1-6-2. Photochemistry of Porphyrins and Phthalocyanines

Overview

Porphyrin is the basic skeleton of molecules that play important roles in biological systems, such as chlorophylls and hemes of hemoglobin, which are responsible for the light-harvesting/charge separation in photosynthesis and the transportation of oxygen in the blood. Phthalocyanines, one of the porphyrin analogs, are functional molecules, which are practically used as the blue pigment in Shinkansen trains, the CYAN dye for inkjet printers, and the photoconductor in photocopiers. The research has expanded beyond basic molecular studies to their modifications onto supports and their uses as components of functional materials.

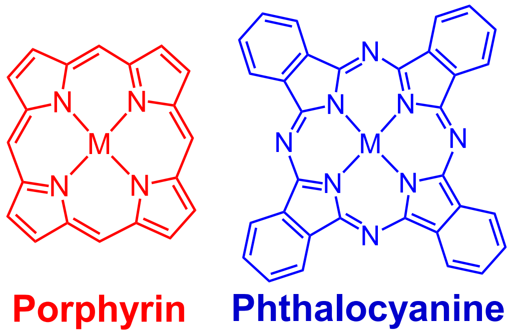

Figure 1. Molecular structures of Porphyrin and Phthalocyanines.

Current Status and Frontiers

Various studies on the photochemistry of porphyrins and phthalocyanines have been conducted due to the fundamental scientific interests mentioned above. Numerous Japanese researchers have led this field since the 1970s. For a comprehensive overview up to the mid-2000s, refer to Section "1-6-2. Photochemistry of Porphyrins and Phthalocyanines" in the Photochemistry Div Report described in Japanese. URL: https://division.csj.jp/div-report/02/0210602.pdf Recently, research on these compounds as components of functional materials has progressed, and several development examples are presented below.

1. Synthesis and properties of porphyrin derivatives

Porphyrin derivatives can change their Q absorption bands from the visible to near-infrared region by changing their molecular structures or oligomerization (e.g., Osuka, Furuta, and Kobayashi). As will be mentioned later, these can be used as building blocks for light-harvesting antenna, electron donor/acceptor, and singlet oxygen generators. In recent years, the attempts to improve their stability during photocatalytic cycles have been reported (Furukawa, Suzuki, Ishii, et al.).

2. Hybridization with inorganic compounds

The attempts to hybridize them with clay (Inoue, Takagi et al.), silica gel (Shirakami, Ishii et al.), semiconductor quantum dots, gold nanoparticles, and so on, have been reported for preparing solid materials.

3. Fundamental research on artificial photosynthesis

Self-assembled chlorophyll aggregates have been studied as light-harvesting antennas (Tamiaki et al.). By linking porphyrin to the CO_2 reduction catalyst, $Re(bpy)(CO)_3$, CO_2 photoreduction catalysts that can work even upon red light irradiation have been developed (Kuramochi et al.).

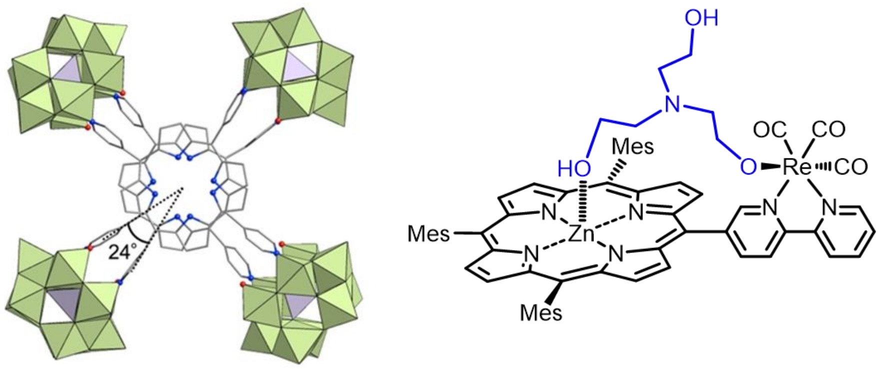

Figure 2. A porphyrin dimer photocatalyst that can stably generate singlet oxygen (left) and a porphyrin-$Re(bpy)(CO)_3$-based CO_2 photoreduction catalyst (right).

4. Photobiological applications

Phthalocyanines with strong Q-band absorption have been developed as fluorescence probes and photosensitizers for photodynamic therapy using red and near-infrared light ($\geq$ 650 nm), which can highly penetrate living tissues (Ishii et al.). In photodynamic therapy, singlet oxygen generated by the energy transfer from the excited triplet photosensitizers attacks cancer cells. Porphyrin derivatives, i.e., Chlorin e6 and so on, are practically used as photosensitizers. In photoimmunotherapy using antigen-antibody interactions, the phthalocyanine conjugated to antibodies is used (Kobayashi, Ogawa et al.).

References

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2. Y. Kuramochi, Y. Fujisawa, A. Satake, *J. Am. Chem. Soc.*, **142**, 705–709 (2020).
3. T. Yokoi, T. Otani, K. Ishii, *Sci. Rep.*, **8**, 1560 (2018).
4. K. Murata, et al., *Chem. Commun.*, **58**, 11280–11283 (2022).

Future Perspectives and Directions

Issues to be solved or realized in the next decade: Development of photocatalysts for CO_2 reduction, H_2 production, ammonia conversion, and so on, and components for optical memory and optical quantum information.

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