

Intramolecular Electron Transfer of Diporphyrins Comprised of Electron-Deficient Porphyrin and Electron-Rich Porphyrin with Photocontrolled Isomerization

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Abstract: New azobenzene-linked diporphyrin Zn complexes and free base analogues were synthesized in an attempt to develop new materials for molecular electronics. These diporphyrin Zn complexes and the corresponding diporphyrins consist of electron-deficient porphyrin Zn complex and electron-rich porphyrin Zn complex or electron-deficient porphyrin and electron-rich porphyrin. These compounds, which are a new family of diporphyrins, exhibited the photoresponsive property with a structural change in the antenna; the trans–cis photoisomerization and cis–trans thermal recovery occurred and this process was reversible. A particularly noteworthy characteristic of the diporphyrin Zn complex is that its fluorescence spectrum changes with isomerization; the fluorescence intensity of the cis-isomer produced by photoirradiation is smaller than that of the trans-isomer. This fluorescence quenching of the cis-isomer arises from the intramolecular electron transfer from electron-rich porphyrin Zn complex to electron-deficient porphyrin Zn complex. Similar phenomena were observed for azobenzene-linked diporphyrins. This discovery that intramolecular electron transfer between the porphyrin rings is caused by photocontrolled isomerization is worthy of notice. Additionally, these compounds bearing eight fluorine atoms at the β -position of one porphyrin ring are the ideal materials for the practical application, because of their robust properties. This finding clearly suggests that new molecules are particularly useful in the development of photocontrolled molecular electronics such as molecular switches.

Introduction

Studies on the photoinduced interactions between the porphyrins¹ have provided important methods for developing new materials for molecular electronics,² and various porphyrin derivatives for this purpose have been synthesized.³ The most successful porphyrin systems studied to date exhibited the electronic interaction via the bridging group (linker) that links several porphyrins.^{3–6} However, porphyrin systems in which the electron-rich porphyrin directly interacts with the electron-deficient porphyrin in the same molecule seem to be more useful for this purpose. My approach to developing new materials for

molecular electronics is based on the utilization of β -halogenated porphyrin as the electron-deficient porphyrin.^{7–10} In particular, perfluorinated porphyrin (*Teflon porphyrin*), which is an excellent electron acceptor and robust for the light, is considered to be one of the most important materials for new systems.^{7,11} Thus, the fluorinated porphyrin Zn complex has been linked to the electron-rich porphyrin Zn complex by an azobenzene moiety, and new diporphyrin Zn complexes which exhibit the photoresponsive property with a structural change in the antenna have been synthesized. In this paper, the syntheses of the new azobenzene-linked diporphyrin Zn complex and the corresponding diporphyrin and the photocontrolled interaction between the electron-rich porphyrin Zn complex and the electron-deficient

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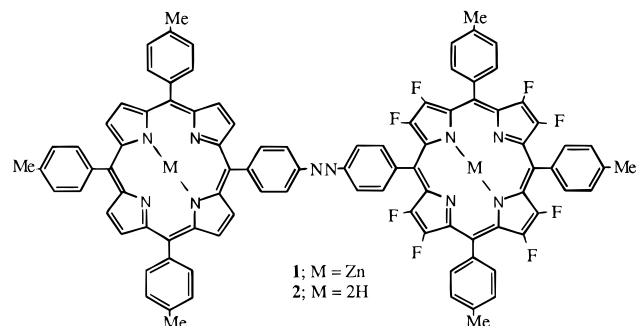
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(11) Usual porphyrins are known to be decomposed under strong light. When the halogen atoms are substituted directly on the porphyrin ring itself, their properties including redox potentials change greatly. In particular, fluorinated porphyrins are very robust toward oxidizing agents and light.

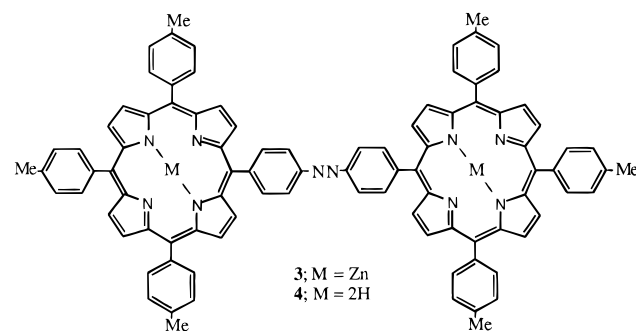
porphyrin Zn complex (or electron-rich porphyrin and electron-deficient porphyrin) in these compounds have been described.

Results and Discussion

The structures of diporphyrin Zn complex **1** linked by an azobenzene bridge and the corresponding diporphyrin **2**, which were synthesized newly by us, are shown below.



This system we present has been designed to take place in the rigid interaction between the two porphyrin rings with photoisomerization. Related diporphyrin Zn complex **3** and the corresponding diporphyrin **4** were synthesized for comparison purposes; it is possible to explore more detailed information about the electronic interaction between the two porphyrin rings by using these compounds.



Properties of β -Halogenated Porphyrin Metal Complexes and Diporphyrin Zn Complexes. The synthetic methods of azobenzene-linked diporphyrin Zn complexes (**1**, **3**) and the starting porphyrin Zn complexes (**5**, **6**) are described in the Experimental Section.

Of particular interest is the role of fluorine atoms at the β -position in changing the electrochemical properties of 5,10,15-tris(*p*-methylphenyl)-20-(*p*-nitrophenyl)porphyrin Zn complex **5**, which is the starting compound, because 5,10,15-tris(*p*-methylphenyl)-20-(*p*-nitrophenyl)-2,3,7,8,12,13,17,18-octafluoroporphyrin Zn complex **6** is expected to be an electron acceptor.¹² The electrochemical properties of β -chlorinated porphyrin Fe^{III}Cl (β -Cl₈TPPFe^{III}Cl) and β -brominated porphyrin Fe^{III}Cl (β -Br₈TPPFe^{III}Cl) already have been studied in detail to explore their catalytic ability and the biological role of the nonplanar porphyrin ring.^{13,14} Thus, the electrochemical characteristics of the β -fluorinated porphyrin metal complex are clarified by comparison between the electrochemical properties of β -fluorinated porphyrin metal complex and those of other β -halogenated porphyrin metal complexes previously reported.

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Table 1. UV–Visible Spectral Data for Diporphyrin Zn Complexes (**1**, **3**) and Their Diporphyrin Analogues (**2**, **4**) in Dichloromethane

comps	λ_{max} , nm (ϵ^a)						fwhm ^c
1	410 ^b	432(100)	558(10)	601(7)			38
2	417 ^b	431(100)	512(19)	544(12)	593(8)	650(4)	
3	395 ^b	426(100)	555(8)	597(4)			19
4	398 ^b	418(100)	516(9)	550(6)	586(4)	643(3)	

^a All extinction coefficients in this table are relative to the Soret maximum in the species and are not absolute nor related to other derivatives. As described in the Experimental section, the absolute extinction coefficients (λ_{max} (ϵ)) of compound **1** are 432 (41000), 558 (4100), 601 nm (2870). ^b The shoulder. ^c Fwhm (nm) of Soret absorption of the diporphyrin Zn complex.

To conduct this comparison, porphyrin Zn complexes **5** and **6** were converted into 5,10,15-tris(*p*-methylphenyl)-20-(*p*-nitrophenyl)porphyrin Fe^{III}Cl **7** and 5,10,15-tris(*p*-methylphenyl)-20-(*p*-nitrophenyl)-2,3,7,8,12,13,17,18-octafluoroporphyrin Fe^{III}Cl **8**, and their redox potentials were measured by cyclic voltammetry. The first reduction potentials (half-wave potentials (V vs SEC)) of **7** and **8** were -0.38 and 0.33 V, respectively. These values suggest that β -fluorinated porphyrin metal complexes **6** and **8** can function as the electron acceptor. The change (0.71 V) of **8** from that of **7** is much larger than those (0.47 and 0.39 V) reported for β -octachlorinated porphyrin Fe^{III}Cl and β -octabrominated porphyrin Fe^{III}Cl.^{13,14} This result revealed that, when the fluorine atoms are substituted directly on the porphyrin ring itself, the fluorinated porphyrin metal complex is the best electron acceptor among halogenated (Br, Cl) porphyrin metal complexes.

The coupling reaction of electron-rich porphyrin Zn complex **5** and electron-deficient porphyrin Zn complex **6** afforded diporphyrin Zn complex **1**. This diporphyrin Zn complex **1** showed several pronounced characteristics in the UV–visible spectrum that are distinct from a reported diporphyrin system; that is, the Soret band is highly red-shifted (from 422 to 432 nm) and is greatly broadened with fwhm of 38 nm. These shifts and band broadening do not arise from the π -system interaction as observed for cofacial diporphyrins,¹⁵ because this diporphyrin Zn complex **1** has a trans form at the azobenzene bridge due to the steric interaction between porphyrin Zn complexes, and the two porphyrin rings do not interact directly with each other.

Diporphyrin Zn complex **3** was prepared from porphyrin Zn complex **5**. The Soret absorption of diporphyrin Zn complex **3** (dimer) exhibits a wavenumber shift from 421 to 426 nm and is slightly broadened with fwhm of 19 nm, compared with the fwhm (13 nm) of starting porphyrin Zn complex **5** (monomer). It has been reported that the diarylethyne-linked porphyrin dimers exhibit the trend observed for this system (427 nm, fwhm = 18.7 nm).^{6b} Diporphyrins **2** and **4** were prepared successfully from the corresponding diporphyrin Zn complexes **1** and **3** by using trifluoroacetic acid in dichloromethane. The spectroscopic data and the results of elemental analysis of diporphyrin Zn complex **1** were described in the Experimental Section. The UV–visible absorption characteristics of diporphyrin Zn complexes (**1**, **3**) and the corresponding diporphyrins (**2**, **4**) in dichloromethane are summarized in Table 1.

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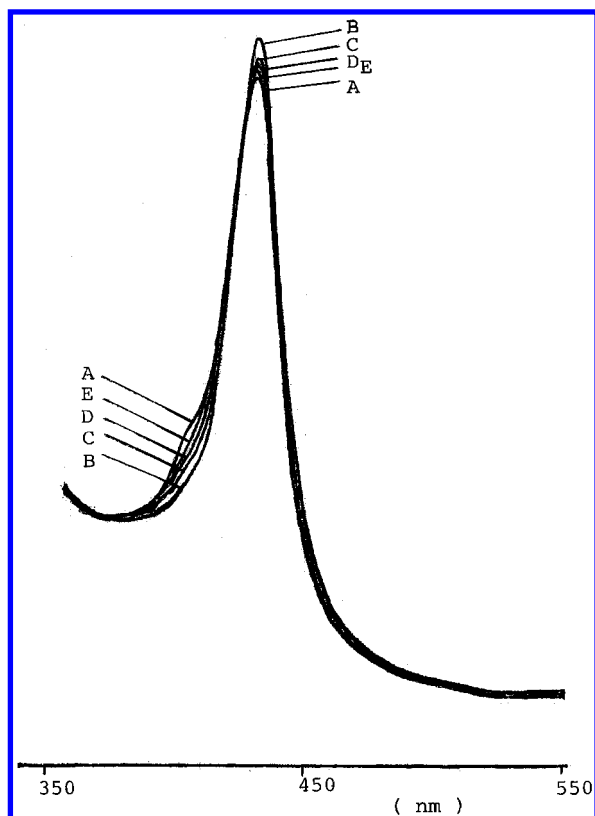


Figure 1. UV-visible spectral changes of diporphyrin Zn complex **1** in acetonitrile: A, diporphyrin Zn complex **1**; B, diporphyrin Zn complex **1** after photoirradiation; C, D, E, spectral changes with time after photoirradiation, after 1 h in the dark, this returned to original band A.

Photoisomerization of Diporphyrin Zn Complexes. Initially, we need to explore the photoresponsive property of diporphyrin Zn complex **1**, which consists of electron-deficient porphyrin Zn complex (fluorinated porphyrin Zn complex) and electron-rich porphyrin Zn complex. The photoisomerization of diporphyrin Zn complex **1** was therefore examined by Xe lamp irradiation (10 min) or high-pressure Hg lamp irradiation (5 min).¹⁶ Diporphyrin Zn complex **1** in acetonitrile exhibited three peaks and one shoulder before photoirradiation.¹⁷ After photoirradiation, the Soret band of diporphyrin Zn complex **1** in acetonitrile was red-shifted from 430 to 432 nm and its peak height increased by 8.5% as shown in Figure 1. It should be noted that the shoulder at 408 nm disappeared. The position of this shoulder is close to that (π - π^*) reported for *trans*-azobenzene and the starting porphyrin Zn complexes **5** and **6** do not have this shoulder. It was also reported that the absorption coefficient of *trans*-azobenzene of bis(crown ether) with an azo linkage is 26 700.^{18,19} Presumably, this shoulder at 408 nm would be assigned to the *trans*-azobenzene moiety of diporphyrin Zn complex **1**. Thus, the disappearance of shoulder would result from *trans*-*cis* isomerization. The changes of Soret band noted above also support this fact. The thermal recovery (*cis*-

trans thermal isomerization) was also observed; after 1 h in the dark, the peak height and the position of the Soret band of diporphyrin Zn complex **1** returned to the original band before photoirradiation and the shoulder appeared again as shown in Figure 1. This procedure of *trans*-*cis* and *cis*-*trans* photoisomerization was repeated several times and the same result was obtained. Thus, these results imply that the isomerization process between *trans*-isomer and *cis*-isomer is reversible.

Relative Fluorescence Quantum Yields of Diporphyrin Zn Complex and Porphyrin Zn Complex. Since the Soret band broadening (fwhm = 38 nm) is observed for the *trans*-isomer of diporphyrin Zn complex **1**, there is a possibility that significant interaction between two porphyrin Zn complexes via the linking azobenzene moiety occurs. The strong interaction between porphyrin Zn complex and free base porphyrin via the diarylethyne linker in the porphyrin dimer has been reported already.⁶ To confirm this type of the interaction, the relative fluorescence quantum yields of the *trans*-isomer of diporphyrin Zn complex **1** and the starting porphyrin Zn complex **5** were measured in benzene. The relative fluorescence quantum yield (0.029) of porphyrin Zn complex **5** is essentially identical with that (0.030) of tetraphenylporphyrin Zn complex (ZnTPP). However, the relative fluorescence quantum yield (0.0095) of the *trans*-isomer of diporphyrin Zn complex **1** is smaller than that (0.029) of the starting porphyrin Zn complex **5**. This suggests that the intramolecular interaction via the azobenzene linker that bridges the electron-rich and electron-deficient porphyrin rings occurs in the *trans*-isomer. However, since this relative fluorescence quantum yield (0.0095) is larger compared with other systems of multiporphyrin arrays,^{3,4,6} it seems that the azobenzene moiety that bridges the electron-rich and electron-deficient components of diporphyrin Zn complex **1** is not an efficient linker in mediating the electronic interaction.

In addition, the relative fluorescence quantum yields of diporphyrin **2** and porphyrin **9** were measured for comparison purposes, and their values were 0.0237 and 0.1, respectively. The ratios of relative fluorescence quantum yields of the *trans*-isomers of diporphyrin Zn complex **1** and diporphyrin **2** for the starting porphyrin Zn complex **5** and porphyrin **9** are 0.33 and 0.24, respectively, suggesting the larger interaction between the porphyrins compared with the porphyrin Zn complexes.

Photocontrol of Intramolecular Electron Transfer. As mentioned previously, UV-visible spectra of diporphyrin Zn complex **1** showed the isomerization process (*trans*-*cis* and *cis*-*trans*). The fluorescence intensity measurements of these two isomers provided interesting results. The fluorescence intensity of the *cis*-isomer produced by photoirradiation was much smaller than that of the *trans*-isomer as shown in Tables 2 and 3; the *cis*-isomer exhibited only 61% of the fluorescence intensity of the *trans*-isomer. As described in the above section, since the fluorescence intensity of the *trans*-isomer decreased by the interaction via the azobenzene linker (0.0095), the *cis*-isomer of diporphyrin Zn complex **1** exhibited 20% of the fluorescence intensity of the starting porphyrin Zn complex **5** (monomer). The changes of fluorescence intensity with *trans*-*cis* and *cis*-*trans* isomerization were reversible as with the UV-visible measurements.²⁰ The larger fluorescence quenching observed for the *cis*-isomer can be explained in terms of an intramolecular electron-transfer mechanism. As seen in the following scheme, since the distance between the two porphyrin

(16) The light with longer wavelength (>440 nm) was cut off by using a Toshiba glass filter (UV-D33S), and then, the region of UV was used for photoirradiation.

(17) All of the experiments of photoirradiation were conducted in acetonitrile, because the decomposition of dichloromethane under Xe lamp irradiation was observed.

(18) In the case of azobenzene-linked bis(crown ether), the absorption bands of the *trans* form and the *cis* form are λ_{max} 376 nm, ϵ_{max} 26700 and λ_{max} 445 nm, ϵ_{max} 2890, respectively.¹⁹

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Table 2. Relative Fluorescence Intensities of Isomers of Diporphyrin Zn Complex **1** and Its Diporphyrin Analogue **2** in Acetonitrile^a

	excitation wavelength (nm)	rel intensity ^b
diporphyrin Zn complex 1		
trans-isomer	431	1.0
cis-isomer	431	0.61
diporphyrin 2		
trans-isomer	430	1.0
cis-isomer	430	0.46

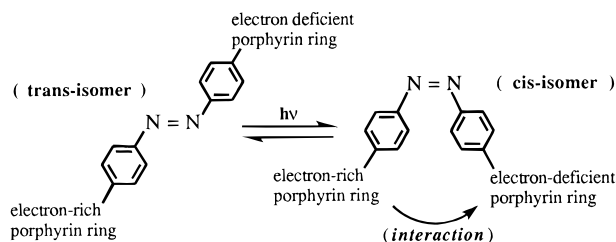
^a The concentrations of diporphyrin Zn complex **1** and diporphyrin **2** used for measurements were 1×10^{-5} M and their fluorescence measurements were carried out under an argon atmosphere at 20 °C. The cis-isomer was produced by Xe lamp irradiation for 10 min. After photoirradiation, the cis configuration of the linking azobenzene moiety was confirmed by the UV–visible spectrum. After fluorescence measurements, the cis-isomer was confirmed again by the UV–visible spectrum. After 1 h in the dark, the cis-form isomerized to the trans-form. The UV–visible spectrum of the trans-isomer after thermal isomerization did not give any evidence of decomposition of diporphyrin Zn complex **1** and diporphyrin **2** by photoirradiation. ^b (Isomer)/(trans-isomer).

Table 3. Relative Fluorescence Quantum Yields (Φ) of Diporphyrin Zn Complex **1**, Its Diporphyrin Analogue **2**, and Related Compounds **5** and **9** in Benzene

	diporphyrin Zn complex 1	diporphyrin 2
trans	0.0095	0.0237
cis (Φ_{dc})	0.0058	0.0109
	porphyrin Zn complex 5 ^a	porphyrin 9 ^a
(Φ_s)	0.029	0.10
(Φ_{dc})/(Φ_s) ^b	0.2	0.109

^a The starting porphyrin Zn complex **5** and its porphyrin analogue **9** (monomer). ^b (Relative fluorescence quantum yield of the cis-isomer)/(relative fluorescence quantum yield of the starting compound).

rings in the trans-isomer is long, the possibility that the electron-rich Zn porphyrin and electron-deficient Zn porphyrin interact mutually is very small. In contrast, the distance between the two porphyrin rings of the cis-isomer is sufficiently close to enable direct interaction. Thus, it is considered for the cis-isomer that intramolecular electron transfer from the electron-rich porphyrin Zn complex moiety to the electron-deficient porphyrin Zn complex moiety would take place and as a consequence, the larger fluorescence quenching is observed.^{21,22}



To explore whether the fluorescent behavior is affected by the interaction between two identical porphyrin Zn complexes

(21) The decrease (67%) of fluorescence intensity of the trans-isomer of diporphyrin Zn complex **1** for the monomer **5** is caused from the interaction via the azobenzene linker, while for the cis-isomer, the larger decrease (80%) of fluorescence intensity for the monomer **5** would arise from direct interaction between two porphyrin Zn complexes.

(22) The relative fluorescence intensities of diporphyrin Zn complexes with other β -halogen atoms were measured for comparison purposes. The relative intensities of the cis-isomers of β -brominated diporphyrin Zn complex **16** and β -chlorinated diporphyrin Zn complex **17** were 0.79 and 0.73, respectively. The ratios of fluorescence quenching of these diporphyrin Zn complexes (**16**, **17**) are smaller, suggesting that the electron-transfer interaction may be controlled by both steric and electronic factors of β -halogen atoms on one porphyrin ring. The synthetic methods of Zn complexes (**16**, **17**) were described in the Experimental Section.

in the one molecule, similar fluorescence measurements on diporphyrin Zn complex **3**, which consists of two identical electron-rich porphyrin Zn complexes, were carried out. The fluorescence intensity of the cis-isomer produced by photoirradiation was almost the same as that of the trans-isomer, though the UV–visible spectrum measurements of diporphyrin Zn complex **3** showed a trans–cis and cis–trans isomerization process like that of the diporphyrin Zn complex **1**. This fact supports the conclusion described above; that is, intramolecular electron transfer from electron-rich porphyrin Zn complex to electron-deficient porphyrin Zn complex (fluorinated porphyrin Zn complex) is the important factor causing the fluorescence quenching in the cis-isomer of diporphyrin Zn complex **1**.

Since some properties of TPP are different from those of ZnTPP, there is the possibility that the isomerization and the fluorescence quenching are affected by the centrally coordinated zinc atom. To explore this, the same experiments were therefore conducted by using diporphyrins **2** and **4** in acetonitrile.¹⁷ After photoirradiation, the Soret band of diporphyrin **2** comprised of electron-rich porphyrin and electron-deficient porphyrin was red-shifted to 433 nm, a 5% decrease of its peak height was observed, and the shoulder at 416 nm disappeared. After 1 h in the dark, Soret and shoulder peaks returned to those before photoirradiation. The fluorescence measurements of diporphyrin **2** gave the same trend as diporphyrin Zn complex **1** as shown in Table 2; the cis-isomer exhibited 46% of the fluorescence intensity of the trans-isomer. This is about 11% of the starting porphyrin **9** (monomer) as shown in Table 3. On the other hand, in the case of diporphyrin **4** comprised of two identical porphyrins, the fluorescence intensities of the trans-isomer and the cis-isomer are almost constant. Thus, the result of the diporphyrins is in good agreement with diporphyrin Zn complexes, and shows that the isomerization process and the trend of fluorescent behavior are not affected by the zinc atom coordinated.

The fluorescence quenching is known to be closely related to the lifetime of fluorescence, and it has been reported that the lifetimes of TPP and ZnTPP are 13.2 and 2.2 ns, respectively.^{6c} Thus, it is expected that there is a large difference in the ratio of the fluorescence quenching between diporphyrin Zn complex **1** and diporphyrin **2**. In this case, the ratios (Φ_{dc}/Φ_s) of the relative fluorescence quantum yields of diporphyrin Zn complex **1** and diporphyrin **2** for the starting compounds (monomer, **5** and **9**) are 0.2 and 0.109, respectively, as shown in Table 3. The difference in the ratios between diporphyrin Zn complex and diporphyrin is smaller than that expected from their lifetimes. One of the reasons is that some interaction between the porphyrin rings and the azobenzene moiety would probably contribute to the fluorescence quenching of this system. However, we do not have a definite explanation for this experimental result.

Electron-Transfer Phenomenon. As stated above, the experimental results suggest that intramolecular electron transfer from electron-rich porphyrin to electron-deficient porphyrin is one of the important factors to occur in fluorescence quenching. However, further evidence for electron transfer is required. The electron-transfer phenomenon is generally confirmed when the large overlap between the absorption of the UV–visible spectrum and the absorption of the fluorescence spectrum does not exist,²³ and the fluorescence quenching is observed with the addition of acceptor (quencher) to the solution of donor.

(23) When the large overlap between the absorption of UV–visible spectrum and the absorption of fluorescence spectrum exists, there is the possibility that the intramolecular energy transfer occurs.

Attempts were therefore made, using related electron-rich porphyrin (donor) and electron-deficient porphyrin (acceptor), to confirm the electron-transfer phenomenon by the fluorescence quenching arising from intermolecular electron transfer. The electron-rich porphyrin and electron-deficient porphyrin used in this study are 5,10,15,20-tetrakis(2',4',6'-trimethylphenyl)-porphyrin (**11**) and 5,10,15,20-tetrakis(2',4',6'-trimethylphenyl)-2,3,7,8,12,13,17,18-octafluoroporphyrin (**15**). Since **11** is more electron rich compared with diporphyrin **2**, porphyrin **11** as the electron donor is expected to afford more distinct evidence about the electron transfer. In fact, when the acetonitrile solution (1×10^{-5} M) of electron-rich porphyrin **11** and the acetonitrile solution (1×10^{-5} M) of electron-deficient porphyrin **15** were mixed, a 38% decrease of fluorescence intensity compared with the original fluorescence intensity was observed. This result suggests the formation of an electron-transfer complex (charge-transfer complex) between electron-rich porphyrin **11** and electron-deficient porphyrin **15** or the electron transfer between these species. This decrease of fluorescence intensity caused by the intermolecular electron transfer would be further evidence that the smaller fluorescence intensity of cis-isomer arises from the electron transfer.

Other evidence of electron transfer is to confirm the existence of the porphyrin radical pair, which is generated by the electron transfer. As shown in Table 3, the ratios of quantum yields of the diporphyrin system for the starting compounds (monomer) are 0.2 and 0.109. Thus, there is the possibility that the radical of the cis-isomer is explored by spectroscopic methods. Porphyrin radicals have been investigated by UV-visible spectrum measurements. For example, UV-visible spectra of the radicals of porphyrin metal complexes (anion and cation) were found to exhibit broad absorption from 600 to 800 nm.^{24,25} We also found this broad absorption in the UV-visible spectrum of the π cation radical of dodecarylporphyrin Fe complex.²⁶ Just after photoirradiation, the UV-visible spectrum of the cis-isomer of diporphyrin Zn complex **1** in CH₃CN exhibited broad absorption (550–800 nm) centered at 685 nm, the maximum of which was obscured. This broad absorption was independent of temperature from 25 to 0 °C. This absorption observed in the UV-visible spectrum may be due to the existence of stable radicals of diporphyrin Zn complex.²⁷ On the other hand, the trans-isomer did not show any absorption in the same region. Thus, these experimental results²⁷ would support the above explanation that intramolecular electron transfer from the electron-rich porphyrin Zn complex moiety to the electron-deficient porphyrin Zn complex moiety in one molecule occurs.

Conclusion

Azobenzene-linked diporphyrin Zn complex **1** and its free base analogue **2** showed photoisomerization and subsequent thermal isomerization, and this isomerization process (trans–cis and cis–trans) was reversible. The noteworthy characteristics of compounds **1** and **2** are that the fluorescence intensity of the

cis-isomer produced by photoisomerization is smaller than that of the trans-isomer, and this fluorescence quenching is attributed to the intramolecular electron-transfer interaction between the two porphyrin Zn complexes or the two porphyrins. Additionally, though some decomposition of diporphyrin Zn complex **3** and its free base analogue **4** was observed under Xe lamp irradiation, the spectroscopic data of these compounds (**1** and **2**) containing the porphyrin ring with eight fluorine atoms at the β -position^{7–10,29} did not give any evidence of decomposition, thereby meeting an important requirement for practical applications.^{6f,11} The discovery that intramolecular electron transfer between the porphyrin rings is caused by photocontrolled isomerization is worthy of note. These facts clearly suggest that new diporphyrin Zn complex **1** and its free base analogue **2** are particularly useful in the development of photocontrolled molecular electronics, such as molecular switches,^{30–32} and are the ideal materials to enable the construction of practical systems. In addition to being a useful material for molecular electronics, new compounds **1** and **2** might also serve as a potential model for the photosynthetic electron-transport system,¹ because the product from photoinduced intramolecular electron transfer is very stable at room temperature.

Experimental Section

Materials. All solvents and reagents were purchased commercially. Dry solvents were distilled from CaH₂ or LiAlH₄. Acetonitrile for photoirradiation experiments was distilled from CaH₂ under an argon atmosphere and stored over molecular sieves. Other solvents were used as received. Iron powder was converted to Fe^{II}Br₂ by a literature procedure³³ and Fe^{II}Br₂ was used to prepared the iron(III) complexes of new porphyrins and diporphyrins.

Physical Measurements. NMR spectra (JEOL GX270) and UV-visible spectra (Hitachi 340) were collected routinely. The extinction coefficient for the diporphyrin Zn complex **1** in dichloromethane at room temperature has been determined at the Soret band. The fluorescence spectra were collected by using a Shimadzu RF-5300PC and a JASCO FP-770 under an argon atmosphere at room temperature.³⁴ The relative fluorescence quantum yields of diporphyrin Zn complex

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(27) To obtain further evidence about this, the preliminary ESR measurements of diporphyrin Zn complex **1** in butyronitrile were carried out at room temperature. The ESR spectrum of the cis-isomer after photoirradiation showed the broad peak, suggesting the existence of radicals.^{3f,25a,26,28} This broadening is probably due to intramolecular dipolar–dipolar and exchange interaction among the radicals.

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(34) The relative fluorescence quantum yields of compounds (**1**, **2**, **5**, and **9**) were summarized in Table 3. The measurements of the relative fluorescence quantum yields of other diporphyrin Zn complexes and diporphyrins have been tried by using several methods (Ogawa, S.; Tsuchiya, S. *Chem. Lett.* **1996**, 709). The results of these measurements will be published in the future.

1, its diporphyrin analogue 2, porphyrin Zn complex 5, and its porphyrin analogue 9 in benzene were determined by the corrected fluorescence spectra of ZnTPP (0.030) and TPP (0.11).³⁵ Cyclic voltammograms were obtained by using a Nikkou Keisoku potentiogalvanostat. Cyclic voltammograms were recorded in the three-electrode system, consisting of a glassy carbon working electrode, a platinum wire as a counter electrode, and a Ag/AgCl reference electrode. Porphyrin Fe^{III} Cl complexes (7, 8) were measured in PhCN with 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. PhCN was thoroughly degassed with argon prior to recording cyclic voltammograms. The photoirradiation of acetonitrile solution containing diporphyrin Zn complexes or diporphyrins was made with use of a Xe lamp (Ushio Electronic Inc.) or a high-pressure Hg lamp.¹⁶ All compounds for physical measurements were purified by high performance liquid chromatography (HPLC) and their purities were confirmed by both methods of TLC and HPLC. HPLC used in this procedure was assembled by Hitachi L-6050 pump, Hitachi L-6250 Intelligent pump, Hitachi L-4200 UV-visible Detector, Hitachi AS-400 Intelligent Autosampler, and Hitachi L-5200 Fraction Collector.

Syntheses. 5,10,15-Tris(*p*-methylphenyl)-20-(*p*-nitrophenyl)porphyrin Zn complex 5 was synthesized by using *p*-tolualdehyde (4 g, 0.0336 mol), *p*-nitrobenzaldehyde (1.7 g, 0.0112 mol), pyrrole (3 g, 0.0448 mol), zinc acetate (3 g, 0.0168 mol), and collidine (20 mL).³⁶ The reaction mixture was heated at reflux under an argon atmosphere, during which time the peak height of the product in the UV-visible spectrum gradually changed. The reflux was continued until the change of the peak height was not observed and then the reflux of the reaction mixture was stopped. At this time, the maximum yield of porphyrin Zn complex was obtained (total yield 65%). Zinc complex 5 was separated and purified by silica-gel column chromatography (dichloromethane-hexane), because the pure porphyrin Zn complex 5 was required for the following reactions.

5,10,15-Tris(*p*-methylphenyl)-20-(*p*-nitrophenyl)porphyrin (9) was prepared from Zn complex 5 by using trifluoroacetic acid in dichloromethane. 5,10,15-Tris(*p*-methylphenyl)-20-(*p*-nitrophenyl)porphyrin Fe^{III} Cl complex 7 was prepared by the reaction of porphyrin 9 and Fe^{II}Br₂ in refluxing dimethylformamide under an argon atmosphere and the anion exchange by HCl solution (1 N).

5,10,15,20-Tetrakis(2',4',6'-trimethylphenyl)porphyrin Zn complex 10 and its porphyrin 11 were prepared by the method described for the syntheses of porphyrin Zn complex 5 and porphyrin 9.³⁶

The halogenations of pyrrole moieties of porphyrin Zn complex 5 and porphyrin Fe complex 7 were carried out by using the procedure already described for other porphyrin metal complexes^{7,8,13,37} and have been successfully accomplished.³⁸ That is, β -bromination and β -fluorination were carried out by using porphyrin Zn complex 5 and *N*-bromosuccinimide⁸ or porphyrin Zn complexes 5 and Co^{III}F₃.³⁷ β -Chlorination of porphyrin Fe complex 7 was carried out by using Fe^{III}Cl₃ and chlorine gas (Cl₂).¹³ These halogenation reactions were accomplished by monitoring the reaction process by means of the measurement of the UV-visible spectrum. This procedure was very important for the β -halogenation of the porphyrin metal complexes. Since the porphyrin metal complexes were often decomposed under severe conditions, the reaction conditions had to be controlled by

monitoring the reaction process during halogenation reactions. After column chromatography (silica or alumina) and recrystallization, 5,10,15-tris(*p*-methylphenyl)-20-(*p*-nitrophenyl)-2,3,7,8,12,13,17,18-octabromoporphyrin Zn complex 12, 5,10,15-tris(*p*-methylphenyl)-20-(*p*-nitrophenyl)-2,3,7,8,12,13,17,18-octafluoroporphyrin Zn complex 6, and 5,10,15-tris(*p*-methylphenyl)-20-(*p*-nitrophenyl)-2,3,7,8,12,13,17,18-octachloroporphyrin Zn complex 13 were obtained.²² 5,10,15-Tris(*p*-methylphenyl)-20-(*p*-nitrophenyl)-2,3,7,8,12,13,17,18-octafluoroporphyrin (14) and 5,10,15,20-tetrakis(2',4',6'-trimethylphenyl)-2,3,7,8,12,13,17,18-octafluoroporphyrin (15) were prepared by using their Zn complexes and trifluoroacetic acid in dichloromethane. 5,10,15-Tris(*p*-methylphenyl)-20-(*p*-nitrophenyl)-2,3,7,8,12,13,17,18-octafluoroporphyrin Fe^{III}Cl 8 for the measurement of cyclic voltammetry was synthesized by the reaction of fluorinated porphyrin 14 and Fe^{II}Br₂ in refluxing dimethylformamide under an argon atmosphere and the anion exchange by HCl solution (1 N).

The coupling reaction of two porphyrin Zn complexes was the same as that reported for bis(crown ether) with an azo linkage.¹⁹ The coupling reaction of porphyrin Zn complex 5 and β -halogenated porphyrin Zn complex with zinc powder afforded the corresponding diporphyrin Zn complexes (β -fluorinated diporphyrin Zn complex 1, β -brominated diporphyrin Zn complex 16, β -chlorinated diporphyrin Zn complex 17).²² Since diporphyrin Zn complex 1 with eight β -fluorine atoms has the best property for this study, the synthetic method for preparing diporphyrin Zn complex 1 is described; that is, the coupling reaction of porphyrin Zn complex 5 and β -fluorinated porphyrin Zn complex 6 is as follows.

Diporphyrin Zn Complex 1. One gram of NaOH in 1 mL of water and 0.025 g (3.2×10^{-5} mol) of 5,10,15-tris(*p*-methylphenyl)-20-(*p*-nitrophenyl)porphyrin Zn complex 5 and 0.029 g (3.2×10^{-5} mol) of 5,10,15-tris(*p*-methylphenyl)-20-(*p*-nitrophenyl)-2,3,7,8,12,13,17,18-octafluoroporphyrin Zn complex 6 in 8 mL of benzene were heated to 80 °C. The solution was stirred vigorously, and KOH (2 g) and zinc powder (0.5 g) were added. After the mixture was stirred for 10 h, zinc powder (0.5 g) was added again. This reaction mixture was then heated to 90 °C and stirred for 10 h. This hot solution was filtered, and the solid was washed with 5 mL of methanol. Air was introduced in this solution for 5 h. The resultant solution was neutralized by HCl solution (1 N) and filtered again. An excess of dichloromethane (50 mL) was added and the organic layer was separated and dried by sodium sulfate. The solvent was evaporated to dryness, and to this residue was added dichloromethane (20 mL) again. The solvent was removed in vacuo and the product as the solid was obtained. This crude diporphyrin Zn complex 1 was purified by silica-gel column chromatography (dichloromethane-hexane). The yield was 37%. When lithium aluminum hydride was used in place of zinc powder, the same product 1 was prepared in 21% yield. IR (KBr disk), $\nu(\text{N}=\text{N})$ 1625 cm⁻¹. Mass spectrum, C₉₄H₅₈F₈N₁₀Zn₂: Calcd av mass, 1610.31; obsd *m/z* 1610.10. ¹H NMR (CDCl₃) δ 2.71 (18H, ArCH₃), 7.25–8.15 (32H, ArH), 8.70–9.90 (8H, β -pyrrole). ¹⁹F NMR (CDCl₃) δ -139.0. Visible spectrum (CH₂Cl₂) λ_{max} (ϵ) 410 nm (shoulder), 432 (41000), 558 (4100), 601 (2870). Anal. Calcd for C₉₄H₅₈F₈N₁₀Zn₂: C, 70.11; H, 3.63; N, 8.70. Found: C, 69.95; H, 3.67; N, 8.65. The value (δ = -139) of ¹⁹F NMR of diporphyrin Zn complex 1 in CDCl₃ is very close to that (δ = -141) of the starting porphyrin Zn complex 6.

The procedures for the synthesis of other diporphyrin Zn complexes (3, 16, 17) were the same as that of diporphyrin Zn complex 1 described above. The spectroscopic data for these compounds (3, 16, 17) and the results of physical measurements of compounds (16, 17) will be discussed in a future paper.^{22,39}

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(39) For example, the absorption of $\nu(\text{NN})$ of diporphyrin Zn complex 3 is 1617 cm⁻¹. The syntheses of Zn complexes (18, 19) of tetrakisphenylporphyrin dimer with an azo linkage at the 2' or 4' positions of the phenyl moiety at the meso position were conducted, and similar values of $\nu(\text{NN})$ were obtained. Diporphyrin Zn complexes (3, 16, 17) gave satisfactory elemental analyses for C, H, and N and parent peaks in the mass spectrum in agreement with the calculated values.

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(38) Since first syntheses of perhalogenated porphyrins having eight halogen atoms at β -position were carried out by us,⁸ a variety of perhalogenated porphyrins have been synthesized by many investigators.^{7,9,10,13,14,29} First syntheses of dodecaarylporphyrins with twelve aryl groups on the porphyrin ring were carried out by us (Tsuchiya, S. *Chem. Phys. Lett.* **1990**, 169, 608. *J. Chem. Soc., Chem. Commun.* **1991**, 716; **1992**, 1475). In particular, dodecaarylporphyrin with twelve pentafluorophenyl groups on the porphyrin ring (F₆₀ porphyrin = *superteflon porphyrin*) is expected to have this excellent property; the synthesis of diporphyrin containing this dodecaarylporphyrin is in progress.