

論文の内容の要旨

論文題目 New Crystalline Porous Materials with Photophysical and
Photochemical Functions
(光物理・光化学的機能を有する新規結晶性多孔質材料)

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[1] Introduction

Crystalline porous solids are of particular scientific and technological importance due to their ability to interact with atoms, ions, and molecules at both the surfaces and throughout the bulk of the interior of the materials. In the past several decades, there have been significant advances in the ability to fabricate new porous solids with ordered structures from a wide range of materials by synthetic chemistry. Taking porous silica and zeolites for example, those two classes of crystalline porous materials show a wide range of applications for traditional use as catalysts and adsorbents. To meet the demand for more advanced applications, such as fuel storage, sensors, drug delivery, and optoelectronics, there has been an ever increasing need to engineer greater uniformity in pore size, geometry and pore surface at the molecular level. In this regard, one of the most important sub-disciplines of supramolecular chemistry, metal-organic frameworks (MOFs), stands out as optimal materials to address these issues. MOFs are constructed by the coordination of transition metal ions (Zn^{2+} , Cu^{2+} , Cd^{2+} , Eu^{3+} , Zr^{4+} , etc.) and di-/polytopic organic linkers. They possess permanent porosity and well-defined pore structures. More importantly, this class of crystalline porous solids enables chemists and materials scientists to tailor the functionalities of the pore space in the MOFs by the rational design of building blocks at a molecular level for specific recognitions toward various ions, gaseous molecules, or even small drugs, which extends the applications of MOFs to more sophisticated systems. The manipulation of the MOFs' functionality via remote and noninvasive methods through the incorporation of light-responsive building blocks is a promising area of research. Inspired by several pioneering works in photo-responsive porous crystalline solids, the research projects I have worked on mainly emphasize the design and synthesis of novel crystalline porous materials featuring photophysical and photochemical functionality.

[2] Crystalline Nanochannels with Pendant Azobenzene Groups

The integration of photoresponsive functional groups, such as azobenzenes, diarylethenes, aryl azides, and nitrobenzyl moieties, into MOFs is a leading strategy for realizing remote or noninvasive manipulation of their properties. Azobenzene derivatives are well-known photoswitches that provide large geometrical changes based on their photochemical isomerization with ultraviolet (UV) and visible light. This isomerization also provides a remarkable change in polarity because the dipole moments of the *trans*- and *cis*-isomers of non-substituted azobenzene are approximately zero and 3.1 D, respectively. While azobenzene moieties have previously been incorporated into crystalline porous solids, to the best of my knowledge, no claim was given as to how the change in polarity of the pore surfaces upon the *cis*-/*trans*- isomerization affects the diffusion kinetics of gaseous molecules through MOFs.

Herein, we report on the synthesis of a zirconium-based metal-organic framework with pendant azobenzene groups (^{Azo}MOF). It consists of small tetrahedral and large octahedral pores, which are connected heterotropically through shared triangular windows. Upon irradiation with ultraviolet (UV) light at 365 ± 10 nm, ^{Azo}MOF underwent a 20% conversion of *trans*-to-*cis* isomerization of its pendant azobenzene moieties (^{Azo}MOF^{21%}) in 30 min at the photostationary state. The reverse process, isomerization from *cis*-to-*trans*, could be achieved upon either irradiation with visible light (420–480 nm) or heating. The isomerization exerts a significant effect on the adsorption of CO₂ but not on the adsorption of Ar in the ^{Azo}MOF. These contrasting behaviors are quite interesting, as the kinetic diameters of CO₂ (3.3 Å) and Ar (3.4 Å) are nearly identical to one another. However, CO₂ has a quadrupole moment (-14.9×10^{-40} C m²), although both CO₂ and Ar are apolar. When erythrosine B, a polarity-sensitive agent, was used as the guest, it showed a red shift upon exposure of ^{Azo}MOF^{20%} EB to visible light, indicating that the interior environment of ^{Azo}MOF becomes less polar as the *trans*-isomer content increases. This apparent change in the pore environment of ^{Azo}MOF strongly influences the kinetic diffusion behavior on gaseous molecules with dipole/quadrupole moment based on the double exponential model.

In conclusion, we demonstrated that ^{Azo}MOF provides the first porous crystalline nanochannel to photochemically modulate the diffusion kinetics of CO₂ by alteration of the dipole/quadrupole interactions within the azobenzene-appended channel wall.

[3] Self-Assembled Porphyrin-Based Crystalline Microstructure

Nano- or microstructures constructed from electrically and optically active organic molecules display unusual optoelectronic properties, often quite different with respect to the single molecules or the bulk materials. Porphyrins (**Por**) are particularly attractive building blocks for self-assembled nano- or microstructures because of its square-planar nature. Several unique **Por**-based nanostructures, such as nanofibers, nanotubes and nanosheets, have been fabricated *via*

host-guest interactions, vaporization-condensation-recrystallization, and other methods. These assemblies have been shown to exhibit intriguing optoelectronic or catalytic properties.

Herein, we report a serendipitous discovery that a new **Por**-based crystalline microstructure was obtained from a reaction mixture of *meso*-tetra(4-carboxyphenyl)porphine (**^{2H}Por**), 4,4'-azopyridine (**^{Azo}Py**) and $\text{Zn}(\text{NO}_3)_2$ in DMF/EtOH by a solvothermal reaction. This crystalline microstructure possessed a peripheral square crystal and a cubic crystal centered on the corresponding peripheral crystal. The concentration of reaction mixture as well as the reaction time plays a key role for the nucleation and crystal growth of these crystalline microstructures. ^1H NMR and diffusion reflectance spectroscopic analyses revealed that the peripheral crystal was consisting of zinc porphyrin (**^{Zn}Por**) only, but the cubic crystal was composed of **^{Zn}Por** and **^{Azo}Py** with a molar ratio of 1 to 1. A layer-by-layer structure was observed in both the cubic and peripheral parts by scanning electron microscopy, atomic force microscopy and transmission electron microscopy. By combining selective area electron diffraction on TEM and powder X-ray diffraction analyses, two-dimensional networks of zinc-metalated porphyrins connected by paddle-wheel-like zinc-carboxylate clusters were the basal structures in both cubic and peripheral crystals. It is noteworthy that the cubic crystal could be isolated from the crystalline microstructure; and the attained cubic crystal exhibited a dichroism phenomenon under linearly polarized light (LPL). When an intact co-crystal was placed under confocal laser scanning microscopy (CLSM) with an excitation laser with a wavelength of 488 nm, it exhibited unique photoluminescence properties. The peripheral crystal showed a bright fluorescence emission but no fluorescence emission was observed from the cubic crystal. When the cubic crystal was isolated from the corresponding crystalline microstructure, the hollow peripheral crystal still retained strong fluorescence emission. Surprisingly, a fluorescence emission was observed in the cubic crystal under CLSM, in sharp contrast to that of the case in the intact porphyrin-based crystalline microstructure. We assume that this anisotropic fluorescence in the cubic crystal might be due to wave-guiding phenomenon in the cavities of the cubic crystal.

In summary, we synthesized a novel porphyrin-based crystalline microstructure with intriguing photophysical properties. The structures and compositions of this crystalline microstructure were investigated by SEM, TEM, PXRD and ^1H NMR analyses.

[4] Conclusion

My research projects emphasize the novel properties of azobenzene-functionalized metal-organic frameworks and porphyrin-based crystalline microstructure. Both of them exhibit unprecedented photophysical and photochemical properties. What I have achieved in my research projects shall be an important and insightful complement to the fundamental photochemistry of crystalline porous materials.