1-8-5. Photochemical Reactions in the Solid State

Overview

Among solid-state materials, crystals are the ultimate molecular assemblies in which molecules are regularly arranged. Photochemical reactions in crystals are governed by both the photoreactivity of the molecules themselves and the crystal structure, often producing products that differ from those formed in solution and exhibiting high regioselectivity and high stereoselectivity. Recently, the scope of target crystals has expanded to include photochromic crystals and metal–organic frameworks (MOFs), and research has progressed from photoreactions themselves to new functions and applications of crystals created by photoreactions.

Current Status and Frontiers

Research on photochemical reactions in crystals began in the 1960s with the [2+2] photocycloaddition reaction studied by Schmidt and colleagues, introducing the concept of topochemical reactions. In Japan, many researchers have been leading this field since the 1970s. An overview up to the mid-2000s is presented below; for details, refer to Section "1-8-5. Photochemical Reactions in the Solid State" in the Photochemistry Div Report described in Japanese. URL: https://division.csj.jp/div-report/02/0210805.pdf

Various photoreactions such as addition, elimination, substitution, oxidation, and reduction have been developed. Furthermore, combining electron donors and acceptors into cocrystals has enabled photoinduced electron-transfer reactions. A distinguishing feature of solid-state photoreactions is their ability to yield products with high regioselectivity and stereoselectivity, often differing from those in solution. Absolute asymmetric synthesis has also been achieved: chiral products can be obtained by photoreactions in chiral crystals spontaneously formed from achiral molecules without any chiral auxiliary. Because molecular motion is restricted in crystals, single-crystal-to-single-crystal transformations occur occasionally, allowing the reaction pathway to be traced by X-ray crystallographic analysis, one of the advantages of solid-state reactions.

Since the mid-2000s, the main solid-state photoreactions under continuous investigation include [2+2] cycloadditions of olefins leading to dimerization or polymerization, and [4+4] cycloadditions of anthracenes forming dimers. Unlike in solution, crystal photoreactions proceed cooperatively under the spatial constraints of surrounding molecules. Recently, kinetic analyses at the molecular level have been conducted and related to the propagation of the reaction in macroscopic crystals. Furthermore, research has expanded beyond the study of the photoreactions themselves to creating new functions and applications based on structural changes caused by

photochemical reactions. Examples of these developments are described below.

1. Creation of photomechanical functions through photoreactions in crystals

When light is irradiated onto single crystals of photoisomerizable compounds such as diarylethene, azobenzene, and salicylideneaniline, various mechanical motions—bending, twisting, jumping, or locomotion—can be caused. Many such photomechanical crystals have been developed over the past decade, with promising applications to actuators and soft robots.

2. Functionalization of metal–organic frameworks (MOFs) via photoreaction

MOFs are porous crystalline materials composed of metal–organic complexes and have attracted significant attention due to their functions in adsorption, storage, separation, and catalysis. The design of the pore structure is crucial, and photochemical reactions within MOFs have also been explored. For instance, by incorporating both CO_2 adsorption sites and photocatalytic centers into MOFs, photochemical reduction of CO_2 has been achieved. Moreover, the photoreaction transformed the structure of the MOF itself from a two-dimensional array structure to a three-dimensional structure.

References

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Future Perspectives and Directions

Challenges to be resolved or realized within the next 10 years: Pioneering new solid-state photoreactions, particularly intermolecular reactions within cocrystals. Elucidation of reaction mechanisms. Creation of diverse functions through crystalline photoreactions. Practical application of crystalline state photoreactions.

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