

Host–Guest Systems

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Porous Coordination Polymer with π Lewis Acidic Pore Surfaces, $[[\text{Cu}_3(\text{CN})_3\{\text{hat}(\text{CN})_3(\text{OEt})_3]\}_n \cdot 3\text{THF}]_n^{}$** *Daisuke Tanaka, Shigeyuki Masaoka, Satoshi Horike, Shuhei Furukawa, Motohiro Mizuno, Kazunaka Endo, and Susumu Kitagawa**

Modification of chemical properties of porous coordination polymers (PCPs) is very topical in the area of materials

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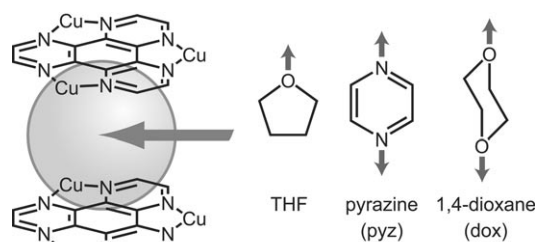
[**] hat = hexaazatriphenylene. This work was supported by a Grants-in-Aid for Scientific Research in a Priority Area "Chemistry of Coordination Space" (#434) and a Grant-in-Aid for Young Scientists (B) (#17750125) from the Ministry of Education, Culture, Sports, Science and Technology, Government of Japan.

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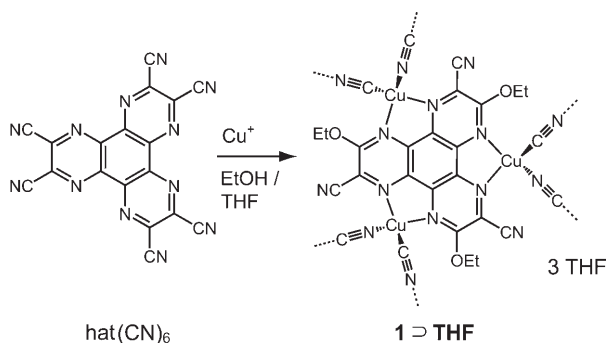
chemistry.^[1] PCPs with functional groups such as open metal sites or metal-free organic groups in the pores have attracted attention because of their versatile applicability to gas storage, ion exchange, heterogeneous catalysis, and selective guest adsorption. There is no doubt that an adsorption system specific to a target molecule can be realized when multiple interaction sites are located at suitable positions on a regular micropore.^[2] To obtain such systems, aromatic π moieties could be a key component for the effective confinement of guest molecules that is not only shape-selective but also site-selective due to their large surface area and feasibly modifiable functionality, which is responsible for their interaction with guests.^[3] In general, aromatic π faces, such as those of benzene, interact with positively charged groups or hydrogen atoms as a Lewis base (so-called, cation– π ^[4] and XH– π -type interactions, in which X is O, N, C^[5]). These interactions play important roles in chemical and biological recognition as well as in the construction of protein structures.^[6] In contrast, interactions of negatively charged atoms with aromatic rings (i.e., anion– π interactions) are rare. However, several recent reports claimed that electron-deficient π systems could operate as receptors capable of binding an anion or molecule with electronegative atoms.^[7,8] In spite of the importance of this interaction and the interest that it has generated, experimental studies within porous frameworks are still rare and recent reports have focused on interaction of discrete anion receptors.^[8,9] The investigation and discovery of PCPs with neutral π Lewis acidic sites is significant to the design of a new type of interaction site that makes the surface functionality of the pores useful.

To realize PCPs with electron-deficient π systems, hexaazatriphenylene (hat) derivatives were chosen as building units^[10–12] as they have electron-deficient heterocyclic cores responsible for anion– π interactions^[11] and three chelating sites, which are useful for the construction of a coordination network.^[10] Previously, we reported anion-trapping host systems constructed from hat derivatives,^[12a] and a recent theoretical investigation demonstrated that hat derivatives could be used for the molecular recognition of anions.^[11c] Herein, we report a 3D PCP of a hat derivative, which incorporates neutral guest molecules that have electronegative atoms with the aid of an electron-deficient π surface (Scheme 1).

A coordination polymer, $[[\text{Cu}^{\text{I}}_3(\text{CN})_3\{\text{hat}(\text{CN})_3(\text{OEt})_3\}_n \cdot 3\text{THF}]_n$ (**1**·3THF), was prepared by the slow intermixing of a solution of $[\text{Cu}^{\text{I}}_2(\mu\text{-}\eta^2, \eta^2\text{-benzoquinone})(\text{OAc})_2]$ in ethanol and a solution of hat(CN)₆ in THF.^[13] This reaction affords C₃ symmetrical hat(CN)₃(OEt)₃ and CN[−] ions through the substitution of an ethoxy for a cyano group (Scheme 2).^[14] Single-crystal X-ray diffraction measurements confirmed that the distorted tetrahedron around the Cu^I cation consists of two nitrogen atoms from hat(CN)₃(OEt)₃, one nitrogen atom, and one carbon atom from the cyanide anions. These cyanide ligands link the two tetrahedral copper ions to form a 3D (8,3)-c type network (Figure 1).^[15] There are two kinds of pores in this structure: one is a large 1D channel running along the *c* axis with a cross section of $10 \times 10 \text{ \AA}^2$ (Figure 1a); the other pore is just a pocket located along the channel, in which the hat units form a floor and a ceiling and whose



Scheme 1. Inclusion of solvent guest molecules into pores comprising π planes.



Scheme 2. Synthesis of **1**⊃THF.

portals open to three adjacent channels (Figure 1b). The crystal structure in Figure 1c,d reveals that the three THF molecules are accommodated in the cavity. Interestingly, the THF molecules do not sit parallel but perpendicular to the hat plane, and the vertical distance between the hat plane and the oxygen atom is 2.97 Å,^[16] which indicates that there is an attractive interaction between the oxygen atom and the hat π plane that is attributed to an anion- π type interaction.

Thermogravimetric analysis (TGA) of **1**⊃THF shows that the removal of two THF molecules in the temperature range 30–80 °C is accompanied by a severe broadening of the X-ray powder diffraction (XRPD) pattern (see Supporting Information).^[17] Complete removal of three THF molecules was accomplished by putting **1**⊃THF in a vacuum at 50 °C or by washing with EtOH to afford an amorphous guest-free solid, **1**. However, by soaking **1** in THF, a porous framework identical to that of **1**⊃THF returns, as demonstrated by XRPD (see Supporting Information). This phenomenon also occurs with 1,4-dioxane (dox), *N,N*-dimethylformamide (DMF) or in an ethanol solution of pyrazine (pyz; see Supporting Information). Such an amorphous-to-crystal phase transition is associated with the guest (G) inclusion as shown in Equation (1).



In contrast, when **1** is soaked in hydrocarbons (hexane, cyclohexane, and benzene), linear ethers and alcohols (diethylether, methanol, and ethanol), and a large-molecule compound (4,4'-bipyridyl), there are no sharp peaks in the corresponding XRPD patterns. The structural recovery occurs only for guest molecules with at least one electro-

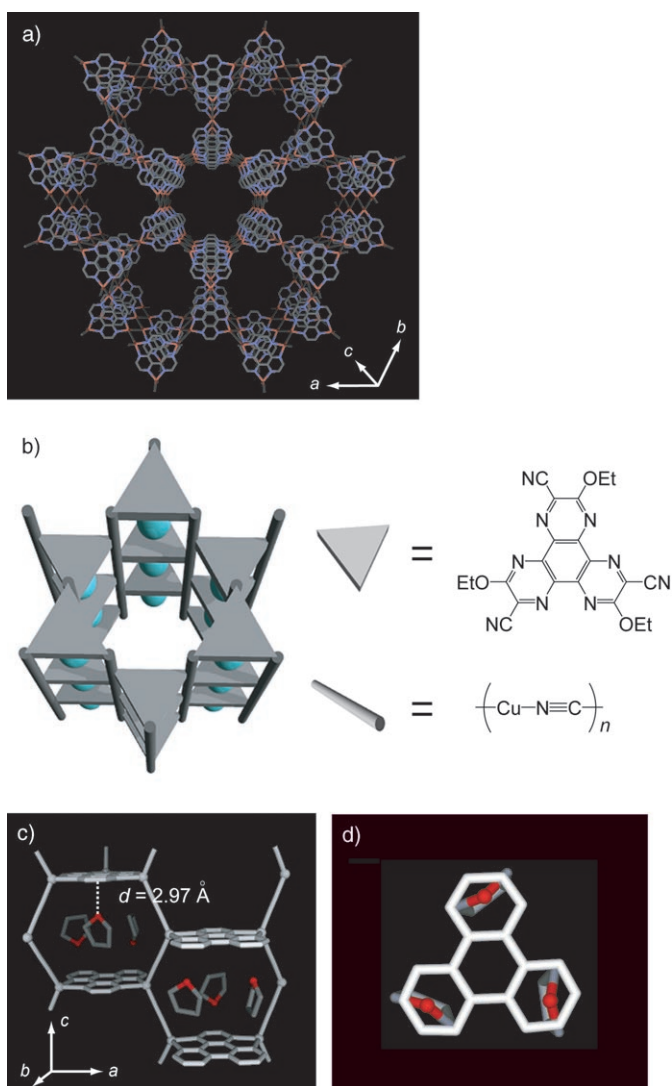


Figure 1. Structural representation of **1**⊃THF. a) 1D channel structure constructed by Cu^I, hat(CN)₃(OEt)₃, and cyanide anions (Cu, red; C, gray; N, blue). The ethoxy and cyano groups of hat and the THF molecules are omitted for clarity. b) Schematic representation of the pore structure of **1**⊃THF. c) Crystal structure of the cavity defined by two hat molecules. (O, red; C, gray) d) View of hat with THF along the *c* axis. Disordered THF molecules are omitted for clarity in (c) and (d).

negative atom, X, and which are the right size for the cavity, thus indicating that the origin of the guest-responsive phase transformation is the guest-selective inclusion in the cavity promoted by X- π (hat) interactions.

To determine the crystal structures of **1** with other guests, single crystals were obtained by the crystal-to-crystal guest exchange of **1**⊃THF with pyz and dox. When single crystals of **1**⊃THF were immersed in an ethanol solution of pyz (0.1 M) at room temperature for several days, the THF molecules in the cavity were replaced by pyz to give **1**⊃pyz without loss of crystallinity. Similarly, single crystals of **1**⊃dox were obtained by immersing single crystals of **1**⊃THF in a mixture of dox/EtOH (1:1 v/v).

The crystallographic analysis reveals that the framework of **1**⊃pyz is isomorphous to that of **1**⊃THF; the pyz molecules

are accommodated within the cavity in place of the THF molecules. The accommodation of pyz involves elongation of the crystal dimension along the crystallographic c axis ($8.7244(9) \text{ \AA} \rightarrow 8.791(2) \text{ \AA}$; $\Delta = 0.07 \text{ \AA}$) and shrinking along the a and b axes ($18.1226(19) \text{ \AA} \rightarrow 18.034(5) \text{ \AA}$; $\Delta = -0.09 \text{ \AA}$). In the cavity, the edge-to-face contact between a nitrogen atom of pyz and the hat π plane is easily identified, with a separation of 3.02 \AA (Figure 2a). The pyz plane disorders over two positions around the C_2 axes with an angle, θ , of 40° (Figure 2b). The short $\pi(\text{hat})\text{--N}(\text{pyz})$ separations indicate that two nitrogen atoms of the pyz molecule interact with the two π planes of the hat moieties.

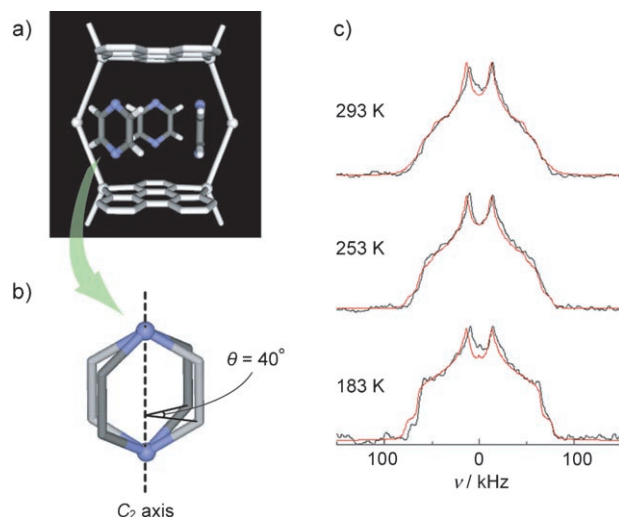


Figure 2. a) Crystal structure of the cavity of **1Dpyz**. The ethoxy and cyano groups and disordered pyz molecules are omitted for clarity. b) Schematic illustration of disordered structure of pyz. c) Selected ^2H NMR spectra (black line: experimental; red line: simulation) of the $[\text{D}_4]\text{pyz}$ molecule of **1D** $[\text{D}_4]\text{pyz}$ (see Supporting Information).

Similarly, the single crystal structure of **1Ddox** shows that the dox molecules are accommodated within the cavity. The $\text{O}\text{--}\pi$ separations are $2.93\text{--}2.95 \text{ \AA}$ (see Supporting Information). In all cases of **1DG**, the $\text{X}\text{--}\pi$ separations indicate that the electronegative atoms of the guest molecules interact with the hat π planes, and the lone pair of X is directed towards the π face as in the case of hexafluorobenzene complexes.^[7c,18] It is worth noting that there are no recognizable specific host–guest interactions except for the $\text{X}\text{--}\pi$ plane contact in the crystal structures of **1DG**. These results confirm that the origin of the guest-selective inclusion of **1** is the interaction between π Lewis acid and electronegative atoms.

Information about the dynamics of the confined guest molecules in the host framework is important for an in-depth understanding of how strongly the guest molecules are accommodated. We acquired solid-state ^2H NMR spectra of **1D** $[\text{D}_4]\text{pyz}$ between 183 and 293 K, which show doublet patterns of $[\text{D}_4]\text{pyz}$ in the cavity over the whole temperature range. The simulation of the signal affords an anisotropic motion of the $[\text{D}_4]\text{pyz}$, which is a pyz ring rotation around the molecular NN axis perpendicular to the hat plane. The motion has two kinds of frequencies and moves over four sites

with angles of 0° , 40° , 180° and 220° . This result is consistent with the crystallographic structure of disordered pyz shown in Figure 2b. The restricted motion is caused by the interaction between two nitrogen atoms of pyz and hat π planes.

TGA and XRPD measurements of heated samples of **1DTHF** show that the crystallinity of **1DG** is not retained upon the loss of the guest molecules (Supporting Information).^[17] Therefore, the presence of guest molecules is essential to maintain the framework. Unlike results obtained from the analysis of **1DTHF**, the results of crystallographic analysis and solid-state ^2H NMR spectra of **1Dpyz** reveal that the pyz molecules behave as if the two nitrogen atoms at both ends of the molecule bind with the two π planes of hat moieties. The multiple interactions in **1Dpyz** could influence the stability of the framework. Indeed, XRPD measurements with heating and TGA show that **1Dpyz** is stable up to 120°C (Supporting Information). Interestingly, placing **1Dpyz** under vacuum or washing the compound with ethanol does not result in the removal of pyz molecules and there is no significant loss in crystallinity. In contrast, **1DTHF** gradually collapses upon the removal of THF molecules under ambient temperature and pressure. Such strong accommodation and enhanced stability of the crystal phase of **1Dpyz** is ascribed to the pillar support of the pyz within the cavity, which arises from the two-point N– π interactions.

In conclusion, we have demonstrated that neutral organic guest molecules can be confined within the cavities of a porous coordination polymer through the interaction between electronegative atoms and electron-deficient π planes, the so-called anion– π interaction. This interaction could be exploited to design a new family of PCPs.

Experimental Section

Synthesis of 1DTHF: hat(CN)₆ was prepared according to reported procedures.^[19] An ethanol solution of $[\text{Cu}^{\text{I}}_2(\mu\text{--}\eta^2, \eta^2\text{--benzoquinone})\text{(OAc)}_2]$ (10 mM, 2 mL), prepared by the in situ reaction of copper (II) acetate with hydroquinone in ethanol,^[13] was carefully layered on a hat(CN)₆ solution in THF, where a mixed solvent of THF/ethanol (1:1 v/v) was placed between the two layers. Dark brown crystals suitable for single-crystal X-ray analysis were obtained after one week. For elemental analysis, these crystals were collected, washed with EtOH and dried in vacuo. Elemental analysis of guest-free solid, **1**, calcd for $\text{C}_{24}\text{H}_{15}\text{Cu}_3\text{N}_{12}\text{O}_3$ (%): C 40.59, H 2.13, N 23.67; found: C 39.65, H 2.42, N 22.72. IR (Nujol): $\tilde{\nu} = 2236 \text{ cm}^{-1}$ (CN from hat(CN)₃-(OEt)₃), 2138 cm^{-1} (cyanide anion).

Physical measurements: XRPD data were collected on a Rigaku RINT 2000 (Ultima) diffractometer by using $\text{CuK}\alpha$ radiation. Elemental analyses were measured on Thermo Finnigan EA1112. TGA was carried out with a Rigaku Instrument TG8120 in a nitrogen atmosphere at 2°C min^{-1} . IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrophotometer with samples prepared with Nujol. Solid-state ^2H NMR spectra were measured by a Varian Chemagnetics CMX-300 spectrometer operated at 45.826 MHz and the quadrupole pulse sequence was used for the measurements. Simulated spectra were produced by using home-written FORTRAN programs.

X-ray structure determination: X-ray structures were determined on a Rigaku Mercury CCD system with $\text{MoK}\alpha$ radiation. In all cases, the structure was solved by direct methods (SIR 97) and refined on F^2 in SHELXL-97. Crystal data for **1DTHF**, $\text{C}_{12}\text{Cu}_4\text{N}_4\text{O}_2$, $M_r = 295.70$, hexagonal, space group $P6_3/mmc$, (no. 194), $a = 18.1226(19)$, $c =$

8.7244(9) Å, $V = 2481.5(4)$ Å³, $Z = 6$, $\rho_{\text{calc}} = 1.187$ g cm⁻³, $F(000) = 870$, $\mu(\text{Mo}_{\text{K}\alpha}) = 1.321$ cm⁻¹, $T = -50$ °C, $2\theta_{\text{max}} = 50.0^\circ$, $\lambda(\text{Mo}_{\text{K}\alpha}) = 0.71070$ Å, reflections collected/unique 17476/858, $R(R_w) = 0.077$ (0.218), GOF = 1.220 and 66 parameters. The residual electron density (min./max.) is $-0.41/0.48$ e Å⁻³. Solvent molecules and some disordered molecules were refined isotropically, whereas other atoms were refined anisotropically. The C–C and C–O bond lengths in THF were restrained to 1.54 Å. Crystal data for **1**⊃pyz, C₁₂H₄CuN₆O, $M_r = 311.75$, hexagonal, space group $P6_3/mmc$, (no. 194), $a = 18.034(5)$, $c = 8.791(2)$ Å, $V = 2476.0(11)$ Å³, $Z = 6$, $\rho_{\text{calc}} = 1.254$ g cm⁻³, $F(000) = 930$, $\mu(\text{Mo}_{\text{K}\alpha}) = 1.326$ cm⁻¹, $T = -50$ °C, $2\theta_{\text{max}} = 50.0^\circ$, $\lambda(\text{Mo}_{\text{K}\alpha}) = 0.71070$ Å, reflections collected/unique 17608/859, $R(R_w) = 0.060$ (0.172), GOF = 1.166 and 67 parameters. The residual electron density (min./max.) is $-0.50/0.59$ e Å⁻³. Disordered atoms were refined isotropically, whereas other non-hydrogen atoms were refined anisotropically. Hydrogen atoms of pyz were placed geometrically and refined by using a riding model with U_{iso} constrained to be 1.2 times U_{eq} of the carrier atom. Crystal data for **1**⊃dox, C₁₂H₄CuN₆O, $M_r = 311.75$, hexagonal, space group $P6_3/mmc$, (no. 194), $a = 18.421(5)$, $c = 8.537(5)$ Å, $V = 2508.8(18)$ Å³, $Z = 6$, $\rho_{\text{calc}} = 1.238$ g cm⁻³, $F(000) = 918$, $\mu(\text{Mo}_{\text{K}\alpha}) = 1.314$ cm⁻¹, $T = -50$ °C, $2\theta_{\text{max}} = 50.0^\circ$, $\lambda(\text{Mo}_{\text{K}\alpha}) = 0.71070$ Å, reflections collected/unique 14492/866, $R(R_w) = 0.067$ (0.175), GOF = 1.137 and 75 parameters. The residual electron density (min./max.) is $-0.53/0.57$ e Å⁻³. Solvent molecules and some of disordered molecules were refined isotropically, whereas other atoms were refined anisotropically. CCDC-600740, CCDC-600741 and CCDC-600742 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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