1-8-2. Photochemistry of Supramolecular Systems

Overview

Supramolecular photochemical reactions utilize both excited- and ground-state interactions to control reactions and have been reported to greatly enhance yield and selectivity. Furthermore, numerous reports describe reactivity and products that differ greatly from those in homogeneous systems based on low-entropy environments. Consequently, this approach is attracting attention as a novel method of controlling photoreactions in fundamental and applied research. Since the 1990s, photoreactions utilizing spatially confined environments, such as cyclodextrins and zeolites, have been developed. Recently, new reaction control methods that incorporate nanotechnology have emerged, such as the utilization of metal-organic frameworks (MOFs), nanocapsulation, and CB[n] systems. Additionally, there have been rapid advancements in asymmetric photoreaction and asymmetric amplification/chirality propagation systems. Further developments are anticipated.

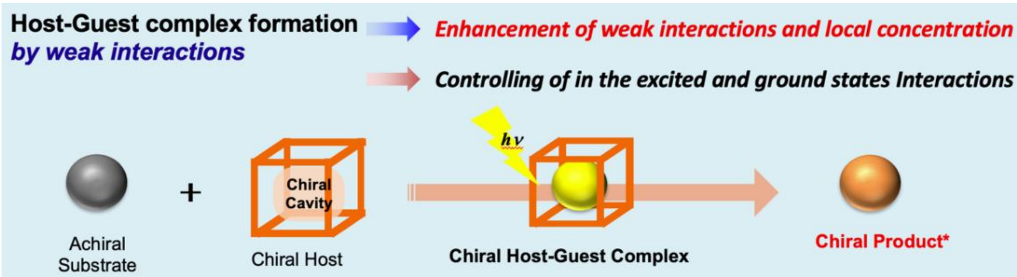

Figure 1. Schematic diagram of supramolecular photochemical reactions.

Current Status and Frontiers

Photoreaction, which proceeds via electronically excited states and exhibits excellent characteristics such as the ability to synthesize compounds with unique structures—including polycyclic and highly strained compounds—in a single step without altering the reaction mechanism across a wide temperature range, is gaining attention as a synthetic method complementary to thermal synthesis. Since the 1990s, supramolecular photoreactions utilizing supramolecular hosts such as cyclodextrins and zeolites as reaction sites have been investigated to construct highly efficient reaction spaces. Within these spatially confined reaction sites possessing nanoscale reaction spaces at the molecular level, the contribution of low-entropy environments—such as (1) the "concentration effect" enhancing local concentration, (2) the "distance effect" reducing intermolecular distances, (3) the "cage effect" suppressing molecular dissipation, and (4) the contribution of a low-entropy environment, such as "reduced solvation and thermal vibrations." Supramolecular photoreactions represent a novel methodology that integrates the characteristics of the aforementioned photoreactions with supramolecular chemistry. They enable the control of highly efficient and selective photoreactions by utilizing not only excited-state interactions but also ground-state interactions. This field was pioneered by N. J. Turro's extension to asymmetric photoreaction systems in 1989. For an overview up to the mid-2000s, refer to Section "1-8-2. Photochemistry of Supramolecular Systems" in the Photochemistry Div Report described in Japanese. URL: https://division.csj.jp/div-report/02/0210802.pdf

Since the mid-2000s, rapid progress has been made with the proposal of host-guest molecular systems utilizing nanotechnology and biotechnology, as well as methods for controlling photoreactions using supramolecular templates. Furthermore, applications have been reported for controlling short-lived processes induced by photoexcitation, such as excimer formation, photon upconversion, and CT excitation, by utilizing ground-state interactions for supramolecular pre-organization of reaction substrates and nano-level confinement effects. This approach is attracting attention as a highly stereoselective and stereospecific method for controlling photoreactions. Specifically, new reaction control methods using metal organic frameworks/MOFs, nanocapsulation, and CB[n] systems are advancing, along with applications to asymmetric photoreaction systems with the utilization of proteins or chiral-modified hosts, and asymmetric amplification/chirality propagation systems. Furthermore, expansion into functional materials represents a new trend, such as:

1. Control of supramolecular structure and function using photoinduction

Development of photoresponsive functional materials is advancing by utilizing light-induced changes in supramolecular structures. Systems enabling on-off control of structure and function in response to irradiation wavelength using photoreversible reactions, as well as self-assembly systems induced by light irradiation, have been reported, with applications to sensors also being explored.

2. Expansion into photoresponsive catalytic systems

Development of supramolecular catalysts with controllable catalytic activity via light irradiation is also progressing. This enables control of reaction selectivity and reaction rate unattainable with conventional chemical reactions. Development of light-controlled supramolecular catalysts based on light-responsive metal complexes and organic molecules is being investigated.

3. Development of light-induced gelation supramolecular materials and applications to self-healing materials

Research on light-induced gelation-type supramolecular materials has also advanced. Materials enabling reversible structural and functional control by utilizing light-induced property changes are attracting attention. Reports describe the application of these light-responsive supramolecular gelation materials to self-healing materials, with anticipated uses in the medical and electronics fields.

Thus, supramolecular photoreactions are increasingly significant not only for fundamental research—such as unique photoreaction environments and asymmetric photoreaction control—but also for applied research, including the development of light-responsive functional materials utilizing these reaction environments. Further advancements are anticipated.

References

1. V. Ramamurthy, J. Sivaguru, *Chem. Rev.*, **116**, 9914–9993 (2016).
2. R. Ham, C. J. Nielsen, S. Pullen, J. N. H. Reek, *Chem. Rev.*, **123**, 5225–5261 (2023).
3. K. Tamaki, S. Yagai, et al., *J. Am. Chem. Soc.*, **146**, 22166–22171 (2024).
4. Y.-W. Su, et al., *Chem. Synth.*, **5**, 10 (2025).
5. D. E. Balderston, J. R. Hiscock, et al., *Chem. Soc. Rev.*, **54**, 8888–8924 (2025).

Future Perspectives and Directions

Challenges to be resolved or realized within the next 10 years: Development of more efficient and selective photoresponsive materials. Overcoming technical challenges for scale-up toward practical application. (Author: Takehiko Wada)