Photoswitchable Complexation of Metalloporphyrins

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The complexation of zinc and magnesium complexes of tetra(3,5-di-*tert*-butylphenyl)porphyrin with 3′,5′-di-*tert*-butyl-2-stilbazole is reversibly photoswitchable by UV and visible light *via trans–cis* isomerization of the stilbazole.

Photocontrol of chemical or physical functions has attracted continuous interest in connection with the photoresponsive systems in nature such as vision[1] and photomorphogenesis in plants,[2] where the isomerization of olefin plays a central role. Representative related compounds are stilbene, and a derivative stilbazole (2-phenylethenylpyridine) is of particular interest since it undergoes the *trans* → *cis* isomerization upon UV irradiation and the reversion by visible light *via* complexation of the pyridine group with metalloporphyrins.[3] The reversible change in the complexation induced by the photoisomerization, however, has not been explored.[3,4] Complexation of metalloporphyrins with bases is of particular importance, since it is essential to the reactivity of metalloporphyrins as observed in haem enzymes. Here we present the first example of the reversibly photocontrolled 'on–off' complexation of zinc and magnesium porphyrins with a well-designed stilbazole derivative induced by the photoisomerization of the stilbazole. This achievement is considered to provide a step toward the photocontrol of chemical reactions on metalloporphyrins.

For the purpose of 'on–off' complexation of a stilbazole to a metalloporphyrin induced by the photoisomerization of the stilbazole, a substantial difference is required in the extent of complexation of the metalloporphyrin with the *trans* and *cis* forms. In general, the complexation constants of metalloporphyrins with pyridine derivatives depend on the basicity of the pyridines.[5,6] On the other hand, the steric hindrance by substituents in the 2 position of pyridine has a great influence on the complexation with metalloporphyrins. For example, in the complexation with zinc or magnesium porphyrin, the complexation constant for 2-methylpyridine is two orders of magnitude less than that of 4-methylpyridine although both ligands have essentially the same basicity.[5,6] Therefore, in the case of 2-stilbazole **1** possessing a styryl group in the 2 position, although there is little difference in pK_a of the conjugate acids of the *trans* and *cis* isomers of the stilbazole,[7] the difference in the structures of the isomers is expected to result in the considerable difference in their complexation constants. Thus the complexations of each geometrical isomer of 2-stilbazole derivatives with zinc porphyrins were investigated.

The complexation of zinc porphyrins with stilbazoles was observed by monitoring changes in visible spectra of the porphyrins, where the absorption bands were shifted to longer wavelength.[8] The complexation constants were determined from the absorbance of the visible (Q) band due to the complexes.[8,9] An intriguing result was obtained in the complexation of 2-stilbazole **1** with (tetraphenylporphyrinato)-zinc [Zn(tpp)] **3** in benzene. As shown in Table 1, the value of the complexation constant (K) for *trans*-**1** is much smaller than that for *cis*-**1** (K_{cis}/K_{trans} = 28). Since the value of K_{cis} is nearly equal to the complexation constant for 2-methylpyridine (K = 200 dm^3 mol^{-1}),[5] the small value of K_{trans} indicates the strong steric repulsion of *trans*-**1** to the metalloporphyrin. A similar result is obtained in the complexation of **1** with zinc etioporphyrin I (K_{cis}/K_{trans} = 14). These results can be explained as shown in Fig. 2: *cis*-**1** can adopt a conformation with no steric problem in complexation with the metalloporphyrin **I**, whereas *trans*-**1** cannot avoid steric repulsion to the metalloporphyrin in any conformations (**III** or **IV**). On the basis of the consideration with CPK (Corey–Pauling–Koltun) models, the introduction of large substituents in the 3′ and 5′ positions of 2-stilbazole and in *meta* positions of the phenyl groups in tetraphenylporphyrin is expected to lead to the absence of complexation of the *trans* isomer due to the steric repulsion between the two components. According to this strategy, 3′,5′-di-*tert*-butyl-2-stil-

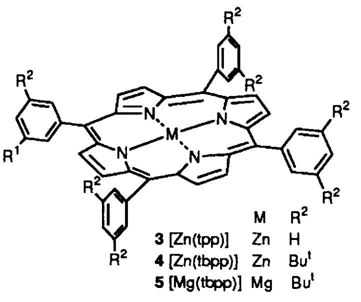

Fig. 1 Structures of stilbazoles (**1** and **2**) and metalloporphyrins (**3–5**)

Table 1 Complexation constants of zinc porphyrins with stilbazoles[a]

Stilbazole	Metalloporphyrin	K_{trans}[b]/ dm^3 mol^{-1}	K_{cis}[c]/ dm^3 mol^{-1}
1	**3**	7	197
1	**6**	12	162
2	**3**	0	279
2	**4**	0	298

[a] Obtained from visible spectra of a mixture of benzene solutions of metalloporphyrins and stilbazoles at 23 °C under argon. [b] Metalloporphyrins (2.0 × 10^{-3} mol dm^{-3}), stilbazoles (2.0 × 10^{-2} mol dm^{-3}). [c] Metalloporphyrins (2.0 × 10^{-4} mol dm^{-3}), stilbazoles (2–10 equiv.).

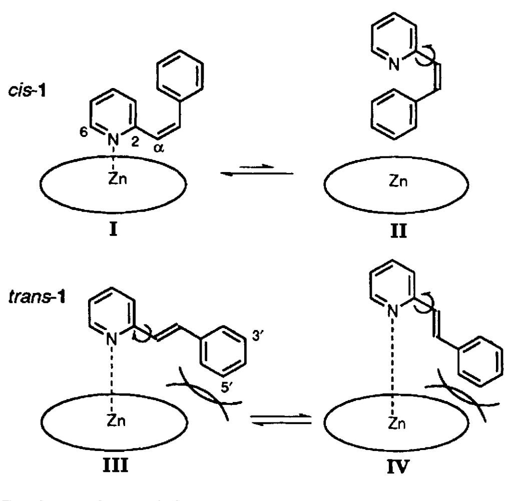

Fig. 2 Conformations of the *cis* and *trans* isomers of 2-stilbazole **1** in the complexations with (tetraphenylporphyrinato)zinc **3**

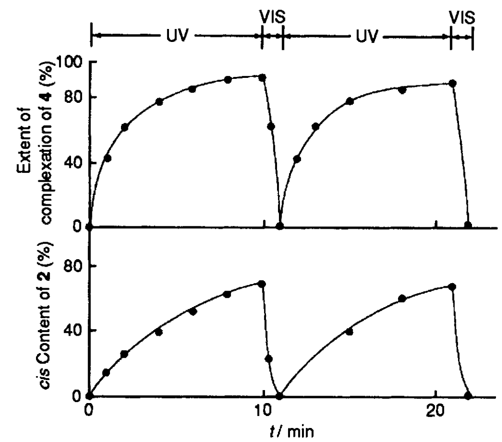

Fig. 3 Reversible change in the complexation of [Zn(tbpp)] **4** with **2** together with the isomerization of **2** upon the periodic irradiation of UV and visible light. The value of the extent of complexation of **4** was determined from the intensity of the absorption band at 601 nm due to the complex. The isomerization of **2** was followed by HPLC analysis.

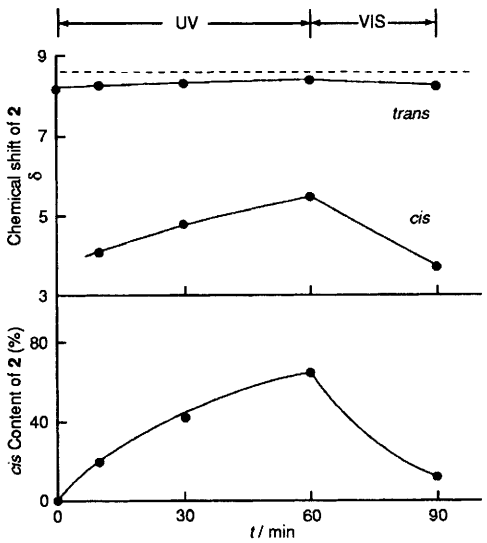

Fig. 4 Reversible change in the NMR chemical shift of the protons in the 6 position of **2** in the presence of [Mg(tbpp)] **5** together with the isomerization of **2** upon the irradiation of UV and visible light. The broken line represents the chemical shift of the proton in the 6 position of **2** in the absence of **5** (δ 8.6); **5**, 2.0 × 10^{-2} mol dm^{-3}, *trans*-**2**, 2.4 × 10^{-2} mol dm^{-3} in C_6D_6.

bazole **2** and [tetra(3,5-di-*tert*-butylphenyl)porphyrinato]-zinc(II) [Zn(tbpp)] **4** were prepared and their complexation was investigated. In the complexation of **2** with [Zn(tpp)] **3**, the value of K_{trans} strikingly decreases to zero from the value of 7 found for **1**. On the other hand, the value of K_{cis} for **2** increases from 197 for **1** to 279, probably because the basicity of the stilbazole increases due to the electron-donating *tert*-butyl groups.[7] Use of [Zn(tbpp)] **4** in place of [Zn(tpp)] **3** affords the same result for *trans*-**2** (K_{trans} = 0).

The substantial difference in the complexation constants of *trans*- and *cis*-**2** with the zinc porphyrins allowed us to control their complexations by the photoisomerization of **2**. When UV light was irradiated on a mixture of benzene solutions of [Zn(tbpp)] **4** (2.0 × 10^{-3} mol dm^{-3}) and *trans*-**2** (2.0 × 10^{-2} mol dm^{-3}) in which the two components are essentially in dissociated form, isomerization of *trans*- to *cis*-**2** took place. This isomerization resulted in the complexation of **4** with *cis*-**2**, as evidenced by the appearance of the absorption due to the complex in the visible spectra of **4**. Furthermore, irradiation of visible light on the resulting solution gave rise to the smooth isomerization of *cis*- to *trans*-**2** and dissociation of the complex occurred as evidenced by the disappearance of the absorption due to the complex. Fig. 3 shows the reversible complexation of **4** with **2** together with the isomerization of **2** upon the periodic irradiation of UV and visible light. The reversibly photocontrolled complexation was observed also in the system of [Zn(tpp)] **3** and **2**. No change was observed in the complexation after leaving the system in the dark for a long time. This makes it clear that the irradiation of UV and visible light causes the change in the complexation.

Furthermore, the photoswitchable complexation was demonstrated with [Mg(tbpp)] **5**. While the formation of a 1 : 1 complex with nitrogen bases causes little change in the visible spectra, complexation causes large upfield ^{1}H NMR shifts of the ligand protons due to shielding by the porphyrin-ring current.[10] The complexation of the 2-stilbazole derivative **2** with [Mg(tbpp)] **5** was investigated by ^{1}H NMR in deuteriated benzene. The 270 MHz ^{1}H NMR spectrum of *cis*-**2** (2.0 × 10^{-2} mol dm^{-3}) in the presence of **5** (1.5 × 10^{-2} mol dm^{-3}) showed large upfield shifts of the protons of *cis*-**2**, especially for the protons in the 6 position (from δ 8.6 to 5.3) and the α position (from δ 7.0 to 4.1). In contrast, only small upfield shifts were observed for *trans*-**2** in the presence of **5** (from δ 8.6 to 8.2 for the proton in the 6 position of *trans*-**2**). These results indicate much stronger complexation of **5** with *cis*-**2** than with *trans*-**2** similarly to the complexation of the zinc porphyrins. Furthermore, upon UV irradiation to a mixture of deuteriated benzene solutions of **5** (2.0 × 10^{-2} mol dm^{-3}) and *trans*-**2** (2.4 × 10^{-2} mol dm^{-3}) in which the two components are essentially in dissociated form, the isomerization of *trans*- to *cis*-**2** resulted in the appearance of the signals due to *cis*-**2** strongly bound to **5** in the ^{1}H NMR spectrum (Fig. 4). The downfield shift for *cis*-**2** along with the increase in the content of *cis*-**2** is attributed to the rapid exchange of complexed *cis*-**2** and uncomplexed *cis*-**2** on the magnesium porphyrin.[10] Successive irradiation with visible light resulted in a shift and the decrease in the intensity of the signals due to *cis*-**2** accompanied by the isomerization of *cis*- to *trans*-**2**. There photoswitchable complexations of metalloporphyrins are expected to provide a step toward photoswitches for chemical reactions of metalloporphyrins, since the complexation of metalloporphyrins with ligands is known to have a significant effect on the reactivity of the metalloporphyrins.

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