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Communication

Stepwise Guest Adsorption with Large Hysteresis in a Coordination Polymer {[Cu(bhnq)(THF)$_2$](THF)}$_n$ Constructed from a Flexible Hingelike Ligand

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Reversible vapochromic behavior of a porous copper(II) coordination polymer {[Cu(bhnq)(THF)$_2$](THF)}$_n$ (**1**; THF = tetrahydrofuran) constructed from a flexible hingelike ligand H$_2$bhnq [2,2′-bis(3-hydroxy-1,4-naphthoquinone)] has been investigated by adsorption measurements. The isotherms show large hysteretic and stepwise profiles, suggesting the occurrence of the guest-induced framework transformation. The dynamic coil-like behavior of **1** can be controlled through the change of the hydrogen-bonding interactions caused by the reversible and selective incorporation of guest molecules.

Considerable effort has been devoted to the synthesis and characterization of new crystalline nanosized porous materials, such as coordination polymers and inorganic zeolites, because of their versatile applicability to gas storage, molecular sieves, size- or shape-selective catalysis, and ion exchange.[1] It has been believed that a robustness of the host porous framework is a prerequisite for their successful performance, while flexibility is incompatible with the porous properties because it would lead to a collapse of the framework.[2] On the other hand, metalloproteins take advantage of their structural flexibility, which is essential for their molecular recognition capability. Induced-fit theory illustrates the high selectivity in the binding of a substrate to an enzyme, which undergoes conformational change to suite the molecular shape.[3] Therefore, the structural flexibility of the host framework would be a key principle for high selectivity recognition, accommodation, and separation of a target molecule. The creation of the host framework that can interact with guest species in a switchable fashion has implications for the generation of previously undeveloped advanced materials with potential applications in molecular sensing. In this context, it is of significance to design and prepare a structure that can both shrink and expand in response to the presence and absence of a guest molecule.[4]

A porous coordination polymer [Cu(bhnq)(L)$_2$]$_n$ [H$_2$bhnq = 2,2′-bis(3-hydroxy-1,4-naphthoquinone; L = solvent] was constructed from a linking ligand with conformational and geometrical flexibility and a copper ion that possesses a degree of flexibility in bond cleavage due to the Jahn−Teller distortion.[5] [Cu(bhnq)(L)$_2$]$_n$ provides vapochromic behaviors, and the color change accompanying the loss and addition of the interstitial and/or coordinated solvents is consistent with that of the conformational change of the bhnq^{2-} anion; that is, the chains easily expand and contract with the loss and addition of the solvent. Therefore, [Cu(bhnq)(L)$_2$]$_n$ is a good

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Scheme 1. Transformation of the Host Framework Induced by the Guest Sorption
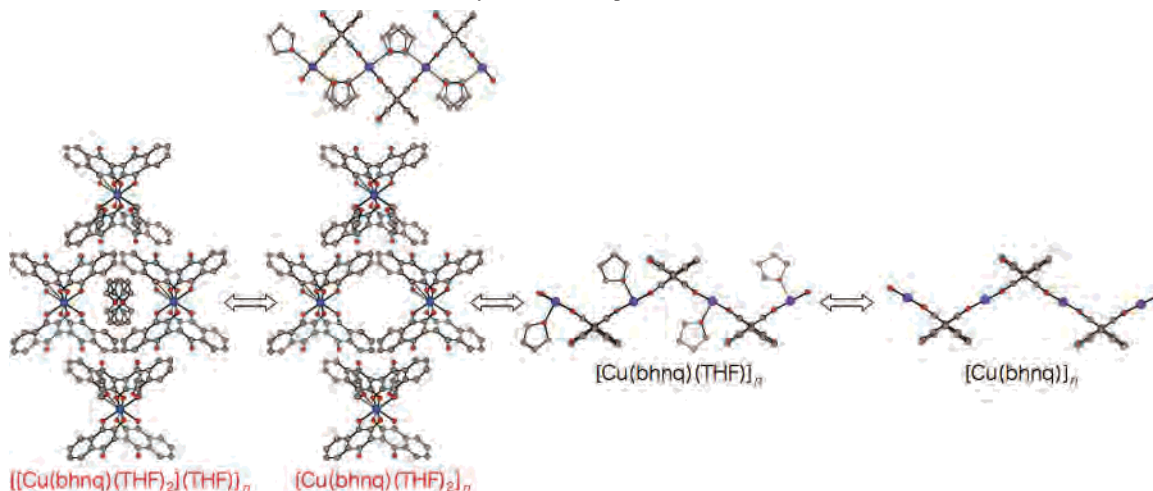
representative of a flexible framework, affording an unprecedented guest shape- and size-responsive fitting capability. In this work, we chose $\{[Cu(bhnq)(THF)_2](THF)\}_n$ (**1**; THF = tetrahydrofuran) as the porous modulator. We have demonstrated the reversible structural transformation with a stepwise sorption of guest molecules by monitoring an adsorption isotherm.

The structure of **1** consists of a one-dimensional chain $[Cu(bhnq)(THF)_2]_n$ and interstitial THF molecules. The chains assemble together to make a channel parallel to the chains. Interstitial THF molecules are introduced to the channel by the hydrogen-bonding interaction.[5] Figure 1 shows the THF
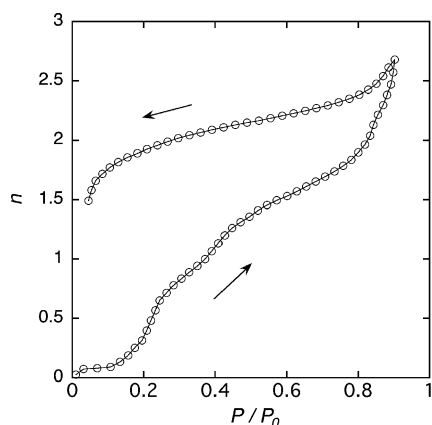
Figure 1. THF adsorption and desorption isotherms at 298 K.

adsorption and desorption isotherms of **1** at 298 K. In this experimental condition,[6] the starting material at $P/P_0 = 0$ is $[Cu(bhnq)]_n$ and the amount resorbed is about three THF molecules per one copper ion at $P/P_0 \sim 0.85$ to form $\{[Cu(bhnq)(THF)_2](THF)\}_n$. The adsorption profile consists of three parts. The adsorption isotherm increases steeply up at $P/P_0 \sim 0.2$ and reaches $n = [THF]/[Cu(bhnq)] = \sim 1$ with pressure $P/P_0 \sim 0.4$ in the first region. It rises gradually up to $n = 2$ ($P/P_0 \sim 0.8$) in the second region. Finally, it attains $n \sim 2.7$ in the third region. These features indicate that the stepwise adsorption occurs under adsorption of THF: stepwise coordinations from 4 to 5 and from 5 to 6 on the copper ion result in the formation of $[Cu(bhnq)(THF)]_n$ and $[Cu$-

$(bhnq)(THF)_2]_n$, respectively, and finally the interstitial THF molecules are introduced to the resulting channel by the hydrogen-bonding interaction. On the other hand, the desorption isotherm does not trace the adsorption one and gradually decreases around $n = 2$ between $P/P_0 = 0.8$ and 0.1, indicative of the high structural stability of $[Cu(bhnq)-(THF)_2]_n$. This hysteretic profile with steps indicates that the shapes of the cavity change as guest molecules are incorporated in the host framework. The transformation of the host framework is induced by the conformational change of the $bhnq^{2-}$ anion, as proposed in the previous paper (Scheme 1). The first and second THF molecules can diffuse into the channels through the coordination bonding interaction between THF and the copper(II) ion, and the hydrogen-bonding interaction in the chain (vide infra) would be strong enough to transform and maintain the channel structure so that the large hysteretic profile appears. Finally, the third THF molecules are incorporated in the cavity formed by $[Cu(bhnq)(THF)_2]_n$ chains with a small framework transformation.

To confirm the conformational flexibility of the $bhnq^{2-}$ anion, we have synthesized a chain compound, $[Cu(bhnq)-(DMF)_2]_n$ (**2**; DMF = *N*,*N*-dimethylformamide).[7] Compound **2** has a chain structure similar to that of **1**, but there is no interstitial solvent molecule. Parts a and b of Figure 2 show the ORTEP drawing and a chain structure of **2**.[8] The chelating $bhnq^{2-}$ anions bridge copper(II) centers to form

(6) The adsorption isotherms and kinetics measurements of gaseous THF were measured by using BELSORP18−Plus volumetric adsorption equipment from BEL Japan. In the sample chamber (17.5 mL) maintained at $T \pm 0.03$ K was placed the adsorbent sample ($\sim$100 mg), which had been prepared at 373 K and 10^{-1} Pa for 7 h prior to measurement of the isotherms. The larger gas chamber (179.85 mL) with a pressure gauge was kept at $(T + 20) \pm 0.1$ K. The THF used to generate the vapor was degassed fully by repeated evacuation and vapor equilibration cycles of the liquid supply side of the vapor reservoir. Helium gas at a certain pressure was introduced to the gas chamber and was allowed to diffuse into the sample chamber by opening a valve. The change in pressure allowed an accurate determination of the volume of the total gas phase. The complexation was monitored in a similar manner by using a guest vapor in place of helium. The amount of guest adsorbed was calculated readily from the pressure difference ($P_{cal} - P_e$), where P_{cal} is the calculated pressure with no guest adsorption and P_e is the observed equilibrium pressure. All operations were computer-controlled and automatic.
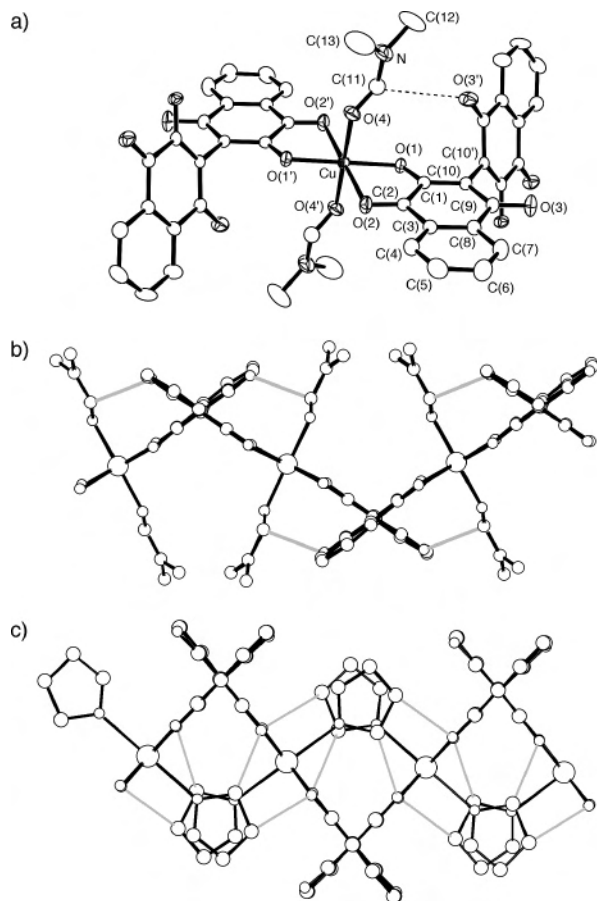
Figure 2. ORTEP drawing of **2** (a; Cu−O(1) 1.935(2) Å, Cu−O(2) 2.322-(2) Å, Cu−O(4), 2.016(2) Å, C(11)−O(3′) 3.163(3) Å, O(1)−Cu−O(2) 77.6(1)°, O(1)−Cu−O(2′) 102.4(1)°) and hydrogen-bonding networks of **2** (b) and **1** (c) in the chains.

zigzag chains. The geometry around the copper ion is similar to that of **1**, consisting of distorted octahedrons involving the four oxygen atoms of two bhnq^{2-} anions and two DMF molecules that are situated in trans positions to one another. The coordinated DMF molecule forms a hydrogen bond with a neighboring bhnq^{2-} anion [C(11)−O(3′): 3.16 Å] in the chain (Figure 2a,b). Interestingly, the dihedral angle of the bhnq^{2-} anion in **2** is 111°, and a Cu−Cu distance in the chain is 7.73 Å while those in **1** are 83.5° and 6.45 Å, respectively. These structural differences are due to the
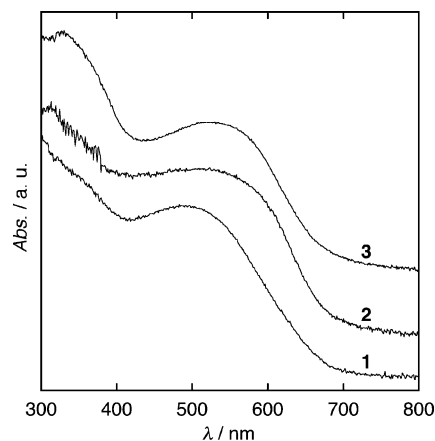
(7) An aqueous solution of copper(II) acetate monohydrate (3 mL, 2.5 mmol L^{-1}) was transferred to a glass tube. A DMF solution (3 mL) of H$_2$bhnq (2.5 mmol L^{-1}) was poured into the tube without mixing the two solutions. Red plate crystals began to form within a week. One of these crystals was used for X-ray crystallography. Physical measurements were conducted on a polycrystalline powder that was synthesized as follows: A solution of H$_2$bhnq (2.5 mmol) in DMF (100 mL) was added dropwise to copper(II) acetate anhydrate (2.5 mmol) dissolved in DMF (100 mL). Upon stirring of the mixture, a dark-red powder appeared immediately. Yield: 40%. Calcd (%) for C$_{26}$H$_{22}$N$_2$O$_8$Cu: C, 56.37; H, 4.00; N, 5.06. Found (%): C, 56.53; H, 4.06; N, 5.24.

(8) Crystallographic data for **2**: C$_{26}$H$_{22}$CuN$_2$O$_8$, M = 554.01, T = 200-(2) K, monoclinic, $C2/c$, a = 15.4329(7) Å, b = 9.9712(4) Å, c = 15.4584(6) Å, β = 97.763(2)°, V = 2357.0(2) Å^3, Z = 4, ρ_c = 1.561 g cm^{-3}, μ(Mo Kα) = 0.983 mm^{-1}, 11 155 reflns collected, 2691 unique (R_{int} = 0.046), R1 [$I > 2\sigma(I)$] = 0.043, wR2 (all data) = 0.119.

Figure 3. UV/vis absorption spectra of **1**−**3**.

differences of the hydrogen-bonding networks between the coordinated solvents and bhnq^{2-} anions (Figure 2b,c), and the conformation of the bhnq^{2-} anion can be controlled by the hydrogen-bonding interaction.

Moreover, the difference in the conformation of the bhnq^{2-} anion is associated with the shift in the absorption bands. Figure 3 shows the UV/vis absorption spectra of these chain compounds. The absorption maximum around 500 nm in **1** is red-shifted in **2**. This red shift is consistent with the π-electron delocalization due to the change of the dihedral angle of the bhnq^{2-} anion and, thus, the one of the desolvated form of **1**, [Cu(bhnq)(THF)]$_n$ (**3**), which has a longer Cu−Cu distance (7.8 Å: calculated by the electron spin resonance−intensity comparison with **1**)[5] and shows an absorption around 540 nm, is concluded to have a larger dihedral angle than that of solvated form **1**. These results show that the dynamic coil-like behavior of the one-dimensional chain, induced by the hingelike properties of the bhnq^{2-} anion, can be controlled through the change of the hydrogen-bonding interactions caused by the reversible and selective incorporation of guest molecules.

The present study has demonstrated a switchable transformation of host frameworks upon adsorption and desorption of guest molecules. The isotherms show large hysteretic and stepwise profiles, suggesting the occurrence of the guest-induced framework transformation. The transformation is based on the reversible shrinking and expanding behaviors of the one-dimensional chain supported by the hingelike properties of linkage ligand bhnq^{2-} and the hydrogen-bonding interactions.

Supporting Information Available: X-ray crystallographic information for **2** (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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