Communication

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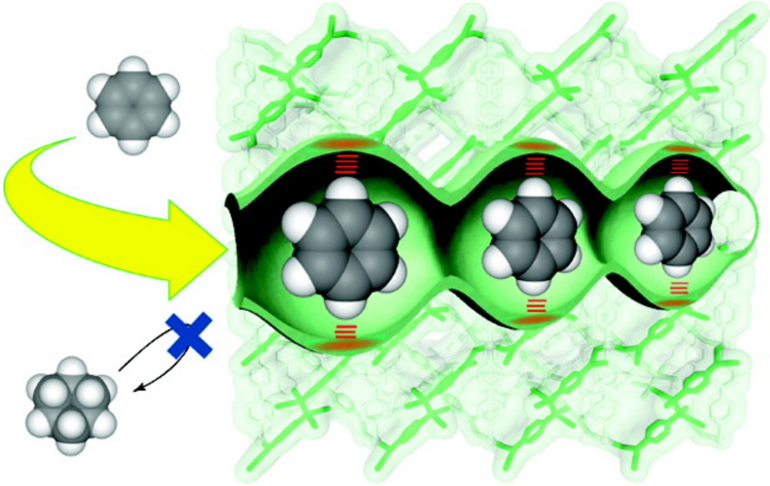

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Guest-Specific Function of a Flexible Undulating Channel in a 7,7,8,8-Tetracyano-*p*-quinodimethane Dimer-Based Porous Coordination Polymer

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In the field of porous coordination polymers (PCPs), separation is one of the most significant topics. PCPs have regularly ordered nanometer-size frameworks with readily modifiable pore surface properties and structural flexibility, which give them potential applications in separation,[1,2] storage,[3] and catalysis.[4] The highly selective separation of hydrocarbons having similar physical properties, such as boiling point and molecular size, remains a significant challenge that has much scientific and commercial value. Because cyclohexane is usually produced by hydrogenation of benzene, in the benzene/cyclohexane-miscible system used in the petrochemical industry, separating their mixture is essential.[5] However, the separation is difficult because these substances have similar boiling points (benzene, 80.1 °C and cyclohexane, 80.7 °C), molecular geometry, and Lennard-Jones collision diameters.[6] To face this chemical similarity, we need to design the high recognition capability system, for instance, in a biological system, which requires the specific binding sites such as cation−π, H−π, and H-bonding-type interaction and the flexible structure to create suitable space for the target molecules.[7,8] 7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ) is a well-known molecule with a large π surface and redox activity. A PCP whose pore surface is formed by TCNQ will have a H−π-type interaction with benzene and achieve selective separation of benzene from cyclohexane with a suitable pore shape for benzene generated from the specific flexibility of the PCP.

Green crystals of $\{[Zn(\mu_4\text{-TCNQ}-\text{TCNQ})bpy]\cdot 1.5\text{benzene}\}_n$ (**1**⊃benzene) were synthesized by reacting $Zn(NO_3)_2\cdot 6H_2O$ with LiTCNQ and bpy (4,4′-bipyridine) in a MeOH/benzene mixture (1:1). The Zn ions are octahedrally coordinated to the four cyanide nitrogen atoms of TCNQ in the equatorial plane and the two nitrogen atoms of the bpy at the axial sites (Figure 1a). The Zn ions are linked by bpy to give a one-dimensional (1D) chain in the direction of the *a*-axis. $[\text{TCNQ}-\text{TCNQ}]^{2-}$ acts as cross-linker connecting the four 1D chains of Zn ions and bpy to form a 3D open framework (Figure 1b). $[\text{TCNQ}-\text{TCNQ}]^{2-}$ is derived from a σ dimerization of two TCNQ^- anions. There are few reports about coordination polymers containing the TCNQ dimer, despite the scarcity, unique shape, and various coordination modes of the dimer making the structures interesting.[9] The dianionic ligand is a nonplanar, staircase motif because of the sp^3 C−C σ bond connecting the two TCNQs, and the two electrons are separated and delocalized in each planar part of the TCNQ. The channels delimited by the ligands are of the undulating form, not a straight but a unique form comprising an alternating arrangement of two types of tubes of large and small diameter. The large diameter space is adequate to accommodate a benzene molecule because of the suitability of the cavity's size and thickness (Figure 1c). The guest benzene molecule is accommodated strongly in the cavity with the size effect and the H−π interaction with the host framework. The distance between the pore wall perpendicular to the benzene molecule, which comprises the electron-rich π surface of the TCNQ dimer and the center of the benzene molecule, is 5.05 Å. This is consistent with the existence of the H−π interaction between the host framework and the guest molecule (Figure 1c).[8]

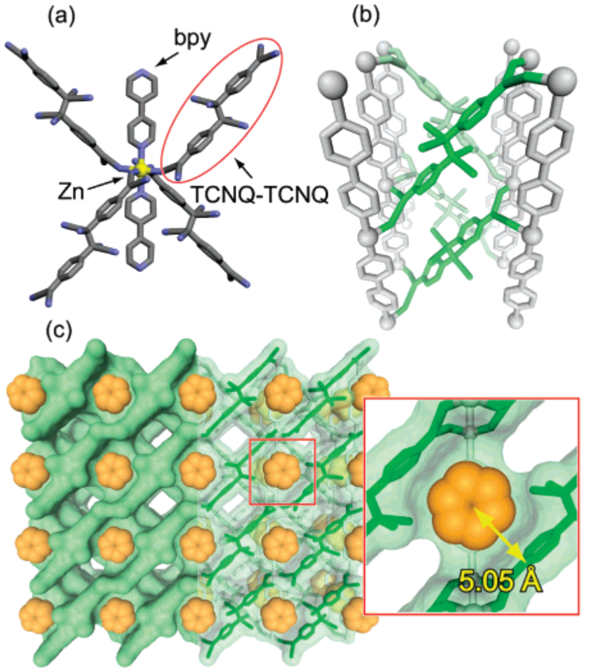

Figure 1. (a) Coordination environment of Zn(II) ion of **1**⊃benzene. (b) TCNQ dimer (green) connected to four 1D chains of Zn and bpy (gray). (c) Benzene arranged in the cage of the undulating channel of **1**⊃benzene. The hydrogen atoms are omitted for clarity.

Interestingly, although the benzene molecule can be removed from and adsorbed to this compound, the aperture of the small tube is not large enough for the benzene molecule to pass through it, indicating that the framework is flexible. The X-ray powder diffraction (XRPD) patterns also show the structural flexibility of this compound, which is classified as a third-generation compound.[10] In the guest-removal process, the crystal is transformed to a guest-free crystal phase **2** (Figure 2). Alternatively, exposing **2** to benzene vapor for 5 h produced the other crystal phase, **3**⊃benzene, whose XRPD pattern quite similar to that of **1**⊃benzene. The flexibility may originate in the freedom in the coordination mode of TCNQ.

The guests of **1**⊃benzene were removed at 413 K for 10 h under low pressure, and the sorption isotherms of benzene and cyclo-

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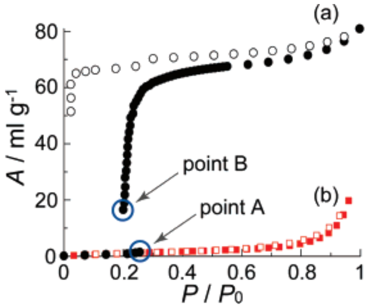

Figure 2. Sorption isotherm for each adsorbate in **2** at 298 K. (a) Benzene adsorption (filled circles) and desorption (open circles). (b) Cyclohexane adsorption (filled squares) and desorption (open squares).

hexane of **2** at 298 K were measured. The profiles differed obviously between each isotherm. In the case of benzene, a flat curve means no adsorption in the lower relative pressure region, although an abrupt increase in adsorption and decrease in relative pressure was observed in the process from point A to point B (see the Supporting Information). This is similar to the gate-open type adsorption behavior,[2,11] which is related to the structural transformation of the host framework. The crystal initially has no gates large enough to receive benzene molecules in its cavities until a certain number of benzene molecules accumulate on the surface. Once the threshold concentration, the so-called gate-opening pressure, is achieved, the crystal begins to accommodate the guests, and the sorption accelerates cooperatively, accompanied by the structural transformation. The driving force to open the gates could be the presence of a higher affinity interaction of the pore surface and guest molecules. In contrast, no adsorption of cyclohexane occurs even in the higher relative pressure region, indicating the gates remain closed for cyclohexane.

The guest-free phase **2** was exposed to the vapor of benzene/cyclohexane mixture at a ratio of 1:1 at room temperature for 5 h. The XRPD pattern was transformed from the guest-free state **2** to the benzene-adsorbed state **3**⊃benzene. This sample was decomposed, and all the organic components were dissolved in DMSO-d_6. The ^{1}H NMR spectrum showed that the ratio of benzene and cyclohexane of this compound was 96:4. This compound maintained the high separation efficiency at least for three times (98:2 (second), 97:3 (third)). At other benzene/cyclohexane mixture ratios (1:3, 1:10), benzene was also selectively adsorbed (96:4, 95:5, respectively). This compound also preferentially adsorbed 1,4-cyclohexadiene from a mixture of equal parts of 1,3-cyclohexadiene and 1,4-cyclohexadiene (23:77), which have almost the same molecular shape and boiling point and differ only in the position of protons in the molecular plane. These properties are linked directly to the strength of the H−π interaction with the host framework. Considering the crystallographic results of **1**, 1,4-cyclohexadiene can interact with this compound with four protons, unlike 1,3-cyclohexadiene, which interacts with three protons. The keys to the success of the separation are the H−π-type host−guest interaction, which triggers the structural transformation from the closed form (**2**) to the open form (**3**) in the sorption process and the undulating channel with cages fitting tightly to the shape of benzene.

In conclusion, we have designed and synthesized a PCP with highly selective capacity to separate benzene from cyclohexane. Synergy of the undulating channel formed gives the PCP structural flexibility to adapt to the target molecular shape and, with the interaction site located in the right position of the pore surface, makes PCPs an effective separation system.

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Supporting Information Available: Experimental methods including synthesis, crystallographic data, NMR spectra, XRPD patterns, and TGA for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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