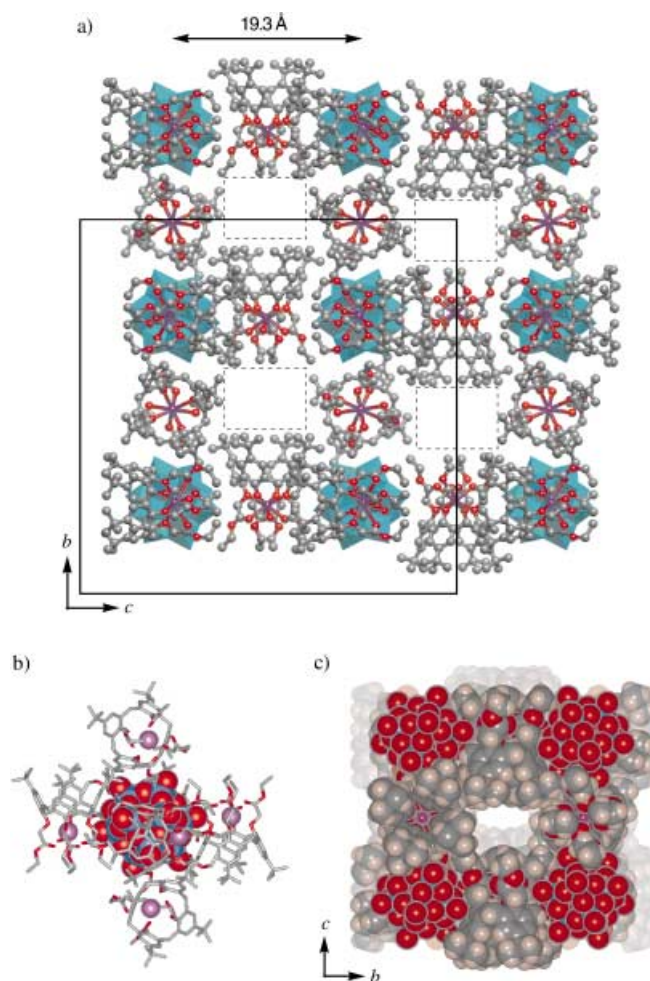

Figure 1. Crystal structure of **3** with solvent molecules omitted. a) A view of the packing structure along the *a* axis illustrating orthogonal stacking of the **1**-Na+ columns running along the *a*, *b*, and *c* axes. b) Octahedral orientation of **1**-Na+ units around a cluster anion. c) A cross section of the microchannel viewed along the *a* axis. The black lines in (a) indicate the unit cell, and the dotted lines the microchannels.

propagate in three directions along the *a*, *b*, and *c* axes and are stacked alternately in orthogonal configurations to generate a three-dimensional gridlike framework, which serves as a scaffold for the α-$[PW_{12}O_{40}]^{3-}$ anions. One anion is surrounded by six **1**-Na+ units, whereby no bonding interactions between sodium and cluster oxygen atoms are observed (Figure 1 b).[5] The side faces of each calix[4]arene unit are involved in weak intermolecular interactions with the anions (e.g., van der Waals forces).[6] Packing of the cationic and anionic components in this manner leaves micropores as the residual space. As shown in Figure 1 a and c, cavities with sizes of about 6×9 Å are created between four calix[4]arene units, which extend along the *a* axis to form channels. Channels are

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also formed in the *b* and *c* directions, and these tridirectional channels intersect each other to form a three-dimensional microporous network. The micropores are occupied by diffuse solvent molecules, and the solvent-accessible volume of the unit cell was estimated, (PLATON program[7]) to be 19 624 Å³, which is approximately 34 % of the unit-cell volume (57 066 Å³).

A porous structure was also observed for the assembly with calix[4]arene **2** ([**2**-Na]$_3$[PW$_{12}$O$_{40}$], **4**), but the fundamental packing profile and the pore characteristics are rather different. As shown in Figure 2a, the crystal structure is constructed by alternating stacking of **2**-Na⁺ and α-[PW$_{12}$O$_{40}$]³⁻ layers on the *bc* plane, whereby one-dimensional channels are created along the [101] direction. The size

and volume percentage of the channels were estimated to be about 4 × 8 Å and 15 %, respectively. The orientation of **2**-Na⁺ around the anion is also different. Two of the six calix[4]arene units surrounding one cluster anion are linked to the anion by Na−O coordinative bonds (Na−O 2.434 Å) to form a 1:2 molecular fragment, while the other four undergo only weak intermolecular interactions with the anion (Figure 2b).[8] The anion surfaces are not completely covered by the calix[4]arene units and are partially exposed to the micropore. Accordingly, as shown in the top view of a microchannel (Figure 2c), the pore wall is constructed from both calix[4]-arene and anion units. This contrasts with **3**, in which the anions are completely shielded by the calix[4]arene units.

These porous architectures containing polyoxometalates prompted us to investigate their guest-sorption capabilities, since such polyoxometalate-based materials have potential for selective reactions and recognition.[9, 10] After evacuation at 100 °C for 2 h, the crystal of **4** showed a powder XRD profile identical to that simulated from the single-crystal data (Figure 3b, I and II), that is, the porous structure shown in Figure 2 was maintained after thermal pretreatment.[11] This pretreated solid efficiently sorbed small alcohols in the one-

Figure 3. a) Sorption isotherms of **4** for ethanol (○, 298 K), methanol (◆, 288 K), water (▲, 298 K), and 1-butanol (□, 303 K). b) XRD profiles of **4** simulated from the single-crystal data (I), before (II) and after (III) ethanol sorption, and after two ethanol sorption/desorption cycles (IV).
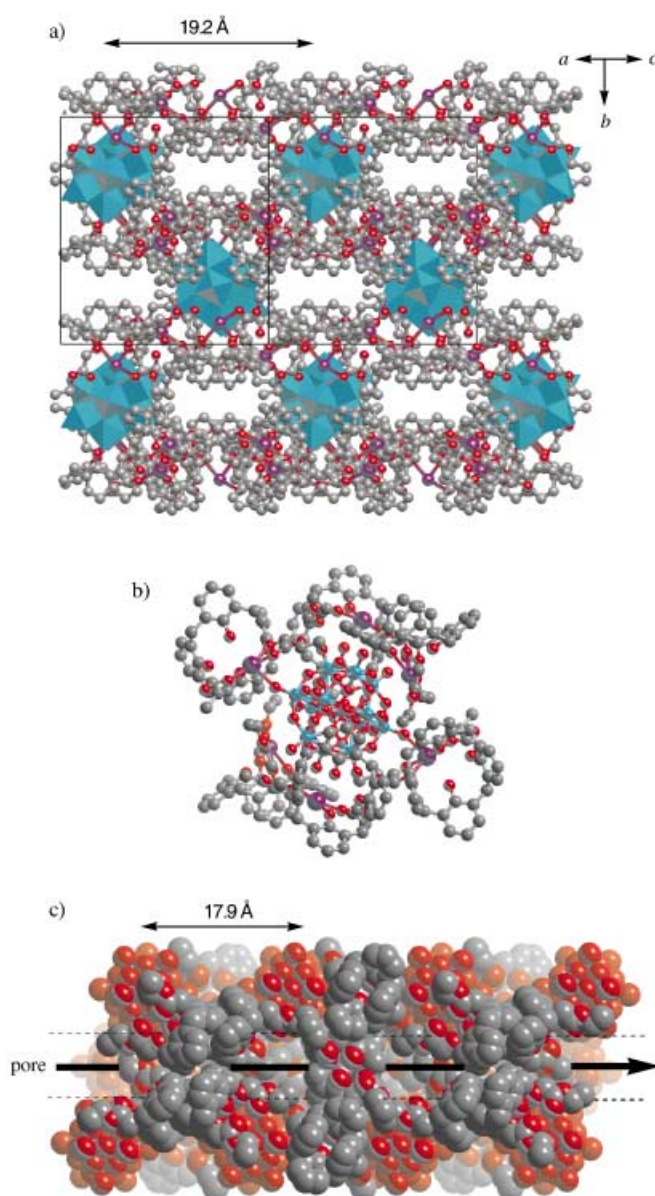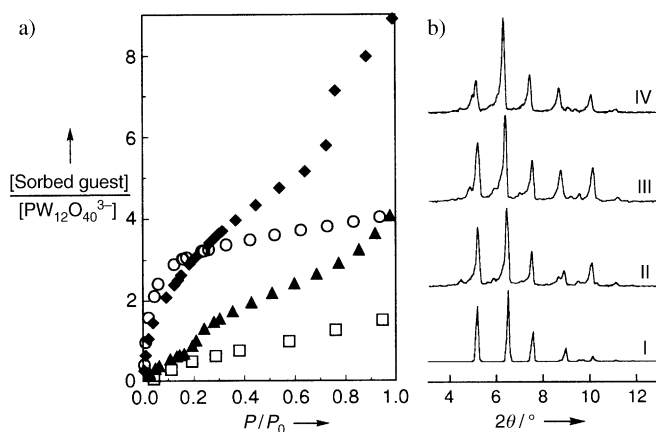
Figure 2. Crystal structure of **4** with hydrogen atoms and solvent molecules omitted. a) View of the packing structure along the 101 direction. b) Orientation of **2**-Na⁺ units around a cluster anion. c) Top view of the microchannel with the anion units above the pore omitted for clarity. The lines in c) represent the pore rims.

dimensional micropores. For example, as shown in Figure 3a, the sorption isotherm of ethanol showed a sharp rise in the low-pressure region, characteristic of sorption in micropores.[12] The sorption/desorption cycle occurred in a completely reversible fashion, and the powder XRD profiles remained unchanged throughout the cycle (Figure 3b).[13] Methanol also showed a reversible sorption/desorption isotherm with retention of the porous structure of the sorbent, but also a second increase in the high-pressure region in addition to the initial sharp increase in the low-pressure region. Interestingly, these alcohols showed higher binding activities than water, which has an inherently strong affinity towards the parent salt Na$_3$PW$_{12}$O$_{40}$. This unique selectivity may arise from the amphiphilic character of the pore wall of **4**, which is constructed from both hydrophobic calix[4]arene and

hydrophilic $[PW_{12}O_{40}]^{3-}$ units. The steric bulk and/or the hydrophobic/hydrophilic balance of guests also appear to be important factors: Higher alcohols such as 1-butanol showed small binding activities.

Assembly **3** also sorbed alcohols, but the broad powder XRD pattern after guest sorption indicated an amorphous character. The broad diffraction pattern did not change on evacuation of the amorphous sample. The strong binding of the guests to the anionic moiety may disturb the orientation of the calix[4]arene units in the original crystalline sorbent (Figure 1) and thus cause irreversible destruction of the crystal lattice.

In conclusion, we have presented two porous organic–inorganic assemblies composed of calix[4]arene–Na$^+$ complexes and polyoxotungstate anions. To the best of our knowledge, assembly **4** is the first porous calixarene-based ionic material to display reversible guest sorption with retention of the original framework.[14] Exploitation of the spatially restricted channels for catalysis is worthy of further investigation.

Experimental Section

3: $Na_3PW_{12}O_{40}$ (198 mg, 0.067 mmol) in EtOH (10 mL) was mixed with **1** (200 mg, 0.20 mmol) in $CHCl_3$ (10 mL), and the resulting clear solution was allowed to stand at room temperature for 7 days to give colorless transparent cubic crystals, which were collected by filtration (325 mg, 82%). Elemental analysis (%): calcd for $[1-Na]_3[PW_{12}O_{40}]\cdot 6H_2O\cdot 2CHCl_3$: C 34.85, H 4.08, Cl 3.39; found: C 34.97, H 3.86, Cl 3.87.

4: $Na_3PW_{12}O_{40}$ (246 mg, 0.083 mmol) in CH_3OH (20 mL) was mixed with **2** (150 mg, 0.25 mmol) in $CHCl_3$ (20 mL), and the resulting clear solution was allowed to stand at room temperature for 2 days to give orange rectangular crystals, which were collected by filtration (278 mg, 70%). Elemental analysis (%): calcd for $[2-Na]_3[PW_{12}O_{40}]\cdot 2H_2O\cdot CHCl_3$: C 26.77, H 2.33, Cl 2.17; found: C 26.41, H 2.39, Cl 2.95.

Crystal data for **3**: $C_{182}H_{320}Cl_6Na_3O_{131}PW_{12}$, cubic, space group Ia-3 (no. 206), $a=b=c=38.5884(9)$ Å, $\alpha=\beta=\gamma=90°$, $V=57460.6(23)$ Å^3, $Z=8$, $\rho_{calcd}=1.647$ g cm^{-3}, $T=153.1$ K, $2\theta_{max}=55°$, $\mu(Mo_{K\alpha})=4.935$ mm^{-1}. 19255 reflections measured, of which 11877 were unique ($R_{int}=0.046$). The carbon atoms of the tBu group (C16–C18, C32–C34) were disordered over two positions and hence were refined isotropically at fixed positions with occupation factors of 0.5. The oxygen atoms of water molecules (O15–O40), which were disordered over multiple positions, were refined isotropically at fixed positions with appropriate occupation factors without hydrogen atoms. Final R and R_w values were 0.046 and 0.058, respectively, for 6774 observed reflections ($I>5.0\sigma(I)$) and 467 variable parameters.

Crystal data for **4**: $C_{108}H_{109}Cl_3Na_3O_{66}PW_{12}$, monoclinic, space group $C2/c$ (no. 15), $a=36.395(8)$, $b=20.451(4)$, $c=19.229(4)$ Å, $\beta=107.0790(9)°$, $V=13680.6(51)$ Å^3, $Z=4$, $\rho_{calcd}=2.401$ g cm^{-3}, $T=153.1$ K, $2\theta_{max}=55°$, $\mu(Mo_{K\alpha})=4.935$ mm^{-1}. 30586 reflections measured, of which 15293 were unique ($R_{int}=0.034$). One of the sodium atoms (Na2) was disordered over two positions, and so was refined isotropically with occupation factors of 0.5. The non-hydrogen atoms of the solvents (chloroform and water), one of the oxygen atoms attached to the phosphorous atom, and the carbon atoms of one of the ethyl groups (C28, C29) were refined isotropically. Final R and R_w values were 0.046 and 0.068, respectively, for 9001 observed reflections ($I>5.0\sigma(I)$) and 926 variable parameters.

Crystal data were collected on a Mercury CCD area detector coupled with a Rigaku AFC-8S diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.7107$ Å) using CrystalClear (Rigaku Co.). Data were corrected for Lorentzian and polarization effects. An empirical absorption correction was applied by using REQABA. The structures were solved with CrystalStructure (Molecular Structure Co.). The initial positions of tungsten atoms were determined by direct methods, and other non-hydrogen atoms were located by Fourier and difference Fourier techniques and refined anisotropically unless otherwise noted. Full-matrix least-squares refinement was employed against F. Hydrogen atoms were located at calculated positions and refined isotropically. CCDC-197385 (**3**) and -227498 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Powder XRD measurements: All spectra were measured with a Rigaku Mini Flex diffractometer using $Cu_{K\alpha}$ radiation ($\lambda=1.54056$ Å, 30 kV, 15 mA). Scans were performed in the range of $2\theta=1.5$–$20°$ at a rate of $0.02°s^{-1}$.

Sorption measurements: The sorption isotherms were measured with a Japan Bel Belsorp 18 sorption instrument.

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