

Photoinduced guest trapping and conversion by photoresponsive nanoporous crystal

Nanoporous compounds are ubiquitous and indispensable in daily life as adsorbents and catalysts. The discovery of a new porous compound having unique properties based on intrinsic nanosized space and surface functionalities is scientifically and technologically important. Surface activity on nanopores is essential for porous properties [1,2]. However, functional species that can be introduced are limited to those that are sufficiently inert so as not to spoil the porous structures. This has prevented access to highly reactive functionalities such as electronically open-shell atoms, which play a pivotal role in many important chemical transformations but often elude isolation and characterization. Furthermore, if it is possible to activate a nanopore surface by external stimuli where and when desired, on-demand gas storage/trapping systems can be realized. Here, we show a new strategy to achieve a crystalline porous material with a pore surface regularly decorated with highly reactive “bare” nitrenes that are photonicly generated from stable “dormant” precursors at will. The bare triplet nitrenes are accessible to and react with adsorbed oxygen molecules, which show not only the activation of the pore surface, but also a high probability of chemical trapping and conversion of guest molecules by light stimulation on demand (Fig. 1) [3]. To achieve the on-demand activation of porous compounds, highly designable host porous frameworks are prerequisite. In this point of view, we adopted porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) [4] as a new platform to create a pore surface having highly reactive species because of their designability based on various functional metal and/or organic sites.

We prepared a linker-type building block having

an azide module, 5-azidoisophthalic acid (H_2N_3 -ipa), because azide modules can be converted to nitrenes, which are reactive open-shell atoms, by photoirradiation. Then, we synthesized single crystals of a new PCP composed of H_2N_3 -ipa ligands, Zn ions and 4,4'-bipyridine (bpy) $[Zn_2(N_3\text{-ipa})_2(\text{bpy})_2(\text{DMF})_{1.5}]_n$ (CID- N_3). CID- N_3 was constructed from interdigitated 2-D layers. A winding 1-D channel with a cross-section of $5 \times 6 \text{ \AA}^2$ runs through the layers, with aryl azides exposed on the channel surface. We studied the sorption properties of dried CID- N_3 which was obtained by heating single crystals of CID- N_3 at 120°C in vacuum for 6 h. The dried CID- N_3 was found to be non-porous for N_2 , O_2 and CO at 77 K because of the slow diffusion of gaseous molecules into the micropore. In contrast, at higher temperatures, the adsorption isotherms of O_2 at 120 K displayed a steep rise in the low-relative-pressure region, indicative of typical physisorption by a microporous compound.

We performed the photoirradiation of CID- N_3 and dried CID- N_3 and tried to observe triplet nitrene species in the frameworks by *in situ* measurements through IR, ESR, and single-crystal X-ray diffraction. The results of the IR and ESR measurements of CID- N_3 and dried CID- N_3 show characteristic signals of triplet nitrene, which ensure the formation of triplet nitrene in CID- N_3 and dried CID- N_3 by photoirradiation. Further clear evidence of the photochemical generation of nitrene species was obtained from crystallographic experiments with the synchrotron X-ray at beamline **BL02B1**. We photoirradiated a single crystal of CID- N_3 for 40 min in vacuum at 77 K and observed a clear change in its diffraction image, which was attributed to a crystal transformation in a space group in a part of the single crystal from $P2/n$ to $C2/m$. The conversion of azide

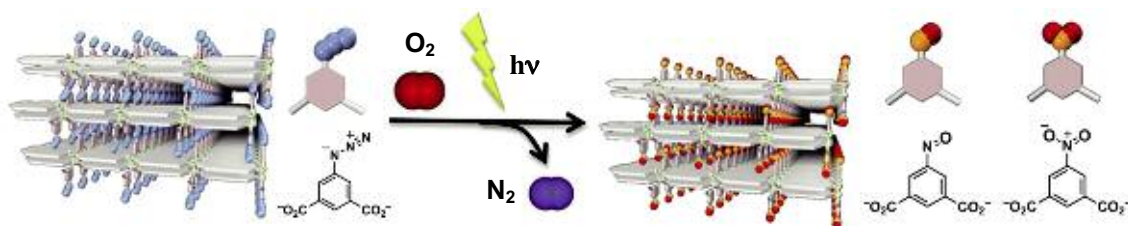


Fig. 1. Schematic representation of concept shown in this work. A new PCP composed of N_3 -ipa (left panel) is converted to NO_2 -ipa- or NO -ipa based PCPs (right panel) by photoirradiation in O_2 atmosphere. N_2 is released during the conversion process.

moieties was estimated to be 31% in the transformed structure from structural analysis. The above-mentioned direct observation indicated that the triplet nitrene anchored on the pore surface was well isolated and sufficiently stable kinetically.

On the basis of the photochemical generation of the highly reactive nitrenes on the pore surface, we sought to demonstrate the usefulness of our porous crystalline material for the on-demand photoactivation of the pore surface. We found that 1) the chemical transformation of adsorbed guest molecules by photoirradiation and 2) the photoinduced adsorption of guest molecules are possible.

We carried out the photoirradiation of dried CID-N₃ in an O₂ atmosphere (80 kPa) at 120 K for 10 h. We confirmed that the photochemical products from dried CID-N₃ were nitro-(NO₂-ipa) and nitroso-(NO-ipa) isophthalic acids by ¹H-NMR. It is worth noting that triplet nitrene is well known to react with oxygen to give a nitro compound, but few reports on the formation of a nitroso compound by the reaction of nitrene and oxygen have been published. These results clearly show that the porous structure is essential so that the photonically generated nitrene can specifically react with oxygen to give NO₂-ipa and NO-ipa in the solid state. We demonstrated that

the *in situ* photoirradiation of dried CID-N₃ remarkably impacts on its sorption property (Fig. 2). As previously mentioned, the original dried CID-N₃ shows an almost non-porous behavior for O₂ at 77 K. However, by *in situ* photoirradiation, the adsorbed amount of O₂ significantly increases in the low-pressure region. An adsorption isotherm of O₂ for the completely converted dried CID-N₃ is obtained considering the photochemical conversion (15%) estimated from the ¹H-NMR spectrum of the photoirradiated sample. According to the isotherm, the photochemically activated dried CID-N₃ can adsorb 29 times as much O₂ at 0.2 kPa compared with the original dried CID-N₃, indicating that photoirradiation achieves a significant enhancement in the adsorption ability of CID-N₃.

Our photoactivation method can be utilized for a wide range of photoreactive species incorporated in PCPs and can be a general strategy to produce PCPs with reactive open-shell atom (ROSA) sites such as radicals and carbenes, which cannot be realized under conventional synthetic conditions. Furthermore, regularly aligned electron deficient species in nanospace are of potential use in selective adsorption for nucleophilic molecules and various topologically controlled chemical reactions. These results will open up a new dimension of porous compounds as platforms for various surface conversions and selective guest trapping.

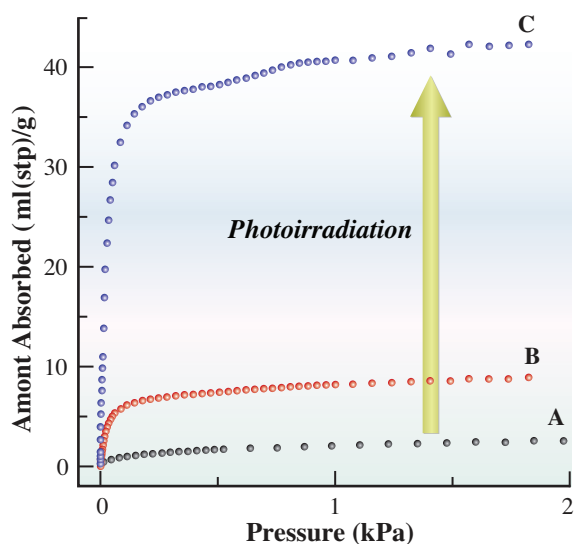


Fig. 2. *In situ* photoactivation of CID-N₃ with adsorption of oxygen. Adsorption isotherms of O₂ at 77 K on dried CID-N₃ without (A) and under (B) photoirradiation, and completely activated CID-N₃ (C). The photochemical conversion (15%) after the adsorption measurement (isotherm b) was estimated from the ¹H-NMR spectrum of the photoactivated sample. The isotherm for completely activated CID-N₃ (C) was obtained from the isotherms (A and B) considering the photochemical conversion (15%).

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