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Application of Benzoyl-substituted Hemithioindigo as a Molecular Switch in Porphyrin-Quinone Recognition

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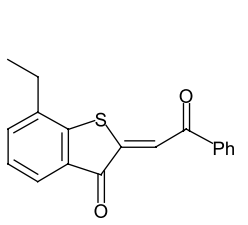
The benzoyl-substituted hemithioindigo 1 with *Z*-configuration was obtained as the sole product from the reaction of 7-ethylbenzo[*b*]thiophen-3(2*H*)-one with phenylglyoxal. Irradiation of 1 produced the [2 + 4] cycloadduct 2, instead of the usual *Z* − *E* isomerization product. The cycloadduct 2 is completely dissociated back to 1 on heating; the interconversion between 1 and 2 shows good repeatability. This reversible property is applied to the molecular switch in the hydrogen-bonded quinone recognition of the 5,15-*cis*-bis(ureidophenyl)-porphyrin 3.

Keywords: Benzoylhemithioindigo; Molecular switch; Ureidoporphyrin; Quinone recognition

INTRODUCTION

Reversible molecular systems provide a tool for manipulating the recognizing ability of a binding site [1–10]. In particular, the photoinduced *E* and *Z* isomerizations of stilbazoles and azopyridines play an important role in the recognition of metalloporphyrins, where the center metals of the porphyrins coordinate with the nitrogen atoms only of the *Z*-stilbazoles and the *E*-azopyridines [11–14]. As a mimic for bacterial photosynthesis, the noncovalently linked porphyrin-quinone assembly has been studied for the construction of an artificial photoelectronic separation system [15–20]. In our previous paper, we showed that 5,15-*cis*-bis[2-(*N′*-ethyl)ureidophenyl]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**3**) and its zinc-porphyrin display significant recognition for *p*-benzoquinones through four-point hydrogen bonding, and that the quinone shuttle between these ureidoporphyrins can be attained by a chemical process such as the addition of a base with affinity for the zinc metal of the zinc-porphyrin [21–23]. Benzoyl-substituted hemithioindigos are expected to be applicable to molecular switches in the hydrogen-bonded porphyrin-quinone recognition because they have two carbonyl moieties that are good acceptors for hydrogen bonding. Here, we demonstrate the application of 2-benzoylmethylene-7-ethylbenzo[*b*]thiophen-3(2*H*)-one (**1**) as the photochemically controlling molecular switch in the hydrogen-bonded quinone recognition of the 5,15-*cis*-bis(ureidophenyl)porphyrin **3**.



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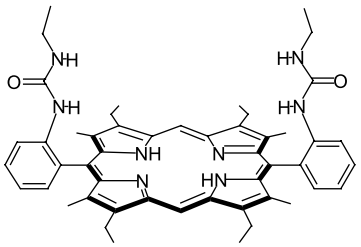

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RESULTS AND DISCUSSION

As reported in our preliminary communication [24], the hemithioindigo **1** was synthesized in 46% yield by the reaction of 7-ethylbenzo[*b*]thiophen-3(2*H*)-one with phenylglyoxal. From the reaction mixture, only the *Z* isomer was isolated; the formation of the other isomer was not detected. The *Z*-configuration of the product was determined by the deshielded olefinic proton (δ8.11) in the ^{1}H NMR spectra. A toluene solution of **1** is yellow and

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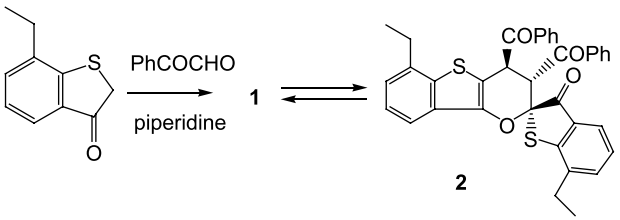


SCHEME 1 Synthesis of **1** and interconversion between **1** and **2**.

absorbs at λ_{max} 463 nm; when irradiated with 463 nm light, **1** produced the [2 + 4] type of the colorless cycloadduct **2**, instead of the usual $Z - E$ isomerization product [25–30] (Scheme 1). Structures of **1** and **2** were confirmed by X-ray analysis and their ORTEP diagrams are shown in Fig. 1 [31]. The cycloadduct **2** is thermally stable and remained unchanged for more than 2 days at room temperature. However, heating at 70°C accelerates the dissociation into **1**; the time-dependent change in the dissociation follows a first-order reaction and the rate constant is estimated to be $k = 0.22\,h^{-1}$ (70°C). Heating at 100°C for 10 min resulted in complete recovery of **1**. Reversible interconversion between the photoinduced dimerization of **1** and the thermal dissociation of **2** was monitored several times using a $C_6D_5CD_3$ solution of 1×10^{-2} M, showing good repeatability between **1** and **2** (Fig. 2).

Complexation of the hemithioindigo **1** with the 5,15-*cis*-bis(ureidophenyl)porphyrin **3** was evaluated using ^{1}H NMR spectroscopy. Addition of one molar ratio of **1** to a $C_6D_5CD_3$ solution of **3** ([**3**] = 1×10^{-3} M) caused an upfield shift of the methylene and methyl protons of **1** from δ2.33 to δ2.17 and from δ1.01 to δ0.91, respectively, due to the diamagnetic ring current of the porphyrin ring. An upfield shift from δ10.37 to δ10.10 of the *meso*-protons of **3** can be ascribed to the diamagnetic ring current of the benzene and the benzothiophenone rings of **1**. The 3-protons of the benzene rings of **3** were deshielded from δ9.13 to δ9.36, as observed in the cases of the complexations of **3** with various quinones. Although signals of NH_a and NH_b protons of **3** and the olefinic proton of **1** were not observed distinctly in $C_6D_5CD_3$, either because of the disappearance in the complexation or because of solvent contaminants, the shielding from δ8.11 to δ7.41 for the olefinic proton and the deshielding from δ6.22 to δ6.45 for the NH_a protons and from δ4.27 to δ4.42 for the NH_b protons were confirmed in CCl_4/CD_3CN (5:1) (Fig. 3). These results support a four-point hydrogen-bonded structure, where **1** is situated above the porphyrin ring (Fig. 4).

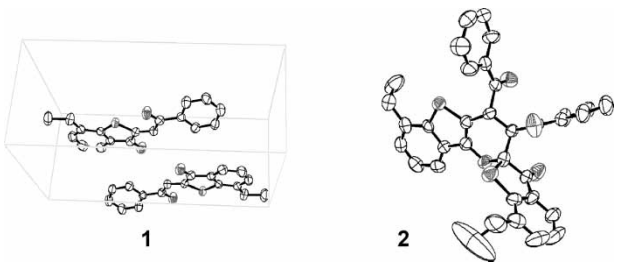


FIGURE 1 ORTEP views of **1** and **2**.

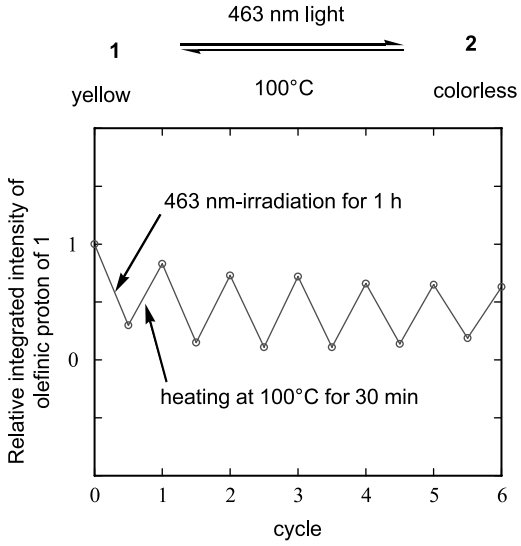


FIGURE 2 Repeatability between **1** and **2**. [**1**] = 1×10^{-2} M in $C_6D_5CD_3$.

The association constant for the complexation of **1** with the porphyrin **3** was determined by ^{1}H NMR titration using the largely shielded chemical shift of the *meso*-protons, whose signal appears very sharp at lower magnetic field [17,21–23]. The ^{1}H NMR titration in $C_6D_5CD_3$ supported the 1:1 complexation. The association constant determined at 293 K is $1.3 \times 10^3\,M^{-1}$, which is appreciably larger than the value ($8.5 \times 10^2\,M^{-1}$) for tetramethoxy-*p*-benzoquinone (**4**). This significant difference in the association constants is important for the functioning of **1** as a molecular switch in the porphyrin-quinone recognition. The temperature dependence of the association constants was also evaluated by ^{1}H NMR titration and the results are summarized in Table I. The thermodynamic parameters were estimated from the van't Hoff plot (Fig. 5, Table II), which included data for the complex **3**·**4** [22,23]. The free energy ΔG° of **1** is larger than that of **4**. This difference is ascribed mainly to the smaller entropy change $T\Delta S^\circ$ of **1** compared with that of **4**. The smaller number of substituents in **1**, compared with **4**, seems to be reflected in the smaller entropy change of **1**.

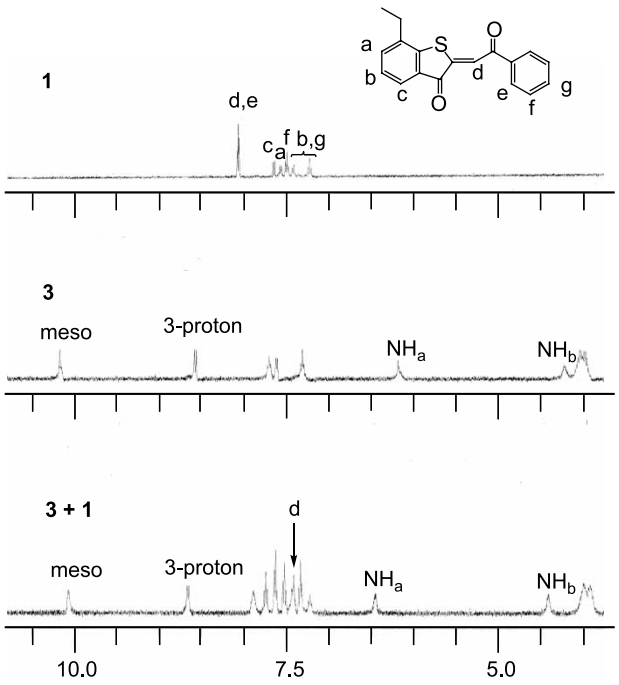
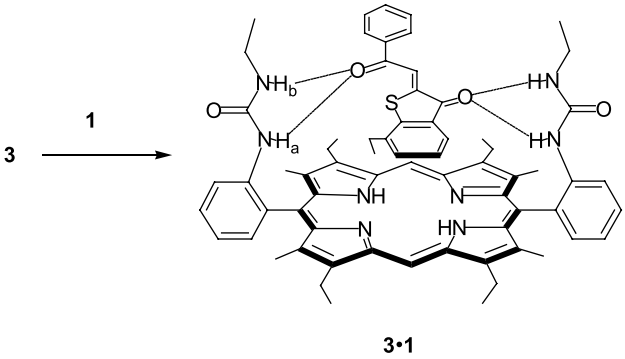


FIGURE 3 ^{1}H NMR spectral change of **3** on addition of **1**. Solvent: $CCl_4/CD_3CN = 5/1$. $[\mathbf{1}] = [\mathbf{3}] = 1 \times 10^{-3}$ M.

The complexation of the cycloadduct **2** with the porphyrin **3** was contradicted by the fact that no chemical shift of any proton of **3** and **2** showed any change on the addition of **2** ($[\mathbf{3}] = [\mathbf{2}] = 1 \times 10^{-3}$ M). Little or no ligation with **2** is important for the functioning of the **1**–**2** system as the molecular switch. The repeatable capture of **1** by the porphyrin **3** and its release from **3** through the photochemical process was confirmed by the ^{1}H NMR analysis. A mixture of **1** (1×10^{-2} M) and **3** (2×10^{-3} M) in $C_6D_5CD_3$ was irradiated at 463 nm, where **3** does not absorb, for 1 h and then heated at 100°C for 30 min; this cycle was repeated three times. At each stage, the chemical shifts of the *meso*-protons and the 3-protons of the benzene rings of **3** were monitored (Fig. 6). Figure 6 shows that when the mixture was irradiated, the 3-protons of the benzene rings shifted upfield, indicating that **1** captured by the porphyrin **3** is released from **3**. This is ascribed to the conversion of **1** to the cycloadduct **2**. The subsequent heating of the mixture returned its chemical shift to the previous value, due to the return of the thermally reproduced **1** to the porphyrin **3**. A similar scenario can be described from the chemical shift change of the *meso*-protons of **3**. The cycle of irradiation and heating was repeated three times and good repeatability was confirmed. These observations indicate the potential of the **1**–**2** system as a photochemically controlling molecular switch in the hydrogen-bonded quinone recognition of **3**.

The capability of **1** as a molecular switch is demonstrated by the following observations. A mixture of **1** and **3** was irradiated and then heated in the presence of the quinone **4** ($[\mathbf{1}] = 1 \times 10^{-2}$ M, $[\mathbf{3}] = 2 \times 10^{-3}$ M and $[\mathbf{4}] = 2 \times 10^{-4}$ M in $C_6D_5CD_3$) and the movement of **4** was again monitored by ^{1}H NMR. The change in the chemical shift of the 3-protons of the benzene rings of **3** was very small at each stage, because both **1** and **4** deshield these protons when captured by **3**. However, the chemical shift of the *meso*-protons of **3**, which is not affected by the complexation with **4**, moved to a lower field on irradiation and then returned to the original value on heating. Moreover, the methyl protons of **4** were shifted upfield on irradiation and returned to the prior position on heating (Fig. 7), which supports the conclusion that a relatively large amount of **4** was captured by **3** on irradiation and the captured **4** was released from **3** on heating. These observations reveal that the photoinduced **1**–**2** interconversion system controls the equilibrium between **3** and **3**·**1** and then that between **3** and **3**·**4**; that is, the conversion of **1** (possibly including the captured **1**) to **2** on irradiation shifts the equilibrium from the **3**·**1** side to the **3** side, which moves the equilibrium between **3**·**4** and **3** to the **3**·**4** side. As a result, a relatively large amount of the quinone **4** is captured by the porphyrin **3**. On heating, the equilibria reverse, resulting in the release of **4** from **3**·**4** (Fig. 8).



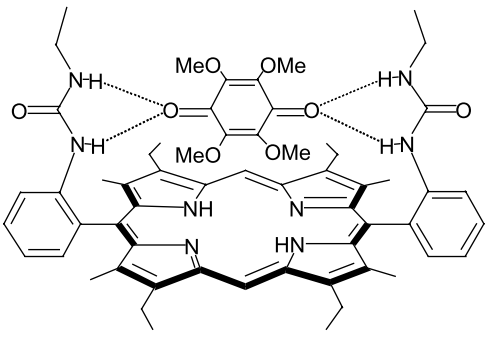


FIGURE 4 Complexation of **3** with **1**.

TABLE I Association constants (K, M^{-1}) for the complexation **3**–**1** in $C_6D_5CD_3$

	293 K	303 K	318 K	333 K	343 K
3·1	1.3×10^3	9.0×10^2	5.1×10^2	3.0×10^2	2.1×10^2

Errors in values are ≤15%.

TABLE II Thermodynamic parameters for the complexation **3**–**1** in $C_6D_5CD_3$

	ΔG°_{293}/kcal mol^{-1}	ΔH°/kcal mol^{-1}	$T\Delta S^\circ_{293}$/kcal mol^{-1}
3·1	− 4.18	− 7.38	− 3.19
3·4*	− 3.92	− 7.42	− 3.50

Errors in values are ≤10%.* See ref. [22,23].

CONCLUSIONS

We have demonstrated that the benzoyl-substituted hemithioindigo **1** performs a novel type of interconversion based on photodimerization; that is, irradiation of **1** produces the cycloadduct **2**, which is completely dissociated back to **1** on heating, and the interconversion between **1** and **2** shows good repeatability. This reversible interconversion was applied to a photoswitch for porphyrin **3**-quinone **4** recognition based on the control of the equilibrium between **3** and **3·1** and that between **3** and **3·4**.

EXPERIMENTAL

FTIR spectra were run in a CCl_4 solution. UV–vis spectra were recorded in toluene of the highest quality for spectroscopy (Kokusan Chemical Co.) without further purification. ^{1}H NMR spectra were measured using tetramethylsilane as internal standard; the chemical shifts are given in δ/ppm downfield. Samples were taken in $C_6D_5CD_3$ and CCl_4/CD_3CN. Preparation of the porphyrin **3** was carried out by the method described previously [22].

2-Benzoylmethylene-7-ethylbenzo[*b*]thiophen-3(2*H*)-one (1) and its Cycloadduct 2

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 previous reports [28,29].

A solution of the residual mixture of 7-ethylbenzo[*b*]thiophen-3(2*H*)-one (300 mg), phenylglyoxal (200 mg, 1.49 mmol) and a drop of piperidine in 5 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 hydrogensulfite solution to remove the unreacted aldehyde, and then with brine and water. The mixture was dried over magnesium sulfate and evaporated to dryness. The resulting solid was chromatographed on silica gel (toluene) to give 200 mg (46% yield) of **1**. Recrystallization from hexane-acetone was carried out in the dark to give red crystals of **1**: mp 125–126°C; FT/IR (CCl_4) ν 3059, 2963, 1686, 1635, 1594, 1575 cm^{-1}; UV/vis (toluene) λ_{max} (log ϵ/L mol^{-1} cm^{-1}) 463 nm (3.84); ^{1}H NMR (400 MHz, CCl_4/CD_3CN = 5/1): δ 1.36 (t, J = 7.6 Hz, 3H), 2.78 (q, J = 7.6 Hz, 2H), 7.28 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H), 7.66 (d, J = 7.6 Hz, 1H), 8.11 (d, J = 7.6 Hz, 2H), 8.11 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 26.0, 118.7, 124.7, 126.6, 128.5, 128.9, 129.0, 133.7, 135.5, 137.3, 139.9, 147.52, 147.53, 189.3, 189.9. Anal. Calcd for $C_{18}H_{14}O_2S$(%): C, 73.44; H, 4.79. Found: C, 73.67; H, 4.76.

Compound **1** (150 mg, 0.51 mmol) was dissolved in hexane-acetone by heating. The resulting solution was irradiated for 2 h with a xenon lamp using a UV39 filter. The solution was then left in the dark for crystallization to take place. Pale yellow crystals of **2** (120 mg, 80%) were formed and collected on a filter. The crystals melt at 117–126.5°C to give a red oil because of the dissociation to **1**. Characterization of **2**: FT/IR (CCl_4) ν3060, 2966, 1714, 1678, 1595, 1577 cm^{-1}; ^{1}H NMR (400 MHz, CCl_4/CD_3CN = 5/1): δ 1.27 (t, J = 7.7 Hz, 6H), 2.60 (q, J = 8.5 Hz, 2H), 2.70 (q, J = 7.6 Hz, 2H), 5.29 (d, J = 10.5 Hz, 1H), 5.82 (d, J = 10.5 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 7.14 (d, J = 6.8 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 2H), 7.39 (d, J = 6.8 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.52 (d, J = 7.6 Hz, 1H), 7.60 (d, J = 7.4 Hz, 2H), 7.63 (t, J = 7.3 Hz, 2H), 7.75 (t, J = 7.3 Hz, 1H), 8.17 (d, J = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.2, 13.4, 26.1, 26.7, 43.9, 49.5, 95.4, 109.8, 118.4, 124.0, 124.8, 125.1, 125.9, 128.2, 128.4, 128.8, 129.0, 129.4, 130.5, 133.4, 134.4, 135.6, 135.9, 136.0, 136.9, 137.8, 139.1, 144.4, 148.7, 195.8,

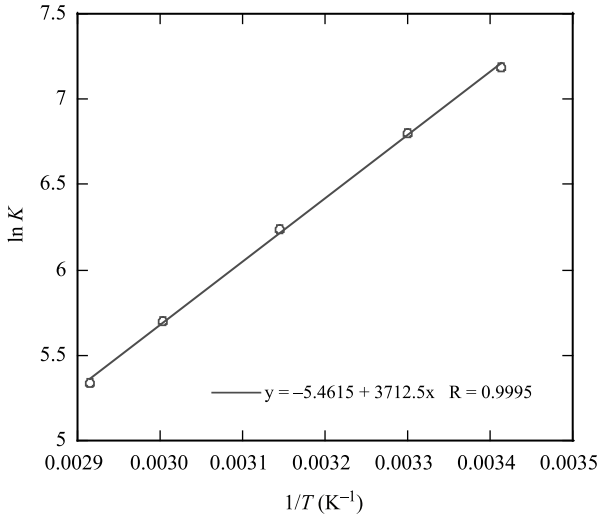


FIGURE 5 van't Hoff plot of the **3**–**1** complexation in $C_6D_5CD_3$.

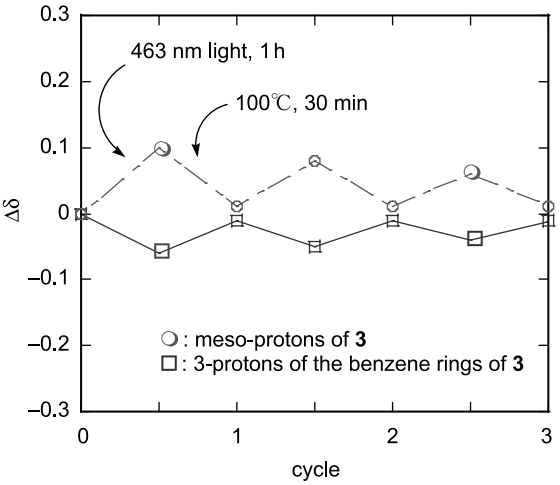


FIGURE 6 Chemical shift difference during three cycles of the reversible process. $\Delta\delta = \delta$ (**3** + **1** after irradiation or heating) $- \delta$ (**3**+**1**). [**1**] $= 1 \times 10^{-2}$ M and [**3**] $= 2 \times 10^{-3}$ M in $C_6D_5CD_3$.

195.9, 196.7. Anal. Calcd for $C_{36}H_{28}O_4S_2$(%): C, 73.44; H, 4.79. Found: C, 73.09; H, 4.45.

X-ray Crystal Structures for 1 and 2

Compound **1**: $C_{18}H_{14}O_2S$, $M = 294.37$, monoclinic, space group $P2_1/a$, $a = 7.288(2)$, $b = 15.455(3)$, $c = 13.091(2)$Å, $\beta = 103.54(2)°$, $V = 1433.6(5)$Å^3, $T = 296$ K, $Z = 4$, $D_c = 1.364$ g cm^{-3}, $\lambda = 0.7107$ Å, 3296 reflections measured, 3294 unique. $R_1 = 0.0704$ (1128) and $R_w = 0.1604$ (1128). CCDC deposition number 232403. Compound **2**: $C_{72}H_{56}O_8S_4$, $M = 1177.47$, triclinic, space group $P\bar{1}$, $a = 16.19(1)$, $b = 23.206(8)$, $c = 8.154(2)$Å, $\alpha = 90.10(2)$, $\beta = 100.61(4)$, $\gamma = 81.66(5)°$, $V = 2978(2)$Å^3, $T = 296$ K, $Z = 2$, $D_c = 1.313$ g cm^{-3}, $\lambda = 0.7107$ Å, 14156 reflections measured, 13681 unique. $R_1 = 0.0825$ (4145) and $R_w = 0.2732$ (4145). CCDC deposition number 232404.

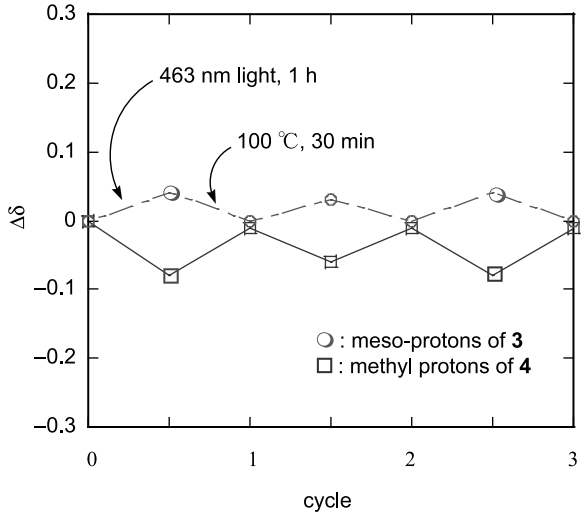


FIGURE 7 Chemical shift change during three cycles of the reversible process in the presence of quinone **4**. $\Delta\delta = \delta$ (**3** + **1** + **4** after irradiation or heating) $- \delta$ (**3** + **1** + **4**). [**1**] $= 1 \times 10^{-2}$ M, [**3**] $= 2 \times 10^{-3}$ M and [**4**] $= 2 \times 10^{-4}$ M in $C_6D_5CD_3$.

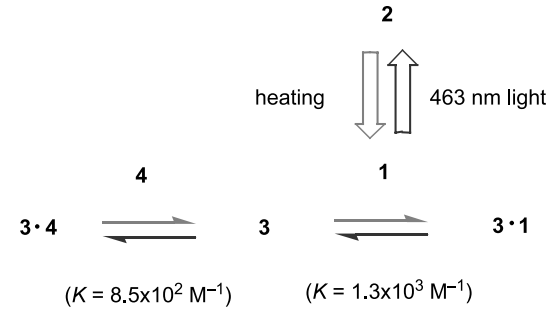


FIGURE 8 Photochemically controlled porphyrin-quinone complexation based on the reversible interconversion between hemithioindigo **1** and its cycloadduct **2**. Association constants at 293 K are shown in parentheses.

Acknowledgements

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