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Synthesis and photochemical properties of porphyrin–azobenzene triad

Takashi Yamamura,[a] Atsuya Momotake[b] and Tatsuo Arai[a,*]

[a]*Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1, Tennodai, Tsukuba 305-8571, Ibaraki, Japan*
[b]*Research Facility Centre for Science and Technology, University of Tsukuba, Tsukuba 305-8571, Ibaraki, Japan*

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Abstract—Porphyrin–azobenzene triad ***E*-2**, having ester spacers between the chromophores, was synthesized and its photochemical and thermal isomerization properties were investigated. Triad ***E*-2** showed little electronic communication among the chromophores according to a comparison of the steady-state absorption and fluorescence spectra of ***E*-2** and their model compounds. ***E*-2** showed photochemical *E*–*Z* isomerization and subsequent thermal *Z*-to-*E* isomerization. The porphyrin chromophore in ***Z*-2**, obtained by photoisomerization, did not strongly affect the transient state of thermal *Z*-to-*E* isomerization of the azobenzene unit. The high *E*-isomer composition at the photostationary state indicates the occurrence of triplet energy transfer between porphyrin and azobenzene. ***E*-2** forms a 1:1 complex with 4,4′-bipyridyl (**Bipy**). The stability constant for ***E*-2** with **Bipy** was determined ($\log K = 4.20$ $mol^{-1} dm^3$) by iterative least-squares fitting to a 1:1 binding model.

The structure–property relationship of a variety of dimeric porphyrins has been studied as model systems for primary charge separation in photosynthesis,[1,2] which can be applied to molecular photonic wires,[3,4] molecular gates,[5] chemo sensors,[6,7] and so on. The distance or angle[8] between porphyrins is crucial for the electronic communication and can be controlled by using different linkers such as an alkyl or ether chain[6,7] 1,2-polyphenylene,[9] alkyne,[10–12] and even a heterometallic metal–metal bond.[13] When two porphyrins are bridged by photoresponsive chromophore, the interporphyrin distance can be controlled by light.[14] In order to prove this problem that the distance between porphyrins can be controlled by light, porphyrin–azobenzene triad ***E*-2** (Fig. 1) was designed and synthesized. The photochemical and the thermal isomerization and the complexation behaviors of ***E*-2**, were examined using UV absorption and fluorescence spectra.

Photoisomerization of azobenzenes is a clean reaction. The *E*-isomer is thermodynamically more stable than the *Z*-isomer and the *Z*-isomer can be converted back to the *E*-isomer thermally in the dark as well as photochemically. In addition, the two isomers exhibit different absorption spectra and the simplicity of the synthesis of

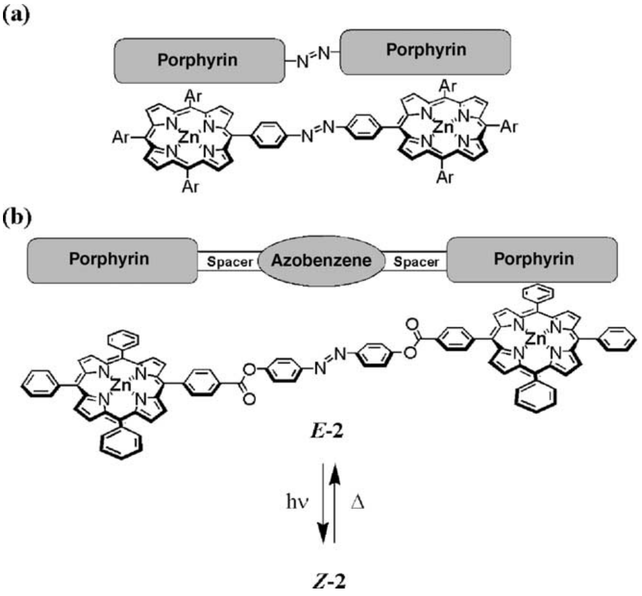

Figure 1. Chemical structures of azo-bridged diporphyrins (a) and porphyrin–azobenzene triad with ester spacers **2** (b).

Keywords: Porphyrins; Azobenzenes; Photoisomerization; Thermal isomerization.

[*] Corresponding author. Tel.: +81 298 53 4315; fax: +81 298 53 6503; e-mail: arai@chem.tsukuba.ac.jp

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the azobenzene derivatives is also important in the use of the azobenzene unit to construct photoresponsive molecules. In this respect, we employed azobenzene as a photoresponsive linker between two porphyrins. Photochemical and thermal isomerization takes place even if bulky groups such as dendrons with molecular weight more than 1000 were substituted on both phenyl groups in the azobenzene chromophore.[15–19]

Diporphyrins directly bridged by azo linkage (Fig. 1a)[20,21] have already been synthesized for developing new materials for molecular electronics.[22] In this type of compounds, the azo group behaves as an electron-attracting group[21] and affects the electronic environment of the porphyrin ring, which causes the change in the absorption spectra from that of the original porphyrins. Similar changes in the electronic structure are also observed in other azobenzene-linked porphyrins.[23] These intramolecular electronic communications between azo group and porphyrin units, however, may cause loss of the ordinal feature of azobenzene, such as isomerization property. In fact, some azobenzene–porphyrins did not isomerize by photoirradiation[23] and the reasons for this are still obscure.

We employed the ester spacers between porphyrin and azobenzene, which would be helpful to avoid disrupting the electronic interaction. In this porphyrin–azobenzene triad ***E*-2** (Fig. 2b), the distance between porphyrins can be changed by the isomerization of azobenzene. Furthermore, the difference of the distance of two porphyrin rings in *E*- and *Z*-isomer may give the difference of affinity to other molecules such as 4,4′-bipyridyl, DABCO, or even fullerene so that the photochemical properties of porphyrin and azobenzene in **2** should not be greatly changed from those of the original ones, such as model compounds **3** and **4** shown in Figure 2. It should also be noted that control of the molecular conformation containing more than two azobenzene units[24] seems to be very difficult because the photoirradiation to each azobenzene unit will give a mixture of *E*- and *Z*-isomers.

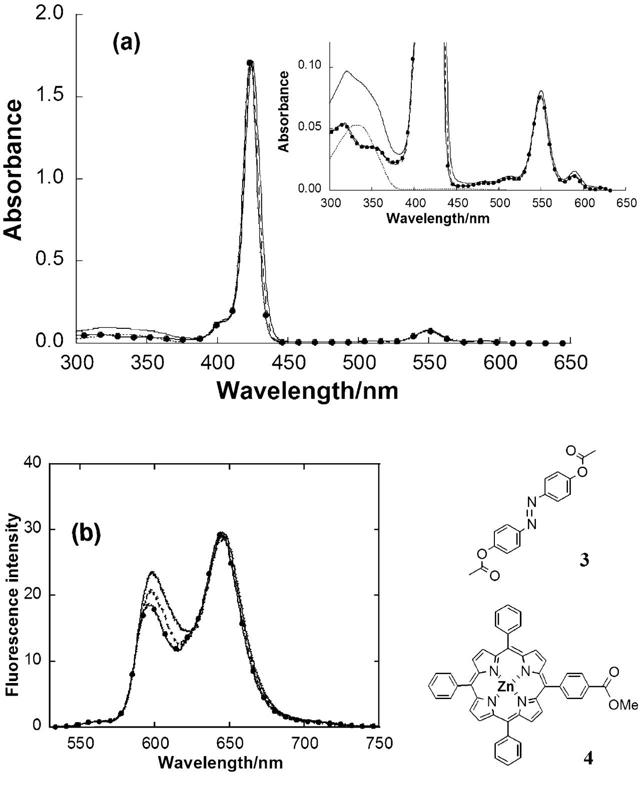

Figure 2. (a) The absorption spectra of ***E*-2** (solid line), **3** (dotted line), **4** (dash line), and **Zn-TPP** (closed circle) in toluene. Inset shows the expanded spectra. Spectra of **4** and **Zn-TPP** are almost identical; (b) the normalized fluorescence spectra of ***E*-2** (solid line), **4** (dash line), and a **Zn-TPP** (closed circle), excited at 424 nm in toluene.

Zn complex ***E*-2** was prepared in two steps starting from TPP-COOH and 4,4′-dihydroxyazobenzene (Scheme 1).[†] The absorption spectra of **2** in toluene is shown in Figure 2a and was compared to the reference compounds, azobenzene **3**, porphyrin **4**, and **Zn-TPP**. Both the Soret-band and Q-band in compound ***E*-2** are very similar to those of **4** and **Zn-TPP**, which indicates that porphyrin units in ***E*-2** do not take either intra- or intermolecular overlapped conformation. In addition, there is little electronic communication between the azobenzene and the porphyrin moieties in ***E*-2** due to the ester spacer. It should be noted that there is a clear difference in the Soret-band in the absorption spectra in ***E*-2** and those in the azo-bridged diporphyrin-type compounds (Fig. 1a), which is red-shifted with broadening of the absorption band by the electronic interaction of porphyrin ring with the N=N bond in their ground state.[20–22] The expanded absorption spectra are shown in the inset in Figure 2. The absorption bands of azobenzene **3** appeared around 340 nm for π–π^* and 440 nm for n–π^* absorption, respectively, and the absorption spectrum of ***E*-2** is almost a summation of the components, azobenzene **3**, and porphyrin **4**. Thus, one can estimate that the π–π^* absorption band of the azobenzene part in ***E*-2** exists around 340 nm as in model compound **3**, and, therefore, the irradiation of ***E*-2** at 340 nm should result in the *E*–*Z* isomerization.

Figure 2b shows the normalized fluorescence spectra of ***E*-2**, **4**, and **Zn-TPP** (excited at 424 nm). All three spectra are similar but the peak intensity of ***E*-2** around 600 nm is slightly larger than that of **4**. In addition, fluorescence quantum yield of ***E*-2** ($\Phi_F = 0.031$) is also close to that of **Zn-TPP** ($\Phi_F = 0.033$).[25] The results indicate that the excited state properties of porphyrin in ***E*-2** are not greatly changed or quenched by intramolecular interaction with azobenzene and the porphyrin ring substituted at the other end of azobenzene.

Figure 3 shows the change in the absorption spectra during the photoisomerization of ***E*-2** in toluene at room temperature. On irradiation at 340 nm light, the absorbance at 300–380 nm, which is attributed to the azobenzene unit, decreased having the isosbestic point at 295 nm. The expanded data are shown in the inset in

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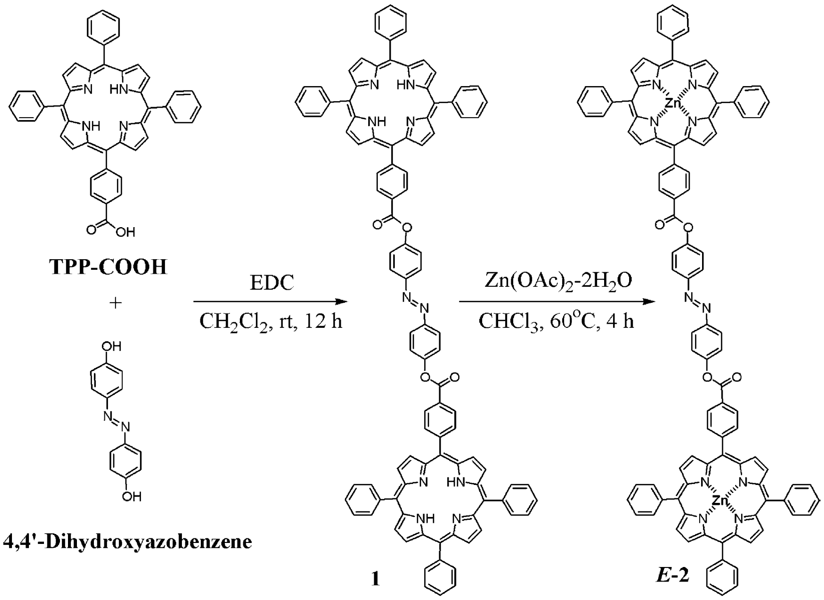
[†] Electronic Supplementary Information (ESI) available: experimental data for **1** and ***E*-2**.



Scheme 1.

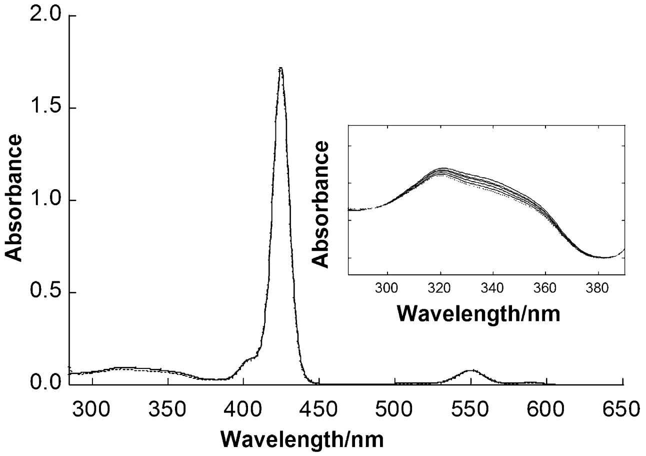


Figure 3. Change in the absorption spectra of ***E*-2** upon the irradiation at 340nm light. Before irradiation (solid line) and at photostationary state (dotted line). Inset shows the expanded spectra for azobenzene unit.

Figure 3. While the absorbance of the azobenzene unit changed by irradiation, neither the Soret-band nor the Q-band of porphyrin changed before and after irradiation. Furthermore, the fluorescence spectra of ***E*-2** also did not change after irradiation. This indicates that two porphyrin units in ***Z*-2**, produced by photoisomerization, do not take the overlapping conformation or do not contact within the distance to have the van der Waals interaction.[9] Since the values of the extinction coefficient of the porphyrine chromophore in both *E*- and *Z*-isomer are the same, the *E*/*Z* ratio at the photostationary state can be obtained by HPLC analysis detected at 424nm; $([E]/[Z])_{\mathrm{pss}} = 80/20$. The composition of the *Z*-isomer of the model compound **3** at the photostationary state was >90%. However, in **2** the *E*-isomer composition at the photostationary state is much higher at 80%. Thus, the Zn–porphyrin moiety in **2** may influence the photostationary state isomer composition by quenching and/or energy transfer processes. The triplet energy of *E*-azobenzene does not strongly depend on the substituent groups and are in the range of 30–35 $\mathrm{kcal\,mol^{-1}}$,[26,27] which are slightly lower than that of Zn–porphyrin ($E^{\mathrm{T}} = 38\,\mathrm{kcal\,mol^{-1}}$). Since both chromophores are connected by the covalent bond, the energy transfer or quenching process should take place not by a diffusion-controlled process but by the small structural change of the covalent bond. The energy transfer from the triplet state **Zn-TPP** should take place in both *E* and *Z*-azobenzene because the triplet energy of the *Z*-isomer is even lower than that of the *E*-isomer.[26] In triplet-sensitized isomerization using sensitizers with triplet energy of 45–67 $\mathrm{kcal\,mol^{-1}}$, the *Z*-isomer composition was only 1–2% at the photostationary state indicating almost one-way *Z*-to-*E* isomerization in the excited triplet state.[28,29] The excitation light at 340nm was absorbed both by the azobenzene chromophore and Zn–porphyrin chromophore. The produced singlet excited state of azobenzene undergoes *E*–*Z* isomerization with favoring the *Z*-isomer composition, while that of Zn–porphyrin undergoes intersystem crossing to the triplet state. The produced porphyrin triplet state ($E_{\mathrm{T}} = 36.6\,\mathrm{kcal\,mol^{-1}}$)[30] should undergo energy transfer to the azobenzene chromophore (30–35 $\mathrm{kcal\,mol^{-1}}$ for both *E*- and *Z*-isomer) to give the azobenzene triplet state. As described above, the *Z*-isomer composition at the photostationary state was only 1–2%, giving almost one-way *Z*-to-*E* isomerization in the triplet state. Therefore, the considerably high *E* isomer composition at the photostationary state in **2** is a compromise of the isomerization in the singlet excited state and the triplet excited state as a different spin state of isomerization.

When an irradiated solution of **2** was kept in darkness, the absorption spectra changed back to that of the *E*-isomer. This spectral change is similar to the well-known

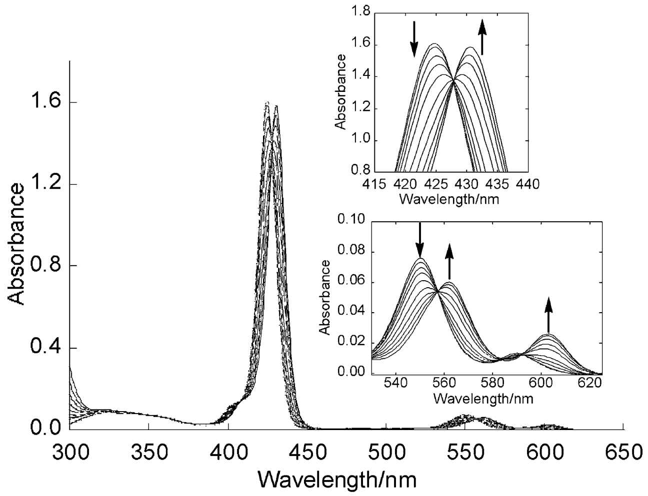


Figure 4. Change in the absorption spectra of ***E*-2** upon the addition of 4,4′-bipyridyl, whose equivalent values are (from top to the bottom at 425 nm); 0, 1, 4, 8, 15, 30, 60, 100, 160, 240 equiv.

cis-to-*trans* thermal isomerization of azobenzene. The observed back-reaction in darkness, therefore, can be assigned to the thermal *Z*-to-*E* isomerization of the azobenzene chromophore. The rate of the thermal isomerization increased at higher temperature. The activation energy ($E_a = 22.9\,\mathrm{kcal\,mol^{-1}}$) and the frequency factor ($A = 1.41 \times 10^{13}\,\mathrm{s^{-1}}$) for thermal *Z*-to-*E* isomerization of **2** were determined by the Arrhenius plot. The activation enthalpy ($\Delta H^{\neq}$) and activation entropy ($\Delta S^{\neq}$) for thermal *Z*-to-*E* isomerization of **2** were also obtained from the Eyring plot: $\Delta H^{\neq} = 22.3\,\mathrm{kcal\,mol^{-1}}$, $\Delta S^{\neq} = -0.61\,\mathrm{cal\,mol^{-1}\,K^{-1}}$. These thermodynamic parameters are not very different from those of model compound **3** (Table 1) or other azobenzene derivatives in organic solvents.[16,17] Thus, the porphyrin chromophore in **2** does not strongly affect the transient state of thermal isomerization of the azobenzene chromophore.

Because of its somewhat flexible structure, some bidentate ligands, such as 4,4′-bipyridyl (**Bipy**) and DABCO, seems to fit the binding site provided by two Zn–porphyrins in ***E*-2**. The binding behavior of ***E*-2** with **Bipy** is monitored by UV–vis spectroscopy (Fig. 4). Upon binding of **Bipy**, the Soret (425 nm) and Q (550 and 590 nm) bands were red-shifted (430, 562, and 603 nm, respectively). In the spectra, isosbestic points were observed at 408, 428, 557, 584, and 592 nm, respectively. The result suggests the formation of one distinct species during the titration. The stoichiometry of the complex was estimated on the basis of Job's plots, which is supporting 1:1 complex stoichiometry. The apparent formation constant ($\log K = 4.20\,\mathrm{mol^{-1}\,dm^3}$) was determined by iterative least-squares fitting to a 1:1 binding model. The formation constant of ***E*-2/Bipy** is larger than that of monomer Zinc-5,10,15,20-tetraphenylporphyrin (**Zn-TPP**)/**Bipy** complex ($\log K = 3.20\,\mathrm{mol^{-1}\,dm^3}$ in CH_2Cl_2)[31]. These results indicate that ligand molecule probably binds in between two porphyrins to give sandwich-type complex (Fig. 5), at least in this concentration range. The exploration of the difference of affinity to other molecules between *E*- and *Z*-isomers is ongoing.

Table 1. The rate constants, activation energy, frequency factor, activation enthalpy, and activation entropy of thermal *Z*-to-*E* isomerization of **2** and **3**

Entry	E_a/kcal mol^{-1}	$A/10^{13}\,\mathrm{s^{-1}}$	$\Delta H^{\neq}$/ kcal mol^{-1}	$\Delta S^{\neq}$/cal mol^{-1} K^{-1}
2	22.9	1.41	22.3	−0.61
3	22.1	0.43	21.5	−2.85

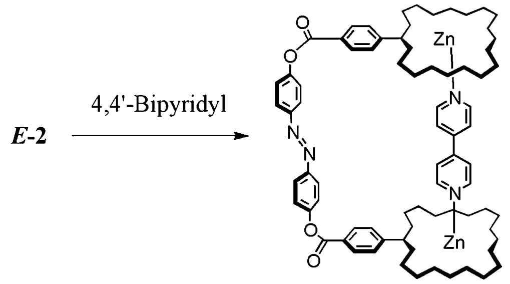


Figure 5. Schematic representation of possible ***E*-2**/4,4′-bipyridyl sandwich-type complex.

In summary, we have newly prepared the porphyrin–azobenzene triad ***E*-2**, possessing ester spacers between the azobenzene and porphyrin chromophores. The electronic communication between the azobenzene and porphyrin chromophores as well as two porphyrins was not detected according to a comparison of the steady state absorption and fluorescence spectra. ***E*-2** showed photochemical *E*–*Z* isomerization and subsequent thermal *Z*-to-*E* isomerization. Neither the absorption nor fluorescence spectra of the porphyrin moiety in **2** changed after irradiation. The results indicate that two porphyrins in the *E*- or *Z*-isomer do not take the overlapping conformation. The high *E*-isomer composition at the photostationary state indicates the occurrence of triplet energy transfer between porphyrin and azobenzene and therefore, **2** should have observable interaction between azobenzene and porphyrin only in the triplet state. ***E*-2** forms a 1:1 complex with **Bipy** and the stability constant between E-2 and **Bipy** ($\log K = 4.20\,\mathrm{mol^{-1}\,dm^3}$) was determined to be considerably higher than that between **Zn-TPP** and **Bipy**.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2004.10.076.

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