Photoregulated Fluorescence Switching in Axially Coordinated Tin(IV) Porphyrinic Dithienylethene

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Photochromic fluorophore **Sn(TTP)(DTE)₂**, in which two phenolic derivatives of 1,2-dithienylethene are axially coordinated to (5,10,15,20-tetratolylporphyrinato)tin(IV) in trans position, has been synthesized and fully characterized by various spectroscopic methods. We have also investigated the photoregulated fluorescence switching behavior of **Sn(TTP)(DTE)₂**. The fluorescence of the porphyrin macrocycle in **Sn(TTP)(DTE)₂** greatly depends on the state of the 1,2-dithienyletene photochromic switch. In the open state (**Sn(TTP)(o-DTE)₂**), the porphyrin exhibits high fluorescence intensity at 609 and 664 nm when excited at 410 nm. When the photocyclization reaction was carried out by irradiating **Sn(TTP)(o-DTE)₂** with the UV light (∼365 nm), the fluorescence intensity of the porphyrin macrocycle decreased. Back irradiation with visible light at wavelengths greater than 500 nm regenerated **Sn(TTP)(o-DTE)₂** and almost restored the original fluorescence spectrum. The fluorescence intensity of the porphyrin fluorophore is efficiently regulated by photochromic switching between **Sn(TTP)(o-DTE)₂** and **Sn(TTP)(c-DTE)₂** in several cycles, clearly demonstrating that the **Sn(TTP)(DTE)₂** can act as a system for reversible data processing using fluorescence as the detection method.

Introduction

The molecular photochromes responding to specific light energy, during which they undergo reversible changes in their structures and properties, have drawn great attraction as they have the potential to significantly impact technologies in the applications for photonic devices such as ultrahigh-density erasable data storage systems and optical switches.[1] Aiming at molecular-level optical information processes, bistable photochromic switching of the fluorescence emission can be a promising signaling mode because the fluorescence signals can be readily and sensitively recognized.[2] Among various photochromes, the 1,2-dithienylethene derivatives have been largely considered for molecular photonic devices such as erasable memory media and optical switches because of their

thermal stability, excellent photofatigue resistance, and high efficiency of photoisomerizations.[3] The porphyrin complexes are also well suited for molecular devices of nondestructive optical memory because their intense luminescence is at wavelengths far into the visible spectral region where the one photochromic isomer (open form) of 1,2-dithienylethene

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is more likely to be transparent and the other one (closed form) absorbs the light emitted from the porphyrin fluorophore. The photochromism of dithienylethenes has been successfully utilized in regulating the fluorescence intensity of free base porphyrins, in which the two chromophores are covalently linked, for the application of nondestructive information processing.[4,5] The regulation of ruthenium(II) porphyrins' phosphorescence was also investigated for the Ru(II) porphyrins with the axial coordination of pyridyl appended dithienylethenes.[6] Despite promising potential in application as molecular-scale photoelectronic devices, porphyrinic photochromes have not been explored at great length. In the course of our research on photoelectronic molecular devices with metalloporphyrins, we thus decided to investigate the optical properties of tin(IV) porphyrins in conjunction with the photochromism of dithienylethenes because tin(IV) porphyrins have intense fluorescence and attractive coordination properties.

A resurgence of interest in tin(IV) porphyrins in recent years in large part is due to the attractive properties conferred by the highly charged main group metal center.[7] The preferential coordination of the tin(IV) porphyrins to oxy anionic ligands has been used in the construction of elaborate multiporphyrin arrays.[8] Noncovalent self-assembly of tin(IV) porphyrins can afford porous structures with uniform channels.[9] Tin(IV) porphyrins have been also investigated for interesting applications such as catalysis,[10] biomedicine,[11]

and syntheses of nano materials.[12] We have also studied tin(IV) porphyrins bearing photoelectronically active components such as fullerene[13] and ferrocene.[14] We here report that photochromic fluorophore **Sn(TTP)(DTE)₂**, in which two phenolic derivatives of 1,2-dithienylethene are axially coordinated to (5,10,15,20-tetratolylporphyrinato)tin(IV) in trans position, has been synthesized and fully characterized by various spectroscopic methods. More importantly, we demonstrate modulated fluorescence signaling behavior of **Sn(TTP)(DTE)₂** by photochromic regulation of the dithienylethene ligands in this work.

Experimental Section

trans-Dihydroxo(5,10,15,20-tetratolylporphyrinato)tin(IV) **Sn-(TTP)(OH)₂**[12f,15] and the phenolic derivative of dithienylethene **DTE**[16] were prepared by the reported procedures. Toluene was purified by distillation from a sodium/benzophenone ketyl solution. Steady-state UV–vis and fluorescence spectra were recorded on a Hewlett-Packard 8453 diode array and a Shimadzu PF-5300PC spectrophotometers, respectively. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DRX-500 spectrometer. Electrospray ionization (ESI) mass spectra were recorded on a Thermo Finnigan linear ion trap quadrupole mass spectrometer. Elemental analyses were performed on a ThermoQuest EA 1110 analyzer.

Synthesis of Sn(TTP)(DTE)₂. *trans*-Dihydroxo(5,10,15,20-tetratolylporphyrinato)tin(IV) (174 mg, 0.21 mmol) and phenolic derivative of 1,2-dithienylethene (250 mg, 0.47 mmol) were dissolved in anhydrous toluene (100 mL). The reaction mixture was heated at reflux for 2 h. After cooling to room temperature, the solvent was evaporated under reduced pressure to give a crude product. It was then recrystallized from toluene/CH₃CN solution to afford purple solids of **Sn(TTP)(DTE)₂.** Yield: 200 mg (51%). ^{1}H NMR (500 MHz, CDCl₃): δ 9.10 (s, 8H, β-pyrrolic H, ^4J(SnH) = 15.9 Hz), 8.04 (d, 8H, tol, J = 7.6 Hz), 7.56 (d, 8H, tol, J = 7.6 Hz), 7.50 (d, 4H, DTE-Ph, J = 7.4 Hz), 7.34 (m, 6H, DTE-Ph), 7.23 (s, 2H, DTE-thiophene), 6.66 (s, 2H, DTE-thiophene), 5.83 (d, 4H, DTE-OPh, J = 7.4 Hz), 2.73 (s, 12H, tol-CH₃), 1.84 (s, 6H, DTE-CH₃), 1.84 (s, 3H, Ph-DTE-CH₃), 1.82 (s, 3H, OPh-DTE-CH₃), 1.80 (d, 4H, DTE-OPh, J = 7.4 Hz). ^{13}C NMR (CDCl₃): δ 147.6, 143.4, 142.2, 138.4, 138.2, 135.1, 133.6, 132.7, 129.2, 127.9, 126.1, 125.8, 124.1, 123.8, 122.6, 122.1, 118.2, 31.1, 21.8, 14.7, 14.6. UV–vis (CH₂Cl₂, nm): λ_{max}(log ε) 303(4.46), 426(5.27), 561(3.60), 604(3.42). MS (ESI): m/z 1857.9 [M⁺ requires 1858.32], 1323.3 [(M-DTE)⁺ requires 1323.26]. Anal. Calcd. For C₁₀₂H₇₀-

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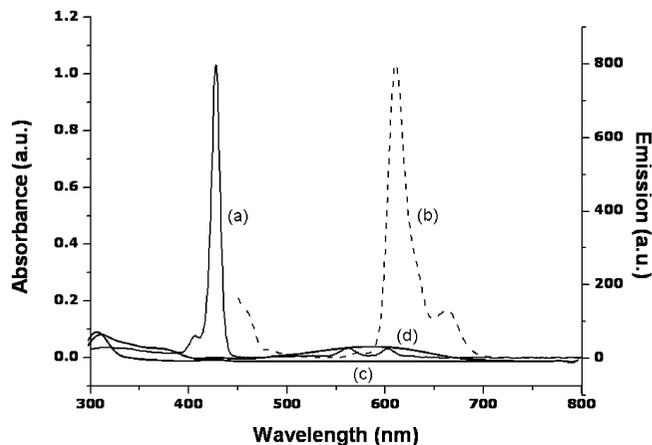
Figure 1. (a) UV–vis absorption and (b) fluorescence spectra of **Sn(T-TP)(OH)₂**, UV–vis absorption spectra of (c) free **DTE** before and (d) free **DTE** after irradiation with 365 nm light. All spectra were taken with 2 × 10^{-6} M CH₂Cl₂ solutions at room temperature.

F₁₂N₄O₂S₄Sn·CH₂Cl₂: C, 65.00; H, 3.86; N, 3.21; S, 6.23. Found: C, 63.59; H, 3.71; N, 2.88; S, 6.59.

Measurement of Modulated Fluorescence. The changes of fluorescence intensity of **Sn(TTP)(DTE)₂** in a toluene (5 × 10^{-6} M) solution were recorded on a SLM-AMINCO SLM-4800 spectrofluorometer during alternating irradiation with UV and visible lights. Fluorescence intensity at 609 nm after every irradiation was recorded by exciting at 410 nm of the same intensity. After fluorescence measurement of the initial state, the solution was irradiated with UV light (~365 nm) irradiation for 15 s by using a UV lamp (Viler Lourmat, Model VL-4.LC), and the fluorescence intensity changes were recorded at 5 s intervals. Visible light irradiations were performed with a 450 W mercury lamp passed through a 500 nm cutoff filter. During the visible irradiation of 120 s, fluorescence intensity changes were recorded at 30 s intervals. Such alternating irradiation cycles were repeated six times per experiment. The fluorescence intensity changes were finally plotted with values obtained by averaging data measured over 15 experiments.

Results and Discussion

We have chosen a class of 1,2-dithienylethene compounds as a photochromic chromophore in this work not only because the 1,2-dithienylethene compound shows a highly efficient bistable photochromism but also because it has negligible absorbance at around the Soret absorption band of the porphyrin chromophore both in the open form and in the 365 nm photostationary state, as shown in Figure 1. Tin(IV) porphyrins can be regarded as an attractive component in the molecular design for optical data storage devices because of their favorable optical and axial coordination properties. For example, *trans*-dihydroxo(5,10,15,20-tetra-tolylporphyrinato)tin(IV) complex **Sn(TTP)(OH)₂** emits intense fluorescence in the range of 550–700 nm upon the excitation of the Soret band,[17] and the wavelength range of the fluorescence is considerably superimposed with the absorption band of the closed form of 1,2-ditheylethene

photochrome (Figure 1). Therefore, the fluorescence of the tin(IV) porphyrin can be largely affected by the state of the 1,2-dithenylethene photochromic switch in the molecular system consisting of the two chromophores. The preferential and rigid coordination of the tin(IV) porphyrins to carboxy-lates and phenolates can be utilized to easily construct molecular materials with high thermal stability. Furthermore, the trans-diaxial coordination of tin(IV) porphyrins would be useful in the vertical architectures of the self-assembled layers on surfaces by modular methods.[18]

The (5,10,15,20-tetratolylporphyrinato)tin(IV) complex coordinated by the phenolic 1,2-dithienylethene derivative, **Sn(TTP)(DTE)₂**, was synthesized by the reaction of *trans*-dihydroxo(5,10,15,20-tetratolylporphyrinato)tin(IV) complex **Sn(TTP)(OH)₂** with 2 equiv of the phenol derivative of 1,2-dithienylethene in toluene, as shown in Scheme 1. The complex **Sn(TTP)(DTE)₂** was fully characterized by various spectroscopic methods and elemental analysis. In the ¹H NMR spectrum of **Sn(TTP)(DTE)₂**, the most diagnostic signals judging the formation of the complex are the phenolic resonances which are shifted significantly to higher field (Δδ H_α −5.75 and H_β −1.03 ppm). The significant upfield shifts of these resonances as a result of the large shielding by the porphyrin ring current strongly support that the **DTE** moiety is linked to the Sn(IV) porphyrin moiety via Sn−phenoxide coordination.[19] The ESI mass spectrum of **Sn(TTP)(DTE)₂** exhibits a molecular ion peak at $m/z = 1857.9$, which is consistent with the desired molecular formula. We also obtained a satisfactory result from the elemental analysis.

The photochromic isomerization of **Sn(TTP)(DTE)₂** was examined by spectroscopic methods. A solution of **Sn(T-TP)(DTE)₂** in toluene readily turned to deep blue upon irradiating it with the UV light. The color change implies that the photochromic isomerization of 1,2-dithienylethene moiety from the open to the closed form occurs efficiently in **Sn(TTP)(DTE)₂** as shown in Scheme 1. Figure 2 illustrates the changes in the UV–vis absorption spectra of **Sn(TTP)(DTE)₂** in toluene upon irradiation with 365 nm light. The UV–vis absorption spectrum of **Sn(TTP)(DTE)₂** is almost equivalent to the sum of the absorption spectra of each molecular component (**Sn(TTP)(OH)₂** and free **DTE** ligand) comparing spectra in Figure 1 and Figure 2. It indicates that there is little change in the ground-state of either chromophore in **Sn(TTP)(DTE)₂**. The absorbance in the Q-band region (500–700 nm) was obviously increased because of the appearance of the absorption band of the closed isomer of the **DTE** ligand in **Sn(TTP)(DTE)₂**. The concomitant decrease of absorbance at 303 nm was also

(17) The fluorescence quantum yield of Sn(TTP)(OH)₂ was reported to be Φ = 0.048 by using tetraphenylporphyrin such as H₂TPP (Φ = 0.11 in CH₂Cl₂) or Zn(TPP) (Φ = 0.036 in CH₂Cl₂) as the standard. See ref 8(e).

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(19) (a) Because of the high oxophilicity nature of the Sn(IV) center, the Sn(IV) porphyrin complexes with various phenoxide axial anions are readily prepared and purified even by column chromatography on neutral alumina. This fact strongly supports the high formation constants of aryloxo Sn(IV) porphyrin complexes as well as their stability to hydrolysis. (b) Arnold, D. P. *Polyhedron* **1986**, *5*, 1957. (c) Langford, S. J.; Lee, M. A.-P.; MacFarlane, K. J.; Weigold, J. A. *J. Inclusion Phenom. Macrocyclic Chem.* **2001**, *41*, 135.

Scheme 1. Synthetic Scheme and Photochromic Isomerization of **Sn(TTP)(DTE)₂**
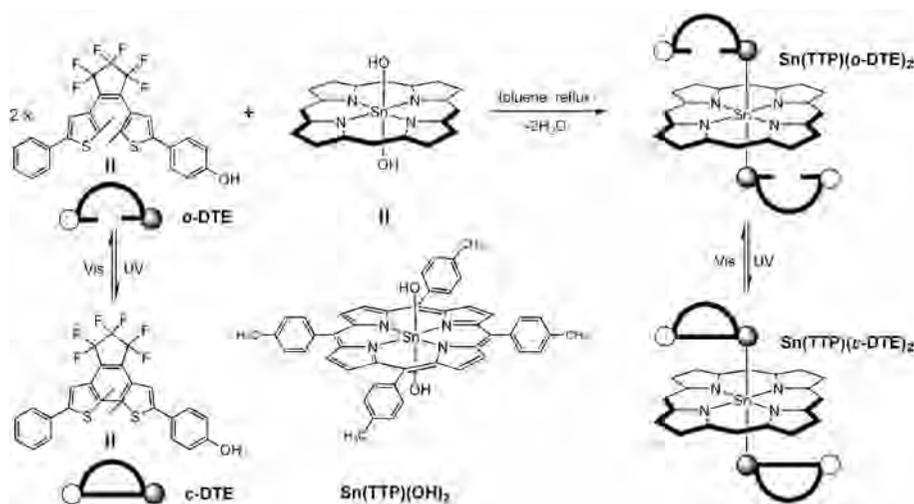
observed during the irradiation periods. Upon UV irradiation of the free **DTE** ligand, the broad absorption band centered at 590 nm attributable to the closed isomer of the free **DTE** ligand appears as shown in Figure 1d. The changes in the two absorptions indicates that the population of the closed form **Sn(TTP)**(*c*-DTE)₂ in the solution gradually increases upon irradiation. More interestingly, the spectral change in the Soret absorption shows an isosbestic point with a new red-shifted absorption band centered at 429 nm.[20] Prolonged irradiation (20 min) results in no observable spectral changes as monitored by absorption spectroscopy. The isosbestic change in the Soret absorption evidently suggests that the photochromic isomerization of the two DTE ligands occurs efficiently and simultaneously in **Sn(TTP)(DTE)₂** without any transient species on the time scale of UV–vis absorption spectroscopy. This simultaneous photochromism of the two coordinated DTE ligands indicates lack of electronic communication between the two DTE ligands in **Sn(TTP)-**

(DTE)₂.[21] On the other hand, partial[22] or sequential[23] photochromic isomerizations have been observed in some conjugated 1,2-dithienylethene oligomers. Upon UV irradiation, we also observed by ¹H NMR spectroscopy that the new resonances appeared at 2.08 and 2.06 ppm with the concomitant decrease in intensity of the resonances at 1.83 and 1.82 ppm assigned to methyl protons in the DTE ligand. After 5 min of continuous irradiation (2×10^{-4} M, CDCl₃), the photostationary state was reached and identified by ¹H NMR spectroscopy as consisting of 63% of the closed isomer **Sn(TTP)**(*c*-DTE)₂.[24]

Irradiation of the closed isomer **Sn(TTP)**(*c*-DTE)₂ with visible light at wavelengths greater than 500 nm resulted in the rapid ring-opening photoreaction and the regeneration of the open isomer **Sn(TTP)**(*o*-DTE)₂. The reversible photoisomerization was verified by monitoring the changes in the UV–vis absorption spectra. As depicted in Figure 3a, back irradiation at wavelengths greater than 500 nm regenerated **Sn(TTP)**(*o*-DTE)₂ and restored the original UV–vis absorption spectrum. The presence of the Soret absorption band centered at 426 nm for **Sn(TTP)(DTE)₂** allows for the porphyrin chromophore to be selectively irradiated in a region of the spectrum where the 1,2-dithienylethene photochromic
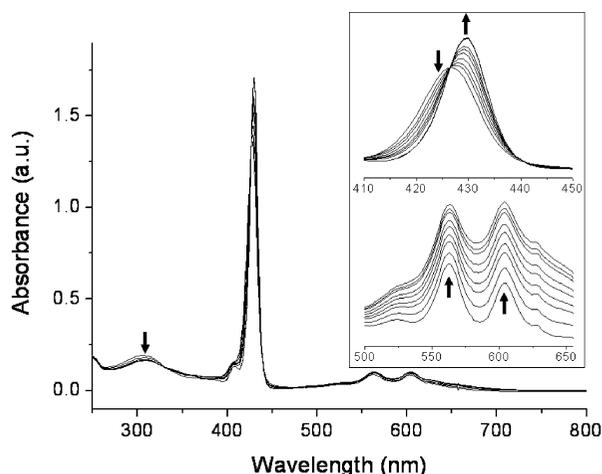

Figure 2. Changes in the UV–vis absorption spectra of a toluene solution of **Sn(TTP)(DTE)₂** (5×10^{-6} M) upon irradiation with 365 nm light. Inset shows enlargements of Soret (top) and Q-bands (bottom) regions. The solution was irradiated for 10 s intervals up to 80 s.

(20) Absorption properties of Sn(IV) porphyrins seem to be affected by the electronic nature of the axial ligands. The electronic absorption data for some Sn(IV) porphyrins have been summarized in ref 7(a), showing Soret absorptions at different wavelengths in variation of the axial ligands.

(21) The simultaneous electrochemical responses of the two axial ligands such as porphyrin and ferrocene derivatives in Sn(IV) porphyrins, revealing the absence of electronic interaction between them, were also observed. See ref 8(e) and 14(b).

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(24) Although the conversion ratio in this work is not high, it is comparable to that (69%) for the covalently linked porphyrinic dithienylethene reported in ref 4.
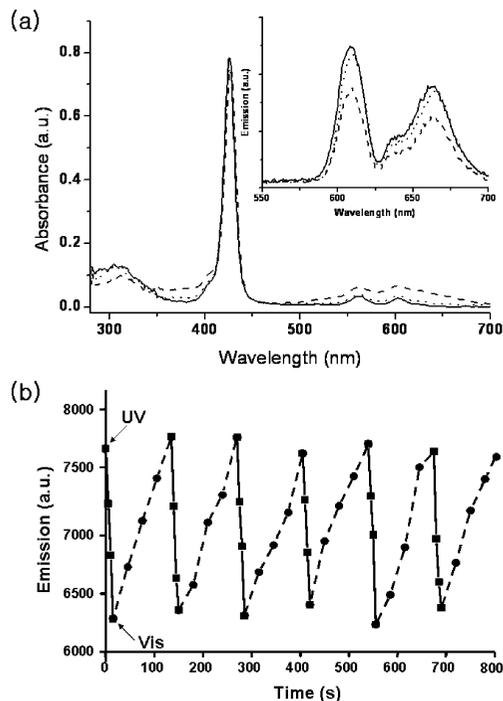
Figure 3. (a) UV–vis absorption spectra of **Sn(TTP)(DTE)₂** on each photostationary state achieved by alternating irradiation with the lights of 365 nm (dashed line) and >500 nm (dotted line). The spectrum of **Sn(TTP)(DTE)₂** without any irradiation is represented by a solid line. The inset shows fluorescence spectra of **Sn(TTP)(DTE)₂** on each state. (b) Modulation of the porphyrin fluorescence with the interconversion of **Sn(TTP)(o-DTE)₂** and **Sn(TTP)(c-DTE)₂** induced by alternating irradiation at 365 (solid line) and >500 (dashed line) nm. All spectra were run in deoxygenated toluene (λ_{ex} = 410 nm, λ_{em} = 609 nm).

ligand of **Sn(TTP)(DTE)₂** is transparent. The fluorescence of the porphyrin macrocycles in **Sn(TTP)(o-DTE)₂** and **Sn(TTP)(c-DTE)₂** obviously depends on the state of the 1,2-dithienyletene photochromic switch. In the open form **Sn(TTP)(o-DTE)₂**, the porphyrin exhibits high fluorescence intensity at 609 and 664 nm when excited at 410 nm. When the photocyclization reaction was carried out by irradiating **Sn(TTP)(o-DTE)₂** with UV light, the fluorescence intensity of the porphyrin macrocycle decreased through formation of the closed form **Sn(TTP)(c-DTE)₂**. Back irradiation at wavelengths greater than 500 nm regenerated **Sn(TTP)(o-DTE)₂** and almost restored the original fluorescence spectrum.[25] Such spectral changes of the fluorescences are illustrated in the inset of Figure 3a. The fluorescence quenching in **Sn(TTP)(c-DTE)₂** is attributed to the intramolecular energy transfer from the excited Sn−porphyrin macrocycle to the closed dithienylethene units,[26] because the spectral overlapping in the range of 550–700 nm between

the emission band from the Sn-porphyrin macrocycle and the enhanced absorption band of the closed dithienylethene ligands in **Sn(TTP)(c-DTE)₂** (Figure 1). Because of the energy transfer, the closed dithienylethene ligands in **Sn(TTP)(c-DTE)₂** absorb the emitted light of the Sn−porphyrin macrocycle around 600 nm so that the higher fluorescent open form **Sn(TTP)(o-DTE)₂** can be partially regenerated even under the UV irradiation, and the fluorescence quenching is relatively small (about 16%).[27] It is apparent that the fluorescence intensity of the porphyrin chromophore is efficiently regulated by photochromic switching between **Sn(TTP)(o-DTE)₂** and **Sn(TTP)(c-DTE)₂** using alternate irradiations at 365 nm and at greater than 500 nm (Figure 3b), clearly demonstrating that the **Sn(TTP)(DTE)₂** can act as a system for reversible data processing using fluorescence as the detection method.

Conclusion

In this report, we have successfully synthesized and fully characterized the 1,2-dithienylethene derivative axially coordinated to the (5,10,15,20-tetratolylporphyrinato)tin(IV) complex **Sn(TTP)(DTE)₂**. We also revealed that the fluorescence intensity of the tin(IV) porphyrin fluorophore is efficiently regulated by photochromic switching between **Sn(TTP)(o-DTE)₂** and **Sn(TTP)(c-DTE)₂** using alternate irradiations with the UV light and the visible light beyond 500 nm. Such photoregulated fluorescence switching of **Sn(TTP)(DTE)₂** can be applied to potential technologies for ultrahigh-density erasable optical data processing.

(25) Lack of full restoration may be due to the re-conversion of **Sn(TTP)**(o-DTE)2 to **Sn(TTP)**(c-DTE) 2 caused by the exciting irradiation while measuring fluorescence.

(26) The fluorescence quenching of the porphyrin excited state by energy transfer to the closed-dithienylethene unit has been manifested in a covalently linked DTE-porphyrin-fullerene triad, Liddell, P. A.; Kodis, G.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **2002**, *124*, 7668.

(27) The reviewers pointed out that the small changes of fluorescence intensity in the fluorescence modulation as well as the low conversion ratio in the photostationary state estimated by ^{1}H NMR spectral data may indicate the formation of a partial photo-isomerized product **Sn(TTP)**(o-DTE)(c-DTE) with less quenched fluorescence. Although we have obtained no direct evidence for the formation of this possible species, the existence of this species in the photostationary state cannot be excluded.