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Title	Highly Selective Sorption of Small Polar Molecules by a Nonporous Ionic Crystal of a Lacunary Keggin-type Heteropoly Anion and Alkali Metal Cations
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Supporting information for

**Highly selective sorption of small polar molecules by a nonporous ionic crystal of
a lacunary Keggin-type heteropoly anion and alkali-metal cations**

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Experimental

Synthesis of $\text{K}_7\text{PW}_{11}\text{O}_{39}\cdot n\text{H}_2\text{O}$:

$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$ (20.7 g, 6.29 mmol) was dissolved in water (100 mL), followed by addition of KCl (1.00 g, 13.4 mmol) with vigorous stirring. To the resulting solution, an aqueous solution of KHCO_3 (1 mol L^{-1}) was added, and the pH of the solution was adjusted to *ca.* 5.5. The resulting solution was filtered to remove insoluble material. The filtrate was concentrated on a rotary evaporator at 313 K to afford a white precipitate. After the white solid ($\text{K}_7\text{PW}_{11}\text{O}_{39}\cdot n\text{H}_2\text{O}$) was separated by filtration, it was dried under ambient conditions.

Synthesis of $\text{Cs}_7\text{PW}_{11}\text{O}_{39}\cdot n\text{H}_2\text{O}$:

2 was recrystallized to synthesize $\text{Cs}_7\text{PW}_{11}\text{O}_{39}\cdot n\text{H}_2\text{O}$ as follows: Ten gram of **2** was added to water (100 mL) and heated at 343 K with stirring. After insoluble matter was filtered off, an aqueous solution of CsCl (0.5 mol L^{-1} , 20 mL) was added to the filtrate at room temperature and allowed to stand for several days. The formed white-solid was collected by filtration (yield; 4.5 g). A portion of the solid (0.2 g) was added to water (10 mL) again and heated at 343 K with stirring. After insoluble matter was filtered off, an aqueous solution of CsCl (0.5 mol L^{-1} , 10 mL) was added to the filtrate at room temperature and allowed to stand for several days. Finally, the resulting solid ($\text{Cs}_7\text{PW}_{11}\text{O}_{39}\cdot n\text{H}_2\text{O}$, yield; 0.12 g) was dried under ambient conditions.

The elemental analysis showed that the compositions of Cs, K, P, and W were 27.2, 0.028, 0.92, and 54.1 wt%, respectively, which were basically consistent with those calculated based on the formula $\text{Cs}_7\text{PW}_{11}\text{O}_{39}$ (Cs 25.8, K 0, P 0.86, and W 56.1 wt%).

Synthesis of $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$:

The material was prepared following a published procedure (T. Okuhara, H. Watanabe, T. Nishimura, K. Inumaru and M. Misono, *Chem. Mater.*, 2000, **12**, 2230–2238).

Characterization:

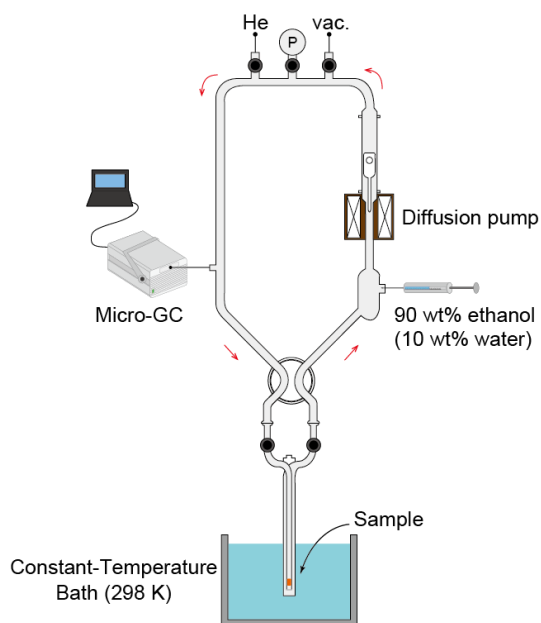
Nitrogen adsorption isotherm was measured at 77 K using a BELSORP-mini (BEL Japan Inc.) after pretreatment at 473 K for 2 h under N₂ flow (50 mL min⁻¹). Elemental analysis was carried out by Mikroanalytisches Labor Pascher (Remagen-Bandorf, Germany) for H, K, Cs, P, and W. Infrared spectra of the samples were measured as KBr disks on a FT-IR-230 (JASCO). Powder X-ray diffraction (XRD) patterns of the solid samples were measured on an XRD diffractometer (Miniflex, Rigaku) with CuK α radiation. Thermogravimetric analysis (TG) was performed using a Thermo Plus TG8120 (Rigaku) in a He flow (50 mL min⁻¹) at a rate of 10 K min⁻¹.

Vapor sorption measurement:

Sorption isotherms of various molecules (water, methanol, ethanol, 1-propanol, *n*-hexane, benzene, and acetonitrile) were acquired on a BELSORP-18 (BEL Japan Inc.) at 298 K. Before measurement, the sample was pretreated in a vacuum at 473 K for 3 h or at 298 K overnight.

Selective removal of water in water-ethanol mixed gas:

Selective removal of water in water-ethanol mixed gas was carried at 298 K in a closed gas-circulation system with an online gas chromatograph (Agilent Technology Co. Ltd, 3000 A Micro GC) shown below.



The sample (0.2 g) was pretreated at 473 K for in a vacuum before the removal experiment. After the temperature of the sample was decreased to 298 K, first He was introduced to the system at 101.7

kPa and then a mixture of ethanol (1.17 mg, 25.4 μmol) and water (0.13 mg, 7.2 μmol) was introduced. The concentrations of ethanol and water in the gas phase were periodically measured with the gas chromatograph.

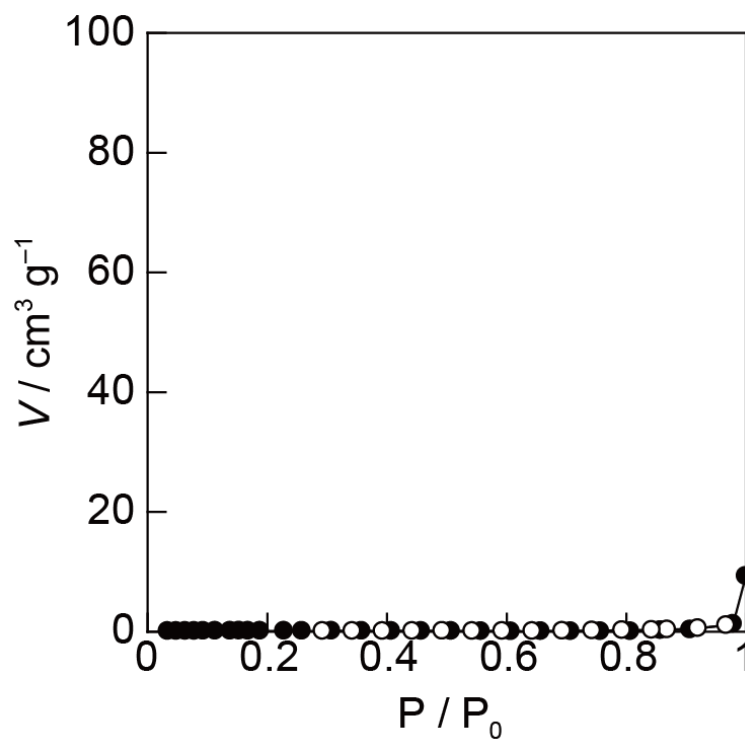


Figure S1 Adsorption-desorption isotherm of N_2 for **1** at 77 K. The BET surface area of **1** was calculated to be $0.9 \text{ m}^2 \text{g}^{-1}$.

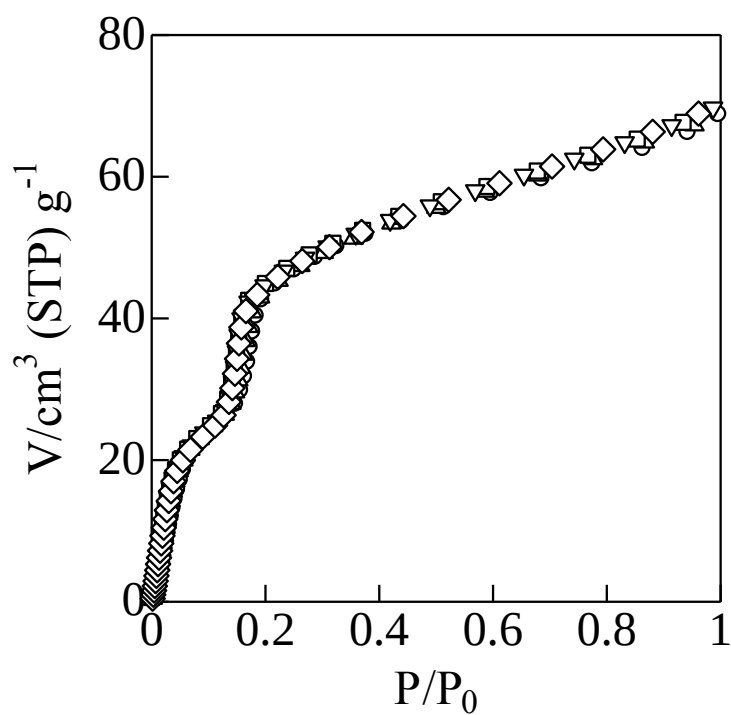


Figure S2 Sorption isotherms of water for **1** at 298 K. Before the first measurement, **2** was pretreated at 473 K in a vacuum for 3 h to transform it into **1**. After the completion of the first measurement, the sample was again treated at 473 K in a vacuum for 3 h, and then the next sorption isotherm was acquired. The sorption isotherms were measured five times in total. The five sorption isotherms were consistent.

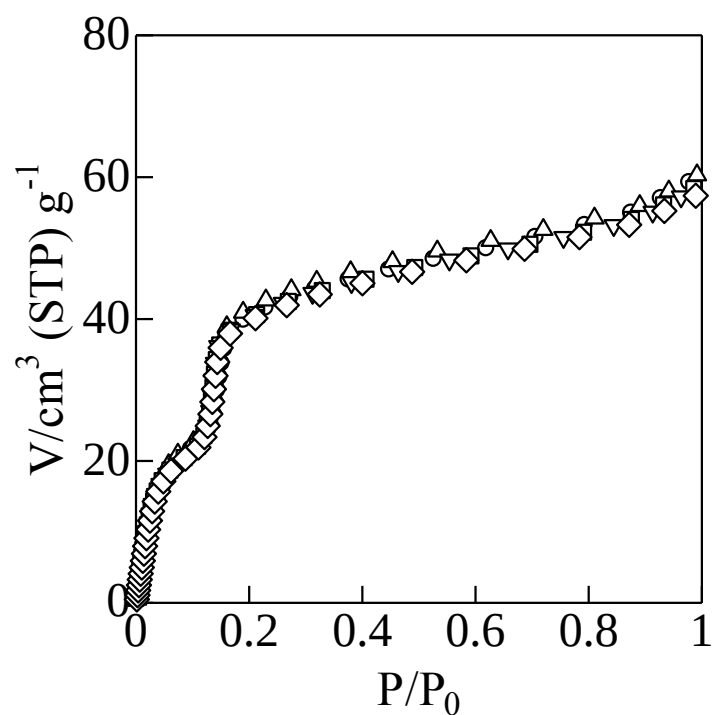


Figure S3 Sorption isotherms of water for **1** at 298 K. Before the first measurement, **2** was pretreated in a vacuum at 298 K overnight. After the completion of the first measurement, the sample was treated again in a vacuum at 298 K overnight, and then the next sorption isotherm was acquired. The sorption isotherms were measured five times in total. The five sorption isotherms were consistent.

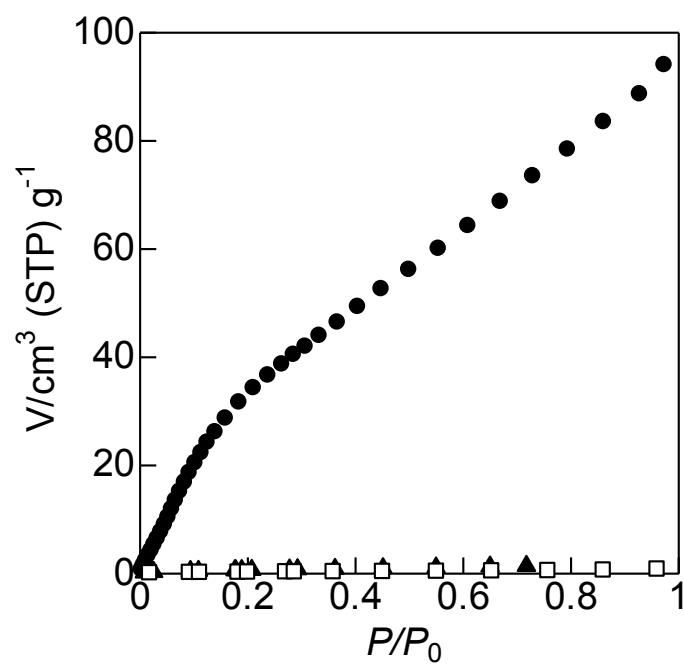


Figure S4 Sorption isotherms for $\text{K}_7\text{PW}_{11}\text{O}_{39}$ at 298 K. ($\bullet$) water, $P_0 = 3.17$ kPa, ($\blacktriangle$) methanol, $P_0 = 16.9$ kPa, and ($\square$) ethanol, $P_0 = 7.87$ kPa.

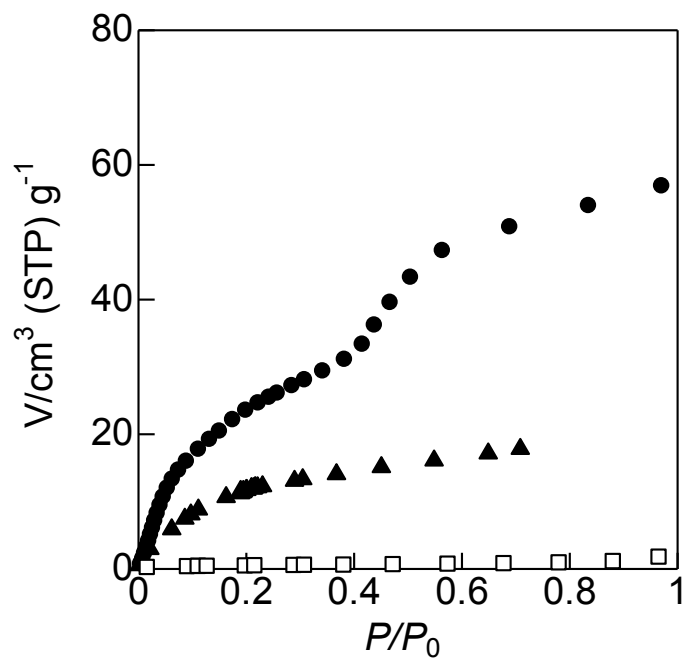


Figure S5 Sorption isotherms for $\text{Cs}_7\text{PW}_{11}\text{O}_{39}$ at 298 K. ($\bullet$) water, $P_0 = 3.17$ kPa, ($\blacktriangle$) methanol, $P_0 = 16.9$ kPa, and ($\square$) ethanol, $P_0 = 7.87$ kPa.

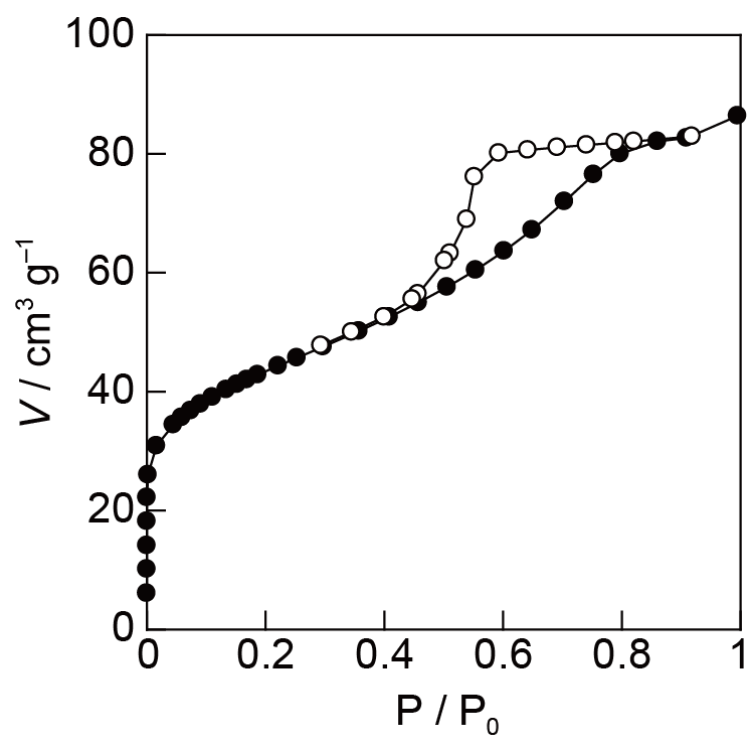


Figure S6 Adsorption-desorption isotherm of N_2 for $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ at 77 K. The BET surface area of **1** was calculated to be $130 \text{ m}^2 \text{g}^{-1}$.

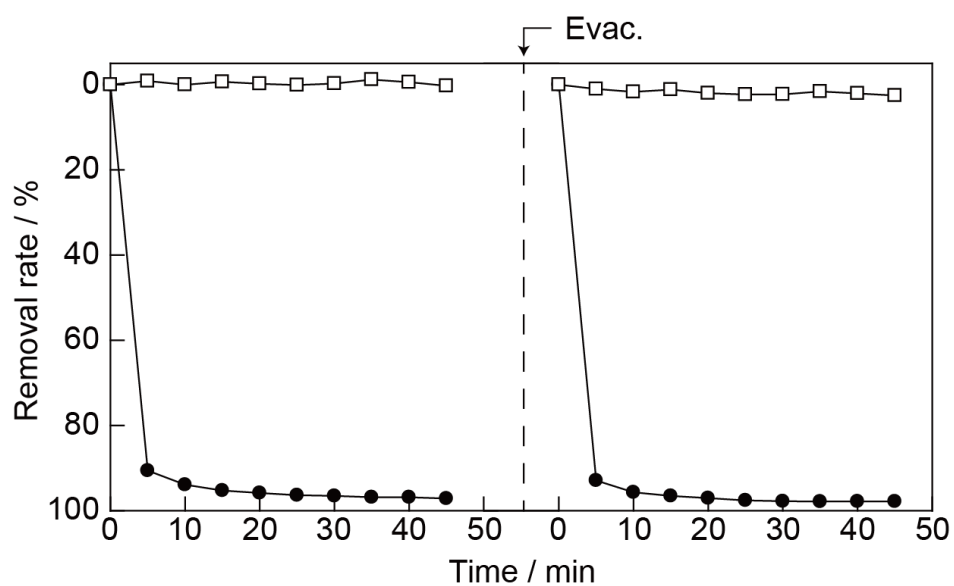


Figure S7. Reusability test of **1** in selective removal of water- from water-ethanol mixed gas at 298 K. (●) water and (□) ethanol. After the first run, the whole system including the sample holder filled with **1** was evacuated at 298 K overnight and then the mixture of water and ethanol was introduced. The experimental conditions were the same as those for Figure 4.

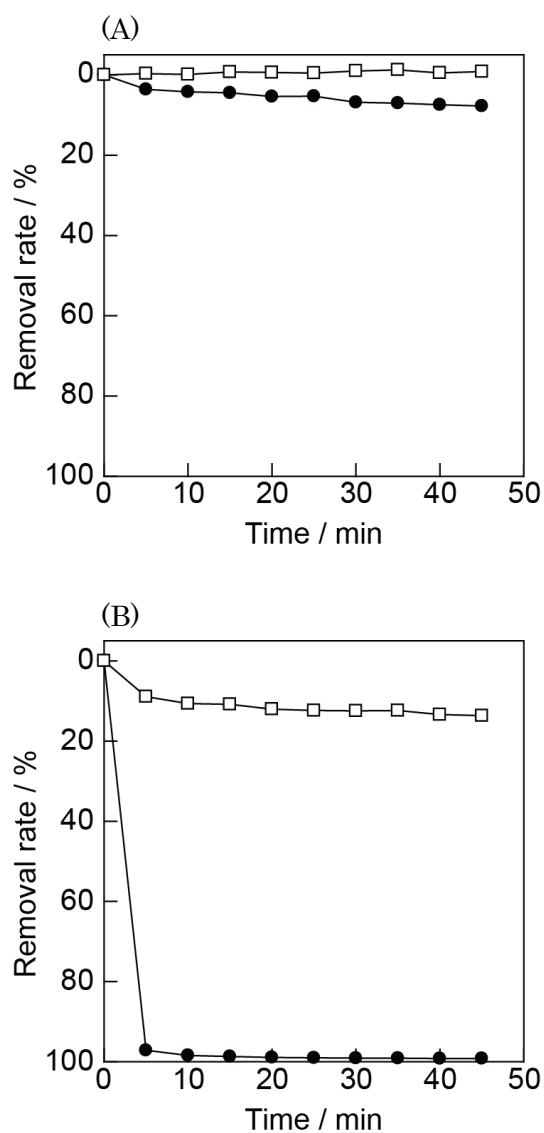


Figure S8. Removal of water- from water-ethanol mixed gas over (A) Na_2SO_4 and (B) molecular sieves 3A at 298 K. (●) water and (□) ethanol. The experiment was carried out in a closed gas-circulation system. Initial amounts of water and ethanol were 7.2 and 25.4 μmol , respectively and weight of the sample was 0.2g. Before the experiment, Na_2SO_4 and molecular sieves 3A were pretreated in a vacuum for 2 h at 473 and 673 K, respectively.