A Breathing Ionic Crystal Displaying Selective Binding of Small Alcohols and Nitriles: $K_3[Cr_3O(OOCH)_6(H_2O)_3][\alpha\text{-}SiW_{12}O_{40}]\cdot 16\,H_2O$**

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The fabrication of nanostructured materials has produced a variety of materials with unique physical or chemical properties. Aluminosilicate zeolites and their inorganic analogues possess well-defined pores, which show shape-selective adsorption of molecules and are widely applied to adsorption, separation, and catalytic processes.[1] Recently, “organic zeolites” based on organic or organometallic building blocks have been synthesized.[2] These organic zeolites can be easily functionalized at the atomic/molecular level by the appropriate selection of the metals, ligands, or chemical bonds and show unique inclusion properties.[2] For example, the compound Co-benzenetricarboxylate (Co-BTC) absorbs only aromatics but not acetonitrile or 1,2-dichloroethane[2f] and the compound Zn-BTC absorbs only alcohols among various polar organic molecules.[2i, 2k] As for the separation of alcohol molecules, the Ca-A zeolite[3] adsorbs 1-butanol from a mixture of its isomers and the compound Zn-BTC [2i] distinguishes alkyl alcohols from aromatic alcohols, although little is known of the separation of smaller alcohols ($< C_3$).

Polyoxometalates are discrete metal – oxygen cluster anions and have notable redox or acid – base properties.[4] Some polyoxometalate compounds possess micropores in the crystal structure[5, 6] or between the nanocrystallites.[7] For example, Müller et al. synthesized a supramolecular molybdenum oxide cluster with cavities.[6] Some polyoxometalate complexes contain acetonitrile or methanol as guests, but do not show reversible inclusion and removal.[8] An acid-type polyoxometalate, $H_3PW_{12}O_{40}$, absorbs polar molecules in the pseudoliquid phase, but the absorption is not selective because of the strong interaction of protons with absorbates.[9] All these compounds do not show selective binding of polar organic molecules.

Herein we report the selective binding of small alcohols and nitriles smaller than C_3 by complex **1**, which is synthesized by the complexation of the Keggin-type $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ polyoxometalate ion with the large macro cation $[Cr_3O(OOCH)_6(H_2O)_3]^+$, and the separation of methanol from a mixture of alcohols.

$K_3[Cr_3O(OOCH)_6(H_2O)_3][\alpha\text{-}SiW_{12}O_{40}]\cdot 16\,H_2O$ **1**

The crystal structure of **1** (see Figure 1) shows polyoxometalates and macro cations lined up along the *c* axis to from a column and that three potassium ions balance the negative charge. The columns are hexagonally arranged to construct a straight channel with an opening of around 0.5 × 0.8 nm (36 % of the unit cell).[10] The use of the macro cation with a large size (ca. 0.7 nm) and small charge (+1), which reduces the ion – ion interaction among the constituent ions, is essential to the formation of the channels. The water of crystallization is in the channels, and is weakly hydrogen bonded to ligand water molecules of the macro cations and oxygen atoms of the polyoxometalates. These water molecules were easily desorbed by the evacuation at 298 K (guest-free phase, **2**; Figure 1). The weight loss was 7.6 %, consistent with the removal of the water of crystallization. The BET surface area of **2** with N_2 adsorption was 2.0 m^2g^{-1} and no micropores were observed.

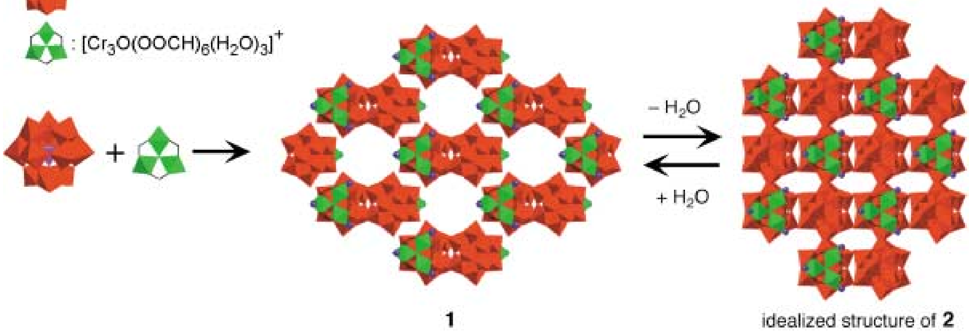

Figure 1. Synthesis and crystal structure of **1** and the ideal closest-packing model of **2**. The water of crystallization is omitted for the clarity; small blue spheres = K^+ ions.

Figure 2 a and b show the powder X-ray diffraction patterns of **1** and **2**, respectively. Broad lines are observed in Figure 2 b. This pattern is explained by a calculation with a closest-packing model of the columns, which is in accord with the low BET surface area and that no micropores were observed for **2**.[11] Compound **2** absorbs water molecules upon exposure to saturated water vapor (ca. 3 kPa) at 298 K with the restoration of the powder X-ray diffraction pattern (Figure 2 c). On the other hand, the binding of methanol by **2** changed the powder X-ray diffraction pattern (Figure 2 d). No satisfactory fits were observed by changing the dimension of the channel in **1**. This occurrence is probably caused by the structure change

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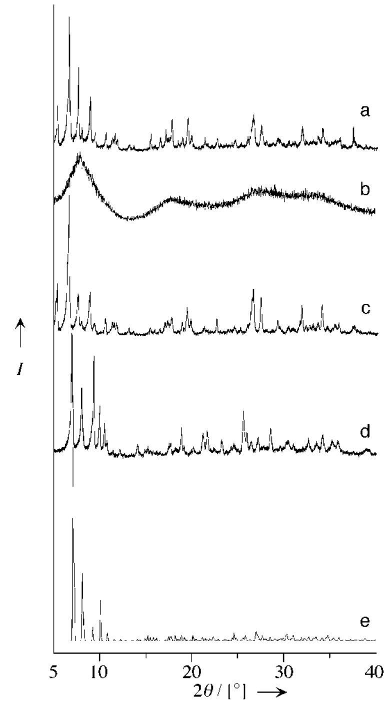

Figure 2. Observed powder X-ray diffraction patterns. a) **1**, b) **2**, c) rehydrated **2**, d) **2** after exposure to saturated methanol vapor for 5 min at 298 K, and e) calculated pattern for $K_3[Cr_3O(OOCH)_6(H_2O)_3][\alpha\text{-}SiW_{12}O_{40}]\cdot n\,CH_3OH$ based on that for $K_2[Cr_3O(OOCH)_6(H_2O)_{2.5}(CH_3OH)_{0.5}]_2[\alpha\text{-}SiW_{12}O_{40}]\cdot n\,CH_3OH$.

with the methanol inclusion. Some organometallic complexes exhibit structure change upon the inclusion of guests, such as alcohols, amides, and nitriles, which have hydrogen-bonding nature.[12] At present, the pattern in Figure 2d was only approximately reproduced by the calculation on the assumption that the occupancies of the $[Cr_3O(OOCH)_6(H_2O)]^+$ and K^+ ions are fixed to 0.5 in the $[Cr_3O(OOCH)_6(H_2O)]^+$ sites of the known compound $K_2[Cr_3O(OOCH)_6(H_2O)_{2.5}(CH_3OH)_{0.5}]_2[\alpha\text{-}SiW_{12}O_{40}]\cdot 8\,CH_3OH$ to give a theoretical pattern for $K_3[Cr_3O(OOCH)_6(H_2O)_3][\alpha\text{-}SiW_{12}O_{40}]\cdot n\,CH_3OH$ (Figure 2e).[13] No changes in the IR and diffuse reflectance UV/Vis spectra were observed upon the repetitions (even after more than five) of the absorption–desorption cycles of either water or methanol, which shows the maintenance of the structures of the $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ and $[Cr_3O(OOCH)_6(H_2O)_3]^+$ ions in **1**.

Figure 3 shows the sorption isotherm of C_1–C_4 alcohols. The amounts of the surface adsorption of alcohols calculated from the BET surface area was 0.24–0.40 $cm^3\,g^{-1}$ and was almost negligible. The amount of methanol increased with an increase in P/P_0. The sorption amount reached 80 $cm^3\,g^{-1}$ (13 molecules per **2**) at $P/P_0 = 0.6$, which shows the sorption of methanol into the bulk material. On the other hand, the amount of ethanol sorption was less than that for the surface adsorption below $P/P_0 = 0.5$ and a sudden rise was observed around $P/P_0 = 0.6$. These unique adsorption phenomenon are explained by the structure change associated with the hydrogen-bond-regulated guest inclusion.[14, 2k, 2q] Above $P/P_0 = 0.6$, ethanol molecules can diffuse into the bulk. 1-Propanol and 1-butanol were completely excluded. Figure 4 shows the sorption isotherms of the nitriles. Acetonitrile showed a similar isotherm to that of ethanol while propionitrile and butylonitrile were excluded. The nonsaturation behavior at a high P/P_0 value is probably caused by the multilayer sorption on the surface.

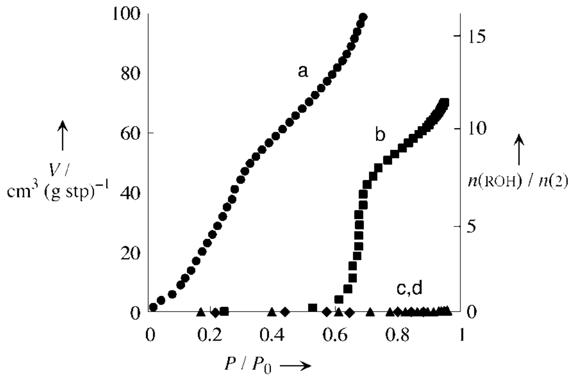

Figure 3. Sorption isotherm of alcohols at 298 K with **2** (0.1 g, 2.85×10^{-2} mmol): a) methanol (●, $P_0 = 15.6$ kPa), b) ethanol (■, $P_0 = 6.67$ kPa), c) 1-propanol (▲, $P_0 = 2.67$ kPa), and d) 1-butanol (◆, $P_0 = 1.35$ kPa).

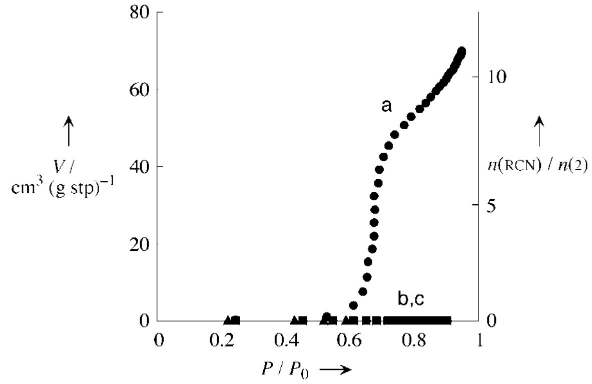

Figure 4. Sorption isotherm of nitriles at 298 K with **2** (0.1 g, 2.85×10^{-2} mmol): a) acetonitrile (●, $P_0 = 10.7$ kPa), b) propionitrile (■, $P_0 = 6.27$ kPa), and c) butylonitrile (▲, $P_0 = 2.67$ kPa).

The amounts of alcohols and nitriles absorbed decreased in the order of methanol > ethanol > 1-propanol ≈ 1-butanol ≈ 0 and acetonitrile > propionitrile ≈ butylonitrile ≈ 0. The same order was observed for the hydrophilicity. In addition, the more hydrophobic methane and nitrogen monoxide, the sizes of which are smaller than the C_1–C_3 alcohols and nitriles, were excluded. Therefore, the sorption properties of **2** are chiefly associated with the hydrogen-bonding interaction between the polar molecules and oxygen atoms of $[Cr_3O(OOCH)_6(H_2O)_3]^+$ and $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$.[15]

Next, **2** was applied to the selective sorption from a mixture of alcohols. Figure 5 shows the separation of methanol from a mixture of C_1–C_3 alcohols under dilute conditions (0.4 M of each alcohol in 1,2-dichloroethane). Methanol was selectively absorbed and the amount reached up to approximately 1.8 molecules per **2**, while ethanol and 1-propanol were excluded.[16] Thus methanol could be separated from other C_1–C_3 alcohols. Therefore, all the present results show the novel molecular sieving for small molecules.

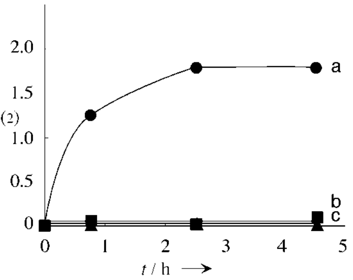

Figure 5. Selective binding of methanol in 1,2-dichloroethane at 298 K with **2** (0.74 g, 2.12×10^{-1} mmol): ● methanol (0.4 M), ■ ethanol (0.4 M), ▲ 1-propanol (0.4 M); conditions: 1,2-dichloroethane (16 mL), methanol:ethanol:1-propanol:1,2-dichloroethane = 1:30:30:30:900.

Experimental Section

1: $K_4[\alpha\text{-}SiW_{12}O_{40}] \cdot n H_2O$ (0.23 mmol) and $[Cr_3O(OOCH)_6(H_2O)_3](OOCH) \cdot n H_2O$ (0.27 mmol) were dissolved into dilute aqueous HNO_3 (pH 2, 30 mL). KCl (6.8 mmol) was added. The solution was filtered after 30 min and the filtrate was kept in air at room temperature for 1–2 days. Green crystals were isolated in about 50% yield. IR (KBr): 1634 and 1378 (vs, OCO), 981 (s, W=O), 929 (br, Si-O), 887 (m, W-O-W), 791 (br, W-O-W), 660 cm^{-1} (m, Cr_3-O). Elemental analysis (%) calcd for $C_6H_{44}Cr_3K_3O_{72}SiW_{12}$: C 1.91, H 1.01, Cr 4.13, K 3.09, Si 0.74, W 59.90; found: C 1.92, H 1.10, Cr 4.10, K 3.35, Si 0.80, W 59.91.

X-ray crystal determination of **1**: X-ray intensity data were collected on a Rigaku AFC-5R diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å, 50 kV-150 mA). Lorentz polarization and empirical absorption correction based on ψ scan were carried out with TEXSAN. Tungsten and chromium atoms were located by direct methods and other non-hydrogen atoms were found by successive differential Fourier syntheses. Refinements were carried out by SHELX97. Monoclinic $C2/m$, $a = 27.258(4)$, $b = 15.764(6)$, $c = 17.285(4)$ Å, $\beta = 102.73(2)^\circ$, $V = 7245(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 3.396$ g cm^{-3}, $T = 293(2)$ K, 10885 unique reflections with $I > 2\sigma(I)$, $2.56 < \theta < 29.97$, 449 parameters, final R factors $R_1 = 0.059$; $wR_2 = 0.1446$. Only 12 out of 16 water molecules per **2** were located. CCDC 160502 (**1**) contains 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 X-ray diffraction measurements: All spectra were measured with a MXP^3 diffractometer (Mac Science) using $Cu_{K\alpha}$ radiation ($\lambda = 1.54056$ Å, 30 kV-40 mA). The scannings were in the range of $2\theta = 2-40^\circ$ at a rate of 0.5° min^{-1}.

Calculation of the powder X-ray diffraction pattern: Calculations were carried out by drawing the presumed structure with Crystal Maker (CrystalMaker Software) and displaying the pattern with Crystal Diffraction (CrystalMaker Software). The particle size (i.e. coherent length), which was translated to the half width of the reflection, was altered to give the best fit.

Sorption measurements: The sorption isotherms of **2** were measured with an automatic sorption apparatus Omnisorp 100CX (Coulter corporation). The uptake of alcohols by **2** was confirmed by the changes in the alcohol concentrations, which were detected by GC (Shimazu GC-8A model with a Porapak QS column and a TCD detector). Methanol, ethanol, and 1-propanol (each 6.36 mmol) were added to 1,2-dichloroethane (ca. 16 mL 0.2 mmol) the anhydride (0.74 g, 2.12×10^{-1} mmol) was added to give a heterogeneous mixture.

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[10] The volume was estimated by considering ionic radii (Cr^{3+}) or van der Waals radii (other atoms) of the constituent atoms.

[11] A similar closest packing to **2** was observed for the complex of Keggin-type polyoxometalate $[CoW_{12}O_{40}]^{6-}$ with $[Cr_3O(OOCH)_6(H_2O)_3]^+$ ions. The channel volume of this complex was 17% of the unit cell, which was comparable to the ideal closest packing model of **2** (20%). The details will be published elsewhere.

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[13] K$_2$[Cr$_3$O(OOCH)$_6$(H$_2$O)$_{2.5}$(CH$_3$OH)$_{0.5}$]$_2$[α-SiW$_{12}$O$_{40}$]·8CH$_3$OH was crystallized from a methanol solution of **2**. Crystallographic data for K$_2$[Cr$_3$O(OOCH)$_6$(H$_2$O)$_{2.5}$(CH$_3$OH)$_{0.5}$]$_2$[α-SiW$_{12}$O$_{40}$]·8CH$_3$OH: orthorhombic $Pna2_1$, $a = 24.796(6)$, $b = 15.406(3)$, $c = 22.042(5)$ Å, $Z = 4$, $R_1 = 0.0480$; $wR2 = 0.0480$.

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[15] In the crystal structure of K$_2$[Cr$_3$O(OOCH)$_6$(H$_2$O)$_{2.5}$(CH$_3$OH)$_{0.5}$]$_2$-[α-SiW$_{12}$O$_{40}$]·8CH$_3$OH, methanol molecules are hydrogen bonded to the oxygen atoms of the bridging units of the macro cations.

[16] The amount of methanol absorbed in Figure 5 seemed to be different from that in Figure 3a. This can be explained by the different equilibrium in the liquid–solid phase from that in the gas–solid phase.

A Self-Assembled Porphyrin Box from *meso–meso*-Linked Bis{5-*p*-pyridyl-15-(3,5-di-octyloxyphenyl)porphyrinato zinc(II)}[**]

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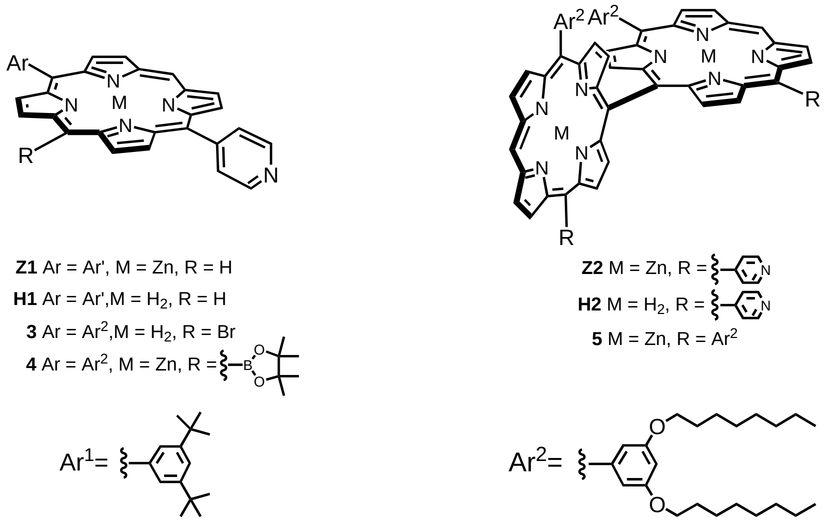
Well-ordered architectures of self-assembling porphyrins[1] have been attracting considerable interest in light of potential applications in material science,[2] template-directed synthesis,[3] reaction catalysis,[4] and duplication of photosynthetic functions of light harvesting and charge separation.[5] Among these, the coordination interaction between zinc porphyrin and pyridine groups have been often used to construct self-assembled porphyrin architectures both in infinite and discrete forms.[1–6] Fleischer and Shachter have reported a linear infinite polymeric aggregate from 5-*p*-pyridyl-10,15,20-triphenylporphyrinato zinc(II),[6] whereas Hunter and co-workers reported the formation of a cyclic tetramer from a zinc(II) porphyrin bearing a *p*-(isonicotinamide)phenyl group[7] and Imamura and co-workers reported a similar cyclic tetramer from 5-*p*-pyridyl-10,15,20-triaryl porphyrinato ruthenium(II),[8] both without X-ray crystal structures. Herein, we report a self-assembling cyclic tetramer of 5-*p*-pyridyl-15-(3,5-di-*tert*-butylphenyl)porphyrinato zinc(II) (**Z1**) with its X-ray structure and a self-assembling box-shape tetramer of *meso–meso*-linked bis{5-*p*-pyridyl-15-(3,5-di-octyloxyphenyl)porphyrinato zinc(II)} (**Z2**; Scheme 1). In the latter case, a very stable supramoleuclar aggregate is constructed as a result of many cooperative interactions with simultaneous structural rigidification, as suggested by its unique absorption and fluorescence spectra.

5-*p*-Pyridyl-15-(3,5-di-*tert*-butylphenyl)porphyrin (**H1**) was prepared by condensation of 4-pyridinecarboxaldehyde and 3,5-di-*tert*-butylbenzaldehyde with 2,2′-dipyrrylmethane in 8% yield, and subsequent zinc insertion with Zn(OAc)$_2$ afforded **Z1** quantitatively. The ^{1}H NMR spectrum of **Z1** in CDCl$_3$ is concentration independent at >3 mM and exhibits large upfield shifts for the pyridyl protons at $\delta = 6.18$ and 2.17 ppm in comparison to those of **H1** at $\delta = 8.29$ and 7.81 ppm, which indicates the coordination of the pyridyl group to zinc(II) porphyrin. As judged from the chemical shifts of the pyridyl group, **Z1** forms a similar aggregate in C$_6$D$_6$ ($\delta = 5.94$ and 2.59 ppm) but exists in a monomeric form in [D$_8$]THF ($\delta = 8.97$ and 8.31 ppm). The latter result suggested the coordination of THF to the zinc center, thus preventing self-assembling. Vapor pressure osmometry (VPO) in CHCl$_3$ afforded average molecular weights of 2760 ± 370 g mol^{-1} for **Z1** and 550 ± 20 g mol^{-1} for **H1** in a range of $3.0–13.0 \times 10^{-3}$ M, which correspond to (**Z1**)$_4$ and monomeric **H1**, respectively. The absorption spectrum of **Z1** in CHCl$_3$ is concentration dependent in an range of roughly $10^{-6}–10^{-5}$ M and shows the Q-band at 540 nm at $<10^{-6}$ M and at 549 nm at $>$ about 10^{-5} M (Figure 1), which correspond, respectively, to four-coordinate and five-coordinate zinc porphyrin units. A good fit for the observed sigmoidal curve is obtained by assuming porphyrin tetramer formation ((**Z1**)$_4$), which gives an association constant of $K_4 = 1.4 \times 10^{15}$ M^{-3}.[9]



Scheme 1.

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