2-5-6. Organic Photochromic Materials

Overview

In applying photochromic molecules to life sciences and materials science, it is of critical importance that they can be driven by visible or near-infrared (NIR) light, which is mild to both biological systems and materials. In recent years, not only one-photon photochromism driven by visible and NIR light but also two-photon photochromism and negative photochromism, both offering superior wavelength selectivity and penetration depth, have attracted increasing attention. Future developments are anticipated in diverse fields such as light-driven molecular machines, photomechanical effects, and optical control of biological functions.

Current Status and Frontiers

Organic photochromic materials have been widely employed not only as optical recording and light-modulating materials but also for controlling diverse physicochemical properties by light. Since the 1970s, numerous researchers in Japan have played leading roles in this field. For studies on applications to photonic devices up to the mid-2000s, refer to section "2-4-5. Organic Photochromic Materials" in the Photochemistry Div Report described in Japanese. URL: https://division.csj.jp/div-report/02/0220204.pdf Representative photochromic molecules include azobenzenes, spiropyrans, indigoids, diarylethenes, and hexaarylbiimidazoles (HABIs). More recently, rational structural modifications have yielded a variety of derivatives that respond to visible and NIR light, and some of these research developments are highlighted below.

1. Azobenzene derivatives

Herges et al. developed diazocines by ethylene-bridging the o,o′-positions of azobenzenes; Woolley et al. introduced electron-donating methoxy groups at the ortho position; and Hecht et al. employed electron-withdrawing fluorine atoms. These modifications enabled reversible E–Z photoisomerization under visible light. Notably, these derivatives exhibit well-separated absorption bands for the Z- and E-isomers, allowing selective excitation of each isomer.

2. Diarylethene derivatives

The open-ring isomer of diarylethenes absorbs only in the UV region. Two principal strategies to achieve visible-light response are: (1) extension of the π-conjugated system and (2) introduction of light-harvesting antenna units. Lehn et al. first reported a

diarylethene with oligothiophenes, shifting the absorption of the open-ring isomer to 450 nm. Fukaminato and Irie synthesized derivatives bearing perylenediimide (PDI) at the reactive carbon of oxidized benzothiophene diarylethenes, achieving a bathochromic shift of the open-ring isomer to 554 nm while retaining photoreactivity.

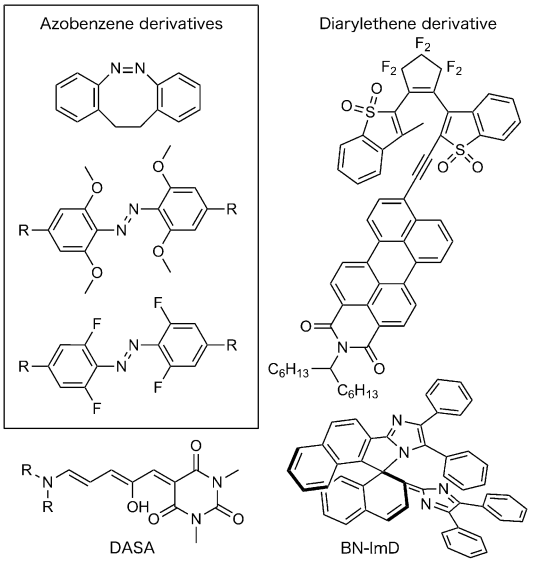

Figure 1. Visible-light-responsive photochromic molecules

3. Negative photochromic molecules

The negative photochromism of Stenhouse salts was first reported by Honda et al. in 1982, though the structural changes and mechanisms were not elucidated at that time. In 2014, Read de Alaniz et al. developed a general synthetic method, leading to robust derivatives collectively termed donor–acceptor Stenhouse adducts (DASAs). The extended, colored form of DASAs absorbs at 500–600 nm and is converted into a compact, colorless form upon visible-light irradiation, which thermally reverts to the stable colored form. Abe et al. reported binaphthyl-bridged imidazole dimers (BN-ImDs), derived from HABIs, exhibiting unique negative photochromism involving three species—colored, radical, and colorless isomers—with the additional feature of a rapid thermal recovery from the metastable colorless state to the stable colored form.

References

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Future Perspectives and Directions

Challenges and goals expected to be addressed within the next decade include: the development of water-soluble photochromic molecules responsive to visible and NIR light; orthogonal dual-wavelength photochromic systems addressable by visible and NIR irradiation; and light-driven molecular machines capable of operating reliably under real-world conditions.

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