Supporting Information

A Photochromic Porphyrin-perinaphthothioindigo Conjugate and its Two-photon Absorption Properties

Joanne T. Dy,[†] Rena Maeda,[†] Yasunori Nagatsuka,[†] Kazuya Ogawa,[†]* Kenji Kamada,[‡] Koji Ohta,[‡] and Yoshiaki Kobuke[†]*

Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0101 and Photonics Research Institute, National Institute of Advanced Industrial Science and Science and Technology, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

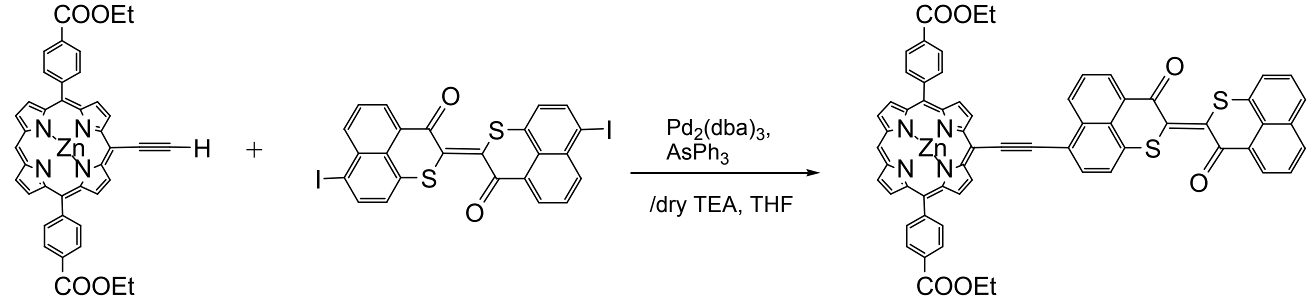
Detailed procedures of synthesis and characterization.

Experimental Section

General. THF used in photophysical measurements was distilled prior to use. All samples were deoxygenated by bubbling nitrogen into the solvent. Solvents for NMR analysis were used as purchased.

^{1}H and COSY NMR spectra were obtained in $C_2D_2Cl_4$/Pyridine-D_5 unless noted otherwise, with Me_4Si as the internal standard (δ 0 ppm) and recorded on either JEOL JNM EX270, JEOL ECP 500, or JEOL ECP 600. UV-vis spectra were obtained on either Shimadzu UV-1650PC or UV-3100PC UV Visible Spectrophotometer. Fluorescence measurements were performed on a Hitachi F-4500 Fluorescence Spectrophotometer. MALDI-TOF mass spectra were obtained on Perseptive Biosystems Voyager DE-STR and Shimadzu/KRATOS Axima-CFR Kompact MALDI with dithranol (Aldrich) as the matrix. Analytical GPC measurements were performed on a Shimadzu Liquid Chromatography series LC10-AD with a TSK-GEL G2500H_{HR} column. Reactions were monitored on silica gel 60 F_{254} TLC plates (Merck). The silica gel utilized for column chromatography was purchased from Kanto

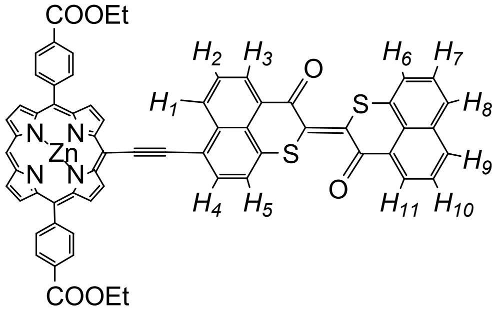
Chemical Co. Inc.: Silica Gel 60N (Spherical, Neutral) 60-210 μm and 40-50μm (Flash). The alumina used for column chromatography was purchased from Merck: Aluminum oxide 90 active basic.



2 **3** **1**

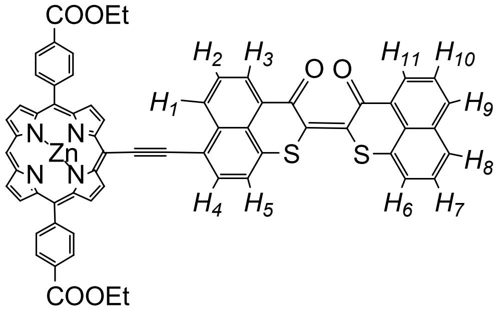
The starting compounds, **2**[1] and **3**[2], were synthesized according to reported procedures.

Porphyrin 1. Under argon atmosphere, **3** (21 mg, 32.4 μmol) in 135 mL THF was sonicated for 10 min (Compound **3** is almost insoluble in any organic solvent, less than 10^{-6} M. So this reaction is inhomogeneous.). Triethylamine (15 mL), tris(dibenzylideneacetone)bispalladium(0) (1.8 mg, 1.7μmol), and triphenylarsine (6 mg, 19.5μmol) were added and the reaction mixture was degassed by 3 freeze thaw cycles. **2** (10 mg, 14.4μmol) in THF (10 mL) was added dropwise during 2 min. After stirring for 2h at 35°C, additional tris(dibenzylideneacetone)bispalladium(0) (1.8 mg, 1.7μmol), and triphenylarsine (6 mg, 19.5μmol), and **2** (5 mg, 7.2 μmol) in THF (5 mL) were added. After a total of 6h, half of the solvent was evaporated and the mixture was washed with water, extracted with $CHCl_3$, and dried over anhydrous Na_2SO_4. The spectra of the crude mixture showed productions of **1** (a single iodine in **3** reacted with **2** and the other iodine was replaced by hydrogen due to reduction) as the main product and bisporphyrin-substituted perinaphthothioindigo. Remaining **3** was removed from the crude by passing through a silica gel column (eluent: $CHCl_3$/THF). The crude material was then reprecipitated in THF from diethyl ether and further purified by preparative GPC (TSK-GEL $G2500H_{HE}$, eluent: pyridine, flow rate: 3.0 mL/min) to give 3 mg (20%) of the target compound. MS (MALDI-TOF Mass, dithranol); Found *m/z* = 1088.34 [M], calcd for $C_{76}H_{74}N_{12}O_4$ 1088.53.



1_{trans}

***Trans* isomer of porphyrin 1 (1_{trans}).** The pure *trans* compound was collected from preparative GPC in pyridine (TOSOH TSK-GEL G2500H_{HR}; flow rate: 3.0 mL/min). ^{1}H NMR (500 MHz, $C_2D_2Cl_4$/Pyridine-D_5) δ 10.07 (s, 1H, Por *meso*), 9.81 (d, *J* = 4.5 Hz, 2H, Por *β*), 9.31 (d, *J* = 8 Hz, 1H, H_1), 9.23 (d, *J* = 4.5 Hz, 2H, Por *β*), 8.92 (d, *J* = 4.5 Hz, 2H, Por *β*), 8.83 (d, *J* = 4.5 Hz, 2H, Por *β*), 8.69 (d, *J* = 8 Hz, 1H, H_3), 8.54 (d, *J* = 8 Hz, 1H, H_{11}), 8.37 (d, *J* = 8 Hz, 4H, ph), 8.24 (d, *J* = 8 Hz, 4H, ph), 8.20 (d, *J* = 8 Hz, 1H, H_4), 8.08 (d, *J* = 8 Hz, 1H, H_9), 7.98 (t, *J* = 8 Hz, 1H, H_2), 7.77 (d, *J* = 8 Hz, 1H, H_5), 7.70 (d, *J* = 8 Hz, 1H, H_6), 7.68 (t, *J* = 8 Hz, 1H, H_{10}), 7.62 (H_8, overlaps with pyridine peak), 7.46 (t, *J* = 8 Hz, 1H, H_7), 4.49 (q, *J* = 7.5 Hz, 4H, -$COOC\underline{H_2}CH_3$), 1.48 (t, *J* = 7.5 Hz, 6H, -$COOCH_2C\underline{H_3}$). UV-vis (λ_{abs}, $CHCl_3$): 435, 575, 655 nm. Fluorescence (λ_{em}, λ_{ex} = 444 nm, $CHCl_3$): 721, 800 nm.



1_{cis}

***Cis* isomer of porphyrin 1 (1_{cis}).** Pure *cis* compound was obtained by irradiating with light >700 nm (0.48 W) for 2 min from a Xe lamp with a 700 nm cutoff filter passed through water to eliminate thermal effects. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$/Pyridine-D_5) δ 10.08 (s, 1H, Por *meso*), 9p-.81 (d, *J* = 4.5

Hz, 2H, Por *β*), 9.34 (d, *J* = 8 Hz, 1H, H_1), 9.23 (d, *J* = 4.5 Hz, 2H, Por *β*), 8.92 (d, *J* = 4.5 Hz, 2H, Por *β*), 8.83 (d, *J* = 4.5 Hz, 2H, Por *β*), 8.55 (d, *J* = 8 Hz, 1H, H_3), 8.41 (d, *J* = 8 Hz, 1H, H_{11}), 8.37 (d, *J* = 8 Hz, 4H, ph), 8.24 (d, *J* = 8 Hz, 4H, ph), 8.21 (d, *J* = 8 Hz, 1H, H_4), 8.11 (d, *J* = 8 Hz, 1H, H_9), 7.98 (t, *J* = 8 Hz, 1H, H_2), 7.78 (d, *J* = 8 Hz, 1H, H_5), 7.76 (d, *J* = 8 Hz, 1H, H_6), 7.68 (t, *J* = 8 Hz, 1H, H_{10}), 7.62 (H_8, overlaps with pyridine peak), 7.49 (t, *J* = 8 Hz, 1H, H_7), 4.49 (q, *J* = 7.5 Hz, 4H, -$COOC\underline{H}_2CH_3$), 1.48 (t, *J* = 7.5 Hz, 6H, -$COOCH_2C\underline{H}_3$). UV-vis (λ_{abs}, THF): 441, 527, 572, 625 nm. Fluorescence (λ_{em}, λ_{ex} = 444 nm, $CHCl_3$): 721, 800 nm.

Quantum yield of photoisomerization. The relative quantum yields of *trans*-to-*cis* and *cis*-to-*trans* photoisomerization of **1** were calculated using thioindigo as the reference (Q.Y. $_{trans\rightarrow cis}$ = 5%).[3] Initially, a 1.99×10^{-5} M (initial abs. at 538 nm = 0.0702) solution of thioindigo in benzene was isomerized from *trans*-to-*cis* by irradiating the sample at 500 nm with a power of 0.57 mW. The conversion from *trans*-to-*cis* was monitored by the absorbance at 538 nm. The absorbances at 538 nm were plotted against their respective irradiation time intervals and the initial rate of conversion (within 5%) was calculated as the initial slope ($Rate_{St}$ = 0.00135).

The same procedure was performed for *trans*-to-*cis* conversion of **1** with a concentration of 1.64×10^{-5} M (initial absorbance at 720 nm = 0.146) which was irradiated with 700 nm light, with a power of 0.38 mW. The *trans*-to-*cis* conversion of **1** was monitored at 720 nm. ($Slope_{1trans\rightarrow 1cis}$ = 0.00149) The same procedure was also performed for *cis*-to-*trans* conversion of **1** with a concentration of 1.64×10^{-5} M (initial absorbance at 500 nm = 0.347) which was irradiated with 500 nm light, with a power of 0.63 mW. The *cis*-to-*trans* conversion of **1** was monitored by the absorbance at 500 nm. ($Rate_{1cis\rightarrow 1trans}$ = 0.00705)

Finally, the quantum yield of isomerization was calculated using the following equation:

$$\Phi_X = \Phi_{St} \times \frac{Rate_X}{Rate_{St}} \times \frac{Abs_{St}}{Abs_X} \times \frac{Power_{St}}{Power_X} \times \frac{Conc_{St}}{Conc_X} \qquad (1)$$

where X = $\mathbf{1_{trans}}\rightarrow\mathbf{1_{cis}}$ or $\mathbf{1_{trans}}\rightarrow\mathbf{1_{cis}}$; St = standard or reference compound (thioindigo); Φ = isomerization quantum yield; *Abs* = absorbance at the monitoring wavelength; *Power* = power of the light irradiated for isomerization; *Conc* = concentration. The quantum yield of *trans*-to-*cis* and *cis*-to-*trans* isomerizations are $\Phi_{\mathbf{1trans}\rightarrow\mathbf{1cis}}$ = 5% and $\Phi_{\mathbf{1cis}\rightarrow\mathbf{1trans}}$ =15%, respectively.

Calculation of *%cis* and *%trans*. The total absorbance, Abs_{Total}, is the sum of the absorbances of the *trans* and *cis* molecules as given in equation (2). The same goes for the total concentration, $Conc_{Total}$, as shown in equation (3).

$$Abs_{Total} = Abs_{cis} + Abs_{trans} = \varepsilon_{cis}Conc_{cis} + \varepsilon_{trans}Conc_{trans} \qquad (2)$$

$$Conc_{Total} = Conc_{cis} + Conc_{trans} \qquad (3)$$

where *Abs* = absorbance; *Conc* = concentration; ε = extinction coefficient.

Combining equations (2) and (3), the concentration of the *cis* and the *trans* molecules in the sample are:

$$Conc_{cis} = \frac{Abs_{Total} - \varepsilon_{trans}Conc_{Total}}{\varepsilon_{cis} - \varepsilon_{trans}} \qquad (4)$$

$$Conc_{trans} = \frac{Abs_{Total} - \varepsilon_{cis}Conc_{Total}}{\varepsilon_{trans} - \varepsilon_{cis}} \qquad (5)$$

Finally, the percentage of *cis* (*%cis*) and *trans* (*%trans*) molecules in the sample can be calculated as:

$$\%cis = \frac{Conc_{cis}}{Conc_{Total}} \times 100\% \qquad (6)$$

$$\%trans = \frac{Conc_{trans}}{Conc_{Total}} \times 100\% \qquad (7)$$

2PA cross-section (2PACS) measurement of 1.[4] *trans*-Rich thioindigoporphyrin (~80%) was dissolved in spectroscopic grade THF. Half of the mixture was used to measure the 2PA of *trans*-rich porphyrin, and half was irradiated with light >700 nm (from a Xe lamp with a 700 nm cutoff filter) in order to generate a 100% *cis*-isomer sample. The samples (0.1-0.3 mM) were placed in a 2 mm cell and were continuously stirred during the measurements.

The 2PACS of the 100% *cis*-isomer sample in THF was measured using the usual method.[3] The open-aperture Z-scan measurements were performed using a femtosecond optical parametric amplifier (Spectra-Physics OPA-800) pumped by a Ti:sapphire regenerative amplifier (Spectra Physics Spitfire). The laser system generated 130 fs pulses with a repetition frequency of 1 kHz and Rayleigh range of ~6 mm. The incident power was varied from 0.05 to 0.5 mW, corresponding to peak intensities of 15-150 GW/ cm^2, for each measurement.

For the determination of the 2PACS value of 100% *trans*-isomer, a *trans*-rich mixture was used. So, it was necessary to isolate the contribution of the *cis*-isomer to the 2PACS value of the mixture in order to obtain the real 2PACS of the *trans*-isomer. In order to calculate the 2PACS value of the *trans*-isomer, the following procedures were employed:

1) The 2PA coefficient of the mixture $\alpha^{(2)}_{\text{mixture}}$ was determined by the usual fitting method of z-scan curve.[3]

2) The 2PA coefficient of the *trans*-isomer $\alpha^{(2)}_{\text{trans}}$ is then calculated using eq (9).

3) Finally, the 2PACS of the *trans*-isomer $\sigma^{(2)}_{\text{trans}}$ was determined by eq (10).

$$\alpha^{(2)}_{\text{mixture}} = \%\, trans * \alpha^{(2)}_{\text{trans}} + \%\, cis * \alpha^{(2)}_{\text{cis}} \tag{8}$$

$$\%\, trans * \alpha^{(2)}_{\text{trans}} = \alpha^{(2)}_{\text{mixture}} - \%\, cis * \alpha^{(2)}_{\text{cis}} \tag{9}$$

$$\sigma^{(2)}_{\text{trans}} = \alpha^{(2)}_{\text{trans}} \times \hbar\omega \,/\, N \tag{10}$$

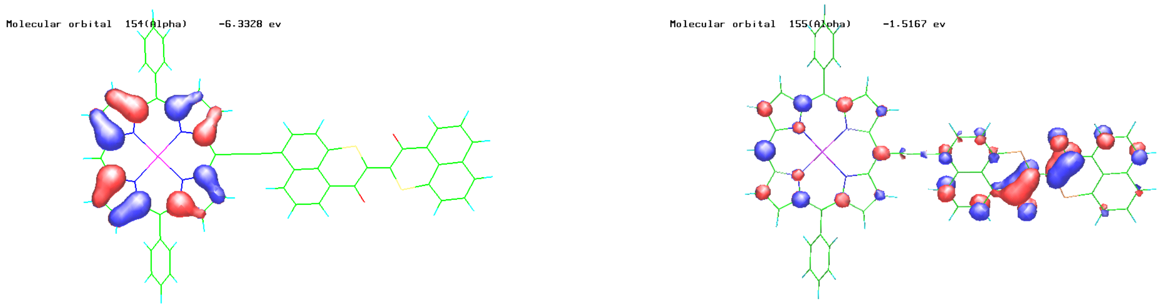
where $\alpha^{(2)}_{\text{mixture}}$, $\alpha^{(2)}_{\text{trans}}$ and $\alpha^{(2)}_{\text{cis}}$ are the 2PA coefficients of the *trans*-rich mixture, pure *trans* compound and pure *cis* compound, respectively; % *trans* and % *cis* are the percentages of the *trans*- and *cis*- compounds, respectively, in the *trans*-rich mixture, these were determined by using the absorption spectra of the samples; $\sigma^{(2)}_{\mathrm{trans}}$ is the 2PACS of the *trans*-isomer; and N is the number density of the solute molecules.

The calculated errors in the *trans*-isomer are much larger than those in the *cis*-compound because in the computation for the $\sigma^{(2)}$ value of $\mathbf{1}_{\mathbf{trans}}$, the error of the $\sigma^{(2)}$ value of $\mathbf{1}_{\mathbf{cis}}$ was also involved.

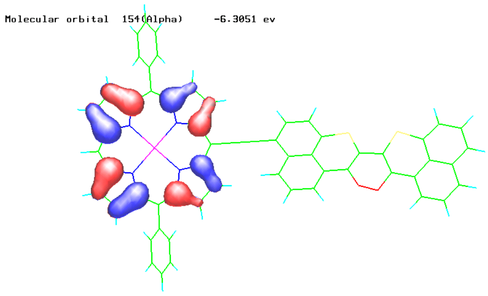
2PA Photoisomerization of 1 and 3. The samples were dissolved in THF (2.5 μM) and were placed in a 1.0 cm cell and degassed by N_2 bubbling. The volume of the samples were set to 1.0 mL and continuously stirred during measurements. The samples were irradiated with a Coherent MIRA 900 Ti:Sapphire laser + focusing lens at 890 nm, with a FWHM of 10 nm, pulse width = 200 fs, peak power = 0.53 GW/cm^2. The progress of isomerization was monitored by measuring the absorption spectra after each time interval. No photoisomerization was observed without the lens.

Molecular orbital calculations. The HOMO and LUMO molecular orbitals of $\mathbf{1}_{\mathbf{trans}}$ and $\mathbf{1}_{\mathbf{cis}}$ were calculated using MOPAC$^{\mathrm{TM}}$ software (WinMOPAC ver. 3.9) with AM1 and INDO-S(CI 30×30 method).

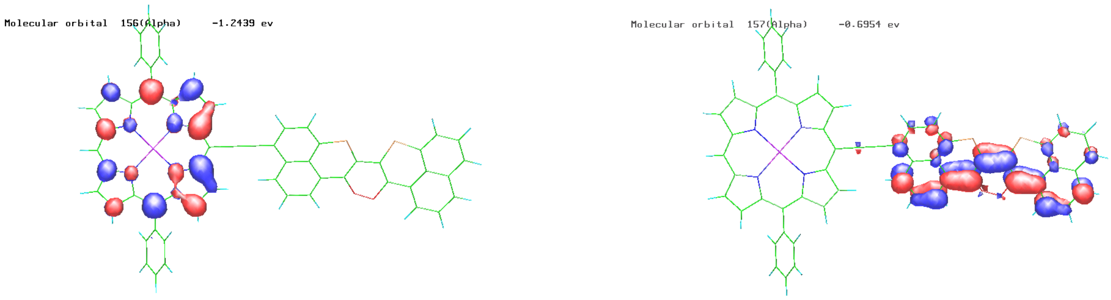
Calculated molecular orbitals of HOMO (left) and LUMO (located at ~660 nm, right) of $\mathbf{1}_{\mathbf{trans}}$. The electronic density of the LUMO orbital is spread throughout the whole molecule.



Calculated molecular orbitals of HOMO (left) of $\mathbf{1}_{\mathbf{cis}}$.



Calculated molecular orbitals of LUMO1 (located at ~620 nm, left) and LUMO2 (located at ~450 nm, right) of $\mathbf{1}_{\mathbf{cis}}$. The electronic density of the LUMO orbital is isolated only in the porphyrin in the case of LUMO1 and only in the PNT unit in the case of LUMO2.



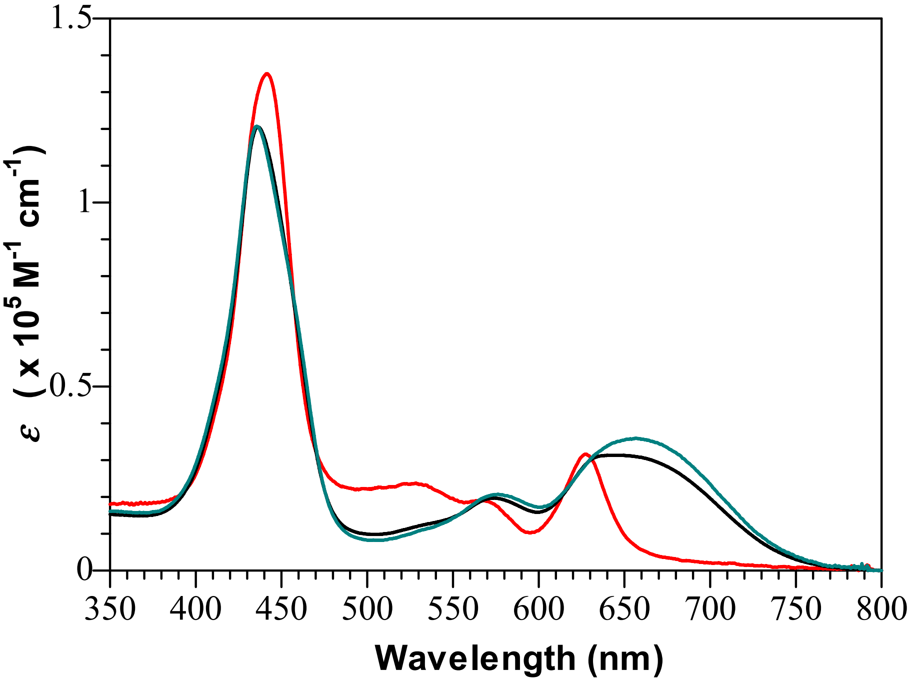
References:

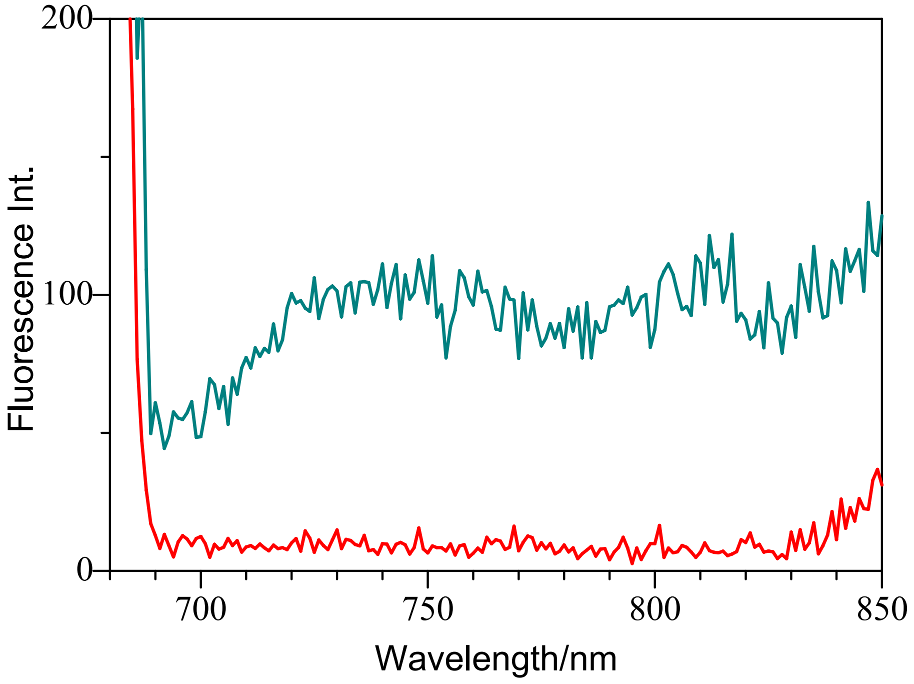
1) Ogawa, K.; Dy, J.; Kobuke, Y. *J. Porphyrins and Phthalocyanines* **2005**, *9*, 735.

2) Leavitt, J. *Chem. Abst.* **1971**, *74*, 113196.

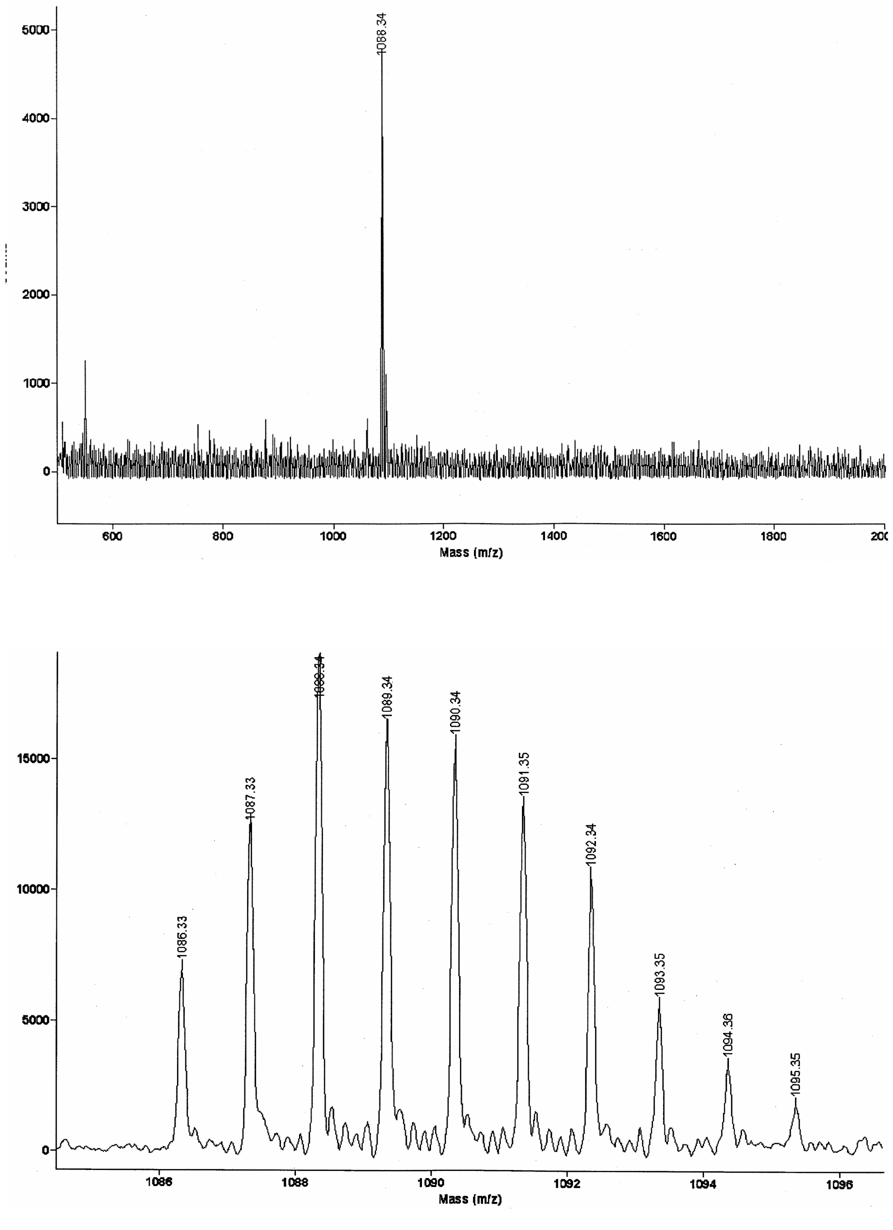
3) Takahashi, T.; Taniguchi, Y.; Umetani, K.; Yokouchi, H.; Hashimoto, M.; Kano, T. *Jpn. J. Appl. Phys.* **1985**, *24*, 173.

4) (a) Kamada, K.; Ohta, K.; Iwase, Y.; Kondo, K. *Chem. Phys Lett.* **2003**, *372*, 386. (b) Iwase, Y.; Kondo, K.; Kamada, K.; Ohta, K. *J. Mater. Chem.* **2003**, *13*, 1573. (c) Ogawa, K.; Ohashi A.; Kobuke, Y.; Kamada, K.; Ohta, K. *J. Am. Chem. Soc.* **2003**, *125*, 13356. (d) Ogawa, K.; Ohashi A.; Kobuke, Y.; Kamada, K.; Ohta, *J. Phys. Chem. B* **2005**, *109*, 22003.

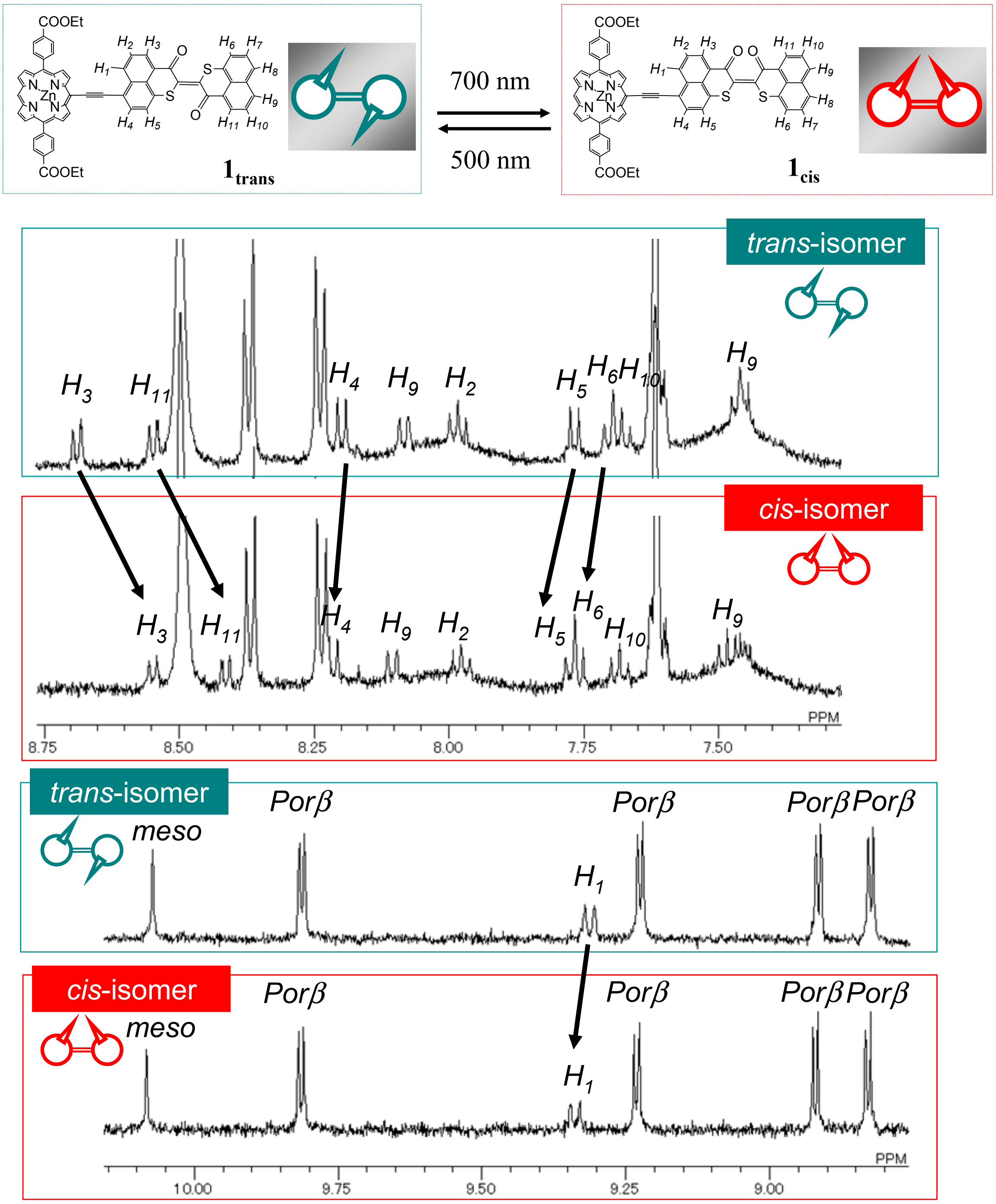




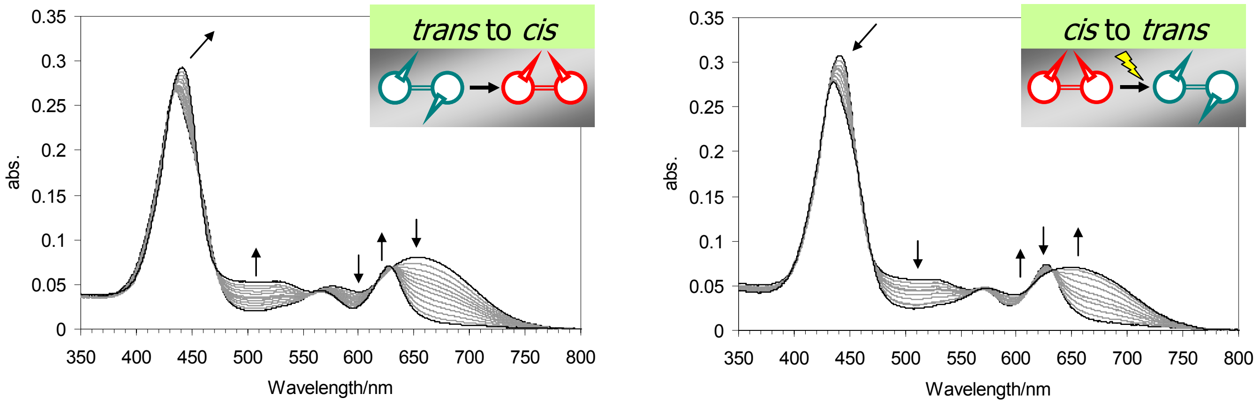
(SI) Figure 1. *Top.* UV-vis absorption spectra of pure $\mathbf{1}_{\mathbf{trans}}$ (blue), $\mathbf{1}_{\mathbf{cis}}$ (red) and photostationary state (black) of **1**. *Bottom.* Fluorescence spectra of $\mathbf{1}_{\mathbf{trans}}$ and $\mathbf{1}_{\mathbf{cis}}$ after 680 nm excitation.



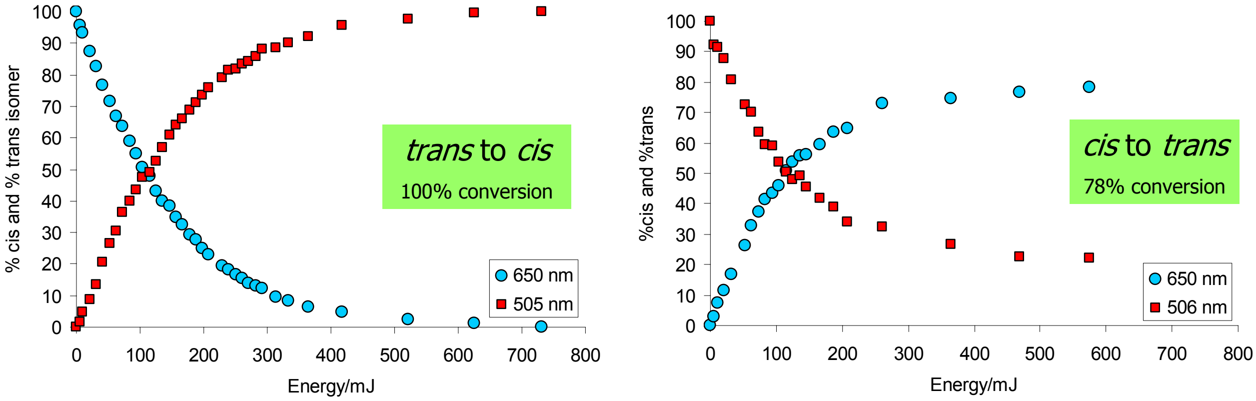
(SI) Figure 2. MALDI-TOF mass spectra of **1** with dithranol, calcd for $C_{64}H_{38}N_4O_6S_2Zn$ *m/z* = 1088.53.



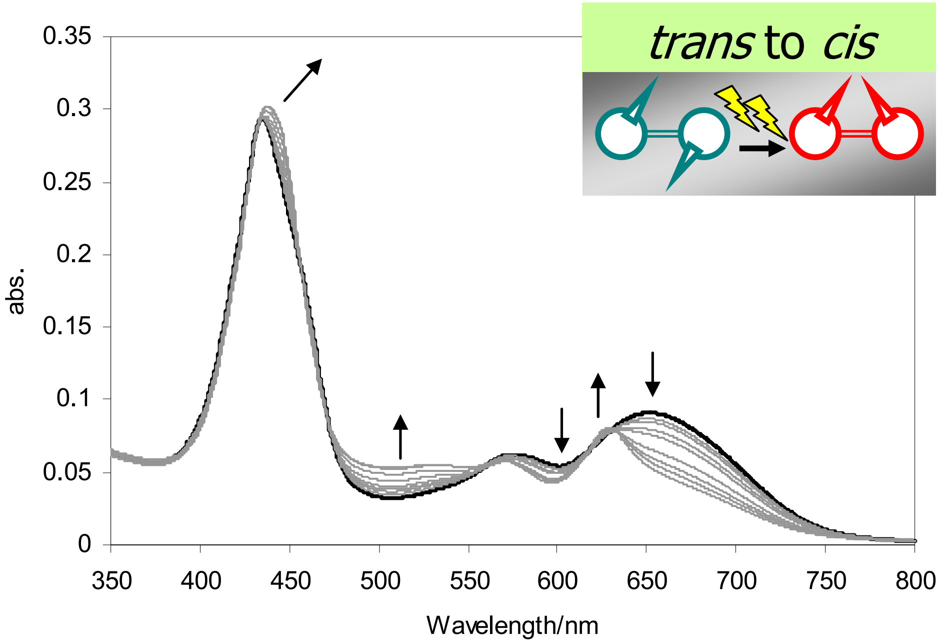
(SI) Figure 3. ^{1}H-NMR spectra of $\mathbf{1}_{\mathbf{trans}}$ (in blue) and $\mathbf{1}_{\mathbf{cis}}$ (in red) in THF-d_8 + Py-d_5, 500 MHz. The thioindigo protons nearest the switching alkene bond, H_3, H_5, H_6, and H_{11}, experience large shifts.



(SI) Figure 4. *Left.* Photoisomerization from *trans* to *cis* of compound **1** (2.2 µM) by 700 nm photoirradiation. *Right.* Photoisomerization from *cis* to *trans* of compound **1** (2.2 µM) by 500 nm photoirradiation.



(SI) Figure 5. *Left.* The progress of isomerization from *trans* to *cis* was monitored at the characteristic wavelength of the *trans*-isomer at 650 nm and the characteristic wavelength of the *cis*-isomer at 505 nm. The *trans*-isomer completely converted to its *cis*-stereoisomer. *Right.* The progress of isomerization from *cis* to *trans* was monitored at the characteristic wavelength of the *trans*-isomer at 650 nm and the characteristic wavelength of the *cis*-isomer at 505 nm. 78% conversion was observed for *cis* to *trans* isomerization.



(SI) Figure 6. Two-photon photoisomerization from *trans* to *cis* of compound **1** (2.5 µM in 1 mL THF with rapid stirring) by 890 nm photoirradiation.