Photoresponsive Coordination of Stilbazoles to Metalloporphyrins

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Abstract: The coordination of stilbazole derivatives to metalloporphyrins was investigated. Among the stilbazoles examined, a stilbazole with a bulky group such as 4-phenyl-3-stilbazole (**4**) showed considerable difference between the trans and cis isomers in its ability to coordinate to aluminum and zinc porphyrins with bulky peripheral substituents. The extent of coordination of **4** to metalloporphyrins could be changed by the trans → cis isomerization of **4** upon UV irradiation.

Introduction

A photoresponsive chemical system is essential to biological functions such as sense of vision[1] and photomorphogenesis in plants.[2] The initial step in the mechanism of vision is the photoisomerization of 11-*cis*-retinal, the chromophore of rhodopsin, to the *all-trans* form,[3] and this isomerization triggers the dissociation of the retinal moiety from the protein and its conformational change at once. It is of considerable interest to mimic such photobiological systems, namely, to construct an artificial system in which the photoisomerization of a chromophore triggers a chemical or physical function.

Recently, azobenzene derivatives have been extensively utilized as chromophores for photocontrolling the conformational change of synthetic polypeptides[4] and other polymers[5] or the binding ability of cyclodextrins[6] and crown ethers.[7] One of the most remarkable observations was reported by Willner et al. about photoswitchable complexation of eosin Y with a viologen derivative bound to azobenzene induced by the photoisomerization of the azobenzene group.[8]

Stilbazole (2-phenylethenylpyridine) is another candidate for a chromophore that can be used as a photoswitch, having a carbon–carbon double bond, and it is more relevant to the behavior of retinal. The stilbazole derivatives are known to undergo trans → cis isomerization by UV irradiation[9] and undergo the reversion by the irradiation of visible light in the presence of a metalloporphyrin.[10] If there exists considerable difference in the extent of complexation of a stilbazole derivative with a metalloporphyrin between the trans and cis isomers, it would be possible to construct a novel photoresponsive system in which the coordination of stilbazole to metalloporphyrin is controlled by the photoisomerization of a stilbazole derivative. Such a photoresponsive metalloporphyrin–stilbazole system is expected to be applied to a photoswitch for a chemical reaction on the metalloporphyrin complexed with stilbazole.

The effect of photoexcitation of metalloporphyrins on their coordination behavior has been extensively studied in connection with the mechanism of ligand binding in heme group compounds. An interesting observation recently reported is the relaxation of the tertiary structure of protein induced by the photodissociation of CO from myoglobin.[11] On the other hand, the photoisomerization of stilbazoles complexed with metalloporphyrins[10] and related compounds of metals such as Ru, Re, and Pd has been reported.[12] However, the change in coordinative behavior of stilbazoles accompanied by the photoisomerization has not been reported.

This paper describes the study of the complexation of a variety of stilbazole derivatives (**1–5**) with aluminum and zinc porphyrins (**6a–e**). In the combination of a stilbazole derivative with a bulky substituent and a bulky metalloporphyrin, considerable differences were observed in the extent of complexation between the trans and cis isomers. The extent of complexation of stilbazoles with the metalloporphyrins could be changed by the trans → cis photoisomerization of the stilbazoles.

Experimental Section

General. Unless noted, solvents and chemicals were purchased and used without further purification. 1,2-Dichloroethane (DCE) was distilled over CaH_2 in a dry nitrogen atmosphere.

Measurements. Melting points were uncorrected. ^1H NMR spectra were recorded on a JOEL JNM-270 spectrometer. Infrared spectra (IR) were recorded on a JASCO FT/IR-5300 spectrometer. UV–vis spectra were recorded on a JASCO U-best 50 spectrophotometer.

General Procedure for the Preparation of Metalloporphyrins. Free-base porphyrins such as tetraphenylporphyrin ($(TPP)H_2$)[13] and tetramesitylporphyrin ($(TMP)H_2$)[14] were prepared in the manner already reported. (TPP)AlCl (**6a**) and (TMP)AlCl (**6b**) were prepared by the equimolar reactions of the free-base porphyrins with Et_2AlCl in CH_2Cl_2 under Ar.[15] (TPP)AlOR (**6c**) was prepared by the polymerization of

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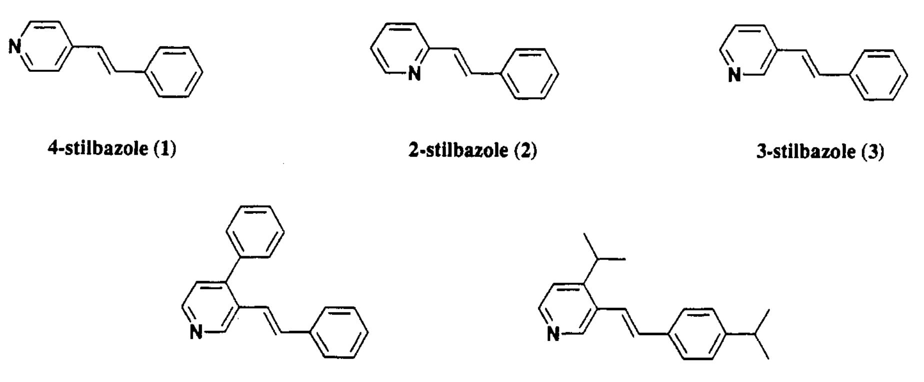
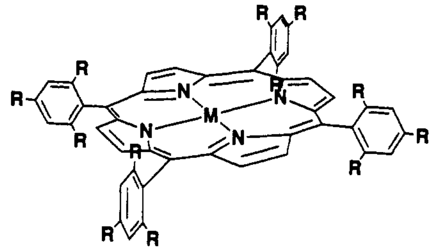
Chart I



4-stilbazole (1) 2-stilbazole (2) 3-stilbazole (3)

4-phenyl-3-stilbazole (4) 4,4'-diisopropyl-3-stilbazole (5)



6a	(TPP)AlCl	R = H,	M = AlCl
b	(TMP)AlCl	= Me,	= AlCl
c	(TPP)AlOR	= H,	= Al(OCHCH$_3$CH$_2$)$_n$Cl (n=5)
d	(TPP)Zn	= H,	= Zn
e	(TMP)Zn	= Me,	= Zn

propylene oxide with **6a** in CH$_2$Cl$_2$ under Ar.[14] (TPP)Zn (**6d**) and (TMP)-Zn (**6e**) were prepared by the reaction of the free-base porphyrins with zinc acetate in CHCl$_3$/MeOH.[16]

General Procedure for the Preparation of Stilbazoles. Stilbazoles were obtained in reasonable yields by Wittig reaction of the corresponding pyridinecarbaldehyde with benzyltriphenylphosphonium chloride. To benzyltriphenylphosphonium chloride (2.0 g, 5.0 mmol) dissolved in dry tetrahydrofuran (15 mL) was added a 1.68 M hexane solution of *n*-butyllithium (3.0 mL, 5.0 mmol) at -78 °C. The mixture was stirred under Ar at -78 °C for 1 h followed by the addition of 4-pyridinecarbaldehyde (536 mg, 5.0 mmol). The reaction mixture was stirred for 2 h, while the reaction temperature was raised from -78 °C to room temperature. The solution was poured into saturated aqueous ammonium chloride (20 mL), and the aqueous layer was extracted with ether (20 mL × 3). The combined organic layers were dried over Na$_2$SO$_4$ and concentrated under reduced pressure to give a mixture of the trans and cis isomers of 4-stilbazole (**1**). Each isomer was separated by silica gel chromatography (hexane/ethyl acetate, 5:1) to afford the cis isomer (oil, 46% yield), which was used without further purification, and the trans isomer, which was recrystallized from hexane (40% yield).

4-Phenyl-3-stilbazole (4). Wittig reaction of 4-phenyl-3-pyridinecarbaldehyde[17] and benzyltriphenylphosphonium chloride gave a mixture of the isomers analogously. Each isomer was separated by silica gel chromatography (hexane/ethyl acetate, 5:1) and recrystallized from hexane to afford the trans isomer (pinkish crystal, 28% yield) and the cis isomer (colorless crystal, 23% yield). Trans isomer: mp 68.0–70.0 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 8.95 (s, 1H), 8.54 (d, J = 5.1 Hz, 1H), 7.23–8.53 (m, 11H), 7.13 (d, J = 16.4 Hz, 1H), 7.03 (d, J = 16.4 Hz, 1H); IR (KBr) 3027, 2924, 2851, 2081, 2033, 1597, 1493, 1476, 1445, 1410, 1314, 1277, 1071, 968, 839, 781, 733, 706, 693, 629, 519 cm^{-1}; UV (DCE) λ_{max} 305 nm (log ϵ 4.41), 255 (4.28). Anal. Calcd for C$_{19}$H$_{15}$N: C, 88.68; H, 5.88; N, 5.44. Found: C, 88.49; H, 5.93; N, 5.62. Cis isomer: mp 95.6–96.6 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 8.50 (d, J = 5.1 Hz, 1H), 8.45 (s, 1H), 7.39–7.50 (m, 5H), 7.29 (d, J = 5.1 Hz, 1H), 7.19–7.23 (m, 5H), 6.68 (d, J = 12.2 Hz, 1H), 6.39 (d, J = 12.2 Hz, 1H); IR (KBr) 3047, 3019, 2924, 2851, 1957, 1896, 1584, 1493, 1472, 1447, 1399, 1159, 1074, 934, 833, 783, 756, 698, 625, 582, 521, 498, 438 cm^{-1}; UV (DCE) λ_{max} 281 nm (log ϵ 4.11), 251 (4.23). Anal. Calcd for C$_{19}$H$_{15}$N: C, 88.68; H, 5.88; N, 5.44. Found: C, 88.45; H, 5.86; N, 5.35.

4,4'-Diisopropyl-3-stilbazole (5) was analogously synthesized by Wittig reaction of 4-isopropyl-3-pyridinecarbaldehyde[17] with the triphenylphosphonium salt of 4-isopropylbenzyl chloride. Purification was performed by column chromatography on silica gel to afford the trans isomer (yellowish oil, 15% yield) and the cis isomer (colorless oil, 34% yield). Trans isomer: ^{1}H NMR (270 MHz, CDCl$_3$) δ 8.70 (s, 1H), 8.44 (d, J = 5.4 Hz, 1H), 7.45–7.49 (m, 2H), 7.23–7.31 (m, 3H), 7.18 (d, J = 5.1 Hz, 1H), 6.99 (d, J = 16.1 Hz, 1H), 3.21–3.36 (m, 1H), 2.86–3.01 (m, 1H), 1.27 (d, J = 6.8 Hz, 6H), 1.27 (d, J = 6.8 Hz, 6H); IR (film) 3023, 2963, 2872, 1640, 1626, 1586, 1512, 1462, 1364, 1233, 1055, 966, 831, 664, 557 cm^{-1}; UV (DCE) λ_{max} 302 nm (log ϵ 4.40). Cis isomer: ^{1}H NMR (270 MHz, CDCl$_3$) δ 8.43 (d, J = 5.4 Hz, 1H), 8.29 (s, 1H), 7.22 (d, J = 4.5 Hz, 1H), 6.95–7.04 (m, 4H), 6.72 (d, J = 12.2 Hz, 1H), 6.58 (d, J = 12.2 Hz, 1H), 3.08–3.24 (m, 1H), 2.74–2.89 (m, 1H), 1.21 (d, J = 6.8 Hz, 6H), 1.18 (d, J = 6.8 Hz, 6H); IR (film) 3019, 2963, 2872, 1634, 1588, 1508, 1462, 1402, 1364, 1285, 1229, 1057, 831, 762, 664 cm^{-1}; UV (DCE) λ_{max} 273 nm (log ϵ 4.05). Anal. as HCl salt. Calcd for C$_{19}$H$_{24}$NCl(hydrochloride): C, 75.60; H, 7.94; N, 4.69. Found: C, 75.30; H, 8.01; N, 4.64.

Complexations of Metalloporphyrins with Stilbazoles. The complexations of metalloporphyrins with stilbazoles were observed by the changes in UV–vis spectra of the metalloporphyrins, where the absorption bands were shifted to longer wavelength.[18]

In the complexations of stilbazoles with (TPP)AlCl (**6a**), (TMP)AlCl (**6b**), (TPP)Zn (**6d**), and (TMP)Zn (**6e**), to 20 mL of a 5.0 × 10^{-5} M DCE solution of the metalloporphyrin (1.0 × 10^{-3} mmol) was added 0.10–0.25 mL of a 2.0 × 10^{-2} M DCE solution of a stilbazole derivative (2.0–5.0 × 10^{-3} mmol) under Ar and the mixture was stirred for 5 min at room temperature. An aliquot of the solution was taken and the UV–vis spectrum was measured with use of a quartz cell (light path length = 1.0 mm). In the case of (TPP)AlOR (**6c**) which is highly air-sensitive, the mixed DCE solution of **6c** (5.0 × 10^{-5} M) and a stilbazole derivative was prepared under Ar in a quartz cell (light path length = 10 mm) equipped with a three-way cock followed by UV–vis measurement.

The extent of coordination (x, %) and the formation constants (K) for the metalloporphyrin–stilbazole complexes were obtained from the UV–vis spectra with the equations

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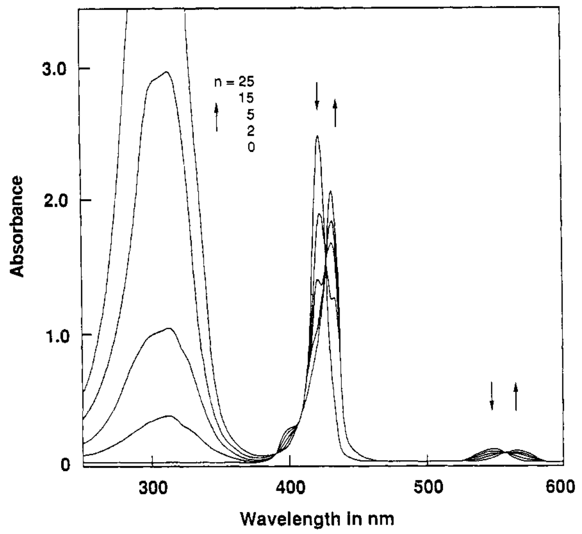


Figure 1. UV–vis spectra of the (TPP)AlCl–*trans*-**1** system in DCE at 25 °C. *n* represents the mole ratio of *trans*-**1** to (TPP)AlCl (1.0 × 10^{-4} M).

$$\frac{x}{100}=\frac{[\mathrm{P{-}S}]}{[\mathrm{P_0}]}=\frac{A_x-A_0}{A_1-A_0}$$

$$K=\frac{[\mathrm{P{-}S}]}{[\mathrm{P}][\mathrm{S}]}=\frac{x}{100-x}\,\frac{100}{100[\mathrm{S_0}]-x[\mathrm{P_0}]}$$

$$[\mathrm{P}]=[\mathrm{P_0}]\left\{1-\frac{x}{100}\right\}$$

$$[\mathrm{S}]=[\mathrm{S_0}]-[\mathrm{P{-}S}]$$

which are similar to the equations reported by Miller et al.[18a] where the band intensity A for the metalloporphyrin, A_x for the sample, A_0 for the free porphyrin, and A_1 for the porphyrin completely complexed with the stilbazole derivative; [P–S], [P], and [S] are the equilibrium concentrations of the complex, free porphyrin, and free stilbazole in the sample, respectively; and [P_0] and [S_0] are the initial concentrations of the porphyrin and the stilbazole derivative, respectively. K values were calculated from the averages of the experiments in different concentrations.

Photoirradiation. In a quartz cell (light path length = 10 mm) 5 mL of a DCE solution of the complex prepared as above was added under Ar. The cell was placed in a thermostated water bath and irradiated with light from a 300 W Xe lamp (ILC Cermax LX-300F), using a Kenko U-330 filter for UV (300–360 nm) or a Kenko BP-43 filter for visible light (around 430 nm) at 25 °C. The distance from the lamp to the cell was 20 cm. The change in the extent of complexation induced by the isomerization of stilbazole derivative was followed by UV–vis measurement for an aliquot of the irradiated solution sample in a quartz cell (light path length = 1.0 mm).

Results and Discussion

Metalloporphyrin–Stilbazole Complexes. UV–vis absorption bands of the metalloporphyrins were found to shift to longer wavelength with the complexation of metalloporphyrins with stilbazoles. As shown in Figure 1, in the case of the (TPP)AlCl (**6a**)–*trans*-4-stilbazole (*trans*-**1**) system, the near-ultraviolet (Soret) and visible (Q) absorption bands of free **6a** appeared at 419 and 550 nm, and those of **6a** complexed with *trans*-**1** appeared at 431 and 564 nm, respectively. The formation constants (K) for the metalloporphyrin–stilbazole complexes were determined by using the intensities of the Soret or Q band at longer wavelength: 431 nm for **6a**, 430 nm for (TMP)AlCl (**6b**), 564 nm for (TPP)AlOR (**6c**), 429 nm for (TPP)Zn (**6d**), and 430 nm for (TMP)Zn (**6e**).

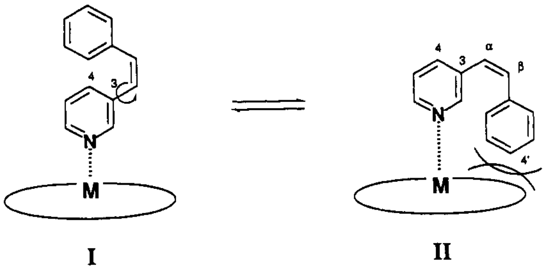
Table I summarizes K values for the complexes of metalloporphyrins with each geometrical isomer of the stilbazoles. Nonsubstituted stilbazoles (4- (**1**), 2- (**2**), and 3-stilbazole (**3**)) were first employed as ligands for (TPP)AlCl (**6a**). In the complexation of **1** with **6a**, the value of K for *trans*-**1** was approximately equal to that for *cis*-**1**. This observation corresponds to the small difference in pK_a values of the conjugate acids between the trans and cis isomers of **1**.[19] No complexation of **2** with **6a** is attributed to the steric hindrance of the 2-substituent of the pyridine group, since it is known that 2,6-lutidine, for example, does not coordinate to metalloporphyrins because of the steric hindrance of the methyl groups at the 2- and 6-positions. In the complexation of **3** with **6a**, the smaller K value than for the **1**–**6a** system corresponds to the lower pK_a value of the conjugate acid of **3** than that of **1**.[19] It is interesting that the value of K for *cis*-**3** was smaller than that for *trans*-**3** (K(trans)/K(cis) = 1.2), although **3** shows little difference in the pK_a values of the conjugate acids between the trans and cis isomers.

Table I. Formation Constants for Metalloporphyrin–Stilbazole Complexes[a]

		$K/\times10^3$ M		
metalloporphyrins	stilbazoles	trans	cis	K(trans)/K(cis)
6a	**1**	10.4	10.5	1.0
	2	0	0	–
	3	2.9	2.4	1.2
	4	9.6	3.0	3.2
6b	**1**	22.6	23.4	1.0
	3	7.4	4.4	1.7
	4	17.5	3.2	5.4
	5	40.3	14.8	2.7
6c	**4**	1.0	0.4	2.3
6d	**1**	16.6	17.1	1.0
	4	19.3	5.3	3.7
6e	**4**	38.2	5.5	6.8

[a] In DCE, metalloporphyrin (5.0 × 10^{-5} M), stilbazole derivative (2–5 equiv) at 25 °C.

Scheme I Coordination of *cis*-3-Stilbazole (**3**) to Metalloporphyrins



Futhermore, in the complexation of 4-stilbazole (**1**) with (TMP)AlCl (**6b**), the increase of K value for **6b** compared with that for (TPP)AlCl (**6a**) is attributed to some electronic effect of the mesityl group in **6b**. The value of K for *trans*-**1** was approximately equal to that for *cis*-**1**. On the other hand, in the complexation of 3-stilbazole (**3**) with **6b**, which is bulkier than **6a**, the value of K(trans)/K(cis) increased up to 1.7 compared with that in the complexation with **6a** (1.2). These observations for the K(trans)/K(cis) value suggest that although *cis*-**3** is considered to prefer conformation I in Scheme I in the complexation with the metalloporphyrin, one of the possible conformations of *cis*-**3** that shows steric repulsion to the metalloporphyrin (II in Scheme I) lowers the coordination ability, while *trans*-**3** has no such steric problem.

On the basis of the above consideration, the introduction of a large substituent at the 4-position of 3-stilbazole (**3**) is considered to be effective in preventing conformation I in Scheme I of *cis*-**3**, and it is anticipated to further lower the coordination ability of the cis isomer leading to a large value for K(trans)/K(cis). According to this strategy, 4-phenyl-3-stilbazole (**4**) and 4,4′-diisopropyl-3-stilbazole (**5**) were prepared and employed as ligands

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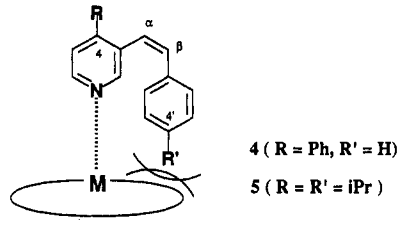
Scheme II Coordination of *cis*-4 and *cis*-5 to Metalloporphyrins[a]



[a] Metalloporphyrins with one and two axial ligands are considered to have square-pyramidal and square-planar structures, respectively.

for metalloporphyrins. In the complexation of **4** with (TPP)-AlCl (**6a**), the value of *K*(trans)/*K*(cis) increased up to 3.2 compared with the 1.2 value for the complexation of **3** with **6a**. Furthermore, in the complexation of **4** with (TMP)AlCl (**6b**), which is bulkier than **6a**, the value of *K*(trans)/*K*(cis) increased up to 5.4 compared with the 1.7 value for complexation of **3** with **6b**. In both systems, the presence of a phenyl group at the 4-position of **4** led to about a 3-fold increase in the *K*(trans) value compared with that for **3**. This is attributed to the higher pK_a value of the conjugate acid of the 4-phenyl derivative as observed for pyridine.[20] On the other hand, there is little change in *K*(cis) for **4** compared with that for **3**. These observations indicate that the phenyl group at the 4-position of 3-stilbazole restrains the conformation of *cis*-**4** to that shown in Scheme II so that the steric repulsion of the phenyl group at the β-position of *cis*-**4** toward the porphyrin ring lowers the binding ability of *cis*-**4** to the metalloporphyrin. On the other hand, in the complexation of **6b** with **5** possessing a bulky isopropyl group at the 4'-position which causes considerable steric repulsion to the porphyrin, the *K* value for *trans*-**5** was much greater than that for *trans*-**4**. That is probably due to the greater value of pK_a of the conjugate acid of the 4-isopropyl derivative than that of the 4-phenyl derivative similarly to pyridine.[20] The value of *K*(trans)/*K*(cis) for **5** was smaller than that for **4**.

Futhermore, coordinations of stilbazoles with other metalloporphyrins in place of the chloroaluminum porphyrins **6a** and **6b** were investigated. In the complexation of 4-phenyl-3-stilbazole (**4**) with aluminum alkoxide porphyrin, (TPP)AlOR (**6c**), *K* decreased compared with the value for (TPP)AlCl (**6a**), probably due to the lower acidity of the aluminum carrying alkoxide group. *K*(trans) was greater than *K*(cis) similarly to the **4**–**6a** system. Zinc porphyrins behaved analogously to aluminum porphyrins. In the complexation of 4-stilbazole (**1**) with (TPP)Zn (**6d**), there was little difference in *K* values between the isomers of **1**. In the complexation of 4-phenyl-3-stilbazole (**4**) with (TPP)Zn (**6d**), a large *K*(trans)/*K*(cis) value of 3.7 was observed. Particularly, in the complexation of **4** with (TMP)Zn (**6e**) which is bulkier than **6d**, the largest *K*(trans)/*K*(cis) value of 6.7 was observed. The increase of *K* value for zinc porphyrin **6e** compared with that for **6d** was similar to the increase for the corresponding aluminum porphyrins.

Photoregulation of Complexation. UV irradiation of the stilbazole derivatives is known to bring about the trans → cis isomerization and the irradiation of visible light in the presence of a metalloporphyrin is known to bring about the reversion. When there is a large difference in the extent of coordination of a stilbazole derivative to a metalloporphyrin between the trans and cis isomers, the complexation of the stilbazole with the metalloporphyrin is expected to be controllable by the photoisomerization of the stilbazole derivative. In order to examine this possibility, the effect of light on the stilbazole–metalloporphyrin system was investigated. The systems containing 4-phenyl-3-stilbazole (**4**) such as **4**–**6b**, **4**–**6d**, and **4**–**6e** were employed because they exhibited large values of *K*(trans)/*K*(cis).

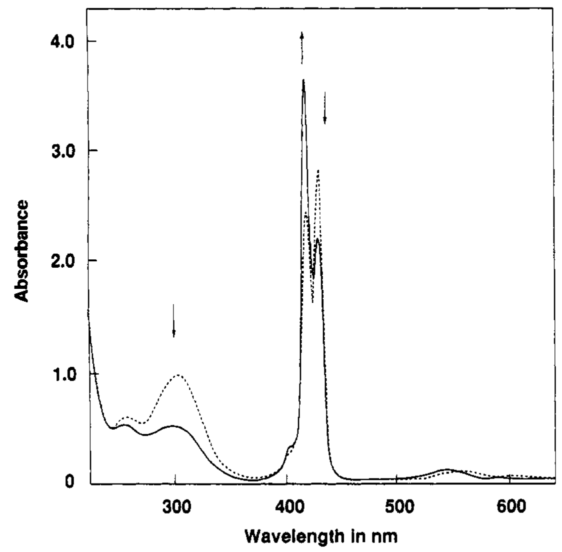


Figure 2. Effect of UV irradiation on UV–vis spectra of a mixture of DCE solutions of (TMP)AlCl (1.0×10^{-4} M) and *trans*-**4** (2.0×10^{-4} M).

Table II. Dissociation of Metalloporphyrin–**4** Complexes Induced by Photoisomerization of *trans*-**4** to *cis*-**4** upon UV Irradiation[a]

metalloporphyrins	time/h	cis content/%	extent of coordination/%
6b[b]	0	0	70
	0.5	60	56
	1.0	72	50
	2.5	80	46
6d[c]	0	0	57
	1.0	80	38
6e[c]	0	0	68
	1.0	80	43

[a] A mixture of DCE solutions (5 mL) of a metalloporphyrin and **4** (2 equiv) was irradiated with UV at 25 °C. [b] 1.0×10^{-4} M. [c] 0.5×10^{-4} M.

When a mixture of DCE solutions of (TMP)AlCl (**6b**) (1.0×10^{-4} M) and *trans*-**4** (2.0×10^{-4} M) was irradiated by UV light for 2.5 h in the manner described in the Experimental Section, the UV–vis spectrum of the solution changed as shown in Figure 2: the absorption maximum at 430 nm due to the **6d**–**4** complex decreased while the absorption at 419 nm due to uncomplexed **6b** increased in its intensity, while the UV irradiation brought about the change in the spectrum around 300 nm due to the trans → cis isomerization of **4**. The cis content of **4** was calculated from the decrease in the absorbance around 300 nm which was about 80% at the photostationary state. The change in the spectrum indicates that the extent of complexation (*x*) decreased from 70 to 46% as the cis content of **4** increased from 0 to 80%. When a mixture of DCE solutions of (TPP)Zn (**6d**) (1.0×10^{-4} M) and *trans*-**4** (2.0×10^{-4} M) was irradiated by UV light for 1.0 h, *x* decreased from 57 to 38%. When a mixture of DCE solutions of (TMP)Zn (**6e**) (1.0×10^{-4} M) and *trans*-**4** (2.0×10^{-4} M) was irradiated by UV light for 1.0 h, *x* decreased from 68 to 43% (Table II). Thus, the dissociation process of the complexes induced by the trans → cis photoisomerization of **4** was achieved.

On the other hand, in the visible light irradiation of a mixture of DCE solutions of **6b** ($1.0\text{-} \times 10^{-4}$ M) and *cis*-**4** (2.0×10^{-4} M), the absorbance in the Soret absorption band of **6b** started to decrease with little change in the absorbance around 300 nm in 30 min. This observation means that *cis*-**4** did not undergo cis → trans isomerization until **6b** started to decompose by the irradiation of visible light. The decreases in the Soret absorption

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(20) Grandberg, I. I.; Faizova, G. K.; Kost, A. N. *Khim. Geterotsikl. Soedin.* **1966**, *4*, 561; *Chem. Abstr.* **1967**, *66*, 10453b.

of the metalloporphyrins were also observed in the irradiation of visible light to **4–6d** and **4–6e** systems.

Conclusion

Among the stilbazole derivatives examined, 3-stilbazole with a phenyl group at the 4-position in order to restrain the conformation (**4**) showed a large difference in the extent of complexation between the trans and cis isomers with both Al and Zn porphyrins (**6a–e**). Thus, by the appropriate design of the structures of stilbazoles and porphyrins, the difference in the coordination ability between the trans and cis isomers can be enhanced. Furthermore, the photoinduced dissociation of metalloporphyrin–**4** complexes was achieved by the trans → cis isomerization of **4** by UV irradiation.

Such a photocontrol of coordination is expected to lead to the photoregulation of a chemical reaction, since the coordination of a ligand to metalloporphyrin is known to have a significant effect on the reactivity of a reaction on the porphyrin.[21] Therefore, this photoresponsive metalloporphyrin–stilbazole system is expected to be applied to a photoswitch for such a chemical reaction on metalloporphyrin complexed with stilbazole.

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(21) For example: ref 15b.