

A photoresponsive molecular switch. Reaction of CO₂ and epoxide regulated by aluminum porphyrin–stilbazole system

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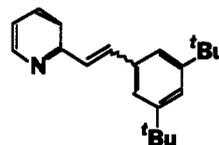
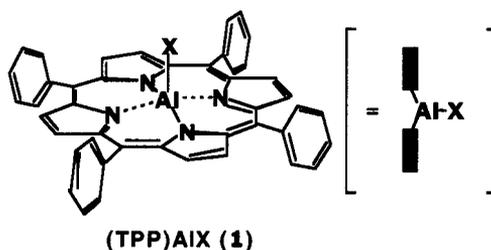
Abstract: A novel example of a 'photoresponsive molecular switch', the light-driven on-off switching system for chemical reaction, composed of aluminum porphyrin and stilbazole is found to regulate the reaction of carbon dioxide and propylene oxide to give propylene carbonate. The reaction is catalyzed by aluminum porphyrin through the photoisomerization of stilbazole.

In the dark, the reaction of carbon dioxide and propylene oxide to give propylene carbonate proceeds very slowly for the methoxyaluminum porphyrin - *trans*-stilbazole system. However, the reaction was accelerated by UV light ($\lambda = 290 - 360$ nm), but less so by visible light ($\lambda > 380$ nm).

INTRODUCTION

Photoresponsive chemical systems are essential to biological functions, such as vision (ref. 1) and photomorphogenesis in plants (ref. 2), and have attracted continuous interests in connection with mimicking such natural photoresponsive systems in order to construct artificial systems. Chemists trying to elucidate the mechanism of photoresponsive natural systems have devoted their efforts to investigation of the physico-chemical properties of light-absorbing molecules, such as photochromism and electron-transfer. However, they have hardly dealt with connecting these properties with biosynthetic chemical reactions to eventually afford the products of the processes induced by photoresponsive molecules. On the other hand, interest in artificial systems which exhibit functions in response to light have increased, as exemplified by the photoregulated interaction between photoresponsive hosts and guests (ref. 3). However, there has been only limited demonstration of reactions regulated by photoresponsive molecules (ref. 4). Therefore, we have sought to construct a novel light-driven switching-system, a 'photoresponsive molecular switch', which functions as on-off switch to start and stop chemical reactions.

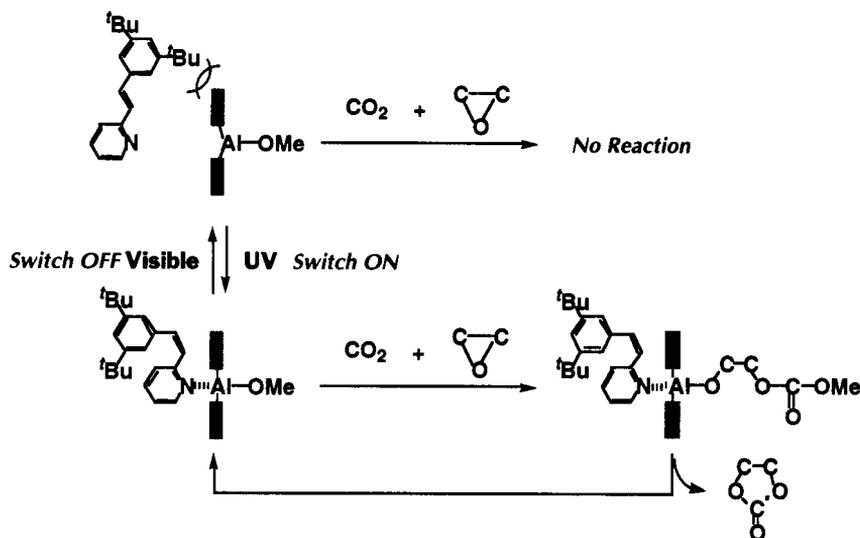
Aluminum porphyrin and stilbazole, a nitrogen-containing base, were chosen as the components of the photoresponsive molecular switch (Scheme 1), since the photoswitchable complexation of a base to metalloporphyrin was anticipated to provide access to a light-driven on-off switch to control a chemical reaction of the metalloporphyrin. For the construction of the photoresponsive switch, stilbazole (2-phenylethenylpyridine, a stilbane derivative which is related to natural photoresponsive molecules, such as retinal), is of much interest, 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 metalloporphyrins (ref. 5). We have recently found that photoisomerizable 2-stilbazole coordinates to zinc porphyrin with different extents depending on the structure of the geometric isomers of stilbazole due to



3',5'-di-*tert*-butyl-2-stilbazole (2)

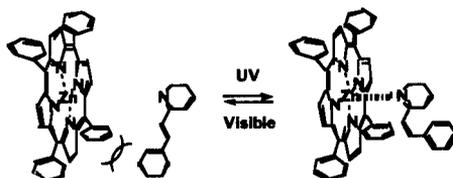
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Scheme 1



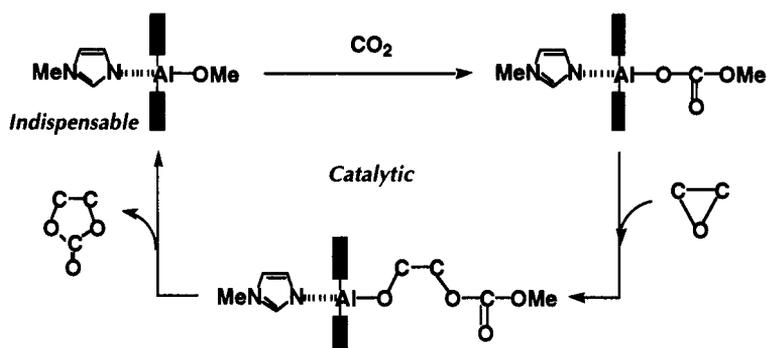
steric repulsion between zinc porphyrin and stilbazole (ref. 6). Thus, the complexation of zinc tetraphenylporphyrin with 2-stilbazole is reversibly photoswitchable by UV and visible lights through the *trans-cis* isomerization of the stilbazole (Scheme 2). On the other hand, complexation of metalloporphyrin with a nitrogen-containing base is of particular importance, since some reactions on metalloporphyrins require the coordination of a base to the central metal of metalloporphyrin, as observed both in natural and

Scheme 2



artificial systems. For example, aluminum porphyrin with an aluminum alkoxide group produces a five-membered cyclic carbonate catalytically by the reaction of carbon dioxide and epoxide only when a nitrogen-containing base, such as 1-methylimidazole, coexisting in the reaction system coordinates to the metalloporphyrin (Scheme 3) (ref. 7). 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.

Scheme 3



RESULTS AND DISCUSSION

Reaction of carbon dioxide and epoxide by an aluminum porphyrin–stilbazole system in the dark

When the reaction of carbon dioxide (CO₂) and 1,2-epoxypropane (propylene oxide; PO) catalyzed by methoxyaluminum tetraphenylporphyrin (**1**, X = OMe) was carried out in the dark at 25 °C, the yields of propylene carbonate (PC) in the presence of *cis*- and *trans*-3',5'-di-*tert*-butyl-2-stilbazole (**2**) were sufficiently different to realize a photoswitching system. With *cis*-**2**, which is expected to readily coordinate to **1** (X = Ome), the reaction of CO₂ and PO (20 equiv with respect to **1**) 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 1,797 cm⁻¹ due to the C=O group of PC in the periodically measured IR spectra of the reaction mixture. The yield of PC, as estimated by ¹H NMR, was 7 and 23 % in 6 and 18 h, respectively (Fig. 1). In the presence of *trans*-**2**, which is expected to coordinate poorly to **1** (X = OMe) under otherwise similar conditions, the reaction of CO₂ and PO by the **1** (X = OMe) - *trans*-**2** system proceeded much more slowly to attain only 1, 2, and 5 % yield in 6, 18, and 30 h, respectively (Fig. 1). These results show that the reaction rate in the presence of *cis*-**2** was sufficiently larger than that in the presence of *trans*-**2** to establish photoswitching of the reaction by the aluminum porphyrin - stilbazole system as the photoresponsive molecular switch through the photoisomerization of 2-stilbazole (Scheme 1).

Reaction of carbon dioxide and epoxide by an aluminum porphyrin–stilbazole system under irradiation

The aluminum porphyrin - stilbazole system under the irradiation with UV light was confirmed to serve as an on-switch to speed up the reaction, while under visible light 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** (X = OMe) - *trans*-**2** system was irradiated with UV light ($\lambda = 290 - 360$ nm) at 25 °C for 18 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 gave 16 and 30 % yields of PC after 18- and 24-h irradiation, respectively (Fig. 1). This corresponds to about a 10-folds acceleration. This observation indicates that irradiation with UV light induces the *trans*-to-*cis* isomerization of **2** and with **2** coordinating to **1** (X = OMe) 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 does not serve as the direct energy for acceleration, which confirms the activation of **1** (X = OMe) by coordination with **2**. In sharp contrast, 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 down the reaction, such that the rate of reaction became to that in the presence of *trans*-**2** in the dark.

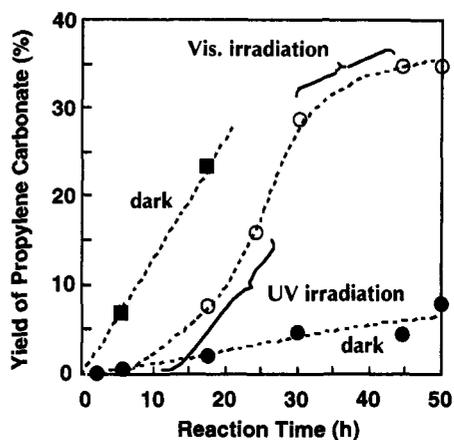


Figure 1. Reaction of carbon dioxide and propylene oxide in a (TPP)AlOMe (**1**) - 3',5'-di-*tert*-butyl-2-stilbazole (**2**) system. ○: initial isomer structure of **2** is the *trans*-form, under irradiation; ●: isomer structure of **2** is the *trans*-form, in the dark; ■: isomer structure of **2**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

Coordination of 2-stilbazole to aluminum porphyrin

In relation to the above results, the complexation behavior between chloroaluminum tetraphenylporphyrin [(TPP)AlCl, **1** with X = Cl] and **2** in CH₂Cl₂ was studied at room temperature. An absorption maximum in the visible region in the spectrum for a mixture of **1** (X = Cl) (1.0×10^{-3} M) and *trans*-**2** (6.0×10^{-2} M) in CH₂Cl₂ was observed at the same wavelength ($\lambda = 548$ nm) as that seen in the spectrum for **1** (X = Cl) alone in CH₂Cl₂, indicating that the two components were in a dissociated form. On the other hand, the red-shift of the absorption maximum from 498 nm to 510 nm and appearance of a new absorption at 603 nm observed for a CH₂Cl₂ solution of **1** (X = Cl) and *cis*-**2** under the identical conditions demonstrated the complexation of **1** (X = Cl) and *cis*-**2**. Furthermore, irradiation with UV light ($\lambda = 290 - 360$ nm) of a CH₂Cl₂ solution of **1** (X = Cl) (1.0×10^{-3} M) and *trans*-**2** (6.0×10^{-2} M), where the isomerization of *trans*-**2** to *cis*-**2** should take place, resulted in the induction of complexation between **1** (X = Cl) and **2** as shown by the gradually increased absorption at 603 nm (Fig. 2). When the resulting solution was irradiated with visible light ($\lambda > 380$ nm), the absorption at 603 nm was decreased gradually, indicating that dissociation of the complex occurred (Fig. 2).

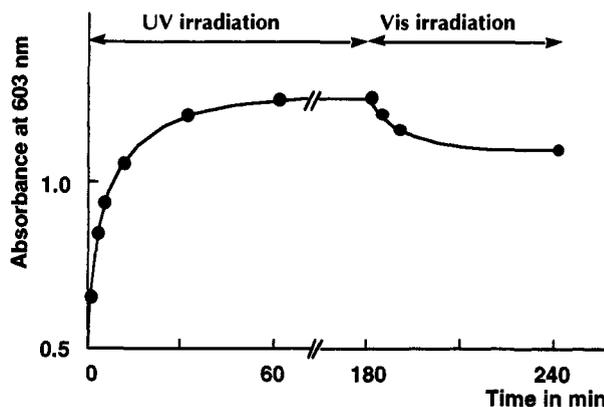


Figure 2. Photoresponsive change of complexation between (TPP)AlCl (**1** with X = Cl) and 3',5'-di-*tert*-butyl-2-stilbazole (**2**) upon the irradiation of UV ($\lambda = 290-360$ nm) followed by visible light ($\lambda > 380$ nm); $[1]_0 = 1.0 \times 10^{-3}$ M, $[trans-2]_0 = 6.0 \times 10^{-2}$ M.

CONCLUSION

The present study demonstrates a novel example of a photoresponsive molecular switch, the light-driven on-off switching system for a chemical reaction, composed of aluminum porphyrin and stilbazole, which regulates the reaction of carbon dioxide and propylene oxide to give propylene.

EXPERIMENTAL SECTION

Materials

Trimethylaluminum (Me₃Al) and diethylaluminum chloride (Et₂AlCl) were fractionally distilled under reduced pressure in a nitrogen atmosphere.

CH₂Cl₂ and CHCl₃ were washed successively with concentrated H₂SO₄, water, and aqueous NaHCO₃, dried over CaCl₂, and distilled over CaH₂ under nitrogen. Deuterated chloroform (CDCl₃) was distilled over CaH₂ under nitrogen. MeOH was purified as follows: 50 mL of MeOH was refluxed over a mixture of Mg (4 g) and I₂ (1 g) until all the Mg was converted to the methoxide, and then 1 L of MeOH was added. The mixture was refluxed and distilled under nitrogen.

1,2-Epoxypropane (propylene oxide, PO) was refluxed over a mixture of KOH and CaH₂, and fractionally distilled under nitrogen atmosphere. Carbon dioxide was passed through a column packed with silica gel, molecular sieves (4A), and P₂O₅ prior to use.

3',5'-Di-*tert*-butyl-2-stilbazole (**2**) was synthesized from 3,5-di-*tert*-butylbenzaldehyde and 2-picoline according to the literature procedure (ref. 8).

Preparation of aluminum porphyrin (**1**)

5,10,15,20-Tetraphenylporphyrin (TPPH₂) was synthesized from pyrrole (0.8 mol) and benzaldehyde (0.8 mol) in propionic acid (2.5 L) under reflux for 0.5 h. The crude product, which precipitated upon allowing

the reaction mixture to stand overnight at room temperature, was recrystallized from $\text{CHCl}_3/\text{MeOH}$ (1/2 in v/v) to give TPPH_2 in 20 % yield (ref. 9).

To a round-bottomed flask (50 mL) equipped with a three-way stopcock containing TPPH_2 (0.5 mmol), CH_2Cl_2 (20 mL) and Me_3Al (0.048 mL, 1 equiv) were successively added by a hypodermic syringe in nitrogen stream. The mixture was stirred for 1 h under a nitrogen atmosphere at room temperature. The volatile fractions were removed from the reaction mixture under reduced pressure to leave methylaluminum tetraphenylporphyrin ((TPP)AlMe; **1**, X = Me) as a purple powder. Methoxyaluminum tetraphenylporphyrin ((TPP)AlOMe; **1**, X = OMe) was prepared by the reaction of (TPP)AlMe with MeOH. To a CH_2Cl_2 (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 under a nitrogen atmosphere at room temperature. The solvent and unreacted MeOH were removed from the reaction mixture under reduced pressure to leave **1** as purple powder (ref. 10).

Chloroaluminum tetraphenylporphyrin [(TPP)AlCl ; **1**, X = Cl] was synthesized from TPPH_2 and Et_2AlCl similarly to the above procedure.

Reaction of carbon dioxide and propylene oxide

A typical procedure for the reaction of carbon dioxide (CO_2) and 1,2-epoxypropane (propylene oxide; PO) by the methoxyaluminum tetraphenylporphyrin (**1**, X = OMe) - 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 CDCl_3 solution (20 mL) of **1** (X = OMe) (1 mmol) under dry CO_2 . With vigorous stirring, CO_2 was passed through the solution for 5 min, and then PO (20 mmol; 1.4 mL) was added to the solution with a hypodermic syringe at 25 °C. A small amount of the reaction mixture was periodically removed with a syringe in a nitrogen stream and subjected to IR and ^1H NMR spectral measurements to estimate the amount 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.

Measurement

^1H NMR spectra was measured in CDCl_3 on a JEOL type GSX-270 spectrometer. The chemical shifts were determined with respect to CHCl_3 (δ 7.28 ppm) as the internal standard. IR spectra were recorded with a JASCO FT/IR-5300 spectrometer.

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