Application of 2-Pyridyl-Substituted Hemithioindigo as a Molecular Switch in Hydrogen-Bonded Porphyrins

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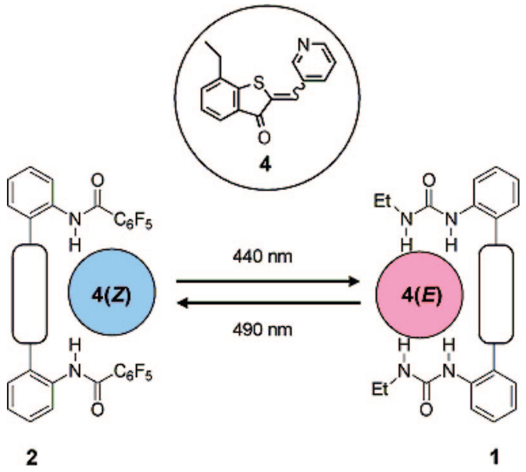

When the photochromism of 2-(3′-pyridylmethylene)-7-ethylbenzo[*b*]thiophen-3(2*H*)-ones (**4**) was investigated, high thermal stability of the *E* isomer of **4**, **4(*E*)** and good repeatability of the photoinduced *E*,*Z*-isomerization were found. Association constants of the 1:1 complexations of **4(*Z*)** and **4(*E*)** with the ureidoporphyrin **1** and with the pentafluorobenzamidoporphyrin **2** were evaluated. We found that **1** captures **4(*E*)** preferentially to **4(*Z*)** and, reversely, **2** prefers **4(*Z*)** to **4(*E*)**. On the basis of these differences in the binding ability, we concluded that the repeatable movement of the hemithioindigo, so-called the hemithioindigo shuttle, between two kinds of porphyrins was controlled by the photoirradiation. These movements were applied to create a molecular switch for changes in the quinone distribution between two kinds of porphyrins.

Introduction

Photochromic molecular systems provide a tool for manipulating the recognizing ability of a binding site.[1] In particular, supramolecular systems controlled by the *E*,*Z*-isomerizations of azobenzenes, stilbenes, and thioindigos have been applied to molecular devices such as molecular shuttles, molecular switches, and molecular machines.[2] In addition, as a model for bacterial photosynthesis, the noncovalently linked porphyrin−quinone assembly has been studied for the construction of an artificial photoelectronic separation system.[3] In our continuing research about the construction of hydrogen-bonded porphyrin−

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(1) (a) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72. (b) Balzani, V.; Credi, A.; Venturi, M. *Molecular Devices and Machines*; Wiley-VCH: Weinheim, Germany, 2003; Chapter 7. (c) Feringa, B. L., Ed. *Molecular Switches*; Wiley-VCH: Weinheim, Germany, 2001; Chapters 6 and 9. (d) Willner, I.; Rubin, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 367.

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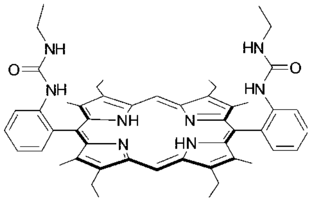
quinone systems controlled by a molecular switch,[4] we have demonstrated the role of (*Z*)-(2-benzoyl)hemithioindigo as a molecular switch. The irradiation of the (*Z*)-(2-benzoyl)hemithioindigo produces the photodimer, which is dissociated back to the hemithioindigo on heating. The hemithioindigo itself is strongly captured by 5,15-*cis*-bis[2-(*N*′-ethyl)ureidophenyl]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**1**) through four-point hydrogen bondings, but the photodimer is not captured by **1** because of its large size. The interconversion between (*Z*)-(2-benzoyl)hemithioindigo and its photodimer and their difference in complexation ability of **1** have been applied to create a molecular switch in the hydrogen-bonded quinone recognition of **1**.[5]

The function of (*Z*)-(2-benzoyl)hemithioindigo as a molecular switch is based on the intermolecular photodimerization; this causes an unnecessarily high concentration of the molecular switch. Therefore, we studied 2-pyridylmethylene-7-ethylbenzo[*b*]thiophen-3(2*H*)-one in detail because it has two acceptors for hydrogen bondings, carbonyl oxygen atom and pyridine nitrogen atom; thus intramolecular *Z*,*E*-isomerization is expected in the irradiation. In this paper, we demonstrate the recognition performance of 2-pyridylmethylene-7-ethylbenzo[*b*]thiophen-3(2*H*)-one with two porphyrins, **1** and 5,15-*cis*-bis(2-pentafluorobenzamidophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**2**), which was reported to be a good acceptor of quinones,[4a] and its applications as a molecular switch in the hydrogen-bonded porphyrin−quinone recognitions.



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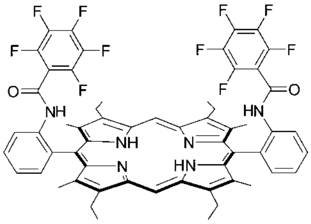

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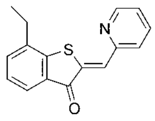
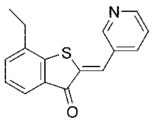
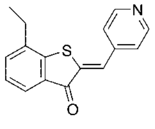


3(Z)



4(Z)



5(Z)

Results and Discussion

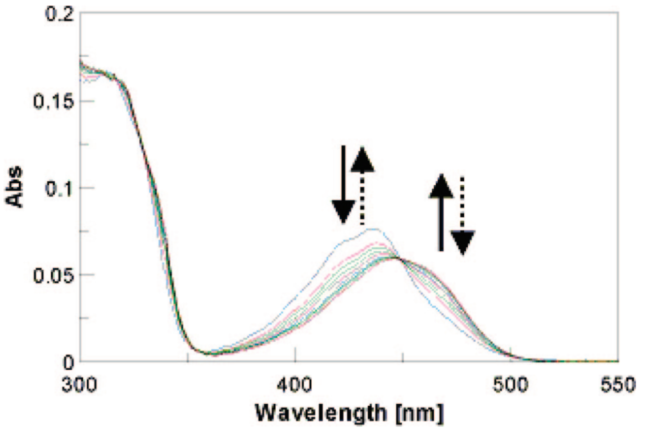


FIGURE 1. Absorption spectra change of **4(Z)**. Solid arrow: Irradiation with 390 nm light for 0 to 10 min. Dotted arrow: Irradiation with 490 nm light for 0 to 2 h. [**4(Z)**] = 1.0×10^{-5} M in toluene.

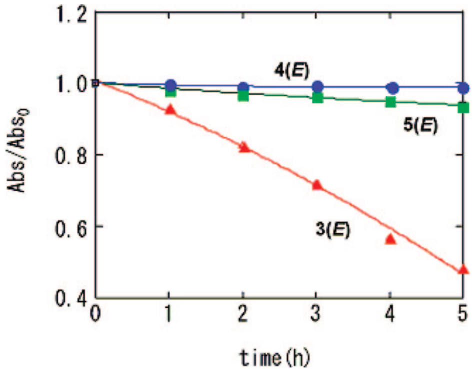


FIGURE 2. Time-dependent changes in absorbance of **3(*E*)**, **4(*E*)**, and **5(*E*)** at 35 °C in the dark. Absorbances at $\lambda = 480$ nm for **4(*E*)** and **5(*E*)** and $\lambda = 500$ nm for **3(*E*)**. **3(*E*)** = **4(*E*)** = **5(*E*)** = 1.0×10^{-5} M.

First, photochromic properties of 2-(2′-pyridylmethylene)-, 2-(3′-pyridylmethylene)-, and 2-(4′-pyridylmethylene)-7-ethylbenzo[*b*]thiophen-3(2*H*)-ones (**3**, **4**, and **5**, respectively) were investigated. These hemithioindigos (**3**, **4**, and **5**) were synthesized in 15, 60, and 12% yields by the reactions of 7-ethylbenzo[*b*]thiophen-3(2*H*)-one with the corresponding pyridinecarbaldehydes. The *Z*-configurations of these products were determined by the deshielded olefinic protons (δ 7.77, 7.84, and 7.82 for **3**, **4**, and **5**) in ^{1}H NMR spectra.[5,6]

The (*Z*)-3′-pyridylhemithioindigo **4** in toluene leads to the reversible *Z*,*E*-isomerization under the photoirradiation; 390 nm light caused a red-shifted absorption due to the *E* isomer, and subsequent irradiation with 490 nm light returned it to the original absorption (Figure 1). Similar changes in the absorption were observed for the other hemithioindigos, **3** and **5**. Some remarkable differences of these hemithioindigos are found in the thermal stability of the *E* isomers. The thermal stability was evaluated by the monitoring of the changes in the absorbance of the photostationary states of the hemithioindigos. The absorbance changes of the λ_{max} of their *E* isomers in toluene were observed with respect to time at 35 °C in the dark (Figure 2). After 5 h, the absorbance of **4(*E*)** did not show any changes; that is in contrast to the slight decrease of **5(*E*)** and to the distinct decrease of **3(*E*)**. The order of the stability was determined to be **4(*E*)** > **5(*E*)** > **3(*E*)**; even after 2 days at room temperature, no change of **4(*E*)** was observed. However, heating at 90 °C accelerates the isomerization into **4(*Z*)**; the time-dependent change follows the first-order reaction, and the rate constant was estimated to be $k = 0.20$ h^{-1} (90 °C), based on the *k* plot using ^{1}H NMR analysis. It should be noted that the order of

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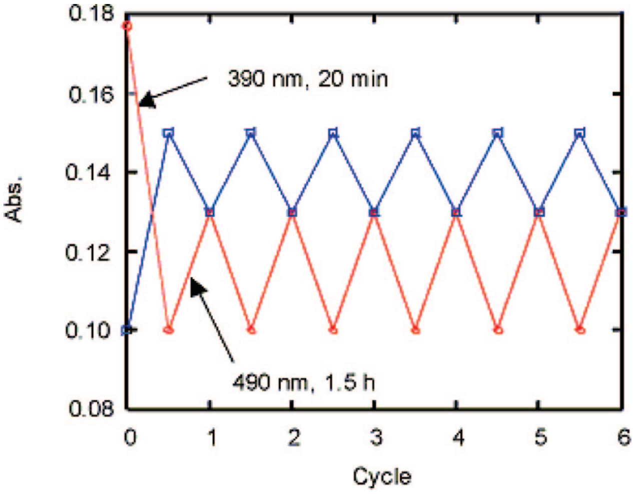
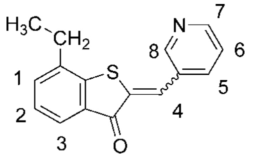


FIGURE 3. Repeatability of *E*,*Z*-isomerization of **4** during six cycles of irradiations. [**4(Z)**] = 3.0 × 10^{-5} M in toluene. Absorbance change at λ = 420 nm (○) and λ = 465 nm (□).

TABLE 1. Chemical Shift Changes of Hemithioindigos 4(*Z*) and 4(*E*) in the Complexations with Porphyrins 1 and 2



	$\Delta\delta^a$			
	1 + **4(Z)**	**1** + **4(*E*)**	**2** + **4(Z)**	**2** + **4(*E*)**
1	−0.04	0.01	−0.02	0
2	0	0.01	−0.01	0
3	−0.08	−0.01	−0.23	−0.02
4	−0.13	−0.15	−0.47	−0.12
5	−0.01	−0.25	−0.01	−0.16
6	−0.03	−0.28	−0.10	0
7	−0.03	−0.19	−0.09	−0.14
8	−0.11	−0.21	−0.16	−0.17
CH_2	0	0.01	0.03	0
CH_3	0.01	0.01	0.03	0

[a] $\Delta\delta = \delta$ (**4**) − δ (porphyrin + **4**). [**1**] = [**2**] = 5.0 × 10^{-4} M, **4(Z)** = **4(*E*)** = 2.5 × 10^{-3} M, solvent: CD_3CN/CCl_4 = 1/10.

the stability (**4(*E*)** > **5(*E*)** >**3(*E*)**) is consistent with the order of the differences in the total energy between *E* and *Z* isomers; the energy differences calculated at B3LYP/6-31G* level are 3.13 kcal mol^{-1} for **4**, 4.05 kcal mol^{-1} for **5**, and 6.31 kcal mol^{-1} for **3**.[7] We assume that the larger energy difference between *E* and *Z* isomers reflects a smaller energy difference of the transition states.

Among the hemithioindigos **3**, **4**, and **5**, the *E* isomer of **4** was found to be most stable and so our investigations were focused on the photochromic properties of **4**. Good repeatability of *E*,*Z*-isomerization was confirmed by the UV−vis spectroscopy results. A toluene solution of **4(Z)** ([**4(Z)**] = 3.0 × 10^{-5} M) was irradiated with 390 nm light for 20 min and then with 490 nm light for 1.5 h, and these irradiations were repeated in six cycles. Absorbance changes at 420 and 465 nm, which are shoulders of the absorption bands of **4(Z)** and **4(*E*)**, are shown in Figure 3. The good repeatability of the *E*,*Z*-isomerization of **4** and the thermal stability of **4(*E*)** are important for applying it as a molecular switch.

The recognition performance of **4** with the ureidoporphyrin **1** was evaluated by ^1H NMR analysis. Addition of half-molar ratio of **4(Z)** to a toluene-d_8 solution of **1** ([**1**] = 1.0 × 10^{-3} M) caused a downfield shift ($\Delta\delta$ +0.50) of PhNH protons of **1**, due to the formation of the hydrogen bonds of PhNH protons of **1** with N and O atoms of **4**, and caused an upfield shift ($\Delta\delta$ −0.07) of meso-protons of **1**, due to the diamagnetic ring current of the benzene and benzothiophenone rings of **4**. The signals of the EtNH protons of **1** were not observed distinctly because of the disappearance of such protons during the complexation. The complexation of **4(*E*)** with **1** was also evaluated by ^1H NMR analysis. The isomer **4(*E*)** was prepared by the irradiation of a mixture of **1** and **4(Z)** with 440 nm light, which is not absorbed by the porphyrin. The presence of **4(*E*)** caused downfield shifts ($\Delta\delta$ +0.05) of the PhNH protons and of the meso-protons ($\Delta\delta$ +0.02), compared with those in the mixture of **4(Z)**.

The chemical shift changes of **4(Z)** by the complexations are measured in CD_3CN/CCl_4 (1/10) and summarized in Table 1, which shows the shielded 3-, 4-, and 8-protons due to the large diamagnetic ring current of the porphyrin ring. On the basis of these chemical shift changes, it is considered that the hemithioindigo is situated almost directly above the center of the porphyrin ring (Figure 4). Meanwhile, the chemical shift changes of **4(*E*)** summarized in Table 1 show the shielded 4-, 5-, 6-, 7-, and 8-protons and the slightly deshielded 1-, 2-, and Et protons. These results may mean that **4(*E*)** is captured in such a way that the pyridine ring is situated above the porphyrin ring but the benzothiophenone ring is off from the porphyrin ring. Thus, the hemithioinzigo **4(*E*)** is situated above the edge of the porphyrin ring, as shown in Figure 4. The movements of the hemithioindigo between the center and the edge of the porphyrin ring can be controlled by the light. These movements were repeated three times by the irradiation with 440 nm light and the subsequent irradiation with 490 nm light; the movements were confirmed by the monitoring of the chemical shift changes of the PhNH protons and the meso-protons (Figure 5a). If one looks at these movements between the center and the edge of the porphyrin ring from a distance, one can imagine a photo-controlled molecular piston of the hemithioindigo over the porphyrin ring.

Stoichiometry for the complexation of **1**−**4(Z)** was determined to be 1:1 on the basis of the Job's plot, and the association constants for their complexations were evaluated from the curve fitting method in the ^1H NMR titration using the change of upfield-shifted meso-protons, the estimated association constant being $K = (4.8 \pm 0.1) \times 10^2$ M^{-1} in toluene-d_8 at 293 K. The association constants at 303, 313, 323, and 333 K were determined, and the thermodynamic parameters were estimated from the van't Hoff plot using these association constants (Figure 6, Table 2). An unexpectedly large association constant was evaluated for the complexation of **1**−**4(*E*)**. Similarly to the above, its association constant was evaluated to be $K = (2.7 \pm 0.7) \times 10^3$ M^{-1} in toluene-d_8 at 293 K. The error of the value is relatively large because of the existence of a small amount of the *Z* isomer (<3%), but the value is substantially larger than that of **1**−**4(Z)**. This unusual result may be ascribed to the tight hydrogen bondings between two NH protons of one ureido group and the pyridine nitrogen atom and the carbonyl oxygen atom, along with the π−π stackings of the porphyrin ring with the hemithioindigo rings.

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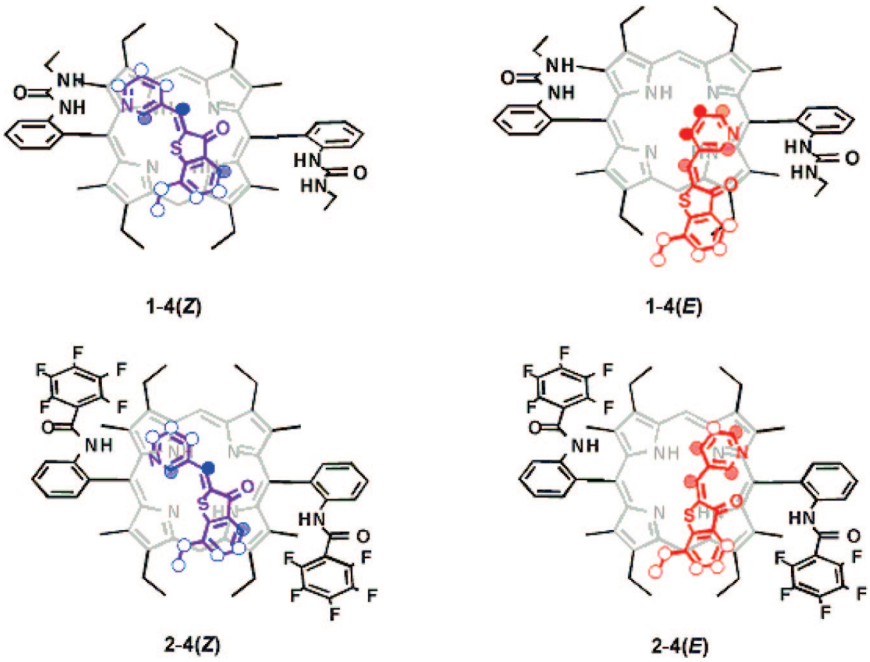
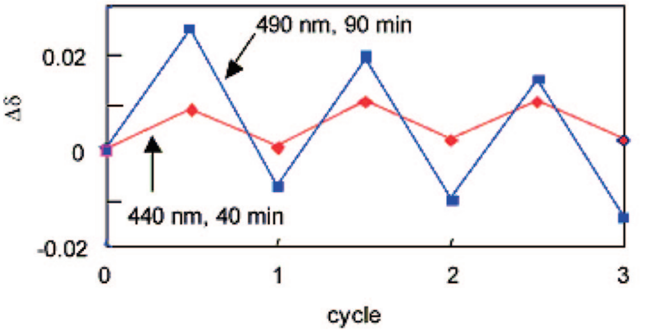


FIGURE 4. Configurations of **1−4(*Z*)**, **1−4(*E*)**, **2−4(*Z*)**, and **2−4(*E*)**.


a) In the presence of 1; [4(Z)] = 5.0x10^{-4} M, [1] = 1.0x10^{-3} M.

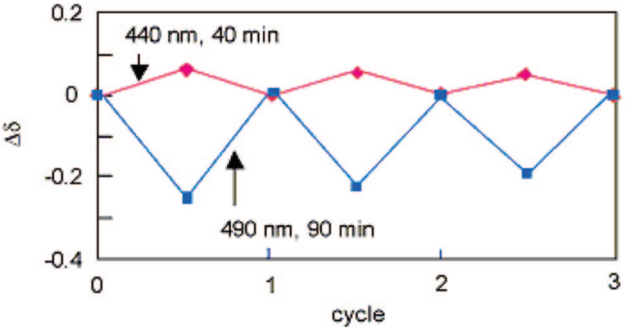

b) In the presence of 2; [4(Z)] = 5.0x10^{-4} M, [2] = 1.0x10^{-3} M.

FIGURE 5. Repeatability of *E*,Z-isomerization of **4** in the presence of **1** or **2** in toluene-d_8, $\Delta\delta$: chemical shift change of (□) PhNH for **1** and amido protons for **2**, and (◇) meso-protons for **1** and **2**.

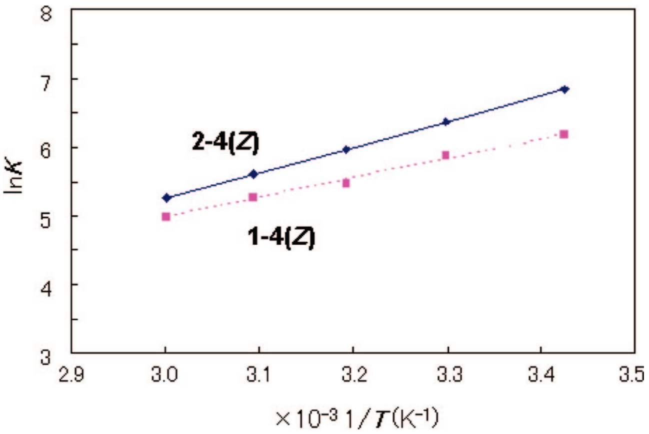


FIGURE 6. The van't Hoff plots of complexations of **2−4(Z)** and **1−4(Z)**.

On the other hand, **4(*Z*)** and **4(*E*)** are also recognized by the pentafluorobenzamidoporphyrin **2**, and **4(*Z*)** is found to be captured more strongly than **4(*E*)**, a tendency that is opposite to the case of **1**. The chemical shift changes of the NH protons and the meso-protons caused by one molar ratio of **4(*Z*)** are $\Delta\delta$ +1.22 and −0.18, respectively. The photoinduced **4(*E*)** caused an upfield shift ($\Delta\delta$ −0.25) of the PhNH protons and a downfield shift ($\Delta\delta$ +0.07) of the meso-protons, compared with those in the mixture of **4(*Z*)**. The chemical shift changes of **4(*Z*)** and **4(*E*)** by the complexations are included in Table 1. From these results, similarly to the case of **1**, **4(*Z*)** is considered to be situated above the center of the porphyrin ring. However, in the case of **4(*E*)**, from the shielded 4-, 5-, 7-, and 8-protons, with no change of 6-protons, it is considered that **4(*E*)** is situated above the side of the porphyrin ring, as shown in Figure 4. The movements of the hemithioindigo between the center and the side of the porphyrin ring are repeated three times by the light (Figure 5b). The 1:1 stoichiometry for the complexation of **2−4(*Z*)** was also determined by the Job's plot. The similarly evaluated association constants for the complexations of **2−4(*Z*)** and **2−4(*E*)** are $K = (9.3 \pm 0.1) \times 10^2$ and $(4.5 \pm 1.8) \times 10^2$ M^{-1}, respectively, in toluene-d_8 at 293 K. The thermodynamic parameters for the complexation of **2−4(*Z*)** were estimated from the van't Hoff plot (Figure 6 and Table 2). With respect to **4(*Z*)**, the sufficiently negative free energy change ($\Delta G° = -4.0 \pm 0.0$ kcal mol^{-1}) of the complex with **2**, compared to that ($\Delta G° = -3.6 \pm 0.0$ kcal mol^{-1}) of **1**, is mainly due to the enthalpy change. This in turn may be ascribed to the strong hydrogen bondings caused by the acidic pentafluorobenzamido protons.

TABLE 2. Association Constants (K/M^{-1}) and Thermodynamic Parameters for Complexations of **1**−**4(Z)** and **2**−**4(Z)** in Toluene-d_8

	K				
	293K	303K	313K	323K	333K
1−**4(Z)**	$(4.8 \pm 0.1) \times 10^2$	$(3.5 \pm 0.0) \times 10^2$	$(2.4 \pm 0.1) \times 10^2$	$(1.9 \pm 0.0) \times 10^2$	$(1.4 \pm 0.0) \times 10^2$
2−**4(Z)**	$(9.3 \pm 0.1) \times 10^2$	$(5.8 \pm 0.1) \times 10^2$	$(3.9 \pm 0.1) \times 10^2$	$(2.7 \pm 0.1) \times 10^2$	$(1.9 \pm 0.1) \times 10^2$
	$\Delta G°_{293}$/kcal mol^{-1}	$\Delta H°$/kcal mol^{-1}	$T\Delta S°_{293}$/kcal mol^{-1}		
1−**4(Z)**	-3.6 ± 0.0	-5.6 ± 0.1	-2.0 ± 0.1		
2−**4(Z)**	-4.0 ± 0.0	-7.4 ± 0.0	-3.4 ± 0.0		

TABLE 3. Association Constants (K/ M^{-1}) for Complexations at 293 K in Toluene-d_8

1−**4(Z)**	$(4.8 \pm 0.1) \times 10^2$
1−**4(*E*)**	$(2.7 \pm 0.7) \times 10^3$
1−**6**	$(2.5 \pm 0.1) \times 10^{2a}$
2−**4(Z)**	$(9.3 \pm 0.1) \times 10^2$
2−**4(*E*)**	$(4.5 \pm 1.8) \times 10^2$
2−**6**	$(1.8 \pm 0.1) \times 10^{2b}$

[a] $K = (6.6 \pm 0.3) \times 10^2$ was determined at 293 K in CDCl$_3$; see ref 4b. [b] $K = (1.7 \pm 0.2) \times 10^2$ was determined at 298 K in toluene-d_8/CDCl$_3$ (10/1); see ref 4a.

Thus, the porphyrin **1** captures **4(*E*)** preferentially to **4(Z)** and, reversely, the porphyrin **2** prefers **4(Z)** to **4(*E*)**, their catch and release being repeated by the photoirradiation. These results suggest that the hemithioindigo plays a role as a shuttle between two kinds of porphyrins; **4(Z)** captured mainly by **2** isomerizes into **4(*E*)** with 440 nm light, and **4(*E*)** released from **2** moves to **1** and the reverse movement from **1** to **2** is triggered by 490 nm light. Such movements of the hemithioindigo as a shuttle were confirmed by the following observations. When a toluene-d_8 solution of **1**, **2**, and **4(Z)** ([**1**] = [**2**] = 1.0×10^{-3} M, [**4(Z)**] = 5.0×10^{-4} M) was irradiated with 440 nm light, the PhNH protons of **1** caused a downfield shift ($\Delta\delta$ +0.05), while the amido protons of **2** showed an upfield shift ($\Delta\delta$ −0.10). Subsequent irradiation with 490 nm light caused the reverse shifts of these NH protons ($\Delta\delta$ −0.04 for PhNH protons of **1**, $\Delta\delta$ +0.09 for amido protons of **2**). It should be added that, under these conditions, estimations on the basis of the association constants (**1**−**4(Z)**: 480, **1**−**4(*E*)**: 2700, **2**−**4(Z)**: 930, **2**−**4(*E*)**: 450) show that 35.0 and 19.7% of **4(Z)** are captured by **2** and by **1**, respectively, and reversely **4(*E*)** is captured in 12.6 and 57.5% by **2** and by **1**. These estimations are performed under the assumption that there is no interaction between the porphyrins **1** and **2**. The movements were repeated three times; the chemical shift changes of these protons are summarized in Figure 7. These results are consistent with the movements of the hemithioindigo as a shuttle between two kinds of porphyrins (Figure 8).

We next demonstrate that the porphyrin−quinone recognitions are controlled by the photoirradiation of the hemithioindigo. The association constants of *p*-benzoquinone (**6**) with the porphyrins **1** and **2** were evaluated in the same conditions at 293 K to be $(2.5 \pm 0.1) \times 10^2$ M^{-1} for **1** and $(1.8 \pm 0.1) \times 10^2$ M^{-1} for **2**. Photoinduced catch and release of **6** could be traced clearly by the monitoring of the chemical shift changes of the olefinic protons of **6**. When a toluene-d_8 solution of **1**, **4(Z)**, and **6** ([**1**] = 2.0×10^{-3} M, [**4(Z)**] = 5.0×10^{-3} M, [**6**] = 2.0×10^{-4} M) was irradiated with 440 nm light, the olefinic protons of **6** shifted to lower fields, which indicates that **6** captured by **1** is released from **1** due to the binding of the photoinduced **4(*E*)** with **1**. Subsequent irradiation with 490 nm light returned it to the original position. By the similar irradiation with 440 nm light using a toluene-d_8 solution of **2**, **4(Z)**, and **6** ([**2**] = 2.0×10^{-3} M, [**4(Z)**] = 5.0×10^{-3} M, [**6**] = 2.0×10^{-4} M), the olefinic protons of **6** reversely shifted upfield, which shows the newly formed binding of **6** with **2** because of a release of the photoinduced **4(*E*)** from **2**. These changes in binding of **6** are consistent with the ones expected on the basis of the determined association constants. The performance was repeated twice, with the chemical shift changes of these protons being shown in Figure 9. Thus, when the movements of the hemithioindigo as a shuttle between two kinds of porphyrins are performed in the presence of the quinone, photoinduced changes in the distribution of the quinone is expected. In this case, the tracing of the quinone is very difficult because the quinone released from one porphyrin will be captured by another porphyrin; the chemical shift changes of the quinone are thought to be small. Such changes are actually very small but are still detectable due to the differences in the recognizing ability of two porphyrins with **4(Z)** and **4(*E*)**. When a toluene-d_8 solution of **1**, **2**, **4(Z)**, and **6** ([**1**] = [**2**] = 2.0×10^{-3} M, [**4(Z)**] = 5.0×10^{-3} M, [**6**] = 2.0×10^{-4} M) was irradiated with 440 nm light, the olefinic protons of **6** shifted to a slightly lower field, which means the release of **6** from the porphyrins. This may be ascribed to the recognizing ability of **1** with the photoinduced **4(*E*)** being larger than those of other complexations: **1**−**4(Z)**,

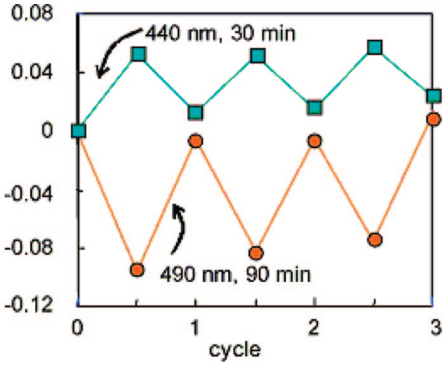


FIGURE 7. Repeatability of molecular shuttle of **4** between **1** and **2**. [**1**] = [**2**] = 1.0×10^{-3} M, [**4(Z)**] = 5.0×10^{-4} M in toluene-d_8; $\Delta\delta$: chemical shift change of PhNH (□) for **1** and amido protons for **2** (○).

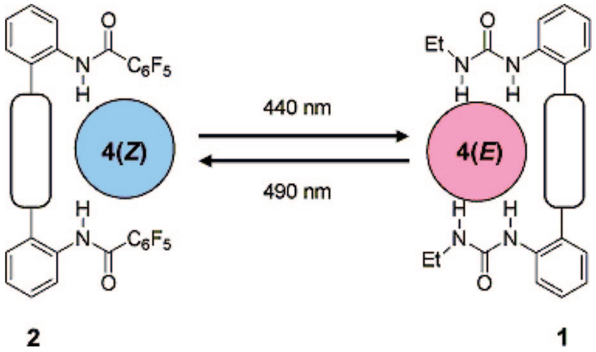
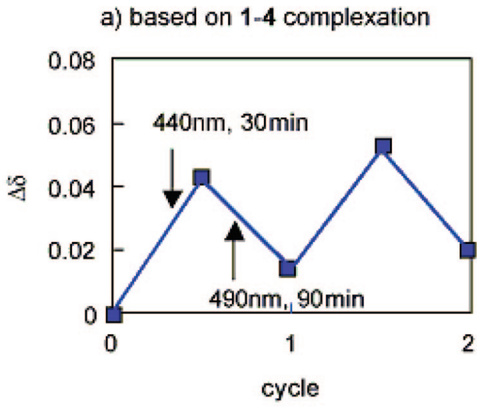


FIGURE 8. Reversible movements of hemithioindigo **4** triggered by *E*,*Z*-isomerization.


a) based on **1-4** complexation

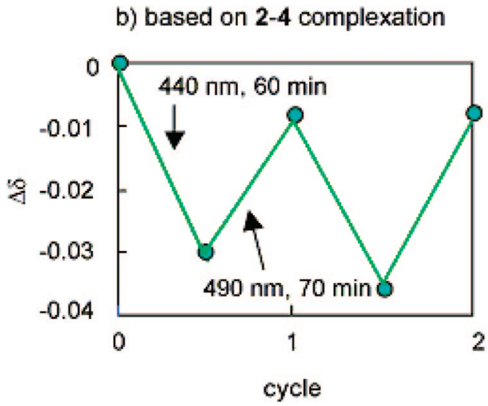

b) based on **2-4** complexation

FIGURE 9. Repeatability of quinone shuttle based on (a) **1−4** complexation and (b) **2−4** complexation. [**1**] = [**2**] = 2.0 × 10^{-3} M, [**4(Z)**] = 5.0 × 10^{-3} M, [**6**] = 2.0 × 10^{-4} M in toluene-d_8; Δδ: chemical shift change of olefinic protons of **6**.

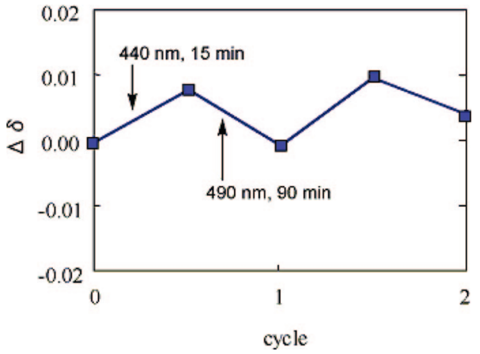


FIGURE 10. Quinone shuttle between **1** and **2** based on *E*,*Z*-isomerization of **4**. [**1**] = [**2**] = 2.0 × 10^{-3} M, [**4(Z)**] = 5.0 × 10^{-3} M, [**6**] = 2.0 × 10^{-4} M in toluene-d_8; Δδ: chemical shift change of olefinic protons of **6**.

2−4(*E*), and **2−4(Z)**. Subsequent irradiation with 490 nm light returned the chemical shift to the original position (Figure 10). These results give indirect support to the conclusion that the reversible changes in the distribution of the quinone between two kinds of porphyrins are triggered by the photoswitched hemithioindigo.

Summary

We studied 2-(2′-pyridylmethylene)-, 2-(3′-pyridylmethylene)-, and 2-(4′-pyridylmethylene)-7-ethylbenzo[*b*]thiophen-3(2*H*)-ones (**3**, **4**, and **5**, respectively). Among the results, the high thermal stability of the *E* isomer of **4**, **4(*E*)**, and its good repeatability during the photoinduced *E*,*Z*-isomerization were found. Association constants of the 1:1 complexations of **4(Z)** and **4(*E*)** with the ureidoporphyrin **1** and the pentafluorobenzamidoporphyrin **2** were evaluated. We found that **1** captures **4(*E*)** preferentially to **4(Z)** and, reversely, that **2** prefers **4(Z)** to **4(*E*)**, their catch and release caused by the porphyrins being triggered by the photoirradiation. On the basis of these differences in the binding ability, the repeatable movements of the hemithioindigo between two kinds of porphyrins, the so-called hemithioindigo shuttle, were controlled by the photoirradiation. These movements of the hemithioindigo were applied to the molecular switch for changes in the quinone distribution between two kinds of porphyrins.

Experimental Section

7-Ethylbenzo[*b*]thiophen-3(2*H*)-one was prepared by the reactions of 2-ethylbenzenethiol with bromoacetic acid and then with thionyl chloride, according to the previously reported paper.[6b] The porphyrins **1** and **2** were prepared using the previously reported methods.[4]

2-(2′-Pyridylmethylene)-7-ethylbenzo[*b*]thiophen-3(2*H*)-one (3(Z)). A solution of 7-ethylbenzo[*b*]thiophen-3(2*H*)-one (0.50 g, 2.8 mmol), 2-pyridinecarbaldehyde (0.30 g, 2.8 mmol), and a drop of piperidine in 12 mL of toluene was stirred at 90 °C for 1 h and then refluxed for 1 h under an argon atmosphere. The reaction mixture was washed with 20% aqueous sodium hydrogen sulfite solution to remove the unreacted aldehyde and then with water and brine. The mixture was dried over magnesium sulfate and evaporated. The resulting solid was chromatographed on silica gel (toluene/ethyl acetate = 9/1) to give 110 mg (15% yield) of **3(Z)**. Recrystallization from hexane/acetone was carried out to give yellow crystals of **3(Z)**: mp 118−120 °C; FT-IR (KBr, cm^{-1}) ν 2964 (C−H), 1673 (C═O); UV−vis (toluene) λ_{max} (log ϵ/L mol^{-1} cm^{-1}) 450 nm (4.07); ^1H NMR (CD_3CN/CCl_4 = 1/10) δ 1.35 (t, *J* = 7.6 Hz, 3H), 2.76 (q, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.25 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.64 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.74 (dd, *J* = 7.6, 7.8 Hz, 1H), 7.77 (s, 1H), 8.80 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 190.1, 153.1, 149.7, 148.6, 139.4, 136.7, 135.0, 134.3, 130.3, 129.4, 127.7, 125.8, 124.3, 123.3, 26.1, 13.8; MALDI-TOF MS *m*/*z* calcd for $C_{16}H_{13}NOS$ $[M + H]^+$ 268.07, found $[M + H]^+$ 268.07. Anal. Calcd for $C_{16}H_{13}NOS$: C, 71.88; H, 4.90; N, 5.24. Found: C, 71.70; H, 5.05; N, 5.14.

2-(3′-Pyridylmethylene)-7-ethylbenzo[*b*]thiophen-3(2*H*)-one (4(Z)). A solution of 7-ethylbenzo[*b*]thiophen-3(2*H*)-one (0.54 g, 3.0 mmol), 3-pyridinecarbaldehyde (0.32 g, 3.0 mmol), and a drop of piperidine in 13 mL of toluene was stirred at 90 °C for 1 h and then refluxed for 1 h under an argon atmosphere. The reaction mixture was washed with 20% aqueous sodium hydrogen sulfite solution to remove the unreacted aldehyde and then with water and brine. The mixture was dried over magnesium sulfate and evaporated. The resulting solid was chromatographed on silica gel (toluene/ethyl acetate = 2/1) to give 480 mg (60% yield) of **4(Z)**. Recrystallization from hexane/acetone was carried out to give yellow crystals of **4(Z)**: mp 131−132 °C; FT-IR (KBr, cm^{-1}) ν 2969 (C−H), 1676 (C═O); UV−vis (toluene) λ_{max} (log ϵ/L mol^{-1} cm^{-1}) 437 nm (3.88); ^1H NMR (CD_3CN/CCl_4 = 1/10) δ 1.34 (t, *J* = 7.6 Hz, 3H), 2.73 (q, *J* = 7.6 Hz, 2H), 7.27 (dd, *J* = 7.6, 7.3 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.42 (dd, *J* = 8.1, 6.8 Hz, 1H), 7.72 (d, *J* = 7.3 Hz, 1H), 7.84 (s, 1H), 8.03 (ddd, *J* = 8.1, 2.0, 1.7 Hz, 1H), 8.55 (dd, *J* = 6.8, 2.0 Hz, 1H), 8.89 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 188.9, 152.4, 150.4, 144.8, 139.2, 136.8, 134.6, 132.8, 130.6, 130.1, 129.3, 126.4, 124.9, 123.9, 26.4, 13.6; MALDI-TOF MS *m*/*z* calcd for $C_{16}H_{13}NOS$ $[M + H]^+$ 268.07, found $[M + H]^+$ 268.07. Anal. Calcd for $C_{16}H_{13}NOS$: C, 71.88; H, 4.90; N, 5.24. Found: C, 71.83; H, 4.85; N, 5.00.

Irradiation of a solution of **4(*Z*)** in CD_3CN/CCl_4 (1/10) with 390 nm light for 1 h caused *Z*,*E*-isomerization to produce the photostationary state which contains more than 97% of **4(*E*)**: ^1H NMR (CD_3CN/CCl_4 = 1/10) δ 1.38 (t, J = 7.6 Hz, 3H), 2.71 (q, J = 7.6 Hz, 2H), 7.23 (s, 1H), 7.25 (dd, J = 7.6, 7.1 Hz, 1H), 7.41 (d, J = 7.1 Hz, 1H), 7.44 (dd, J = 9.3, 4.8 Hz, 1H), 7.69 (d, J = 7.6 Hz, 1H), 8.51 (d, J = 4.8 Hz, 1H), 8.80 (s, 1H), 8.89 (d, J = 9.3 Hz, 1H).

2-(4′-Pyridylmethylene)-7-ethylbenzo[*b*]thiophen-3(2*H*)-one (5(*Z*)). A solution of 7-ethylbenzo[*b*]thiophen-3(2*H*)-one (0.54 g, 3.0 mmol), 4-pyridinecarbaldehyde (0.32 g, 3.0 mmol), and a drop of piperidine in 12 mL of toluene was stirred at 90 °C for 1 h and then refluxed for 1 h under an argon atmosphere. The reaction mixture was washed with 20% aqueous sodium hydrogen sulfite solution to remove the unreacted aldehyde and then with water and brine. The mixture was dried over magnesium sulfate and evaporated. The resulting solid was chromatographed on silica gel (toluene/ethyl acetate = 5/1) to give 100 mg (12% yield) of **5(*Z*)**. Recrystallization from hexane/acetone was carried out to give yellow crystals of **5(*Z*)**: mp 136−137 °C; FT-IR (KBr, cm^{-1}) ν 2976 (C−H), 1681 (C=O); UV−vis (toluene) λ_{max} (log ϵ/L mol^{-1} cm^{-1}) 426 nm (3.86); ^1H NMR ($CDCl_3$) δ 1.33 (t, J = 7.6 Hz, 3H), 2.73 (q, J = 7.6 Hz, 2H), 7.29 (dd, J = 7.6, 7.4 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 6.3 Hz, 2H), 7.81 (d, J = 7.4 Hz, 1H), 7.82 (s, 1H), 8.75 (d, J = 6.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 188.9, 150.7, 144.6, 141.4, 139.2, 135.0, 134.8, 129.7, 129.5, 126.5, 124.9, 124.2, 26.4, 13.7; MALDI-TOF MS *m*/*z* calcd for $C_{16}H_{13}NOS$ $[M + H]^+$ 268.07, found $[M + H]^+$ 268.07. Anal. Calcd for $C_{16}H_{13}NOS$: C, 71.88; H, 4.90; N, 5.24. Found: C, 71.87; H, 5.03; N, 5.13.

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Supporting Information Available: General Information. Absorption spectra changes of **3(*Z*)** and **5(*Z*)** under the photoirradiation. Thermal stability of **4(*E*)** at 90 °C; (a) concentration change and (b) *k* plot. ^1H NMR and ^{13}C NMR spectra of **3(*Z*)**, **4(*Z*)**, and **5(*Z*)**. ^1H NMR spectra of **4(*E*)**. ^1H NMR spectra changes of **1** and **2** induced by the addition of **4** in toluene-d_8. Job's plots in the complexations of **1** and **2** with **4(*Z*)**. Curve fittings for the complexations of **1−4(*Z*)**, **2−4(*Z*)**, **1−4(*E*)**, **2−4(*E*)**, **1−6**, and **2−6**. Optimized geometries obtained from computations. This material is available free of charge via the Internet at http://pubs.acs.org.

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