

Environmentally response materials, Smart materials, Optoelectronic devices Development of stimuli-responsive molecular network crystal capable

of retaining single crystallinity in photoisomerization

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Abstract

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Photochromic molecules are light-responsive molecules that change their molecular structure and thus their optical properties upon photoisomerization reaction. In this study, we aimed to develop photo-responsive porous materials by self-assembling such molecules through intermolecular hydrogen bonding. We synthesized and crystallized a carboxylic acid derivative of photochromic dihydrodimethylbenzo[*e*]pyrene (4BDHP) to construct single crystals of a light-responsive porous hydrogen-bonded organic framework (HOF). We found that 4BDHP was regularly linked into a mesh-like structure by hydrogen bonds between carboxy groups, giving a single crystal of a HOF with internal inclusion spaces. Moreover, the photoisomerization progresses when the single crystals were irradiated with visible light, while the single crystalline nature is mostly maintained.

Background & Results

Crystals composed of photoresponsive molecules have potential applications in optical memory, switches, actuators, and so on. Particularly, photoresponsive porous crystals are promising as smart materials that can selectively adsorb and release chemicals using light stimulation as a driving force. Organometallic structures with photoisomerizable chemical structures (MOFs) and covalent organic structures (COFs) have been reported. Molecular crystalline frameworks called hydrogen-bonded organic structures (HOFs) have recently attracted interest as highly crystalline materials with few structural defects that can be reused. However, there have been no HOFs whose structures and properties can be reversibly modulated by light and whose single-crystallinity can be maintained. In this study, we aimed to develop structurally predictable HOF crystals that can be photoisomerized while maintaining the crystal periodicity. We constructed HOFs using 4BDHP, a carboxylic acid derivative of dihydrodimethylbenzo[e]pyrene, as a building block. We found that HOF 4BDHP-2 photoisomerizes upon irradiation with visible light. Particularly, a single crystal of HOF prepared from a pure enantiomer of 4BDHP remained crystalline after photoisomerization, and its structure was successfully revealed by X-ray structural analysis. The crystals after photoisomerization were found to have a network structure in which the original and photoisomerized molecules were arranged alternately. This isomerization changed the shape of the inclusion space in the crystal. The proof-of-concept system of photoresponsive porous crystals that maintain their crystalline periodicity after photoisomerization may provide new light-driven porous functional materials.

Significance of the research and Future perspective

Light-responsive porous crystals, which can maintain their crystalline periodicity even after photoisomerization of their constituent molecules, can repeatedly release molecules from their crystal vacancies or take up molecules into their vacancies using the non-contact stimulus of light irradiation. If such "open/closeable molecular containers" can be created, the release of drugs from the containers or the collection of locally generated chemical substances into the containers could be controlled in space and time, and thus have potential applications in the medical and environmental fields.



Figure 1



Figure 2

Hisaki, Ichiro et al. Photo-responsive hydrogen-bonded molecular networks capable of retaining crystalline periodicity after isomerization. Angew. Chem. Int. Ed. 2024, 63(24), e202404700. doi: 10.1002/anie.202404700

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Keyword hydrogen bonding, porous frameworks, photo switching, organic crystals