Irreversible photoisomerization behavior of 2-stilbazole† covalently bound to porphyrin

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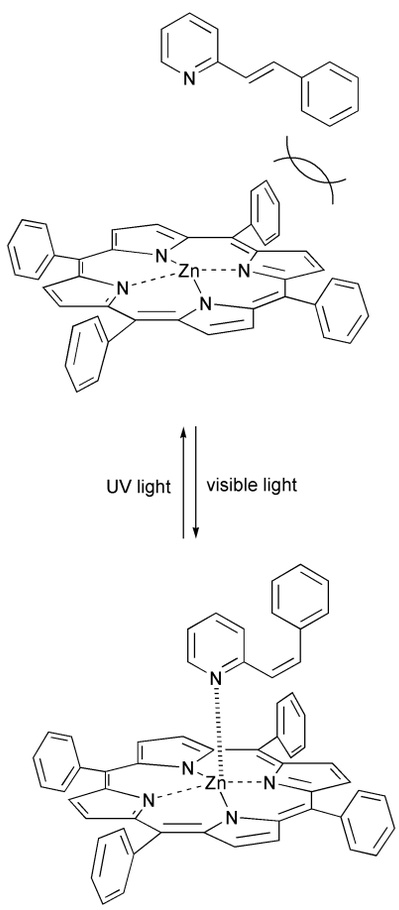
Irreversible *cis*-to-*trans* photoisomerization behavior was observed for a stilbazole–porphyrin (**1**), and its zinc complex (**2**). *trans*-**1** and *trans*-**2** did not isomerize to the corresponding *cis*-isomer under irradiation with UV light, although stilbazoles readily undergo the *trans*-to-*cis* isomerization upon UV irradiation. In contrast, *cis*-to-*trans* photoisomerization was observed for both *cis*-**1** and *cis*-**2**; the isomerization of *cis*-stilbazole readily proceeds by visible light irradiation *via* complexation with metalloporphyrins.

Introduction

Photoresponsive molecules are of much interest and importance in relation to photoresponsive systems in nature and as building blocks to construct photoresponsive supramolecular systems.[1] We have recently found that photoisomerizable stilbazole coordinates to metal complexes of tetraphenylporphyrin to different extents depending on the structure of the geometric isomers of stilbazole due to steric repulsion between the metalloporphyrin and stilbazole.[2] Thus, the complexation of zinc tetraphenylporphyrin with 2-stilbazole is reversibly photoswitchable under the action of UV and visible light through the *trans–cis* isomerization of the stilbazole (Scheme 1).[3] A related compound, stilbene, differs much from stilbazole, since stilbene undergoes both *trans*-to-*cis* and *cis*-to-*trans* photoisomerization under photoirradiation, whereas the *cis*-to-*trans* photoisomerization of stilbazole proceeds less efficiently than the *trans*-to-*cis* process when metalloporphyrins or appropriate sensitizers promote the *cis*-to-*trans* isomerization of stilbazole.[4,5]

More recently, we have demonstrated an interesting novel example of a "photoresponsive molecular switch": a light-driven on–off switching system for chemical reactions, composed of aluminium porphyrin and stilbazole. This system can regulate the reaction of carbon dioxide and propylene oxide to give propylene carbonate, catalyzed by aluminium tetraphenylporphyrin in the presence of 2-stilbazole under UV or visible light through the photoisomerization of stilbazole.[6]

In the course of our related studies on porphyrin–stilbazole chemistry, we synthesized a strategically designed porphyrin having a covalently linked 2-stilbazole moiety in the periphery, such as 5-[2′-(2″-pyridylethenyl)phenyl]-10,15,20-triphenylporphyrin (stilbazole–porphyrin; **1**), in order to produce more efficient photoresponsive systems. Contrary to expectation, we found interesting and unusual phenomena, such as the irreversible photoisomerizations of stilbazole–porphyrin (**1**) and its zinc complex (**2**) in which neither *trans*-**1** nor *trans*-**2** isomerized into the corresponding *cis*-isomer, but, in sharp contrast, *cis*-**1** and *cis*-**2** did undergo photoisomerization. Thus, we wish to report the details of these results in the present paper. ‡



Scheme 1

Results and discussion

5-[2′-(2″-Pyridylethenyl)phenyl]-10,15,20-triphenylporphyrin (stilbazole–porphyrin; **1**) was synthesized by the reaction between 5-(2′-formylphenyl)-10,15,20-triphenylporphyrin (**4**) and (2-pyridylmethyl)triphenylphosphonium bromide *via* 5-[2′-(1″,3″-dithiacyclohexan-2″-yl)phenyl]-10,15,20-triphenylporphyrin, which was prepared from protected *o*-phthalaldehyde, benzaldehyde, and pyrrole (Scheme 2). The product was a mixture of *trans*-**1**, with a *trans* 2-(2′-pyridyl)ethenyl unit in the periphery, and *cis*-**1**, carrying a peripheral *cis*-stilbazolyl unit.

† The IUPAC name for 2-stilbazole is 2-styrylpyridine.
‡ A different type of zinc complex of stilbazole-linked porphyrin was synthesized by Burrell *et al.* in which the structures of molecular assembly were discussed.[15]

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These geometrical isomers were successfully separated by column chromatography on silica gel. ^{1}H NMR and UV–vis spectra for the fractions that eluted faster (**F-1**) and more slowly (**F-2**) showed that they were isomeric stilbazole–porphyrins (**1**) with different geometries of the peripheral stilbazolyl unit. **F-1** exhibited ^{1}H NMR signals in C_6D_6 assignable to olefinic protons at δ 7.5 and 7.9 ppm with $^3J_{HH}$ = 16.0 Hz and its characteristic absorption maximum in the UV due to the stilbazolyl unit occurred at λ_{max} = 302 nm in $CHCl_3$ (ε = 41400). In contrast, the NMR signals assignable to the olefinic protons of **F-2** were observed at δ 6.2 and 6.7 ppm ($^3J_{HH}$ = 12.5 Hz) and an absorption maximum appeared at λ_{max} = 290 nm (ε = 17600) in the UV spectrum. Since geometrical isomers of stilbazole are easily identified by their ^{1}H NMR and UV–vis spectra in which the olefinic protons of *trans*-isomer possess ^{1}H NMR signals at relatively lower magnetic field with larger coupling constants than those of the *cis*-isomer, and the absorption maximum in the UV region for the *trans*-isomer appears at longer wavelength with a larger ε value than that for the *cis*-isomer,[4,7] **F-1** and **F-2** were thus identified as *trans*-**1** and *cis*-**1**, respectively.

Metallation of the two isomers of the stilbazole–porphyrin (*trans*-**1** and *cis*-**1**) by $Zn(OAc)_2$ gave the zinc porphyrins *trans*-**2** and *cis*-**2** almost quantitatively without isomerization, as confirmed by TLC analysis of the reaction mixtures. The UV–vis absorption spectra in $CHCl_3$ for both *trans*-**2** (Soret band: λ_{max} = 428 nm) and *cis*-**2** (λ_{max} = 430 nm) were similar to those of the zinc tetraphenylporphyrin–pyridine complex (428 nm) and zinc tetraphenylporphyrin–*cis*-2-stilbazole complex (430 nm), irrespective of the concentration of **2** ([**2**] = 1.0×10^{-2}–1.0×10^{-6} mol dm^{-3}). Upfield shifts of the signals due to the pyridyl group were observed in the ^{1}H NMR spectra in C_6D_6 for *trans*-**2** and *cis*-**2**, when compared respectively with the spectra of *trans*-**1** and *cis*-**1**. These observations indicate that central zinc atoms of **2** are coordinated by the pyridine moieties.§ As for the structure of *trans*-**2**, molecular modeling studies have shown that the pyridyl group in *trans*-**2** easily coordinates intramolecularly to the Zn atom. On the other hand, since the pyridyl group in *cis*-**2** is considered to experience much difficulty in coordinating to the intramolecular Zn, self-assembled aggregations[8] cannot be excluded, in which no spectral changes were observed for *cis*-**2** over a wide concentration range.

In order to investigate the isomerization behavior of the stilbazolyl groups in the zinc complexes *trans*-**2** and *cis*-**2**, irradiation with UV light or visible light was performed for C_6D_6 solutions of **2** in NMR sample tubes, and ^{1}H NMR spectra were recorded periodically.¶ When solution of *cis*-**2** in C_6D_6 (2.0×10^{-3} mol dm^{-3}) was irradiated with visible light (λ > 380 nm), isomerization of *cis*-**2** to *trans*-**2** was observed to take place (Scheme 3), as demonstrated by the decrease in intensity of the signals due to *cis*-**2** and the increase in those due to *trans*-**2**.

The isomerization proceeded smoothly, and the *trans* content of **2** increased to 38, 67, and 91% after 10, 30, and 60 min, respectively (Fig. 1).

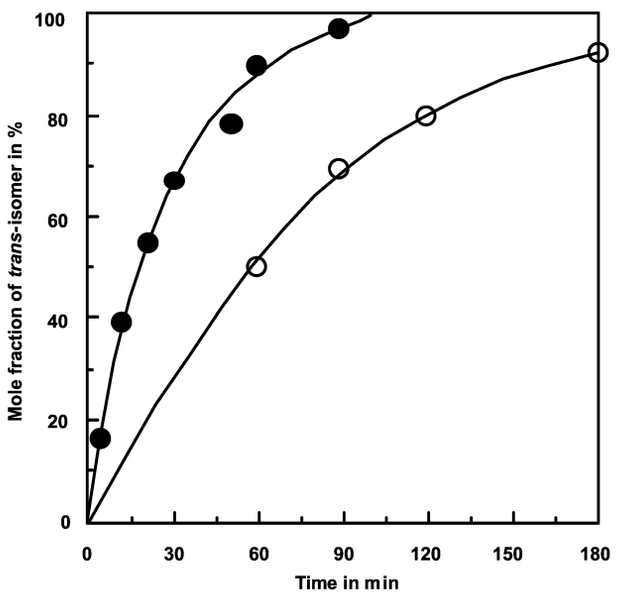
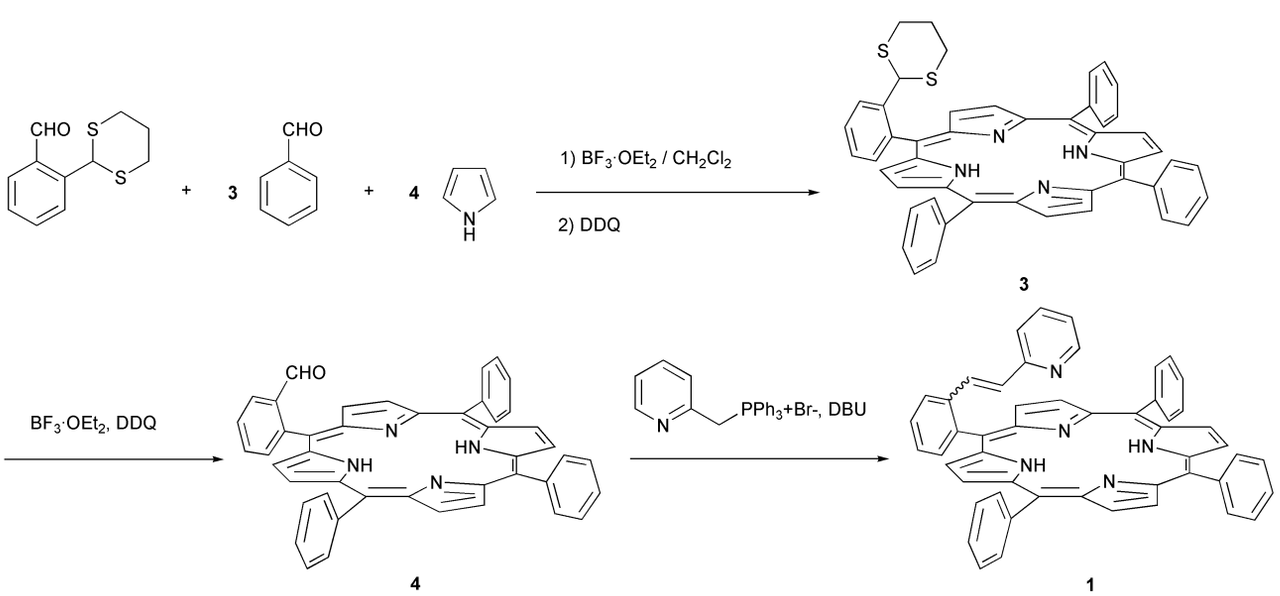


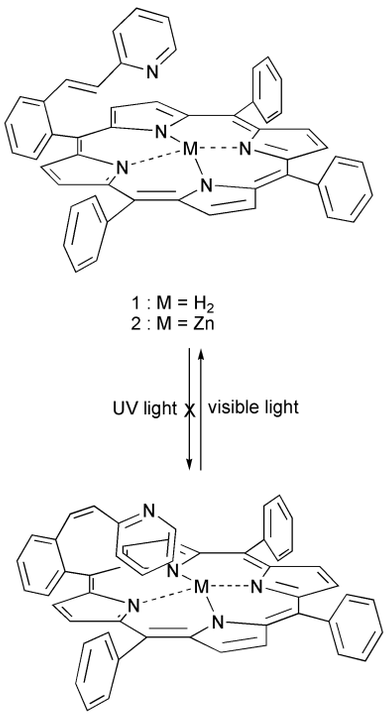
Fig. 1 Time-courses of *cis*-to-*trans* photoisomerization of **1** (○) and **2** (●) under irradiation with visible light (λ > 380 nm) in C_6D_6 ([**1**]$_0$ or [**2**]$_0$ = 2.0×10^{-3} mol dm^{-3}) at 23 °C under nitrogen. Mole fractions of the *trans*-isomers were determined by ^{1}H NMR.

§ The Soret band of zinc tetraphenylporphyrin [Zn(TPP)] in $CHCl_3$ shifts to 420 nm from that of the metal-free tetraphenylporphyrin at 418 nm. The absorption maximum of Zn(TPP) at 420 nm does not change, regardless of the amount of coexisting *trans*-2-stilbazole (1–1000 equiv.), whereas a new absorption maximum appears at 430 nm in the presence of *cis*-2-stilbazole, and the original absorption at 420 nm disappears only when more than 800 equiv. of *cis*-stilbazole, with respect to Zn(TPP), are added to Zn(TPP) ([Zn(TPP)] = 2.0×10^{-2} mol dm^{-3}).

¶ The wavelengths were the same as those employed for photoisomerizations in bimolecular systems.[2,3]



Scheme 2



Scheme 3

In contrast, unexpectedly, isomerization of *trans*-**2** to *cis*-**2** following irradiation with UV light (λ = 290–360 nm) did not occur under similar conditions (Scheme 3), whereas *trans*-2-stilbazole itself readily isomerizes to the *cis*-form following irradiation with UV light[4] under identical conditions. Furthermore, it was confirmed that *cis*-**2** did not isomerize after irradiation with UV light and that *trans*-**2** did not isomerize after irradiation with visible light. An intramolecular coordinative interaction between the central Zn atom and the pyridyl group in *trans*-**2** is thought to prevent the stilbazolyl moiety from isomerizing.

With regard to the unexpected phenomena mentioned above, isomerization of the metal-free porphyrins *trans*-**1** and *cis*-**1** was investigated next in order to further examine the effect of the interaction between the pyridyl group and the Zn on the photoisomerization of the stilbazolyl moiety in **2**. It was found that *trans*-**1** did not isomerize into *cis*-**1** on irradiation with UV light. More unexpectedly, *cis*-to-*trans* photoisomerization of *cis*-**1** was observed under irradiation with visible light (Scheme 3); the *cis*-form stilbazole is known to undergo efficient isomerization upon irradiation with visible light *via* complexation of the pyridine group with metalloporphyrins[4b,9] or in the presence of appropriate sensitizers.[5] We also confirmed that irradiation with UV light did not cause photoisomerization of *cis*-**1**, as observed for *cis*-**2**, and that irradiation with visible light did not bring about the photoisomerization of *trans*-**1**. These results are quite unusual and very interesting because there is, in appearance, no chance for the stilbazolyl moiety of **1** to interact with the porphyrin due to the lack of a central Zn atom. Therefore, the isomerization behavior observed for *trans*-**1** and *cis*-**1** indicates that interactions possibly exist between the porphyrin macrocycle and the stilbazole unit, although the chemical shift value of the signals due to the N–H protons in *trans*-**1** (−2.0 ppm in C_6D_6) and to those in *cis*-**1** (−1.8 ppm) was not very different from the chemical shift value for the N–H signal in tetraphenylporphyrin (−2.1 ppm). The slower isomerization of *cis*-**1** to *trans*-**1** compared with the isomerization of *cis*-**2** to *trans*-**2** (Fig. 1) indicates that the interaction between pyridine and zinc in *cis*-**2** facilitates the isomerization[4b,9] much more than the possible interaction of the stilbazolyl moiety with the metal-free porphyrin in *cis*-**1**. Coordination to zinc is thought to bring the stilbazole group closer to the porphyrin, which is more favorable for energy transfer upon irradiation.

The photoresponses of 2-stilbazole covalently linked to porphyrin, such as 5-[2′-(2″-pyridylethenyl)phenyl]-10,15,20-triphenylporphyrin (stilbazole–porphyrin; **1**) and its zinc complex (**2**), observed in the present study were very different from those of the bimolecular systems composed of zinc porphyrin and stilbazole,[4b,9] and this is the first example of a visible-light driven, irreversible photoisomerization of olefins. In summary, photoisomerization of *cis*-**1** and -**2** occurred only on irradiation with visible light. *trans*-**1** and -**2** did not isomerize following irradiation with either UV light or visible light. Our results are essentially different from the related observation reported by Wildes and Whitten,[9b] since *trans*-to-*cis* photoisomerization was not observed at all in our stilbazole–porphyrin systems (**1** and **2**). Wildes and Whitten reported the efficient *cis*-to-*trans* photoisomerization of 1-(1′-naphthyl)-2-(4′-pyridyl)ethylene in the presence of the magnesium complex of etioporphyrin-I, where *trans*-to-*cis* ratios of 95 : 5–99 : 1 at the photostationary state were reported; they also observed *trans*-to-*cis* isomerization in the same system.

Our observations can be related to the unique isomerization processes of some 1,2-disubstituted olefins having aromatic polycyclic groups that Arai and Tokumaru reported in the 1980s, in which irradiation with UV light caused the olefins to undergo only *cis*-to-*trans* isomerization, and the reverse isomerization from *trans*-form to *cis*-form did not occur. They discussed the mechanism of the irreversible isomerization from the view point of triplet energy surfaces of aromatic olefins.[10] The porphyrin moiety as a triplet sensitizer absorbs visible light and probably undergoes rapid intersystem crossing to the triplet followed by triplet–triplet energy transfer to the stilbazole unit, and thus gives the *trans*-isomer after the possible adiabatic *cis*-to-*trans* isomerization. The excited stilbazole is considered to have an equilibrium between the twisted triplet and the *trans*-triplet states. It is likely that the energy transfer from the stilbazole in the *trans*-triplet state to the porphyrin moiety affords the *trans*-isomer exclusively, while deactivation of the twisted triplet gives a mixture of *trans*- and *cis*-isomers. Since **1** and **2** have both chromophores, such as stilbazole and porphyrin, in the same molecule, the former process should occur in preference.

The participation of visible light in the photoisomerizations of **1** and **2** suggests that the porphyrin moiety plays an essential role. This is of much interest in connection with photomorphogenesis in plants where a tetrapyrrole-containing chromoprotein, such as phytochrome, is involved as photo-transducer.

Experimental

Materials

Dichloromethane (CH_2Cl_2) was washed successively with conc. H_2SO_4, water, and aq. $NaHCO_3$, dried over $CaCl_2$, and distilled over CaH_2 in a nitrogen atmosphere. Deuterated chloroform ($CDCl_3$) was fractionally distilled over CaH_2 under nitrogen. Benzene (C_6H_6) and deuterated benzene (C_6D_6) were distilled over sodium benzophenone ketyl in a nitrogen atmosphere.

Synthesis of 5-[2′-(1″,3″-dithiacyclohexan-2″-yl)phenyl]-10,15,20-triphenylporphyrin (3)[11]

For the preparation of **1**, 5-[2′-(1″,3″-dithiacyclohexan-2-yl)phenyl]-10,15,20-triphenylporphyrin was first prepared according to Lindsey's method. To a 2 L two-necked round-bottom flask connected to a three-way stopcock and a reflux condenser, 2-(1′,3′-dithiacyclohexan-2′-yl)benzaldehyde[12] (1.1

g, 5 mmol), CH_2Cl_2 (2 L), benzaldehyde (1.5 mL, 15 mmol), and pyrrole (1.4 mL, 20 mmol) were added successively, and the flask was wrapped in aluminium foil. After purging of the solution with dry nitrogen for 30 min, BF_3–OEt_2 (0.82 mL, 6.6 mmol) was added *via* a hypodermic syringe, and the mixture was stirred for 1 h at room temperature in a nitrogen atmosphere. Then, 2,3,5,6-tetrachloro-1,4-benzoquinone (DDQ; 3.4 g, 15 mmol) was added to the reaction mixture, and the resulting solution was gently further stirred at room temperature for 1 h. Triethylamine (0.9 mL, 6.6 mmol) was added and the volatile fractions were removed from the reaction mixture under reduced pressure. The resulting dark purple residue was subjected to column chromatography on silica gel (Wakogel C-300) with CH_2Cl_2–*n*-hexane (2 : 1) as eluent. The second fraction, purple in color, was collected and evaporated to dryness. The purple residue was recrystallized from $CHCl_3$–*n*-hexane to give 5-[2′-(1″,3″-dithiacyclohexan-2″-yl)phenyl]-10,15,20-triphenylporphyrin (**3**; 550 mg, 15%) as a purple powder. CHN analysis: found C, 77.81; H, 5.19; N, 7.76 (calcd for $C_{48}H_{36}N_4S_2$: C, 78.66; H, 4.95; N, 7.64%). FAB-MS for $C_{48}H_{37}N_4S_2$ (MH^+): *m*/*z* 733. Mp 320–322 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ −2.7 (s, 2H, NH), 1.6 (m, 2H, $SCH_2CH_2CH_2S$), 1.9 and 2.3 (dt, 4H, SCH_2), 4.8 (s, 1H, SCH(Ph)S), 7.5 (m, 12H, *m*-phenyl and *p*-phenyl), 8.2 (m, 7H, *o*-phenyl), 8.7–8.8 (d, 8H, pyrrole).

Synthesis of 5-(2′-formylphenyl)-10,15,20-triphenylporphyrin (4)[13]

Deprotection of the obtained 5-[2′-(1″,3″-dithiacyclohexan-2″-yl)phenyl]-10,15,20-triphenylporphyrin was achieved by reaction with BF_3–OEt_2 and DDQ. To a CH_2Cl_2 solution (300 mL) of 5-[2′-(1″,3″-dithiacyclohexan-2″-yl)phenyl]-10,15,20-triphenylporphyrin (292 mg, 0.4 mmol) were added BF_3–OEt_2 (5.0 mL, 41 mmol) and DDQ (5.0 g, 22 mmol), and the mixture was stirred at room temperature overnight in the air. The reaction mixture was washed three times with aqueous Na_2CO_3 (10%) and dried over $MgSO_4$. Evaporation to dryness gave a purple powder that was recrystallized from $CHCl_3$–MeOH (1 : 1) to give 5-(2′-formylphenyl)-10,15,20-triphenylporphyrin (**4**; 230 mg, 90%) as purple crystals. CHN analysis: found C, 84.02; H, 4.92; N, 8.63 (calcd for $C_{45}H_{30}N_4O$: C, 84.09; H, 4.70; N, 8.72%). Mp 356–359 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ −2.7 (s, 2H, NH), 7.7 (m, 12H, *m*-phenyl and *p*-phenyl), 8.4 (m, 7H, *o*-phenyl), 8.6 (d, 2H, pyrrole), 8.9 (s, 6H, pyrrole), 9.5 (s, 1H, CHO).

Synthesis of (2-pyridylmethyl)triphenylphosphonium bromide

2-Methylpyridine (18.6 mL, 0.2 mol) and benzoyl peroxide (0.4 g) were added successively to a suspension of *N*-bromosuccinimide (71.2 g, 0.2 mol) in CCl_4 (500 mL) with vigorous stirring, and the mixture was kept at 60 °C for 18 h. The reaction mixture was then cooled in an ice bath and filtered. The filtrate was concentrated to *ca.* 100 mL, washed with water, and then dried over $MgSO_4$. CCl_4 and unreacted 2-methylpyridine were removed under reduced pressure (10 mmHg, 30 °C) to give 2-bromomethylpyridine as a brown oil. This product was used directly in the next step without further purification, since it decomposed easily on standing. ^{1}H NMR ($CDCl_3$): δ 4.7 (s, 2H, CH_2Br), 7.2 (m, 1H, 3-pyridyl-H), 7.5 (d, 1H, 5-pyridyl-H), 7.8 (m, 1H, 4-pyridyl-H), 8.6 (d, 1H, 6-pyridyl-H).[14]

A benzene solution (30 mL) of 2-bromomethylpyridine (4.3 g, 25 mmol) was added to a benzene solution (30 mL) of triphenylphosphine (6.6 g, 25 mmol), and the mixture was stirred at reflux overnight. The precipitates were collected by filtration, and washed with benzene to afford the crude product as a yellow powder. Charcoal was added to a $CHCl_3$ solution of the crude product, and the black suspension was stirred for several minutes before the charcoal was filtered off. The filtrate was evaporated to dryness to leave a white powder. The residual powder was recrystallized from *n*-hexane to give (2-pyridylmethyl)triphenylphosphonium bromide (1.73 g, 17.3%) as white crystals. FAB-MS for $C_{24}H_{21}BrNP$: $C_{24}H_{21}NP^+$; *m*/*z* 354, $(C_{24}H_{21}NP^+)_2Br^-$; *m*/*z* 787. Mp 260–261 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 5.8 (d, 2H, CH_2), 7.1 (d, 1H, 3-pyridyl-H), 7.6–7.9 (m, 16H, phenyl and 5-pyridyl-H), 8.0 (t, 1H, 4-pyridyl-H), 8.3 (s, 1H, 6-pyridyl-H).

Synthesis of 5-[2′-(2″-pyridylethenyl)phenyl]-10,15,20-triphenylporphyrin (stilbazole–porphyrin; 1)

5-(2′-Formylphenyl)-10,15,20-triphenylporphyrin (**4**; 193 mg, 0.3 mmol) and (2-pyridylmethyl)triphenylphosphonium bromide (192 mg, 0.3 mmol) were dissolved in dry CH_2Cl_2 (10 mL) under nitrogen, and the mixture was stirred at room temperature prior to the addition of diazabicyclo[5.4.0]undec-7-ene (0.13 mL, 0.8 mmol). After 30 min, the reaction mixture was directly subjected to column chromatography on silica gel (Wakogel C-300) using CH_2Cl_2 as eluent. The second and third of the three major fractions were collected separately and recrystallized from $CHCl_3$–MeOH (1 : 1) to give (*E*)-5-[2′-(2″-pyridylethenyl)phenyl]-10,15,20-triphenylporphyrin (*trans*-**1**; 101 mg, 47%) and *cis*-**1** (64 mg, 30%), respectively. *trans*-**1**: CHN analysis: found C, 84.25; H, 5.01; N, 9.60 (calcd for $C_{51}H_{35}N_5$: C, 85.33; H, 4.91; N, 9.76%). Mp 251–253 °C (decomp.). FAB-MS for $C_{51}H_{35}N_5$ (MH^+): *m*/*z* 718. ^{1}H NMR (C_6D_6): δ −2.0 (s, 2 H, NH), 6.1 (t, 1H, 5-pyridyl-H), 6.3 (d, 1H, 3-pyridyl), 6.4 (t, 1H, 4-pyridyl), 7.5 and 7.9 (2 d, both 1H, $^3J_{HH}$ = 16.0 Hz, CH=CH), 7.6–7.8 (m, 12H, *m*-phenyl and *p*-phenyl), 7.8 (d, 1H, 6-pyridyl), 8.1–8.4 (m, 7H, *o*-phenyl), 9.1 (m, 8H, pyrrole). UV–vis ($CHCl_3$): λ_{max}/nm (10^{-3} ε_{max}) 646 (4.2), 591 (6.9), 551 (8.5), 516 (21.9), 421 (278), 302 (41.4). *cis*-**1**: CHN analysis: found C, 84.83; H, 5.11; N, 9.74 (calcd for $C_{51}H_{35}N_5$: C, 85.33; H, 4.91; N, 9.76%). Mp 249–251 °C. FAB-MS for $C_{51}H_{35}N_5$ (MH^+): *m*/*z* 718. ^{1}H NMR (C_6D_6): δ −1.8 (s, 2 H, NH), 6.2 and 6.7 (2 d, both 1H, $^3J_{HH}$ = 12.5 Hz, CH=CH), 6.8 (t, 1H, 5-pyridyl-H), 7.2 (t, 1H, 4-pyridyl), 7.5–7.7 (m, 12H, *m*-phenyl and *p*-phenyl), 8.0 (d, 1H, 3-pyridyl), 8.7 (d, 1H, 6-pyridyl), 8.2–8.4 (m, 7H, *o*-phenyl), 9.1 and 9.4 (2 d, 2H and 6H, pyrrole). UV–vis ($CHCl_3$): λ_{max}/nm (10^{-3} ε_{max}) 647 (2.8), 591 (4.3), 550 (5.3), 515 (13.4), 420 (272), 290 (17.6).

Preparation of zinc porphyrin (2)

The zinc complexes of *trans*-**1** and *cis*-**1** (*trans*-**2** and *cis*-**2**) were prepared by the reaction of *trans*-**1** and *cis*-**1** with $Zn(OAc)_2$. To a round-bottom flask (200 mL) containing a $CHCl_3$ solution (100 mL) of *trans*-**1** (143 mg, 0.2 mmol), a saturated MeOH solution of $Zn(OAc)_2$ (7 mL) was added, and the mixture was stirred at room temperature for 2 h. Then, the reaction mixture was washed with brine (100 mL × 3) and dried with Na_2SO_4. After the volatile fractions had been removed under reduced pressure, the purple powder obtained was recrystallized from $CHCl_3$–MeOH to give *trans*-**2** as purple crystals (134 mg, 86%). *trans*-**2**: FAB-MS for $C_{51}H_{33}N_5Zn$ (MH^+): *m*/*z* 780. Mp >237 °C (decomp.). ^{1}H NMR (C_6D_6): δ 5.9 (t, 1H, 5-pyridyl-H), 6.3 (d, 1H, 3-pyridyl), 6.4 (t, 1H, 4-pyridyl), 6.6 and 8.2 (2 d, both 1H, $^3J_{HH}$ = 16.0 Hz, CH=CH), 6.8 (d, 1H, 6-pyridyl), 7.6–7.9 (m, 12H, *m*-phenyl and *p*-phenyl), 8.3–8.6 (m, 7H, *o*-phenyl), 9.2–9.3 (m, 8H, pyrrole). UV–vis ($CHCl_3$): λ_{max}/nm (10^{-3} ε_{max}) 598 (6.6), 558 (22.8), 428 (510.3), 313 (44.7). *cis*-**2** was prepared similarly to *trans*-**2** in 77% yield. *cis*-**2**: FAB-MS for $C_{51}H_{33}N_5Zn$ (MH^+): *m*/*z* 780. Mp >252 °C (decomp.). ^{1}H NMR (C_6D_6): δ 3.5 (br, 1H, 6-pyridyl-H), 5.3 (t, 1H, 5-pyridyl-H), 6.0 (t, 1H, 4-pyridyl), 6.2 and 6.9 (2 d, both 1H, $^3J_{HH}$ = 12.3 Hz, CH=CH), 6.3 (m, 2H, 3-pyridyl), 7.2 (t, 1H, *o*-phenyl), 7.3 (t, 1H, *m*-phenyl), 7.6–7.9 (m, 11H, *m*-phenyl and *p*-phenyl), 8.3–8.8 (m, 7H, *o*-phenyl), 8.9, 9.2, and 9.4 (3 d, 8H, pyrrole). UV–vis ($CHCl_3$): λ_{max}/nm (10^{-3} ε_{max}) 601 (6.2), 560 (19.0), 430 (430.1).

Measurements

Elemental analyses were conducted on a Yanaco MT-6 CHN Corder. ^{1}H NMR measurements were performed using $CDCl_3$ or C_6D_6 as solvent at 22 °C on a Bruker type DPX-400 spectrometer, where the chemical shifts were determined with respect to TMS (δ 0.00 ppm) as internal standard. Mass spectra were recorded on a JEOL JMS-SX102A spectrometer. Melting points were uncorrected.

References

1 Photoregulated interaction between photoresponsive hosts and guests: (*a*) M. Shiga, M. Takagi and K. Ueno, *Chem. Lett.*, 1980, 1021; (*b*) S. Shinkai, T. Nakaji, Y. Nishida, T. Ogawa and O. Manabe, *J. Am. Chem. Soc.*, 1980, **102**, 5860; (*c*) S. Shinkai, T. Minami, Y. Kusano and O. Manabe, *J. Am. Chem. Soc.*, 1983, **105**, 1851; (*d*) S. Shinkai, T. Minami, Y. Kusano and O. Manabe, *Tetrahedron Lett.*, 1984, **23**, 2581; (*e*) S. Shinkai, T. Ogawa, T. Nakaji, Y. Kusano and O. Manabe, *Tetrahedron Lett.*, 1979, **47**, 4569; (*f*) A. Ueno, H. Yoshimura, R. Saka and T. Osa, *J. Am. Chem. Soc.*, 1979, **101**, 2779; (*g*) A. Ueno, R. Saka and T. Osa, *Chem. Lett.*, 1979, 841; (*h*) I. Willner, S. Marx and Y. Eichen, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1243; . Photoregulated reactions by photoresponsive molecules: (*i*) I. Willner, *Acc. Chem. Res.*, 1997, **30**, 347; (*j*) I. Willner and S. Rubin, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 367; . Light-induced conformational and functional changes of polymers having photoisomerizable groups: (*k*) M. Irie, *Adv. Polym. Sci.*, 1990, **94**, 27; (*l*) A. Ueno, K. Takahashi, J. Anzai and T. Osa, *J. Am. Chem. Soc.*, 1981, **103**, 6410; (*m*) O. Pieroni, A. Fissi, A. Viegi, D. Fabbri and F. Ciardelli, *J. Am. Chem. Soc.*, 1992, **114**, 2734; (*n*) H. Yamamoto, A. Nishida and T. Shimozawa, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1477; (*o*) M. Aoyama, J. Watanabe and S. Inoue, *J. Am. Chem. Soc.*, 1990, **112**, 5542; (*p*) M. Irie, Y. Hirano, S. Hashimoto and K. Hayashi, *Macromolecules*, 1981, **14**, 262.

2 Y. Iseki, E. Watanabe and S. Inoue, *J. Am. Chem. Soc.*, 1993, **105**, 7313.

3 Y. Iseki and S. Inoue, *J. Chem. Soc., Chem. Commun.*, 1994, 2577.

4 (*a*) D. G. Whitten and M. T. McCall, *J. Am. Chem. Soc.*, 1969, **91**, 5097; (*b*) D. G. Whitten, P. D. Wildes and C. A. DeRosier, *J. Am. Chem. Soc.*, 1972, **94**, 7811.

5 (*a*) P. Bortolus, G. Favaro and U. Mazzucato, *Mol. Photochem.*, 1970, **2**, 311; (*b*) G. Cauzzo, M. Casagrande and G. Galiazzo, *Mol. Photochem.*, 1971, **3**, 59.

6 H. Sugimoto, T. Kimura and S. Inoue, *J. Am. Chem. Soc.*, 1999, **121**, 2325.

7 F. H. Clarke, G. A. Felock, G. B. Silverman and C. M. Watnick, *J. Org. Chem.*, 1962, **27**, 533.

8 R. A. Haycock, C. A. Hunter, D. A. James, U. M. Michelson, L. R. Sutton and L. R., *Org. Lett.*, 2000, **2**, 2435.

9 (*a*) D. G. Whitten, P. D. Wildes and I. G. Lopp, *J. Am. Chem. Soc.*, 1969, **91**, 3393; (*b*) P. D. Wildes and D. G. Whitten, *J. Am. Chem. Soc.*, 1970, **92**, 7609.

10 T. Arai and K. Tokumaru, *Chem. Rev.*, 1993, **93**, 23.

11 J. S. Lindsey, S. Prathapan, T. E. Johnson and R. W. Wagner, *Tetrahedron*, 1994, **50**, 8941.

12 H. Meier, Y. Kobuke and S. Kugimiya, *J. Chem. Soc., Chem. Commun.*, 1989, 923.

13 J. P. Collman, D. A. Tyvoll, L. L. Chng and H. T. Fish, *J. Org. Chem.*, 1995, **60**, 1926.

14 N. R. Ayyangar, P. Y. Kohle, A. G. Lugade and B. D. Tilak, *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.*, 1980, **19**, 24.

15 A. K. Burrell, D. L. Officer, D. C. W. Reid and K. Y. Wild, *Angew. Chem., Int. Ed.*, 1998, **37**, 114.