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Design of Flexible Lewis Acidic Sites in Porous Coordination Polymers by using the Viologen Moiety**

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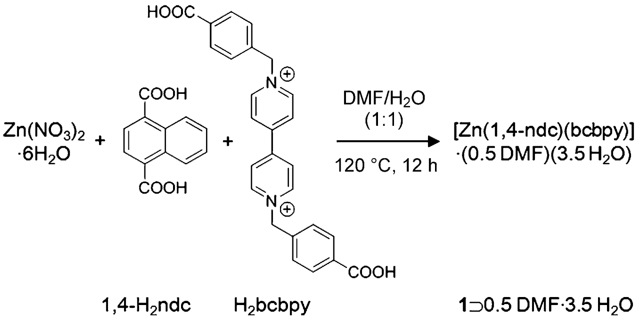
Considerable effort has been devoted to the design of metal–organic architectures and a variety of frameworks have emerged through self-assembly processes involving metal ions and organic linkers.[1] The synthesis of coordination polymers with a channel structure, polymers which have been called porous coordination polymers (PCPs) or metal–organic frameworks (MOFs),[2,3] are of great interest because of their unique functions, such as gas storage,[4] separation,[5] and catalysis.[6,7] Among the PCPs, frameworks having Lewis acidic sites have been highlighted because of their gas-capturing properties[8] or catalytic activities.[7] The main strategy for preparing the Lewis acidic sites is to introduce open metal sites (OMSs). In contrast, we have achieved the fabrication of charged organic surfaces (COSs) using a pyridinium moiety in the porous framework.[9] Because the guest-accessible interior of the pore is mainly organized by the organic moiety, these COSs interact effectively with guest molecules. Another noteworthy point of the introduction of COSs is flexibility, which is based on the flexible nature of the PCP framework.[3,10] PCPs often show a flexible contraction/expansion of the framework through guest accommodation, and if we could incorporate COSs onto the flexible network, the obtained framework would show induced-fit capture of guests at the COSs, a process which is difficult to achieve with the use of OMSs. For the purpose of the construction of flexible COSs, we employed a viologen derivative as an organic linker because of its intrinsic Lewis acidity[11] and the dynamic motion of the aromatic rings.[12] Herein we report the synthesis of a PCP bearing a viologen motif, the strength of the Lewis acidity, and the adsorption properties.



Scheme 1. Synthesis of $\mathbf{1}\supset0.5\,\mathrm{DMF}\cdot3.5\,\mathrm{H_2O}$.

The reaction of $\mathrm{Zn(NO_3)_2\cdot6\,H_2O}$ with 1,4-naphthalenedicarboxylic acid (1,4-$\mathrm{H_2}$ndc) and 1,1-bis(4-carboxybenzyl)-4,4′-bipyridinium bis(hexafluorophosphate) ($\mathrm{H_2bcbpy\cdot2\,PF_6}$) in *N*,*N*′-dimethylformamide (DMF) affords the PCP $\{[\mathrm{Zn(1,4\text{-}ndc)(bcbpy)}]\cdot(0.5\,\mathrm{DMF})(3.5\,\mathrm{H_2O})\}_n$ ($\mathbf{1}\supset0.5\,\mathrm{DMF}\cdot3.5\,\mathrm{H_2O}$) (Scheme 1). The bcbpy, which is a zwitterionic ligand, acts as a neutral organic linker and $\mathbf{1}\supset0.5\,\mathrm{DMF}\cdot3.5\,\mathrm{H_2O}$ does not include any counter anions. The crystal structure of $\mathbf{1}\supset0.5\,\mathrm{DMF}\cdot3.5\,\mathrm{H_2O}$ was determined by single-crystal X-ray crystallography at 223 K. The $\mathrm{Zn^{2+}}$ ion is tetrahedrally coordinated by two 1,4-ndc ligands and two bcbpy ligands (Figure 1 a) to give two-dimensional (2D) interpenetrated layers along the *ac* plane (Figure 1 b). The 2D layers are of the 4^4-sql topology (see Figure S1 in the Supporting Information). The interpenetrated 2D layers are stacked along the *b* axis to form a 3D structure because of the π–π interaction between the 1,4-ndc and the viologen moiety of the bcbpy (Figure 1 c). The $\mathbf{1}\supset0.5\,\mathrm{DMF}\cdot3.5\,\mathrm{H_2O}$ possesses 1D channels along the *c* axis with a cross-section of 4.7×4.1 Å^2 (Figure 1 d). The 0.5 DMF and 3 $\mathrm{H_2O}$ sit in the cavity and the 0.5 $\mathrm{H_2O}$ is between the 2D sheets. The pore surface is formed by bcbpy and 1,4-ndc ligands (Figure 1 e). The carbonyl oxygen atom of the DMF is located 2.48 and 2.64 Å from the two α-hydrogen atoms of the viologen moiety (Figure 2 a), and it forms a C–

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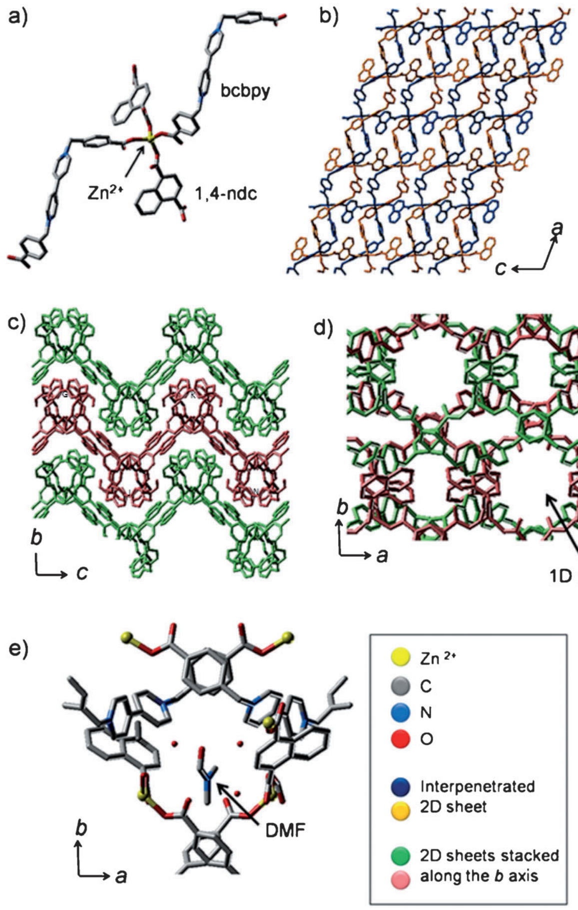

Figure 1. a) Crystallographic environment around the Zn^{2+} ion. b) Interpenetrated 2D sheet. c) 2D sheets stacking along the *b* axis. d) 3D assembled structure of $\mathbf{1}\supset 0.5\,\mathrm{DMF}\cdot 3.5\,\mathrm{H_2O}$. e) Pore surface around the DMF guest. Hydrogen atoms and guests in the pore are omitted.

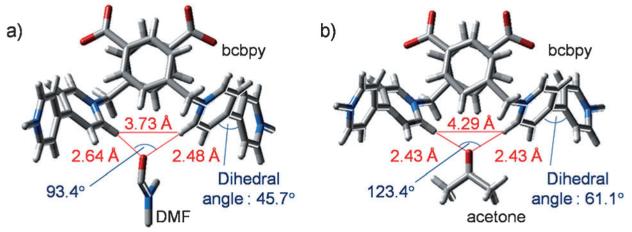

Figure 2. Interaction between the viologen part of bcbpy and DMF in $\mathbf{1}\supset 0.5\,\mathrm{DMF}\cdot 3.5\,\mathrm{H_2O}$ (a) and acetone in $\mathbf{1}\supset 0.5\,\mathrm{acetone}\cdot 3.5\,\mathrm{H_2O}$ (b).

H···O hydrogen bond.[13] Thermogravimetric analysis (TGA) performed on $\mathbf{1}\supset 0.5\,\mathrm{DMF}\cdot 3.5\,\mathrm{H_2O}$ showed a weight loss of 12.4% from 298 to 500 K (see Figure S2). This loss corresponds to the loss of 0.5 DMF and 3.5 H_2O per formula unit (calc. 12.4%).

Table 1: The chemical shift of acetone carbon atom ^{13}C NMR resonance and infrared ν(C=O) band position of acetone absorbed in different PCPs together with those of acetone.

	Interactive site	Acetone as probe	
		δ [ppm]	ν(C=O) [cm^{-1}]
pure acetone (gas)	–	206	1731
HKUST-1⊃acetone	OMS (Cu^{2+})	–[c]	1708
PCP(Na^+)⊃acetone[a]	OMS (Na^+)	212.1	1699
MOF-74⊃acetone	OMS (Zn^{2+})	213.6	–[d]
1⊃acetone	COS (Vio^{2+})[b]	214.2	1695
$1\supset 0.5\,\mathrm{acetone}\cdot 3.5\,\mathrm{H_2O}$	COS (Vio^{2+})[b]	217.1	1690

[a] PCP(Na^+):[CdNa(2-stp)(dabco)$_{0.5}$]. 2-stp = 2-sulfonylterephthalate, dabco = 1,4-diazabicyclo[2,2,2]octane. [b] Charged organic sites by dicationic viologen. [c] Not detected because of paramagnetic Cu^{II} in HKUST-1. [d] Not observed. Vio = viologen.

To investigate the Lewis acidity of the pore surface, we employed acetone as a probe guest. The ^{13}C isotropic chemical shift of carbonyl groups in acetone is sensitive to the interaction of the carbonyl oxygen with Brønsted and Lewis acids.[14,15] When the crystal of $\mathbf{1}\supset 0.5\,\mathrm{DMF}\cdot 3.5\,\mathrm{H_2O}$ was immersed in acetone, acetone was exchanged with DMF to form $\mathbf{1}\supset 0.5\,\mathrm{acetone}\cdot 3.5\,\mathrm{H_2O}$. The chemical shift of the acetone carbonyl carbon atom ^{13}C NMR resonance of $\mathbf{1}\supset 0.5\,\mathrm{acetone}\cdot 3.5\,\mathrm{H_2O}$ appeared at $\delta = 217.1$ ppm, which is downfield from its normal resonance position at $\delta = 206$ ppm (Table 1). The observed downfield shift is larger than that of MOF-74(Zn^{2+})16 ($\delta = 213.6$ ppm) and PCP(Na^+) ($\delta = 212.1$ ppm),[15] both of which have OMSs on the pore surface. In addition, in the infrared spectra of $\mathbf{1}\supset 0.5\,\mathrm{acetone}\cdot 3.5\,\mathrm{H_2O}$, the ν(C=O) band of acetone was observed at $\tilde{\nu} = 1690\ \mathrm{cm^{-1}}$. This band position has a shift that is $\Delta\tilde{\nu} = 41\ \mathrm{cm^{-1}}$ lower than its value of $\tilde{\nu} = 1731\ \mathrm{cm^{-1}}$ when in pure acetone gas.[17] This shift also indicates that the C=O bond of acetone is weakened by the hydrogen bonding between bcbpy and acetone. This ν(C=O) band at $\tilde{\nu} = 1690\ \mathrm{cm^{-1}}$ is lower than that of HKUST-1(Cu^{2+})[18] ($\tilde{\nu} = 1708\ \mathrm{cm^{-1}}$) and PCP($Na^+$) ($\tilde{\nu} = 1699\ \mathrm{cm^{-1}}$). These results demonstrate that **1** has sufficient Lewis acidic sites, probably because of the involvement of the oxygen atom with two C–H groups in the viologen ligand which are comparable to those based on OMSs. To obtain information on the charged state of the viologen compounds, Raman spectra were measured for $\mathbf{1}\supset 0.5\,\mathrm{DMF}\cdot 3.5\,\mathrm{H_2O}$ and $\mathbf{1}\supset 0.5\,\mathrm{acetone}\cdot 3.5\,\mathrm{H_2O}$. Together with the $\tilde{\nu} = 1299\ \mathrm{cm^{-1}}$ obtained for $H_2bcbpy\cdot 2PF_6$, the Raman shifts at $\tilde{\nu} = 1303\ \mathrm{cm^{-1}}$ for $\mathbf{1}\supset 0.5\,\mathrm{DMF}\cdot 3.5\,\mathrm{H_2O}$ and $\mathbf{1}\supset 0.5\,\mathrm{acetone}\cdot 3.5\,\mathrm{H_2O}$ show the dication form of the viologen moiety (see Figure S4 and Table S1 in the Supporting Information).[19]

To observe directly the flexibility of the Lewis acidic site in the framework, the crystal structure of $\mathbf{1}\supset 0.5\,\mathrm{acetone}\cdot 3.5\,\mathrm{H_2O}$ was determined by single-crystal X-ray crystallography at 278 K. The carbonyl oxygen atom of acetone is located 2.43 Å from the two α-hydrogen atoms of the viologen moiety, and results from C–H···O hydrogen bonding, as in the case of $\mathbf{1}\supset 0.5\,\mathrm{DMF}\cdot 3.5\,\mathrm{H_2O}$ (Figure 2). The exchange of guests affords two notable changes in the structure of **1**⊃guests. First, the distance between the two α-hydrogen atoms is 4.29 Å in $\mathbf{1}\supset 0.5\,\mathrm{acetone}\cdot 3.5\,\mathrm{H_2O}$, a distance which is larger than that for $\mathbf{1}\supset 0.5\,\mathrm{DMF}\cdot 3.5\,\mathrm{H_2O}$ (3.73 Å). This change corresponds to the elongation of the interpenetrated 2D sheet along the *a* axis. Second, the dihedral angle of the two pyridyl rings of the viologen moiety in $\mathbf{1}\supset 0.5\,\mathrm{acetone}\cdot 3.5\,\mathrm{H_2O}$ (61.1°) is larger than that in $\mathbf{1}\supset 0.5\,\mathrm{DMF}\cdot 3.5\,\mathrm{H_2O}$ (45.7°), and thus promotes shortening of the distance between the stacked 2D sheets and the pore diameter of the 1D channels along the *b* axis. These structural reorientations suggest that the two bcbpy ligands relocate to capture the acetone molecule suitably with an accompanying rotation of the viologen moiety. Similar behavior in the framework was observed at 298 K by an analysis of the synchrotron X-ray powder diffraction (see Figure S6 and Table S3 in the Supporting Information).[20]

We also investigated the gas adsorption property of guest-free **1** (see Figure S5 in the Supporting Information). After a degassing treatment of $\mathbf{1}\supset 0.5\,\mathrm{acetone}\cdot 3.5\,H_2O$ at 463 K for 12 hours under vacuum, the N_2 sorption isotherm at 77 K for **1** was examined. The adsorption isotherm of nitrogen exhibits Type-I behavior, thus indicating that **1** maintains permanent microporosity. This result corresponds to the cell volume of **1** revealed by the analysis of X-ray powder diffraction. **1** also adsorbs gas-phase acetone from the low pressure region at 298 K, thus suggesting a strong interaction between the acetone and the viologen framework. For acetone absorbed in **1** ($\mathbf{1}\supset$acetone), a ^{13}C chemical shift for the carbonyl carbon atom resonance of $\delta = 214.2$ ppm and ν(C=O) band at $\tilde{\nu} = 1695\ \mathrm{cm}^{-1}$ were obtained. These data lead us to the conclusion that the degassed form of **1** maintains strong Lewis acidic sites originating from the viologen sites. The lack of change in the Raman shift associated with the viologen ligand of $\mathbf{1}\supset$acetone shows that the viologen moiety of the bcbpy ligand remains in the dication form.

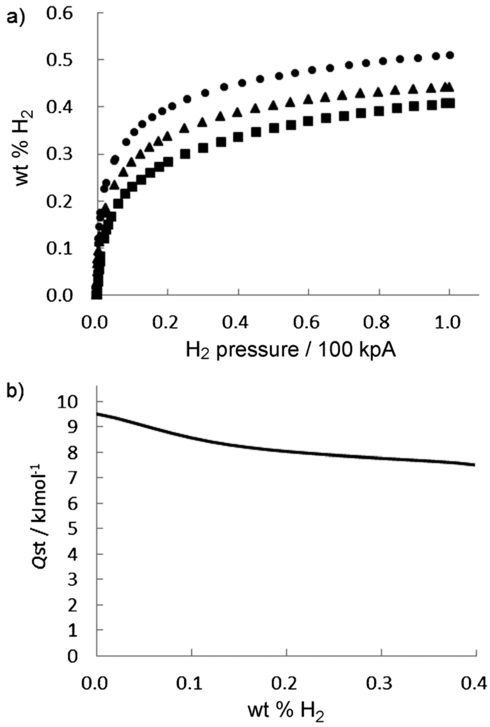

Figure 3. a) H_2 adsorption isotherms for 1 at 77 K(●), 82 K(▲), 87 K(■). b) Isosteric heat of H_2 adsorption (Qst) for 1.

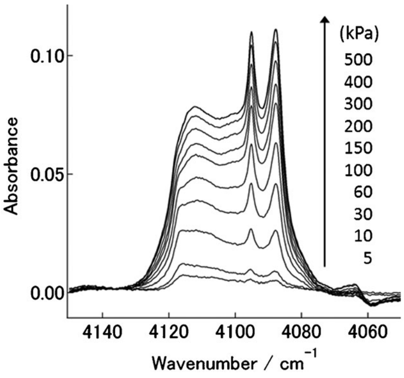

Figure 4. Difference IR spectra in the H—H stretching region for hydrogen adsorbed on 1 at 99 K in the pressure range as shown in the figure. The IR spectrum at 0.5 kPa of H_2 pressure is used as the blank because of a drastic change of spectra from 0 to 0.5 kPa (see Figure S7 in the Supporting Information).

Furthermore to assess the heat of H_2 adsorption for **1**, which bears the flexible Lewis acidic site, H_2 adsorption isotherms were also investigated at 77 K, 82 K, and 87 K (Figure 3). These data were fitted using a virial-type equation (see Figure S7 in the Supporting Information). The heat of adsorption was found to be $9.5\ \mathrm{kJ\,mol^{-1}}$ at zero coverage, finally tending toward $7.5\ \mathrm{kJ\,mol^{-1}}$ at 0.4 wt % (Figure 3 b). These relatively high values of 9.5–$8.5\ \mathrm{kJ\,mol^{-1}}$ at low coverage of 0–0.1 wt % are comparable to those of OMSs[21] despite the organic surface of **1**. To obtain information on H_2 adsorbed on **1**, we carried out variable-temperature infrared (VTIR) measurements below 99 K and at H_2 pressures ranging from 0 to 500 kPa (Figure S8). The VTIR spectra of H_2 adsorbed on microporous materials can be very informative in explaining and differentiating the active sites on the interior surface. The difference VTIR spectra mainly show three peaks at $\tilde{\nu} = 4112$, 4095, $4088\ \mathrm{cm}^{-1}$ (Figure 4) and no other peaks were observed in the region of $\tilde{\nu} = 4040$–$4000\ \mathrm{cm}^{-1}$. This data indicates that there is no chemisorptive site in **1**.[22] The sharp doublet at $\tilde{\nu} = 4095$ and $4088\ \mathrm{cm}^{-1}$ is ascribed to para- and ortho-H_2, respectively, based on previous reports.[22,23] These values are compared with those for PCPs with OMSs such as Mg-MOF-74 ($\tilde{\nu} = 4091$, $4085\ \mathrm{cm}^{-1}$) and for alkali-cation-exchange zeolites such as Li-FER ($\tilde{\nu} = 4090\ \mathrm{cm}^{-1}$). Furthermore they are a lower frequency shift than that for PCPs with OMSs such as HKUST-1 ($\tilde{\nu} = 4097$, $4090\ \mathrm{cm}^{-1}$) and $Cr_3(btc)_2$ ($\tilde{\nu} = 4116$, $4110\ \mathrm{cm}^{-1}$; see Table S4 in the Supporting Information). This comparison, the lack of an exposed Zn^{2+} in **1**, and the result of the NMR and IR (Table 1) spectra allow the assignment of this doublet to para- and ortho-H_2 adsorbed at two of the C—H groups in the viologen ligand. The other peaks from ranging from $\tilde{\nu} = 4130$ to $4100\ \mathrm{cm}^{-1}$ (peak top: $4112\ \mathrm{cm}^{-1}$ at 500 kPa) apparently show a lower shift than that for MOF-5 (peak top: $4130\ \mathrm{cm}^{-1}$) and HKUST-1 (from 4150 to $4120\ \mathrm{cm}^{-1}$; Table S4), and is assigned to peaks adsorbed on the organic moiety in those frameworks. This result indicates that the organic moiety, except for two C—H groups in the viologen ligand, can also perturb H_2 more than neutral organic parts such as terephthalate in MOF-5 and trimesate in HKUST-1. Therefore we can conclude that flexible COSs created by a viologen moiety provide Lewis acidic sites and wide surfaces, which can be effective in strongly adsorbing and perturbing H_2, and is thus comparable to OMSs. The intensities of bands at $\tilde{\nu} = 4112$ and $4088\ \mathrm{cm}^{-1}$ have been measured as a function of temperature (T), and standard enthalpy (ΔH^0) and entropy (ΔS^0) were calculated to be $-5.2\ \mathrm{kJ\,mol^{-1}}$ and $-87\ \mathrm{J\,mol^{-1}\,K^{-1}}$,

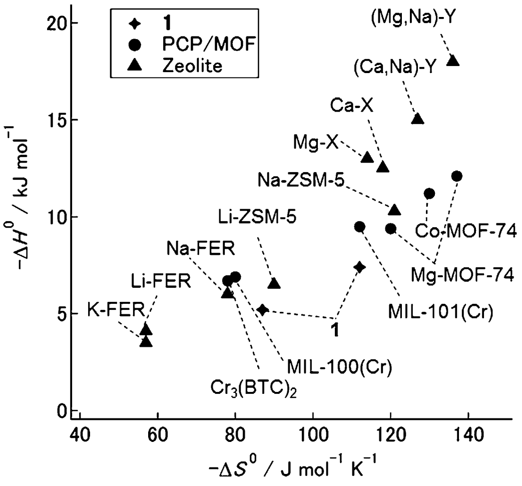

Figure 5. Standard adsorption enthalpy versus entropy for hydrogen adsorption on **1**, PCPs/MOFs reported previously, and zeolite. The points are taken from Table S4 in the Supporting Information.

respectively, at $\tilde{\nu} = 4112\ \text{cm}^{-1}$, and $-7.4\ \text{kJ}\,\text{mol}^{-1}$ and $-112\ \text{J}\,\text{mol}^{-1}\text{K}^{-1}$, respectively, at $\tilde{\nu} = 4088\ \text{cm}^{-1}$ (Figure S9). The order of ΔH^0 is in good agreement with the fact that the lower frequency shift from $\tilde{\nu} = 4161\ \text{cm}^{-1}$ for unperturbed H_2 means adsorption on a more interactive site. The magnitude of ΔH^0 calculated from the VTIR spectra is lower than that estimated from adsorption isotherms, probably because of the difference in analytical methods. The values of ΔH^0 and ΔS^0 show a positive correlation, similar to that reported so far for cation-exchanged zeolites and PCPs[24] (Figure 5). Sorption phenomena of H_2 on adsorptive sites provided by flexible COSs in **1** also follows the enthalpy–entropy compensation rule.

In conclusion, we have synthesized a PCP containing a viologen derivative as a zwitterionic linker and demonstrated that a viologen moiety offers flexible Lewis acidic sites which can strongly interact with carbonyl oxygen atoms and adsorb H_2 molecules. This behavior is comparable to that of the OMSs, and the viologen moiety additionally creates wide surfaces which can perturb H_2 molecules more than the neutral organic moiety in PCP frameworks can. Such flexible COSs, such as viologen in PCPs, are likely to be useful in functional sites providing advanced porous properties such as gas storage and catalytic reactions.

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