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Recognition of Small Polar Molecules with an Ionic Crystal of α-Keggin-Type Polyoxometalate with a Macrocation

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The complexation of Keggin-type polyoxometalates $[\alpha\text{-}XW_{12}O_{40}]^{n-}$ (X = P, Si, B, Co), macrocation $[Cr_3O(OOCH)_6(H_2O)_3]^+$, and alkali-metal ions forms ionic crystals of $Na_2[Cr_3O(OOCH)_6(H_2O)_3][\alpha\text{-}PW_{12}O_{40}]\cdot 16H_2O$ (**1a**), $K_3[Cr_3O(OOCH)_6(H_2O)_3][\alpha\text{-}SiW_{12}O_{40}]\cdot 16H_2O$ (**2a**), $Rb_4[Cr_3O(OOCH)_6(H_2O)_3][\alpha\text{-}BW_{12}O_{40}]\cdot 16H_2O$ (**3a**), and $Cs_5[Cr_3O(OOCH)_6(H_2O)_3][\alpha\text{-}CoW_{12}O_{40}]\cdot 7.5H_2O$ (**4a**). The space volumes of the ionic crystals decrease in the order of **1a** > **2a** > **3a** > **4a**. The water of crystallization in **1a**–**3a** is completely desorbed by evacuation at room temperature, while about 50% of the water of crystallization in **4a** is desorbed. The respective **1a**–**4a** after evacuation at room temperature are denoted by **1b**–**4b**, which show the close packing of the constituent ions. The calculated cell volumes per formula decreased in the order of **1b** > **2b** > **3b** > **4b**, which would be related to the increase in *n*. Compound **1b** sorbs various ≤C5 polar organic molecules such as 1-butanol, valeronitrile, and methyl propionate. Compound **2b** sorbs ethanol, acetonitrile, and methyl formate. Compound **3b** sorbs water and methanol, and **4b** sorbs only water. Thus, the ionic crystals can discriminate ≤C5 polar organic molecules such as alcohols, nitriles, and esters by one methylene chain, and the decrease in *n* of $[\alpha\text{-}XW_{12}O_{40}]^{n-}$ enables the sorption of molecules with the longer methylene chain. The nature of the sorption properties of **1b**–**4b** can be explained by the lattice energy needed for the expansion of **1b**–**4b**. The selective sorption properties of **1b**–**4b** are successfully applied to the separation of mixtures of alcohols, nitriles, esters, and water.

Introduction

Extensive researches have been devoted to the syntheses of microporous materials, which show the unique selectivity in the guest sorption, ion exchange, and catalysis. Zeolites are composed of covalently bonded $[TO_4]$ (T = Si, Al, P, etc.) and $[MO_6]$ (M = Ti, Zr, Sn, etc.) units and show the shape-selective adsorption depending on the pore sizes.[1−3] A classical example is Ca−A zeolite, which adsorbs straight-chain organic molecules but not those that are branched.[4] As for the separation of inorganic gases, Tsapatsis et al. synthesized a microporous titanosilicate, of which the effective pore size can be finely tuned by dehydration at elevated temperatures.[3] The titanosilicate could separate 3−4-Å molecules such as N_2/CH_4, Ar/O_2, and N_2/O_2 by the pressure-swing adsorption.[3]

Recently, much attention has been paid toward the syntheses of porous metal−organic frameworks constructed with metal and organic units.[5−14] The structure and pore size of these compounds can be finely tuned by the choice of building blocks. For example, Yaghi et al. synthesized a series of metal−organic frameworks with zinc benzenecar-

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boxylates, and IRMOF-16 showed the highest free volume (91.1%) and lowest density (0.21 g cm^{-3}) among those reported for crystalline materials.[12] As for the separation of inorganic gases by the metal−organic frameworks, porous manganese formate[13] and lanthanide carboxylate[14] sorbed carbon dioxide but not argon and dinitrogen (kinetic diameters: CO_2 = 3.30 Å, Ar = 3.40 Å, and N_2 = 3.64 Å), showing combined effects of pore sizes and host−guest interactions. Although various kinds of zeolites and metal−organic frameworks can sorb small organic molecules, the discrimination of small organic molecules (especially ≤C3) and/or close-boiling mixtures is still rare.[15−20]

Polyoxometalates are nanosized metal−oxygen macroanions and suitable building blocks of ionic crystals with nanostructures in combination with appropriate macrocations.[21−29] Polyoxometalates show unique redox or acidic properties, which can be controlled at atomic or molecular levels, and have been applied to catalysis.[30−35] We have reported that the complexation of Keggin-type polyoxometalates of $[\alpha\text{-SiW}_{12}O_{40}]^{4-}$ and $[\alpha\text{-CoW}_{12}O_{40}]^{6-}$ with a macrocation of $[Cr_3O(OOCH)_6(H_2O)_3]^+$ formed ionic crystals of $K_3[Cr_3O(OOCH)_6(H_2O)_3][\alpha\text{-SiW}_{12}O_{40}]\cdot 16H_2O$ (**2a**)[36,37] and $Cs_5[Cr_3O(OOCH)_6(H_2O)_3][\alpha\text{-CoW}_{12}O_{40}]\cdot 7.5H_2O$ (**4a**),[38] respectively. The ionic crystals possessed hydrophilic channels filled with the water of crystallization. The former guest-free phase sorbed polar organic molecules up to C2,[36,37] while the latter guest-free phase sorbed only water.[38] In addition, the void sizes of ionic crystals of Dawson-type polyoxometalates ($[\alpha\text{-P}_2V_xW_{18-x}O_{62}]^{m-}$) with the macrocation systematically increased with a decrease in *m*.[39] On the basis of these results, we reached an idea that the changes in the anion charge of the Keggin-type polyoxometalate of the ionic crystals enable the fine control of the sorption of small organic molecules.

In this work, a series of Keggin-type polyoxometalates with anion charges from −3 to −6 ($[\alpha\text{-PW}_{12}O_{40}]^{3-}$, $[\alpha\text{-SiW}_{12}O_{40}]^{4-}$, $[\alpha\text{-BW}_{12}O_{40}]^{5-}$, and $[\alpha\text{-CoW}_{12}O_{40}]^{6-}$) are used as building blocks, and the complexation with the macrocation ($[Cr_3O(OOCH)_6(H_2O)_3]^+$) is reported. The structures of the ionic crystals and the guest-free phases are analyzed by the single-crystal or powder X-ray diffraction (XRD) methods. The effects of the charges of the polyoxometalates on the structures and sorption properties of the ionic crystals are investigated, and the sorption properties are successfully applied to the separation of polar organic molecules (≤C5) by the one methylene chain.

Experimental Section

Syntheses of the Ionic Crystals 1a−4a. $Na_2[Cr_3O(OOCH)_6(H_2O)_3][\alpha\text{-PW}_{12}O_{40}]\cdot 16H_2O$ (**1a**) was synthesized as follows: $H_3PW_{12}O_{40}\cdot nH_2O$[40] (0.9 g, 0.3 mmol) and $[Cr_3O(OOCH)_6(H_2O)_3](OOCH)\cdot nH_2O$[41] (0.18 g, 0.3 mmol) were dissolved in 20 mL of water, and NaCl (0.5 g, 8.5 mmol) was added. Then, the solution was kept at 288 K for 24 h. Green crystals of **1a** were formed (yield 40%). IR spectrum (KBr): 1642 (vs, ν_{asym}(OCO)), 1380 (vs, ν_{sym}(OCO)), 1080 (s, ν_{asym}(P−O)), 982 (s, ν_{asym}(W═O)), 894 (m, ν_{asym}(W−Oc−W)), 795 (br, ν_{asym}(W−Oe−W)) cm^{-1}. Elem anal. Calcd for $C_6H_{44}Cr_3Na_2O_{72}PW_{12}$: C, 1.94; H, 1.18; Cr, 4.21; Na, 1.24; P, 0.84; W, 59.51. Found: C, 1.95; H, 1.10; Cr, 4.19; Na, 1.25; P, 0.81; W, 60.75. $Rb_4[Cr_3O(OOCH)_6(H_2O)_3][\alpha\text{-BW}_{12}O_{40}]\cdot 16H_2O$ (**3a**) was synthesized as follows: $K_5BW_{12}O_{40}\cdot nH_2O$[42] (0.5 g, 0.15 mmol) and $[Cr_3O(OOCH)_6(H_2O)_3](OOCH)\cdot nH_2O$[41] (0.1 g, 0.167 mol) were dissolved in 20 mL of 0.01 M HNO_3 (pH 2), and RbCl (0.4 g, 8.5 mmol) was added. Then the solution was kept at 288 K for 24 h. Green crystals of **3a** were formed (yield 60%). IR spectrum (KBr): 1635 (vs, ν_{asym}(OCO)), 1377 (vs, ν_{sym}(OCO)), 960 (s, ν_{asym}(W═O)), 909 (s, ν_{asym}(B−O)), 823 (br, ν_{asym}(W−Oe−W)) cm^{-1}. Elem anal. Calcd for $C_6H_{44}Cr_3Rb_4O_{72}BW_{12}$: C, 1.81; H, 1.10; Cr, 3.91; Rb, 8.59; B, 0.27; W, 55.39. Found: C, 1.82; H, 1.00; Cr, 3.75; Rb, 8.72; B, 0.28; W, 55.00. The ionic crystals of $K_3[Cr_3O(OOCH)_6(H_2O)_3][\alpha\text{-SiW}_{12}O_{40}]\cdot 16H_2O$ (**2a**) and $Cs_5[Cr_3O(OOCH)_6(H_2O)_3][\alpha\text{-CoW}_{12}O_{40}]\cdot 7.5H_2O$ (**4a**) were synthesized according to refs 36 and 38, respectively. The combinations of the polyoxometalate−macrocation−alkali-metal ion for the complexation were unique, and the complexation did not occur with the other alkali-metal ions.

Preparation of the Guest-Free Phases 1b−4b. The water of crystallization in **1a**−**4a** was desorbed by evacuation or treatment in a dinitrogen flow at 298 K to form the corresponding guest-free phases of **1b**−**4b**, respectively. The weight losses for **1a**−**3a** were 8.2%, 7.6%, and 7.3%, respectively, and the respective values were in good agreement with the calculated amounts (16 mol mol^{-1}) of the water of crystallization of 7.8%, 7.6%, and 7.2%. The weight loss from **4a** to **4b** was 1.8%, and the value corresponded to a loss of 4.0 out of 7.5 mol mol^{-1} of the water of crystallization (calcd 1.7%). The remaining 3.5 molecules were desorbed by evacuation

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at 373 K. It was confirmed by thermogravimetry−mass spectrometry that only water molecules were desorbed by the treatments. The peak positions of the powder XRD patterns of **1b**−**4b** were restored to those of **1a**−**4a** by exposure to the saturated water vapor at 298 K. Therefore, the structure transformation between **1a**−**4a** and **1b**−**4b** proceeded reversibly. The IR spectra of **1b**−**4b** showed characteristic bands of the macrocations and polyoxometalates, indicating that the molecular structures of the constituent ions are retained upon loss of the water of crystallization.

Single-Crystal X-ray Analyses. The diffraction measurements of **1a** were performed on a Rigaku Mercury diffractmeter with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) and a CCD 2-D detector. The unit cell was determined from the reflections collected on the setting angles of seven frames by changing by 0.5° each frame. Two different settings were used, and the angles were changed by 0.5° per frame. Intensity data were collected with a scan width of 0.5°. Empirical absorption correction was performed. The structural analysis was performed by using the *Crystalstructure* crystallographic software package (Rigaku/MSC). The structure was solved by direct methods using the *SIR92* program[43] and expanded using Fourier techniques.[44] In the final cycle of the full-matrix least-squares refinement, tungsten, phosphorus, and chromium atoms were refined anisotropically. The other non-hydrogen elements were refined isotropically. Neutral scattering factors were obtained from the standard source.[45]

The diffraction measurement of **3a** was performed on a Rigaku AFC5R automated four-circle diffractometer. A molybdenum X-ray source equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) was used. The unit cell was determined and refined by a least-squares method using 25 independent reflections. Data were collected with a $\omega-2\theta$ scan technique at room temperature. Three standard reflections were monitored at every 200 measurements. In the reduction of the data, Lorentz and polarization corrections and an empirical absorption correction (ψ scan) were made. The structural analysis was performed by using the *SHELX-97* program.[46] The structure was solved and refined by direct methods and expanded using Fourier synthesis (*SHELX-97*). In the final cycle of the full-matrix least-squares refinement, tungsten, rubidium, chromium, oxygen, and boron atoms were refined anisotropically. Carbon atoms were refined isotropically. Neutral scattering factors were obtained from the standard source.[45] The diffraction measurements and structural analyses of **2a**, **4a**, and **4b** were described in our previous works.[36−38] The single-crystal XRD analyses were carried out at 213−293 K. Lowering the analysis temperature could prevent the removal of the water of crystallization. There are essentially no changes in the lattice parameters at 213−293 K.

Powder XRD Analyses. Powder XRD patterns were measured with XRD-DSCII (Rigaku Corp.) and Cu Kα radiation ($\lambda = 1.540\,56$ Å, 50 kV, 200 mA). The data were collected in the range of $2\theta = 4-38°$ (at 0.01° point and 0.25° min^{-1}). The measurements for **1a**−**4a** were performed in air at 303 K, and those for **1b**−**4b** were performed in a dry dinitrogen flow (300 mL min^{-1}) at 303 K. The structures of **1b**−**3b** were elucidated using Material Studio (Accelrys Inc.). The X-ray scatterings of sodium ions, potassium ions, and water molecules were much lower compared to those of polyoxometalates and macrocations containing heavy atoms (tungsten and chromium) and were negligible. Therefore, sodium ions, potassium ions, and the water of crystallization were omitted from the calculation. The calculation was performed as follows: (i) unit cell indexing and space group determination using X-cell;[47] (ii) peak profile fitting using Pawley refinement;[48] (iii) a starting model created by arrangement of the polyoxometalates and macrocations in the unit cell, the calculated powder XRD pattern compared to the experimental data, and the model optimized by the simulated annealing method;[49] and (iv) final structure refinement using the Rietveld method.[50] The R_{wp} values $[\sum w(y_i - f_i)^2/\sum w(f_i^2)^2]^{1/2}$, where y_i and f_i are the experimental and calculated diffraction intensities, respectively, were shown in parentheses: **1b** (8.93%), **2b** (12.20%), and **3b** (6.83%). The structures of **1b**−**3b** were essentially explained by the close packing of the polyoxometalates and macrocations.

Gas-Phase Sorption Measurements. Prior to the measurements, **1a**−**4a** were evacuated at 298 K to form **1b**−**4b**, respectively, until the weights were unchanged (±0.1 mg) and the pressures reached $<10^{-3}$ mmHg. Vapor sorption isotherms of **1b**−**4b** were measured with an automatic sorption apparatus at 298 K [Hydrosorb or Autosorb (Quantachrome Corp.)]. The liquid used to generate vapor was fully degassed by repeating evacuation. We regarded the following situation as the sorption equilibrium for Hydrosorb (Autosorb): the pressure of the sample cell remained unchanged within an experimental error of 0.02 mmHg (0.6 mmHg) over a period of 180 s (600 s). The saturated vapor pressures are shown in parentheses: water (3.06 kPa), methanol (15.6 kPa), ethanol (6.67 kPa), 1-propanol (2.67 kPa), 2-propanol (5.93 kPa), 1-butanol (0.86 kPa), 2-butanol (2.35 kPa), isobutyl alcohol (1.54 kPa), *tert*-butyl alcohol (5.53 kPa), acetonitrile (10.7 kPa), propionitrile (6.27 kPa), butylonitrile (2.67 kPa), isobutylonitrile (3.93 kPa), valeronitrile (2.62 kPa), benzonitrile (0.40 kPa at 313 K), 1,2-dichloroethane (10.5 kPa), 1,4-dioxane (4.67 kPa), methyl formate (78.0 kPa), methyl acetate (28.8 kPa), methyl propionate (16.0 kPa), ethyl acetate (12.9 kPa), and ethyl propionate (4.97 kPa). The P_0 value for dimethyl ether, nitrogen monoxide, and dinitrogen was 101.3 kPa.

Liquid-Phase Sorption Measurements. The selective sorption of ethanol from a mixture of C2−C4 alcohols by **1b** was carried out under the following conditions: Finely ground **1b** (0.1 mmol) was placed in a Pyrex glass tube with a Teflon-coated stir bar, and 3 mL of a 1,2-dichloroethane solution containing ethanol (1.2 mmol), 1-propanol (1.2 mmol), and 1-butanol (1.2 mmol) was added under an argon flow. The concentrations of alcohols were analyzed by gas chromatography (GC; Shimadzu GC-8A model with a Porapak QS column and a thermal conductivity detector). Chlorobenzene was added as an internal standard. The uptake of alcohols by **1b** was evaluated by the decreases in the alcohol concentrations in the solution (experimental errors, ±10%). The amounts of alcohols sorbed by **1b** were evaluated as follows: After the sorption experiments, the liquid was decanted and the solid was washed with chlorobenzene (three times). Next, 0.5 mL of water was added to the solid, and the suspension was kept at 373 K for 1 h to wash out the alcohols in the solid. The suspension was filtered, and *tert*-butyl alcohol was added to the filtrate (total volume: 3 mL). The amounts of alcohols in the filtrate were analyzed by GC. The selective sorption of valeronitrile from a mixture of valeronitrile

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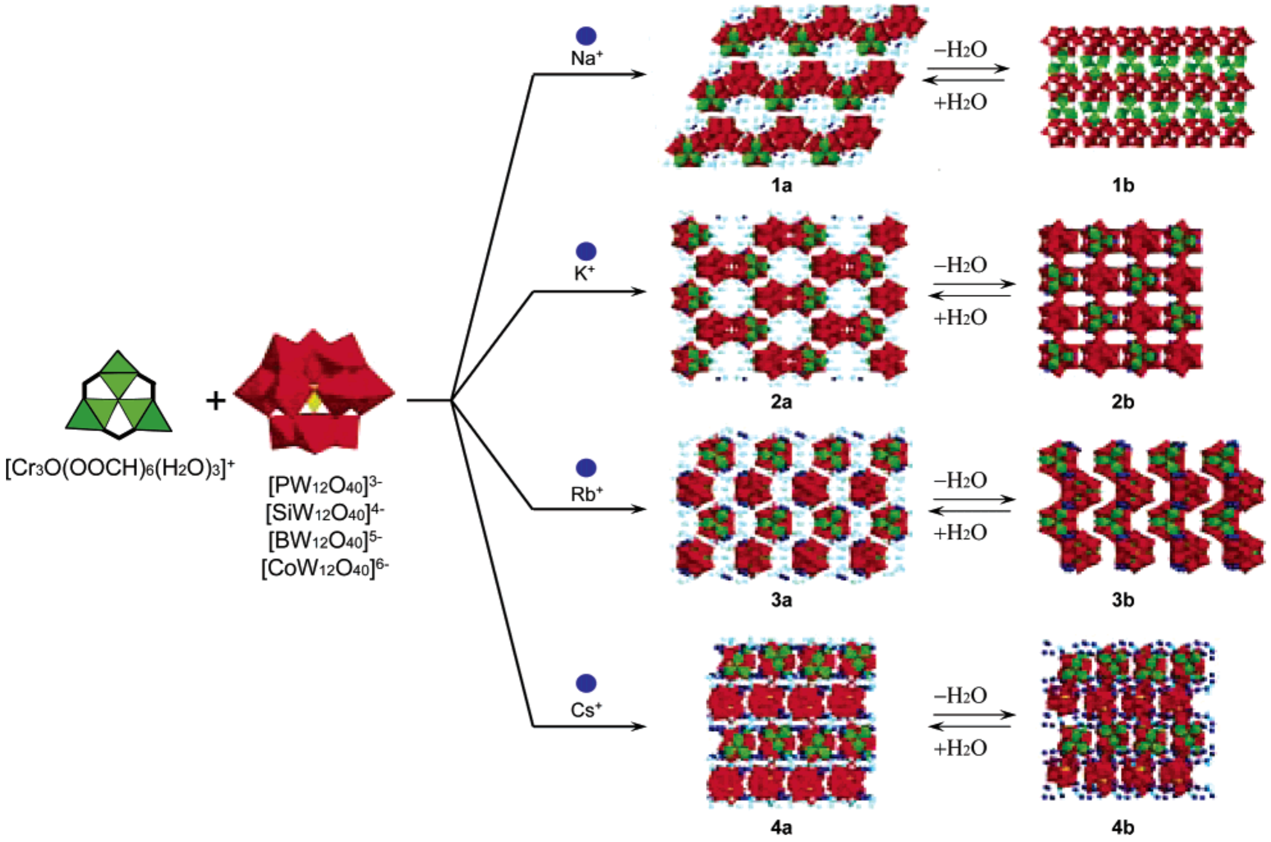

Figure 1. Schematic illustration of the syntheses and crystal structures of **1a**−**4a** and **1b**−**4b**. Red and green polyhedra showed the $[WO_6]$ units of the polyoxometalate and the $[CrO_6]$ units of the macrocation, respectively. Blue and light-blue spheres show the alkali-metal ions and the water of crystallization, respectively.

Table 1. Crystallographic Data

	1a	**2a**	**3a**	**4a**	**4b**
formula	$C_6Cr_3Na_2O_{70.5}PW_{12}$	$C_6Cr_3K_3O_{68}SiW_{12}$	$C_6BCr_3O_{72}Rb_4W_{12}$	$C_6CoCr_3Cs_5O_{63.5}W_{12}$	$C_6CoCr_3Cs_5O_{58}W_{12}$
fw	3639.17	3667.45	3938.74	4173.68	4085.68
crystal system	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$C2/m$ (No. 12)	$Pnma$ (No. 62)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	15.324(3)	27.258(4)	24.680(10)	12.642(3)	12.3267(11)
b, Å	16.398(3)	15.764(6)	16.137(5)	19.337(5)	18.641(2)
c, Å	16.788(3)	17.285(4)	17.281(9)	24.341(6)	24.487(3)
α, deg	60.391(12)	90	90	90	90
β, deg	70.93(1)	102.73(2)	90	89.644(4)	92.332(2)
γ, deg	72.71(2)	90	90	90	90
V, Å^3	3418.6(12)	7245(3)	6882(5)	5950.4(23)	5622.1(10)
Z	2	4	4	4	4
D_c, g cm^{-3}	3.535	3.363	3.803	4.659	4.827
temp, K	213(2)	293(2)	293(2)	123(2)	303(1)
μ(Mo Kα), mm^{-1}	20.731	19.694	23.352	27.050	28.618
no. of measd reflns	27 350	10 885	10 375	48 518	35 028
no. of obsd reflns	12425 [$I > 3\sigma(I)$]	10375 [$I > 2\sigma(I)$]	10375 [$I > 2\sigma(I)$]	13983 [$I > 3\sigma(I)$]	9573 [$I > 3\sigma(I)$]
no. of param refined	469	449	456	479	421
R1,[a] wR2	0.0510, 0.0630	0.0590, 0.1446	0.0649, 0.1497	0.0450, 0.0560	0.0930, 0.1150

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$.

and capronitrile and that of methyl propionate from a mixture of methyl propionate and ethyl propionate by **1b** were carried out under the same conditions as those for the alcohols described above, except for the initial concentrations of esters (0.6 M) and nitriles (2.0 M) in the solution.

The selective sorptions of methanol from a mixture of C1−C3 alcohols, of methyl formate from a mixture of methyl formate and methyl acetate, and of acetonitrile from a mixture of acetonitrile and propionitrile by **2b** were carried out under the same conditions as those for **1b**. The selective sorption of methanol from a mixture of C1−C3 alcohols by **3b** was carried out under the same conditions as those for **1b**. The selective sorption of water from a mixture of water and C1−C2 alcohols by **4b** was also carried out under the same conditions as those for **1b**, except for the initial concentrations of water and alcohols (0.3 M) in the solution.

Results and Discussion

Crystal Structures of 1a−4a. The schematic illustration of the syntheses and crystal structures of compounds **1a**−**4a** is shown in Figure 1. The crystallographic data are summarized in Table 1. Elemental analyses of **1a**−**4a** showed that the macrocation/polyoxometalate ratios were 1:1 and the stoichiometry in the complexes formed did not change among **1a**−**4a**, while the macrocation/polyoxometalate ratio in the synthetic solution was varied. The surplus anion charge was neutralized by the alkali-metal ions. The polyoxometalates and macrocations lined up alternately to form columns, which were arranged in a honeycomb (**1a** and **2a**) or layered structure (**3a**) or were densely packed (**4a**). The distance between the carbon atoms of the bridging formates in the macrocations and the oxygen atoms of the polyoxometalates in the same column were in hydrogen-bonding distances (C−H···O distances were 3.25−3.37, 3.09−3.27, 2.79−3.06, and 2.81−3.07 Å for **1a**−**4a**, respectively). The spaces between the columns were occupied with the water of crystallization, and the space volumes for **1a**−**4a** corresponded to 36%, 36%, 32%, and 17% of the crystal lattices, respectively.

The water of crystallization in **1a**−**4a** was either in the vicinity of the alkali-metal ion or hydrogen-bonded to the constituent ions (polyoxometalate and macrocation) or to the other water molecules. The water of crystallization in **1a**−**3a** was completely desorbed by evacuation at room temperature, while about 50% of the water of crystallization in **4a** was desorbed. The respective **1a**−**4a** after evacuation at room temperature were denoted by **1b**−**4b**. The observed XRD patterns of **1b**−**4b** (Figure 2) were fairly well reproduced by the structures **1b**−**4b** (Figure 1), respectively. The structures **1b**−**4b** showed the close packing of the columns. The calculated cell volumes per formula (V/Z) were in the order of **1b** (1497 Å^3) > **2b** (1467 Å^3) > **3b** (1412 Å^3) > **4b** (1406 Å^3). The decrease in the cell volumes would be related to the increase in the anion−cation interactions because of the close packing of the constituent ions with an increase in n of $[\alpha\text{-XW}_{12}\text{O}_{40}]^{n-}$ (X = Co, B, Si, P). The Brunauer−Emmett−Teller surface areas of **1b**−**4b** were small (<2 m^2 g^{-1}) in accordance with the close packing of the columns where no micropores existed. The crystal structures of **1a**−**4a** were completely restored by exposure of **1b**−**4b** to the saturated water vapor.

Recognition of Small Polar Molecules by 1b−4b. Parts A−C of Figure 3 show the sorption isotherms of **1b** at 298 K. The amount of water sorption increased with an increase in the vapor pressure and reached 16 mol mol^{-1} at P/P_0 = 0.85 (Figure 3A). The amount was equal to the amount of the water of crystallization in **1a**. The desorption branch overlapped with the sorption branch at high pressures, while a hysteresis existed at low pressures. Similar isotherms of polar adsorbents have been reported for montmorillonite. The low-pressure hysteresis has been explained by the specific host−guest interaction, which alters the crystal structure of the host and allows the guest to escape only very slowly during the desorption run.[51−54] A hysteresis similar to that for the water sorption by **1b** was confirmed for the water sorption by **2b** and **3b** and for the sorption of ethanol by **1b** and **2b** (Figures S1 and S2 in the Supporting Information).

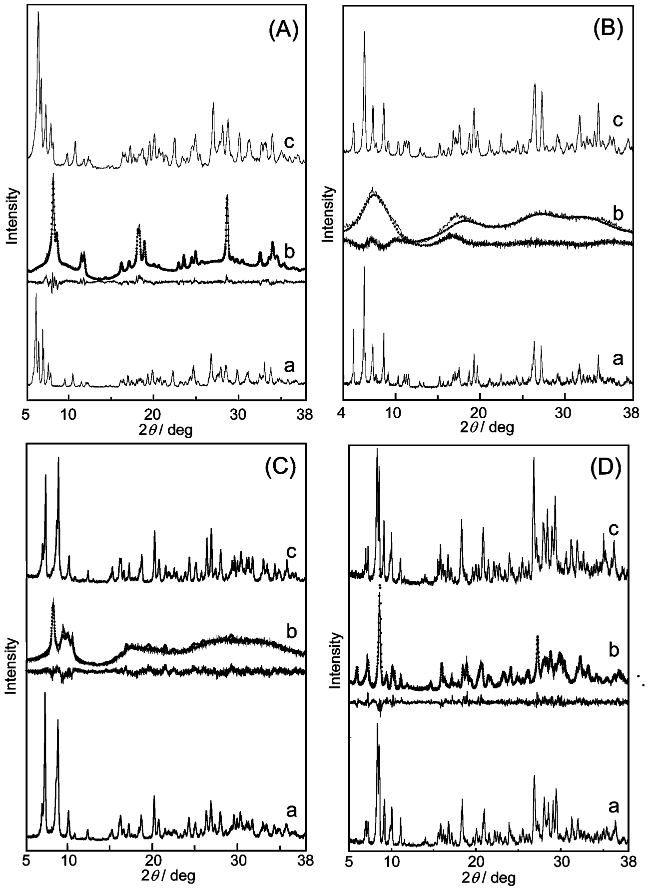

Figure 2. Powder XRD patterns of (A) **1a** (a), **1b** (b), and **1b** (c) after exposure to saturated water vapor, (B) **2a** (a), **2b** (b), and **2b** (c) after exposure to saturated water vapor, (C) **3a** (a), **3b** (b), and **3b** (c) after exposure to saturated water vapor, and (D) **4a** (a), **4b** (b), and **4b** (c) after exposure to saturated water vapor. The calculated patterns (dotted lines) were overlaid with the experimental patterns (solid lines). The difference between the experimental and calculation data was shown under the patterns.

Compound **1b** reversibly sorbed various kinds of polar hydrogen-bonding (hydrophilic) organic molecules such as alcohols, nitriles, and esters as well as water. As for ≥C2 alcohols, nitriles, and esters, the amounts were small at P/P_0 = 0.2 and increased suddenly at definite pressures (gate pressures). Neither non-hydrogen-bonding (hydrophobic) dichloromethane and dichloroethane nor molecules without or with small polarity such as nitrogen monoxide, dinitrogen, and methane were sorbed despite the small sizes. Compound **2b** sorbed water, methanol, ethanol, acetonitrile, and methyl formate (Figure 3D). Compound **3b** sorbed water and methanol, and **4b** sorbed only water (Figure 3E,F). Parts A−D of Figure 4 show the effects of the dipole moments and sizes of guest molecules on the sorption properties of **1b**−**4b** (P/P_0 = 0.8, 298 K). The sorption properties of **1b**−**4b** depended on not only the dipole moments but also the molecular sizes.

Parts A−C of Figure 5 show the effects of the charges of polyoxometalates on the amounts of sorption of polar organic molecules of alcohols, nitriles, and esters. Compounds **1b**−**3b** sorbed alcohols up to C4 (1-butanol), C2 (ethanol), and

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(51) Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*; Academic Press: London, 1982; p 237.
(52) Mooney, R. W.; Keenan, A. G.; Wood, L. A. *J. Am. Chem. Soc.* **1952**, *74*, 1367.
(53) Barrer, R. M.; MacLeod, D. M. *Trans. Faraday Soc.* **1954**, *50*, 980.
(54) Yamanaka, S.; Kanamaru, F.; Koizumi, M. *J. Phys. Chem.* **1974**, *78*, 42.

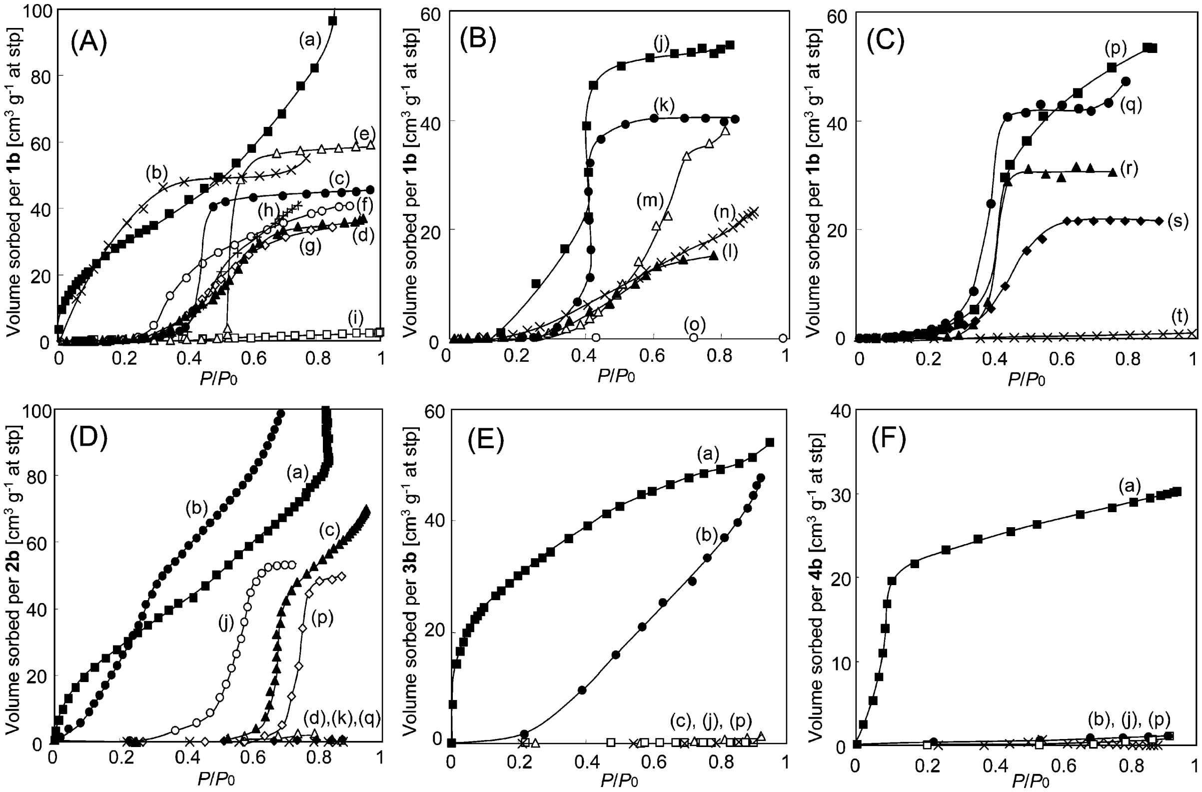

Figure 3. Sorption isotherms of (A) alcohols, (B) nitriles, and (C) esters for **1b** at 298 K. Sorption isotherms for (D) **2b**, (E) **3b**, and (F) **4b** at 298 K. (a) Water, (b) methanol, (c) ethanol, (d) 1-propanol, (e) 2-propanol, (f) 1-butanol, (g) 2-butanol, (h) isobutyl alcohol, (i) *tert*-butyl alcohol, (j) acetonitrile, (k) propionitrile, (l) butylonitrile, (m) isobutylonitrile, (n) valeronitrile, (o) benzonitrile (313 K), (p) methyl formate, (q) methyl acetate, (r) ethyl acetate, (s) methyl propionate, and (t) ethyl propionate.

C1 (methanol), respectively, and **4b** sorbed no alcohols. Compound **1b** sorbed nitriles up to C5 (valeronitrile) while **2b** sorbed only acetonitrile (C2), and **3b** and **4b** excluded even acetonitrile. Compound **1b** sorbed esters up to methyl propionate (C4) while **2b** sorbed only methyl formate, and **3b** and **4b** excluded even methyl formate. Thus, polar small organic molecules such as alcohols, nitriles, and esters (≤C5) could be discriminated with **1b**−**4b**, and an increase in *n* of $[\alpha\text{-XW}_{12}\text{O}_{40}]^{n-}$ enabled the sorption of molecules with the shorter methylene chain.

The nature of the sorption of alcohols by **1b** is probably explained as follows. Because the structures of **1b** showed the close packing of the constituent ions, the lattice volumes of **1b** need to increase with the sorption. The energy needed for the lattice expansion (E_1[55]) is compensated for by the ion−dipole and hydrogen-bonding interactions between the alcohols and **1b** (E_{int}[56]) (Scheme 1), as was reported for the sorption of water by **2b**.[37] If E_{int} is larger than E_1, the guest sorption energy ($E_{\text{int}} - E_1$) becomes >0 and the alcohols can be sorbed into the solid bulk. E_{int} is proportional to the dipole moment of the alcohol and inversely proportional to the ion−dipole (host−guest) distance. The dipole moments of C1−C4 alcohols (1.59−1.70 D) are almost independent of the carbon numbers, while the sizes (4.78−6.34 Å in diameter) increase with the carbon numbers (Figure 4A). Therefore, E_{int} decreases or does not change much with an increase in the carbon numbers. On the other hand, the volumes of alcohols are proportional to the third power of the sizes and increase with an increase in the carbon numbers, resulting in an increase in E_1 (Table S1 in the Supporting Information). Therefore, the value of $E_{\text{int}} - E_1$ turns negative at a certain alcohol (*tert*-butyl alcohol), and **1b** sorbs alcohols up to 1-butanol.

E_1 much increases with an increase in *n* of $[\alpha\text{-XW}_{12}\text{O}_{40}]^{n-}$ (from **1b** to **4b**); for example, 18, 37, 67, and 104 kJ mol^{-1} for the sorption of methanol by **1b**, **2b**, **3b**, and **4b**, respectively. On the other hand, E_{int} probably less increases or decreases because the number of the alkali metal, which can work as a sorption site in addition to the macrocation and polyoxometalate, increases from 2 (**1b**) to 5 (**4b**) while the ionic radii increase and the interaction

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(55) Lattice energies needed for expansion from **1b**−**4b** to the corresponding guest-included phases (1 mol mol^{-1}) were calculated by the equation of $E_1 = \text{A}I/(V/2I)^{1/3}$, where *V* and *I* are the lattice volume (kJ mol^{-1}) and ionic strength ($I = 1/2\sum n_i Z_i$, where n_i is the number of ions with integer charge Z_i), respectively. *A* is a constant (121.4 kJ mol^{-1}). (See: Glasser, L.; Jenkins, H. D. B. *J. Am. Chem. Soc.* **2000**, *122*, 632.) The molecular volumes are calculated with the molecular weights and densities of liquids at 293 K, assuming the cubic close-packed structures of the molecules.

(56) E_{int} between the host−guest can be calculated according to the equation of $E_{\text{int}} = -\sum(Q\mu/4\pi\epsilon_0 r^2) \times N_{\text{A}}$, where *Q*, *μ*, and *r* are the charge of the constituent ion (C), the dipole moment of the guest (D), and the ion−dipole (host−guest) distance, respectively. ϵ_0 and N_{A} are the dielectric constant of vacuum (8.854×10^{-12} J^{-1} C^2 m^{-1}) and Avogadro's number (6.022×10^{23} mol^{-1}), respectively. (See: Atkins, P. W. *Physical Chemistry*; Oxford University Press: Oxford, U.K., 1990; Chapter 22.)

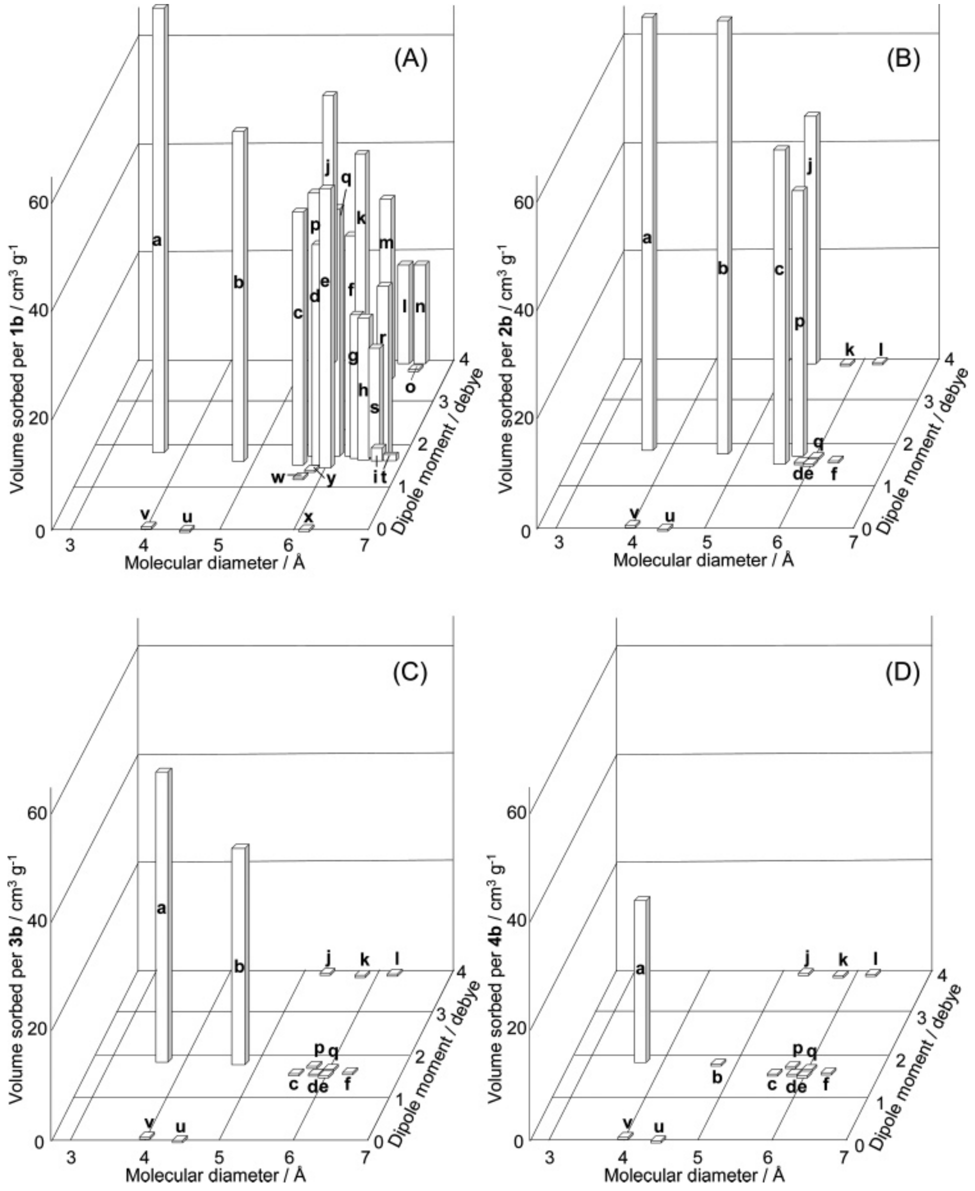
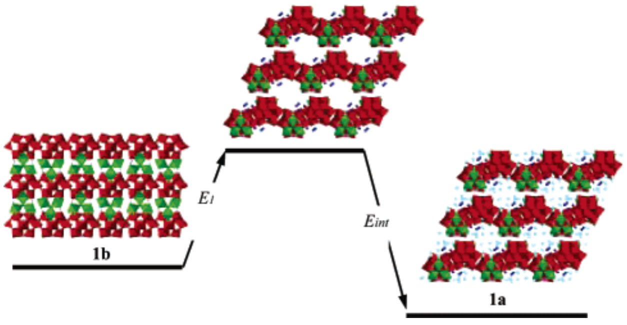


Figure 4. Effects of the sizes and dipole moments of guest molecules on the sorption properties of **1b**−**4b** ($P/P_0 = 0.8$ at 298 K): (A) **1b**; (B) **2b**; (C) **3b**; (D) **4b**. Parts a−t are the same as those of Figure 3. (u) Dinitrogen, (v) nitrogen monoxide, (w) dimethyl ether, (x) 1,4-dioxane, and (y) 1,2-dichloroethane.

is weakened. Therefore, the value of $E_{\text{int}} - E_1$ decreases from **1b** to **4b**, and the upper limit of the carbon numbers of alcohols sorbed into the bulk of **1b**−**4b** decreases with *n*. The nature of the sorption of nitriles and esters by **1b**−**4b** would be explained in the same way as that for alcohols (Tables S2 and S3 in the Supporting Information).

The selective sorption properties of **1b**−**4b** were successfully applied to the separation of mixtures of alcohols, nitriles, esters, and water in 1,2-dichloroethane at 298 K. Ethanol was selectively sorbed by **1b** from a mixture (1:1:1) of C2−C4 alcohols (Figure 6A-1). Methanol was selectively sorbed by **2b** and **3b** from a mixture (1:1:1) of C1−C3 alcohols (parts B-1 and C of Figure 6). Water was selectively sorbed by **4b** from a mixture (1:1:1) of water, methanol, and ethanol (Figure 6D). Thus, ethanol, methanol, and water could be separated from mixtures of C2−C4 alcohols, C1−C3 alcohols, and water + C1−C2 alcohols, respectively. In the case of the separation of nitriles, valeronitrile was selectively sorbed by **1b** from a mixture (1:1) of valeronitrile and capronitrile (Figure 6A-2). Acetonitrile was selectively sorbed by **2b** from a mixture (1:1) of acetonitrile and propionitrile (Figure 6B-2). As for the separation of esters, methyl propionate was selectively

Scheme 1. Model of the Effects of Energy Changes of the Host (**1**) upon the Guest Sorption



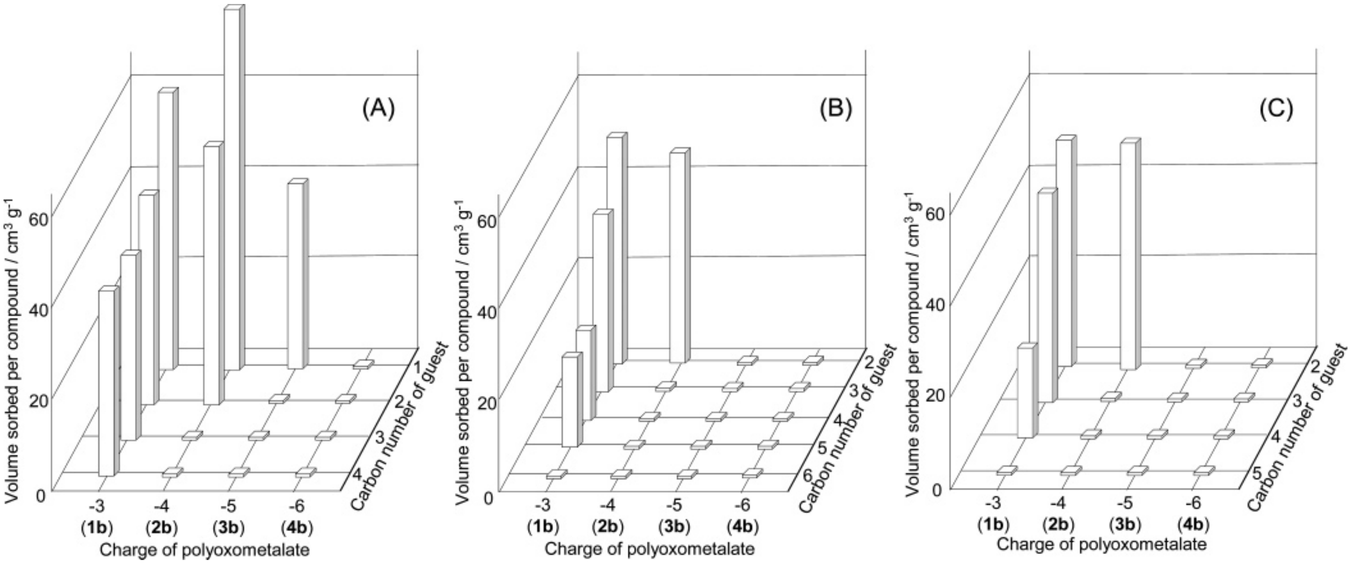


Figure 5. Effects of the charges of polyoxometalates on the amounts of sorption of polar organic molecules ($P/P_0 = 0.8$ at 298 K). (A) Amounts of sorption of alcohols. C1−C4 guests are methanol, ethanol, 1-propanol, and 1-butanol, respectively. (B) Amounts of sorption of nitriles. C2−C5 guests are acetonitrile, propionitrile, butylonitrile, and valeronitrile, respectively. (C) Amounts of sorption of esters. C2−C5 guests are methyl formate, methyl acetate, methyl propionate, and ethyl propionate, respectively.

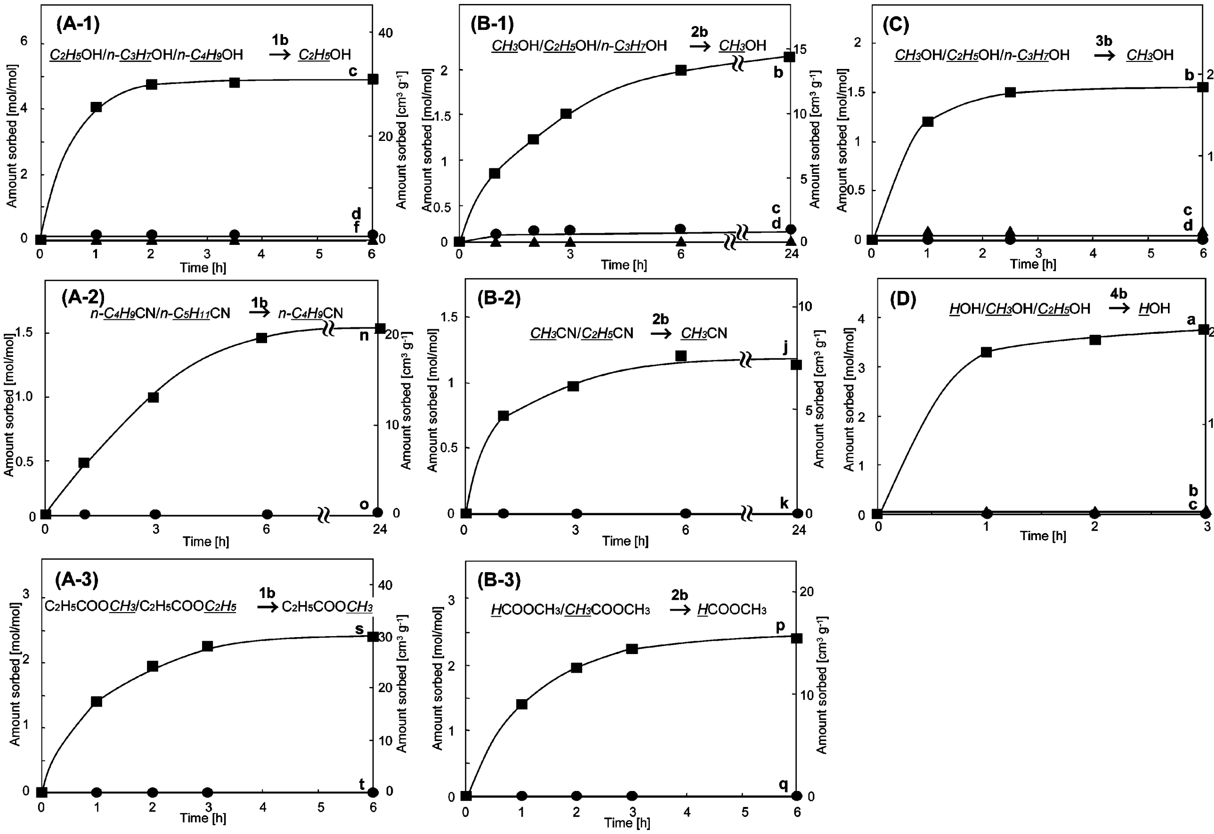


Figure 6. Selective sorption of polar organic molecules by **1b**−**4b** in 1,2-dichloroethane at 298 K. Sorption of (A-1) alcohols, (A-2) nitriles, and (A-3) esters by **1b**. Sorption of (B-1) alcohols, (B-2) nitriles, and (B-3) esters by **2b**. (C) Sorption of alcohols by **3b**. (D) Sorption of water and alcohols by **4b**. Initial conditions: 1.2 mmol of alcohols (1.0 mmol for **4b**), 6.0 mmol of nitriles, or 1.8 mmol of esters; 0.1 mmol of **1b**−**4b**. Total volume of the solution: 3 mL. Internal standard: chlorobenzene. Parts a−d, f, j, k, n, p, q, s, and t are the same as those of Figure 3 except for (o) capronitrile.

sorbed by **1b** from a mixture (1:1) of methyl propionate and ethyl propionate (Figure 6A-3). Methyl formate was selectively sorbed by **2b** from a mixture (1:1) of methyl formate and methyl acetate (Figure 6B-3). Thus, the ionic crystals of **1b**−**4b** could separate polar organic molecules such as alcohols, nitriles, and esters by one methylene chain.

Conclusion

A series of ionic crystals **1a**−**4a** and the respective guest-free phases **1b**−**4b**, composed of α-Keggin-type polyoxometalate ($[\alpha\text{-XW}_{12}O_{40}]^{n-}$), macrocation $[Cr_3O(OOCH)_6(H_2O)_3]^+$, and alkali-metal ion, were synthesized, and the crystal structures were solved by single-crystal or powder XRD methods. The space volumes decreased in the order of **1a** > **2a** > **3a** > **4a**. The cell volumes decreased in the order of **1b** > **2b** > **3b** > **4b**, which would be related to an increase in the anion−cation interactions with an increase in n of $[\alpha\text{-XW}_{12}\text{O}_{40}]^{n-}$ (X = Co, B, Si, P). Compounds **1b**−**4b** discriminated ≤C5 polar organic molecules, and a decrease in n enabled the sorption of molecules with the longer methylene chain. All of these results show the fine control of the sorption properties of small organic molecules with rationally designed ionic crystals.

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Supporting Information Available: Figures S1 and S2 showing the full ethanol sorption isotherms of **1b** and **2b**, respectively, Tables S1−S3 showing the lattice energies needed for the expansion of **1b**−**4b** for ≤C5 molecules (water, alcohols, nitriles, and esters), and X-ray crystallographic files of **1a**−**4a** and **4b** (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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