

Highly selective sorption of oxygen and nitric oxide by an electron-donating flexible porous coordination polymer

The recognition and selective accommodation of gas molecules are vital challenges in the environmental and industrial fields, and fascinating subjects for scientific study. Enhancing the molecular recognition ability of the microporous domain is an important aim of such research; achieving this aim requires providing good affinity for the target molecule and a means to avoid the uptake of other molecules. In the cases of conventional porous materials, there are few molecules applicable to selective accommodation because of the difficulty in designing structures having the properties mentioned above. On the other hand, porous coordination polymers (PCPs) or metal organic frameworks (MOFs) possessing designability that provides various kinds of host-guest interaction, as well as flexibility that allows guest-responsive dynamic accommodation, have attracted much attention as strong candidates for this purpose [1,2]. The design of the pore surfaces to increase the affinity for target molecules is recognized as a good approach to attaining some positive results for selective accommodation. Furthermore, structural flexibility, causing the closed/open-type structural transformation, is the linchpin for the exclusion effect, which enhances the selectivity. For many conventional porous materials, their selective gas sorption properties depend on the size and shape effects, and the dispersion force. Therefore, it is difficult to achieve the retrograde tendency of the selectivity to these factors. Focusing on O₂ as a target adsorbate molecule presents some difficulties in designing the mechanism of O₂ recognition from N₂ and Ar, which have similar molecular shape or size to O₂. Here, we report a PCP having an exceptional selective sorption property for O₂ and NO utilizing the charge transfer interaction between the guest and the host.

A potential mechanism of the gate-opening properties for selective accommodation of target molecules is the structural transformation. The synthesized [Zn(TCNQ-TCNQ)bpy](**1**) has a flexible three-dimensional structure constructed from a Zn(II) cation, 4,4'-bipyridyl (bpy), and a TCNQ dimer, which is the interactive dianion unit for the guest molecule (Fig. 1), and shows the closed/open-type structural transformation accompanying the adsorption/desorption process. These properties make **1** a good candidate adsorbent for selective separation. The channels delimited by the TCNQ dimer have an undulating form, which is unique, comprising an alternating arrangement of two types of tubes of large and small diameters. The electron-rich pore surfaces of **1**

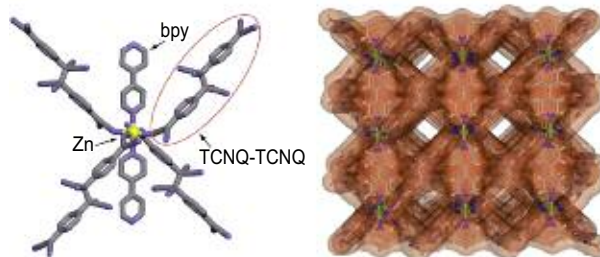


Fig. 1. Crystal structure of **1**. The geometry around the Zn ion (left) and the whole network structure (right) are shown.

should have a good affinity for electron-accepting molecules. This tendency can be observed in the case of gas molecules.

The sorption isotherms of several kinds of gas molecule were measured in the closed form **1** (Fig. 2). Interestingly, only in the cases of O₂ and NO did this compound show the sorption phenomena characteristic of the gate-type sorption behavior: no uptake in the low-concentration region and an abrupt enhancement of adsorption after the threshold concentration. This behavior based on the closed/open-type structural transformation was detected by X-ray powder diffraction (XRPD) analysis. The synchrotron XRPD patterns of the open form and the closed form are distinctly different from each other. Accompanying the accommodation of O₂ and NO, the patterns from the closed form to the new phases with almost the same unit cells as those of the open form was observed. The saturation-adsorbed amount of O₂ was 268 cm³ (at STP)g⁻¹, and that of NO was 322 cm³ (at STP)g⁻¹. In contrast, no sharp uptake over one molecule per

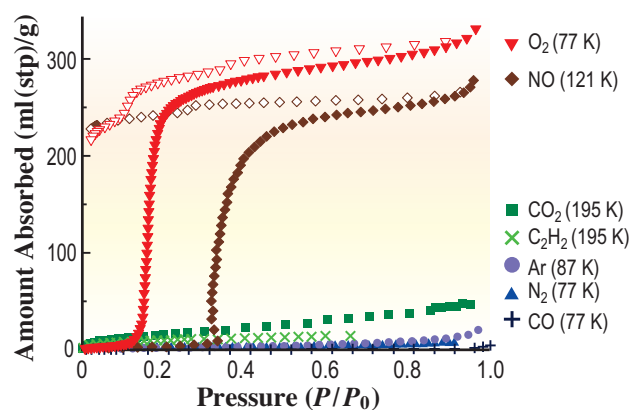


Fig. 2. Adsorption isotherms of several gas molecules on **1**.

formula was observed in the other gas molecules (N_2 , CO , CO_2 , C_2H_2 , and Ar). In this phenomenon, the closed/open transition is important because the trigger of the transformation—the interaction between the host and guest—is an overriding factor for this selectivity. Considering the case of the lack of uptake of CO_2 and C_2H_2 , the quadrupole moment and polarizability, which have a strong effect on the dispersion force of the molecule, have no bearing on this selectivity. In contrast to that in the case of NO , no uptake of CO indicates that the electric dipole moment of guest molecules is not associated with this phenomenon. From these results and background, **1** seems to respond to and recognize some sort of properties common to O_2 and NO .

The Raman spectrum of **1** under the O_2 sorption condition was measured to elucidate the state of **1** and O_2 in the sorption process. The $\nu(\text{O}=\text{O})$ stretch band, which is the index of the physical and chemical states of the O_2 molecule, can be detected directly. As the sorption of the $^{16}\text{O}_2$ molecule progressed, two peaks were observed: a sharp peak at 1454 cm^{-1} and a broad peak at 1449 cm^{-1} . When O_2 was adsorbed on a microporous compound, a slight blue shift of the $\nu(\text{O}=\text{O})$ stretching band by about 10 cm^{-1} was

induced by physical stress in nanospace, the so-called confinement effect. On the other hand, the case of **1** shows a propensity different to that shown in the previous result. The large redshift of the $\nu(\text{O}=\text{O})$ band by about 100 cm^{-1} cannot be induced by the confinement effect. Compared with the reported peak positions of $\nu(\text{O}=\text{O})$ stretching in the various electronic states, the band suggests that O_2 molecules accommodated in **1** have a partial negative charge and that there is no redox reaction with one-electron transfer. This is direct evidence of the existence of the CT interaction between the framework and O_2 molecules and that they are in an exceptional state with an electronic effect and a confinement effect.

We have discovered that **1** shows the selective recognition of O_2 and NO molecules. This specific sorption ability is ascribed to the closed/open-type structural transformation triggered by the CT interaction between the host framework and guest molecule (Fig. 3). The key to this selectivity is the combination of structural dynamics and electron-donating function of the framework, which can be induced by the soft crystallinity and designability of PCPs. PCPs will provide a new platform for selective adsorption systems for small gas molecules.

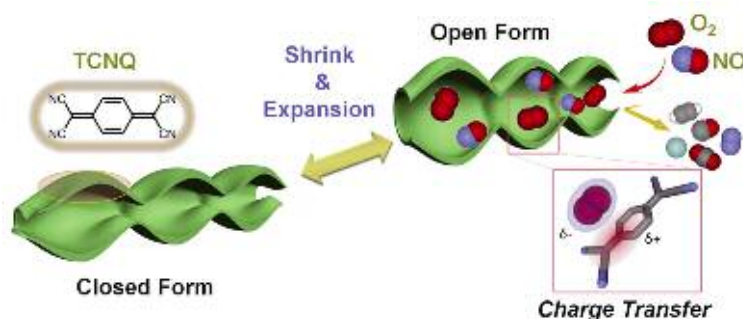


Fig. 3. A schematic representation of the concept shown in this work. The channel formed in TCNQ-based PCP (green tube) shows an expanding/shrinking structural transformation for the NO and O_2 guests, which is induced by the partial charge transfer interaction between the host and the guest.

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