

Photoresponsive Molecular Switch to Control Chemical Fixation of CO₂

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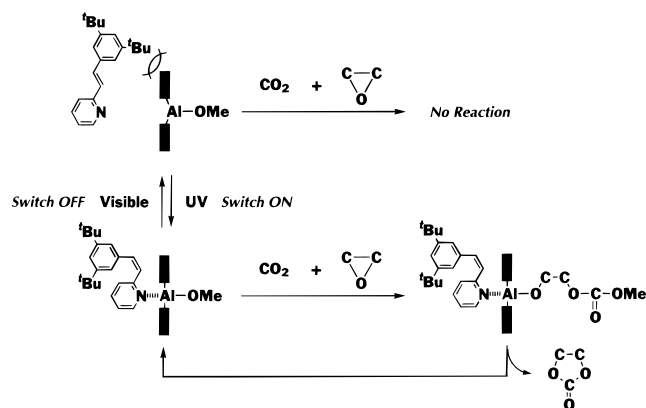
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Photocontrol of chemical or physical functions has attracted continuous interest in connection with the photoresponsive systems in nature, such as vision¹ and photomorphogenesis in plants.² However, chemists trying to elucidate the mechanism of photoresponsive natural systems have devoted their efforts to investigate the physicochemical properties of light-absorbing molecules, such as photochromism and electron-transfer, but have hardly dealt with connection of these properties with biosynthetic chemical reactions eventually affording the products of the processes induced by photoresponsive molecules. On the other hand, interests in artificial systems exhibiting functions in response to light have increased, as exemplified by the photoregulated interaction between photoresponsive hosts and guests.³ However, there have been a few studies demonstrating reactions regulated by photoresponsive molecules.⁴ Therefore, we have been prompted to construct a light-driven switching-system, a "photoresponsive molecular switch", which acts as an on-off switch to start and stop chemical reactions based on a novel concept. Herein we report the photoresponsive molecular switch, consisting of aluminum porphyrin and an olefin, to control the reaction of carbon dioxide and an epoxide through the light-induced structural change, photoisomerization, of the olefin.⁵

To realize a photoresponsive molecular switch, three parts, such as reaction site, reaction control site, and photocontrol site, should be included in the system. The combination of aluminum porphyrin and stilbazole, a nitrogen-containing base, was chosen as the components of a photoresponsive molecular switch (Scheme 1), since the photoswitchable complexation of a base to metalloporphyrin was expected to provide a step toward a light-driven on-off switch to control chemical reactions on metalloporphyrins. For the construction of the photoresponsive switch, stilbazole (2-phenylethenylpyridine), a derivative of stilbene which is one of the representative compounds related to the natural photoresponsive molecules, such as retinal, is very interesting, since it undergoes isomerization from the *trans*-form to the *cis*-form upon UV irradiation and reversion by visible light via the complexation of the pyridine group to the metal center of metalloporphyrins.⁶ Actually, we have recently found that photoisomerizable 2-stilbazole coordinates to zinc tetraphenylporphyrin to different

Scheme 1



extents, depending on the structure of the geometric isomers of stilbazole due to steric repulsion between zinc porphyrin and stilbazole.⁷ Furthermore, the complexation of zinc tetraphenylporphyrin with 2-stilbazole is reversibly photoswitchable by UV and visible lights through the *trans*-*cis* isomerization of the stilbazole. On the other hand, complexation of metalloporphyrin with a nitrogen-containing base is particularly important, since some reactions on metalloporphyrins require the coordination of a base to the central metal of metalloporphyrin, as observed both in natural and artificial systems. For example, aluminum porphyrin with an aluminum alkoxide group produces five-membered cyclic carbonate by the catalytic reaction of carbon dioxide and epoxide only when the nitrogen-containing base, such as 1-methylimidazole, coexisting in the reaction system coordinates to the metal center of metalloporphyrin.⁸ Therefore, the aluminum porphyrin–stilbazole system is expected to serve as a novel photoresponsive molecular switch to control the reaction of carbon dioxide and epoxide.

To establish the photoswitching of the reaction by the aluminum porphyrin–stilbazole system as the photoresponsive molecular switch through the photoisomerization of 2-stilbazole (Scheme 1), the rate of the reaction must differ to a large extent depending upon the isomer structure of stilbazole. When the reaction was carried out in the dark at 25 °C, the yields of the product in the presence of *cis*- and *trans*-3',5'-di-*tert*-butyl-2-stilbazole (**2**) were different from each other enough to realize a photoswitching system. In the case of using *cis*-**2**, which is expected to readily coordinate to methoxyaluminum 5,10,15,20-tetraphenylporphyrin ((TPP)AlOMe, **1**),⁹ the reaction of 1,2-epoxypropane (propylene oxide, PO) (20 equiv with respect to **1**) and CO₂ by the **1**–*cis*-**2** (3 equiv with respect to **1**) system took place as evidenced by the appearance and increase of a peak at 1797 cm⁻¹ due to the C=O group of propylene carbonate (PC) in the periodically measured IR spectra of the reaction mixture, where the yield of PC, as estimated by ¹H NMR, was 7 and 23% in 6 and 18 h, respectively (Figure 1; ■).¹⁰ In the presence of *trans*-**2**, which is

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(4) For reviews, see: Willner, I. *Acc. Chem. Res.* **1997**, 30, 347–356. Willner, I.; Rubin, S. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 367–385.

(5) A part of the present work was presented at the 1st International Conference on Supramolecular Science and Technology, October, 1998, Poland.

(6) Whitten, D. G.; Wildes, P. D.; DeRosier, C. A. *J. Am. Chem. Soc.* **1972**, 94, 7811–7823.

(7) Iseki, Y.; Inoue, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2577–2578.

(8) Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1983**, 105, 1304–1309.

(9) To a round-bottomed flask (50 mL) equipped with a three-way stopcock containing 5,10,15,20-tetraphenylporphyrin (TPPH₂) (0.5 mmol), CH₂Cl₂ (20 mL) and Me₃Al (0.048 mL, 1 equiv) were successively added by a hypodermic syringe in a nitrogen stream, and the mixture was stirred for 1 h in a nitrogen atmosphere at room temperature. The volatile fractions were removed from the reaction mixture under reduced pressure to leave methylaluminum tetraphenylporphyrin ((TPP)AlMe) as a purple powder. Methoxyaluminum tetraphenylporphyrin ((TPP)AlOMe, **1**) was prepared by the reaction of (TPP)AlMe with MeOH. To a CH₂Cl₂ (20 mL) solution of (TPP)AlMe (0.5 mmol), MeOH (5 mL) was added by a syringe in a nitrogen stream, and the mixture was stirred for 15 h in a nitrogen atmosphere at room temperature. The solvent and unreacted MeOH were removed from the reaction mixture under reduced pressure to leave **1** as a purple powder: Takeda, N.; Inoue, S. *Bull. Chem. Soc. Jpn.* **1978**, 51, 3564.

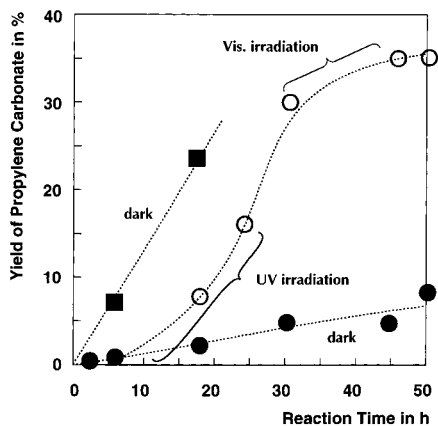
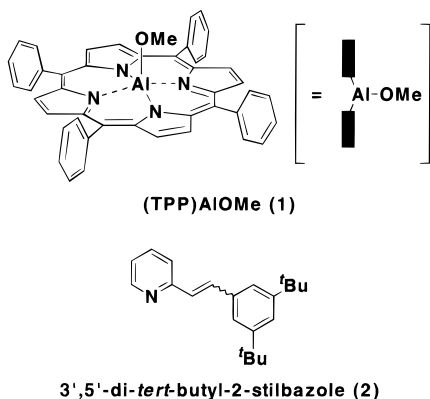


Figure 1. Reaction of carbon dioxide and propylene oxide in a (TPP)-AlOMe (**1**)-3',5'-di-*tert*-butyl-2-stilbazole (**2**) system, initial isomer structure of **2** is the *trans*-form, under irradiation; (●) isomer structure of **2** is the *trans*-form, in the dark; (■) isomer structure of **2** is the *cis*-form, in the dark.



expected to hardly coordinate to **1**, under otherwise similar conditions, the reaction of CO₂ and PO with the **1**-*trans*-**2** system proceeded much more slowly to attain only 1, 2, and 5% in 6, 18, and 30 h, respectively (Figure 1; ●).

As expected from the above results, the (TPP)AlOMe (**1**)-stilbazole (**2**) system under the irradiation with UV light was confirmed to serve as an on-switch to speed up the reaction, while under the visible light irradiation the system worked as an off-switch to reduce the rate of the once accelerated reaction. When the reaction mixture of CO₂ and PO with the **1**-*trans*-**2** system after the 6-h reaction in the dark was irradiated with UV light (λ

= 290–360 nm) at 25 °C for 18 h (total reaction time: 24 h), which induces isomerization of **2** from the *trans*-form to the *cis*-form, the reaction was gradually accelerated. The faster reaction than that in the dark proceeded up to 16 and 30% yield of PC after 18-h irradiation and the following 6-h in the dark, respectively (Figure 1; ○). This corresponds to about 10-folds acceleration. This observation indicates that irradiation with UV light induces the *trans*-to-*cis* isomerization of **2** and thus **2** coordinated to **1** more easily than before irradiation resulting in the enhanced reactivity of **1** with CO₂ and PO to produce PC more efficiently. The fact that the reaction continued at an accelerated speed even after the UV irradiation was stopped indicates that the UV light did not serve as the direct energy for acceleration, to confirm the activation of **1** by coordination with **2**. In sharp contrast, the subsequent irradiation with visible light ($\lambda > 380$ nm), which induces the *cis*-to-*trans* isomerization of **2**, of the reaction system for 18 h slowed the reaction, where the rate of reaction became close to that in the presence of *trans*-**2** in the dark.¹¹

In conclusion, the present study demonstrated an interesting novel example of photoresponsive molecular switch, the light-driven on-off switching system for chemical reaction, composed of aluminum porphyrin and stilbazole, which can regulate the reaction of carbon dioxide and propylene oxide to give propylene carbonate catalyzed by aluminum porphyrin in the presence of stilbazole by the UV or visible light through the photoisomerization of stilbazole. The present results provide a novel concept for the design of photoresponsive systems to regulate the chemical and physical functions by using light as information.

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(10) A typical procedure for the reaction of carbon dioxide (CO₂) and 1,2-epoxypropane (propylene oxide, PO) by the methoxyaluminum 5,10,15,20-tetraphenylporphyrin (**1**)-3',5'-di-*tert*-butyl-2-stilbazole (**2**) system was as follows: *trans*-**2** (3 mmol) was added to a 100-mL round-bottomed flask attached to a three-way stopcock containing a CDCl₃ solution (20 mL) of **1** (1 mmol) under dry CO₂. With vigorous stirring, CO₂ was passed through the solution for 5 min, and then PO (20 mmol, 1.4 mL) was added to the solution by a hypodermic syringe at 25 °C. A small amount of the reaction mixture was periodically taken out by a syringe in a nitrogen stream and subjected to IR and ¹H NMR measurements to estimate the yield of propylene carbonate (PC) formed. Ushio LX-300, a 300-W Xe lamp, with Kenko HA-50 filter for visible light ($\lambda > 380$ nm) or Kenko U-330 filter for UV light ($\lambda = 290$ –360 nm) was used for irradiation at 25 °C.

(11) Although the coordination of stilbazole (**2**) to methoxyaluminum porphyrin (**1**) could not be estimated quantitatively by the spectral analyses, the coordination of a related compound, chloroaluminum porphyrin [(TPP)-AlCl] with *cis*-**2**, but not with *trans*-**2**, was confirmed by UV/vis spectrum. Furthermore, the coordination of **2** to (TPP)AlCl was reversibly controlled by UV and visible light irradiation.