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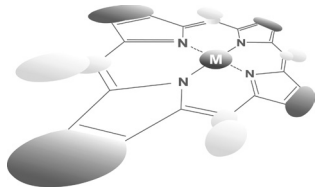

Synthesis and photophysical properties of a porphyrin-perinaphthothioindigo dye

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Dedicated to Professor Evgeny Luk'yanets on the occasion of his 75th birthday

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ABSTRACT: A new porphyrin-perinaphthothioindigo composite, where porphyrin and perinaphthothioindigo dye are connected though a triple bond, was synthesized. In UV-vis absorption spectra of the composite, absorption originating from the *trans*-isomer appeared at 655 nm. Upon photoirradiation at >700 nm, the intensity of this absorption decreased with increase of absorption of the *cis*-isomer around at 530 nm. The HOMO–LUMO absorption of the *cis*-isomer is blue-shifted by 125 nm compared to that of *trans*-isomer due to the lack of π-conjugation. The 2PA cross-section values obtained for both isomers were 2,000 and 700 GM, respectively. The value of 2,000 GM is of the largest class among the values reported for photochromic compounds. The enhancement factors by the connection of porphyrin to perinaphthothioindigo were found to be 3.5–3.9 by measuring cross-section values of bis(TMS-ethynyl) perinaphthothioindigo as the reference compound. Two-photon isomerization of the *trans*-isomer to the *cis*-isomer was successfully conducted using femtosecond pulses.

KEYWORDS: porphyrin, perinaphthothioindigo, two-photon absorption, 3D optical memory, photochromism.

INTRODUCTION

Two-photon absorption (2PA) is a third-order nonlinear phenomenon, wherein excitation occurs by the simultaneous absorption of two photons. The quadratic dependence on the laser intensity allows spatial selectivity using a focused laser beam. This characteristic feature permits a wide variety of optical applications such as photodynamic therapy (PDT) [1–3] and three dimensional (3D) optical data storage [4–9]. Usually, the study of molecular optical memory employs a reversible photochromic transformation between two chemical species on absorbing light at a specific wavelength, where the two species have different absorption and/or emission properties. This property change can be used to record information as the photon-mode optical memory. Some two-photon photochromic compounds have been reported such as diarylethene derivatives that exhibited two-photon photochromism bearing a maximum 2PA cross-section value of ~44 GM ($1\ GM = 10^{-50}\ cm^4.s.molecule^{-1}.photon^{-1}$) at 770 nm [10] and an indolylfulgide yielding a maximum value of 1,030 GM at a wavelength of 775 nm [11]. Unfortunately, the currently

◊ SPP full member in good standing

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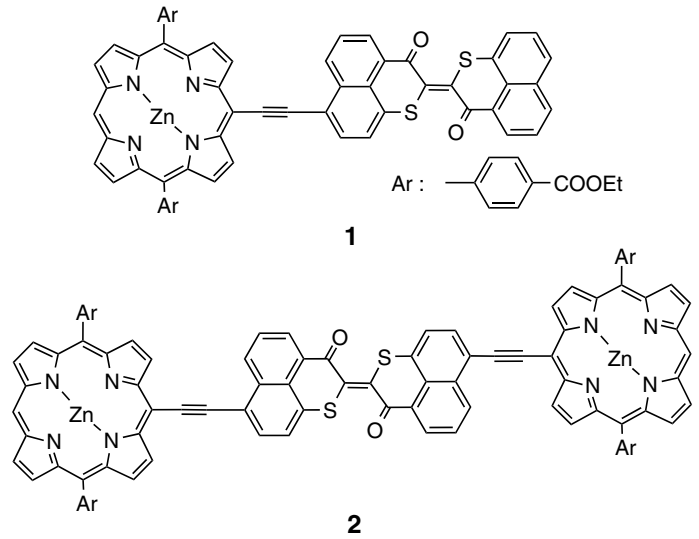
available photochromic molecules lack in strong 2PA to be applied for efficient excitation.

We previously found that an ethynylene linkage between porphyrins significantly enhanced the 2PA efficiency [12, 13]. According to this strategy, we designed a new photochromic molecule having a high 2PA efficiency by conjugating porphyrin and photochromic systems using an ethynylene bridge. In the molecular design, it should be remembered that the energy level of the photochromic moiety must be lower than the S_1 state of the zinc porphyrin part, which is generated by rapid relaxation from the porphyrin S_2 state rose by the two-photon excitation, because this excitation energy must transfer to the photochromic part for switching. Therefore, usual photochromic compounds such as azobenzenes and diarylethenes cannot be used in this system. However, since the S_1 state of the *trans*-isomer of perinaphthothioindigo (PNT, 2.0 eV) [14, 15] is lower than that of zinc porphyrin, isomerization of the PNT part is expected after two-photon excitation of the zinc porphyrin moiety [16]. In this way, at first, we designed a PNT attached-bisporphyrins **2** using an ethynylene bond as a more efficient two-photon absorbing photochromic compound as shown in Scheme 1. However, as described in the section below, unexpected mono-substituted compound **1** was mainly obtained, and thereby was reported first as a communication elsewhere [16]. In this article, details in synthetic parts of **1**, **2**, and related compounds, and photophysical properties including newly obtained 2PA data are reported.

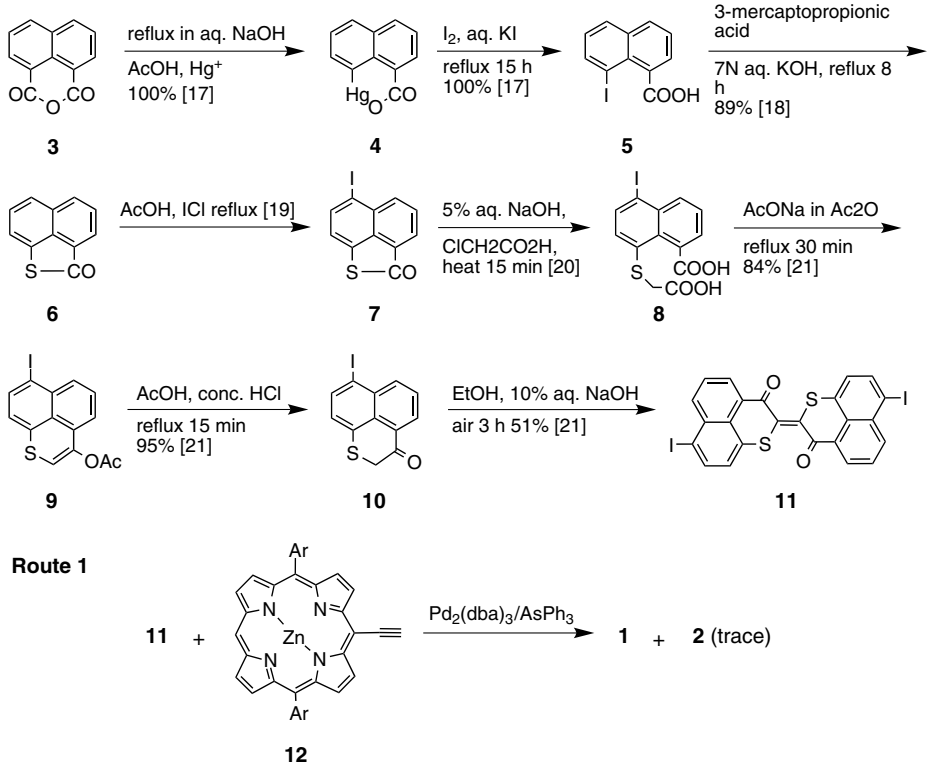


Scheme 1. PNT-conjugated porphyrins

RESULTS AND DISCUSSION

Synthesis

Scheme 2 shows a synthetic route of the target compound. Diiodo-PNT **11** was prepared from 1,8-naphthalic



Scheme 2. Synthetic route of compounds **1** and **2**

anhydride **3** in 8 steps (18%) according to the literatures [17–21]. The synthesis of ethynylporphyrin **12** has previously been reported [22]. A palladium-catalyzed Sonogashira coupling of diiodo-PNT **11** with ethynylporphyrin **12** using tris(dibenzylideneacetone) dipalladium ($Pd_2(dba)_3$) and triphenylarsine as catalysts surprisingly gave monoporphyrin-substituted PNT **1** as the main product in 20% yield. The original target molecule, bisporphyrin-substituted PNT **2**, was expected to exhibit larger 2PA cross-section value because π-conjugation of the molecule might expand. However, only a small amount of **2** was produced probably due to reduction of one of iodines during the reaction route 1, and could not be isolated. So, we decided to isolate **1** and investigate its photophysical properties. In the crude mixture, both the $\mathbf{1}_{trans}$ and $\mathbf{1}_{cis}$ isomers of monoporphyrin-substituted PNT existed. Fortunately, pure $\mathbf{1}_{trans}$ could be separated from $\mathbf{1}_{cis}$ by preparative GPC. One of the iodines in diiodo-PNT **11** was replaced by hydrogen due to reduction and a very small amount of bisporphyrin-substituted PNT **2** was obtained. This reduction occurred even in the presence of Cu(I). The MALDI-TOF mass spectrum of $\mathbf{1}_{trans}$ showed the peak at m/z = 1086.33 ($[M]^+$), which corresponded to the calculated exact value for $C_{64}H_{38}N_4O_6S_2Zn$ m/z = 1086.20 as seen in Fig. 1. Since the MALDI-TOF mass measurement usually detects not only $[M + H]^+$, but also small amount of $[M]^+$, the spectrum was observed as superposition of both the ions. As described below, $\mathbf{1}_{cis}$ was prepared by photoirradiation at > 700 nm. ^{1}H NMR spectra of $\mathbf{1}_{trans}$ and $\mathbf{1}_{cis}$ are shown in Fig. 2. H-H COSY spectra of $\mathbf{1}_{trans}$ were measured to assign the aromatic signals as presented in Fig. 3. After the photoisomerization, large shifts in signals originated from the protons H_3, H_5, H_6 and H_{11} were observed as seen in Fig. 2. Since these protons are closest to the switching moiety of PNT, they should be most sensitive to the stereochemical change. Although bisporphyrin-substituted PNT **2** could not be isolated according to the above scheme, other routes were attempted as shown in Scheme 3 to obtain sufficient amount of **2**. In route 2, starting materials switched to bis(TMS-ethynyl)-PNT **13** and bromoporphyrin **14** [22]. $\mathbf{13}_{trans}$ and $\mathbf{13}_{cis}$ can also be used as reference compounds for 2PA studies because diiodo-PNT **11** could not be used due to its low solubility in any organic solvents. Bis(TMS-ethynyl)-PNT **13** was prepared from the reaction of diiodo-PNT **11** with TMS-acetylene using $Pd(PPh_3)_2Cl_2$ and CuI. Pure $\mathbf{13}_{trans}$ could be isolated after silica gel chromatography. $\mathbf{13}_{cis}$ was prepared by photoirradiation at

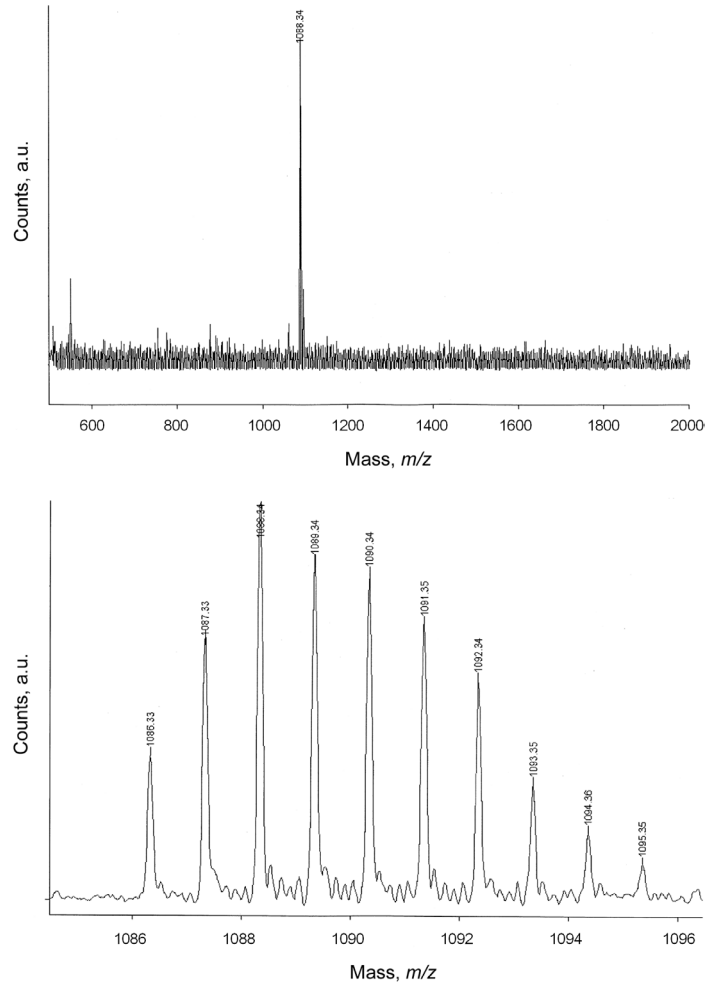


Fig. 1. MALDI-TOF mass spectra of $\mathbf{1}_{trans}$

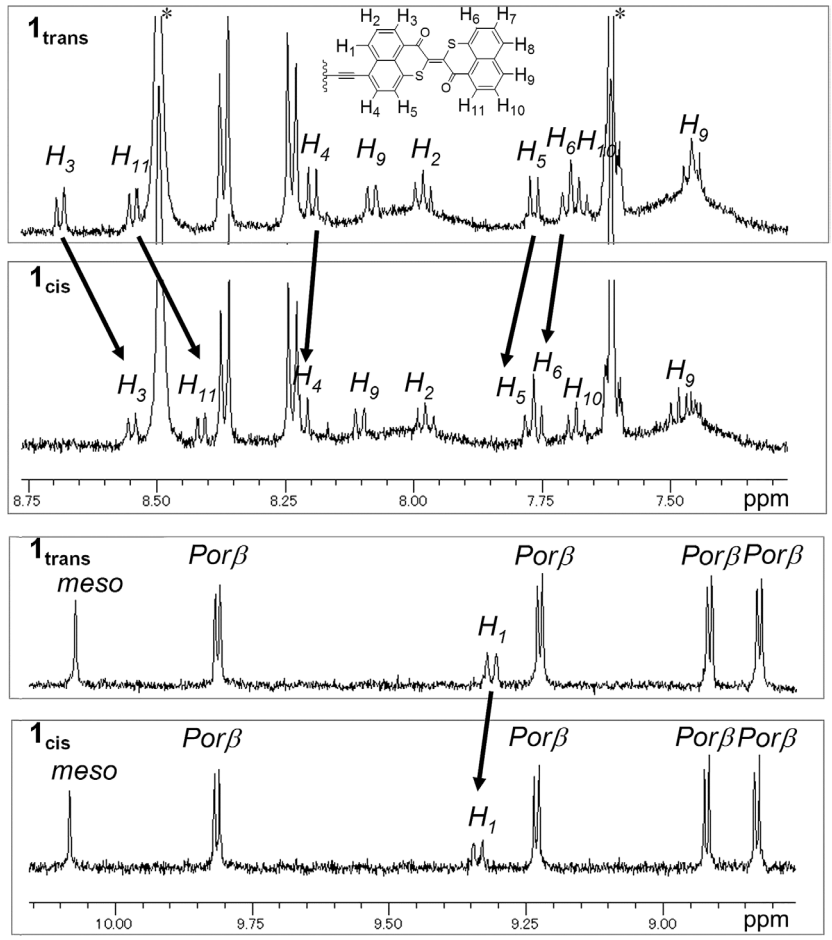


Fig. 2. 500 MHz ^{1}H NMR spectra of $\mathbf{1}_{trans}$ and $\mathbf{1}_{cis}$ in tetrachloroethane-d_2 with a minimum amount of pyridine-d_5. *Marks indicate solvent peaks

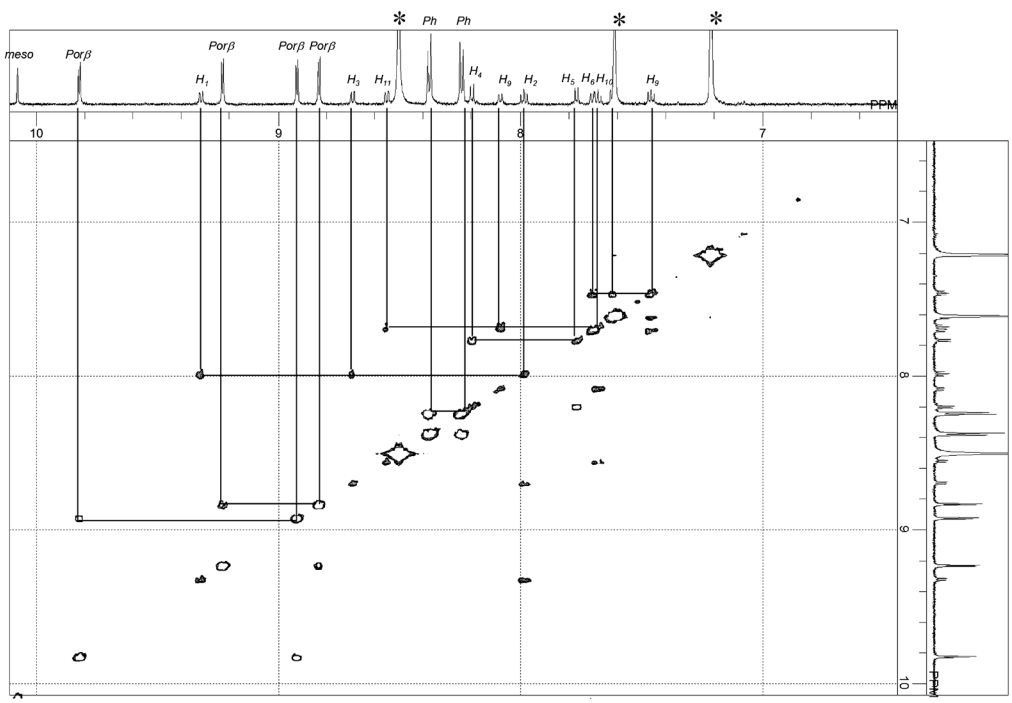
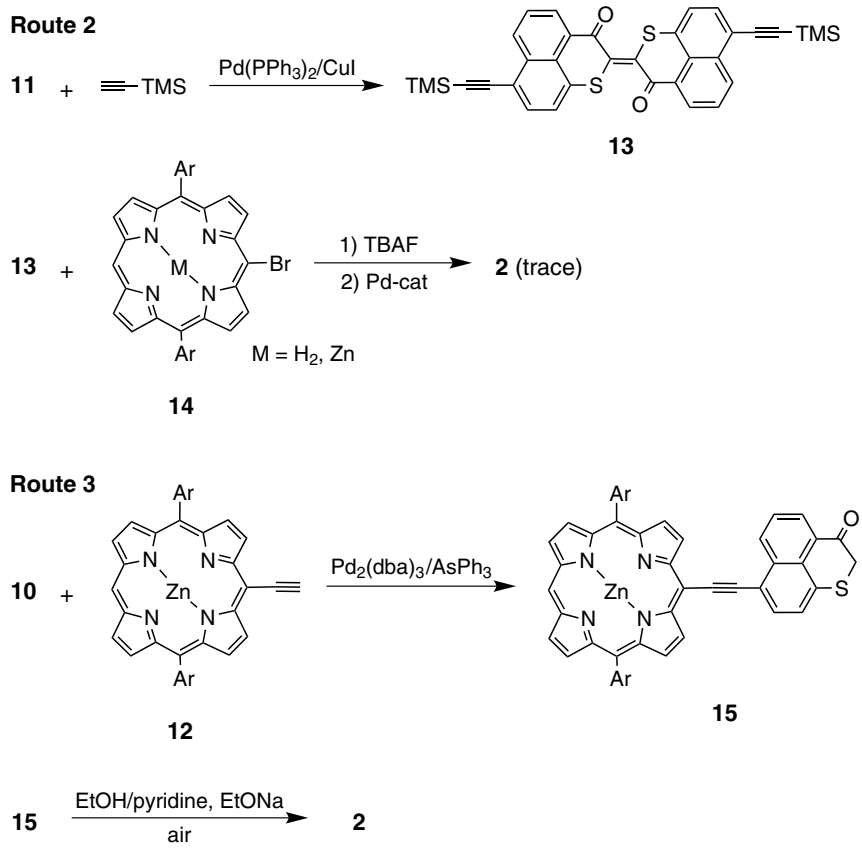


Fig. 3. 500 MHz H–H COSY spectra of $\mathbf{1}_{trans}$ in $CDCl_3$



Scheme 3. Synthetic routes of compound **2**

>660 nm. TMS groups of bis(TMS-ethynyl)-PNT **13** were deprotected using TBAF, and then reacted with bromoporphyrin **14** (H_2 or Zn) using $Pd_2(dba)_3$ and $AsPh_3$ in THF, where deprotection of the TMS group and the coupling reaction were conducted in a one-pot procedure. However, only a small amount of bisporphyrin-substituted PNT **2** was obtained because deprotected-**13** (bisethynyl-PNT) immediately precipitated out before the coupling reaction due to its low solubility.

Next, route 3 was tried, in which the PNT part was synthesized *via* coupling in the last stage of the reactions. First, precursor **15** was successfully prepared from **10** with **12** using $Pd_2(dba)_3/AsPh_3$ in 96.2%. Then, **15** was subjected to the homo-coupling reaction with sodium ethoxide as a base under air bubbling. After 8 h, noticeable **2** was detected in MALDI-TOF spectra as shown in Fig. 4 (found m/z = 1776.28 $[M]^+$, calcd. for $C_{104}H_{64}N_8O_{10}S_2Zn_2$, 1776.28). Reactant **15** (molecular weight = 890.15) almost disappeared. A new peak appeared at m/z = 953, which is larger than the molecular weight of **15** by 63 (= 64 – H) corresponding to two oxygen molecules probably originated from either intermediate or decomposed product. However, after the evaporation of solvent, the product became insoluble in any solvent probably due to aggregation by π–π stacking. Strangely, **1** having only one porphyrin which might work as the solubilizing unit is soluble while **2** bearing two porphyrins is insoluble. We believe that the solubility of **2** can be improved by

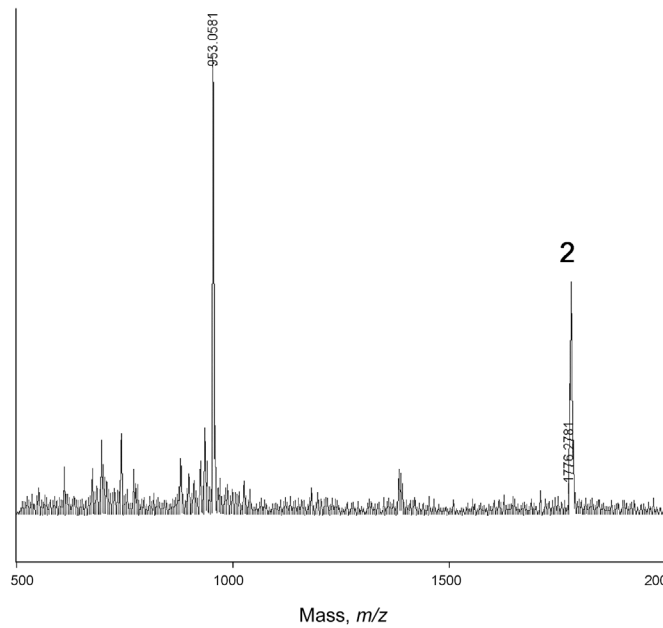


Fig. 4. MALDI-TOF mass spectra of the reaction mixture of **2**

employing more bulky and soluble substituents at the *meso*-positions of the porphyrin part.

Photophysical properties

The photochromic properties of **1** were investigated using one-photon irradiation. $\mathbf{1}_{cis}$ was prepared by photoirradiation at >700 nm with a quantum yield of 5%, which was determined using thioindigo [23] as the reference compound. Figure 5 shows absorption spectra of photostationary state of **1**, $\mathbf{1}_{trans}$, and $\mathbf{1}_{cis}$. In the photostationary state, almost 80% of **1** exists as the *trans* form, indicating that $\mathbf{1}_{trans}$ is more thermally stable than $\mathbf{1}_{cis}$. Figure 6 represents the change in the absorption spectra under photoirradiation at > 700 nm. The intensity of broad absorption of the *trans*-PNT part at 655 nm decreased with increase of absorption of the *cis*-isomer around 500 nm. The Soret-band of the porphyrin part was red-shifted from 435 nm to 440 nm and a sharp Q-band appeared at 625 nm. The HOMO–LUMO absorption of the PNT-part of $\mathbf{1}_{cis}$ at around 530 nm was blue-shifted by 125 nm compared with that of $\mathbf{1}_{trans}$ due to the lack of π-conjugation. Figure 7 shows optimized structures of t*rans*- and *cis*-PNT parts obtained by AM1 calculation. In $\mathbf{1}_{trans}$, carbonyl groups and sulfur atoms are located at opposite sides of the PNT-connecting line each other without steric hindrance, giving planar structure. On the other hand, the carbonyl groups, as well as sulfurs in $\mathbf{1}_{cis}$ are mutually in close proximity, causing steric hindrance. The resulting low planarity of the PNT part reduces the π-conjugation. $\mathbf{1}_{trans}$ can be reversibly generated from $\mathbf{1}_{cis}$ by irradiation at 500 nm with 78% conversion and a quantum yield of 15%, as shown in Fig. 8. In both the photoisomerization experiments, the absorption spectra changed with passing through the clear isosbestic points at 432, 457, 472, 561, 615 and 630 nm. The solution of $\mathbf{1}_{cis}$ in THF showed no change in the UV-vis spectra after keeping in the dark at room temperature for seven days, indicating that the *cis* isomer is relatively stable. $\mathbf{1}_{trans}$ exhibited no change in the UV-vis spectra when it was kept in the dark over several months. $\mathbf{1}_{trans}$ exhibited weak emission when the *trans*-PNT part was selectively excited at 680 nm, as shown in Fig. 9. On the other hand, $\mathbf{1}_{cis}$ showed almost no emission at this excitation wavelength. The difference in the emission property between $\mathbf{1}_{trans}$ and $\mathbf{1}_{cis}$ may be available for data readout.

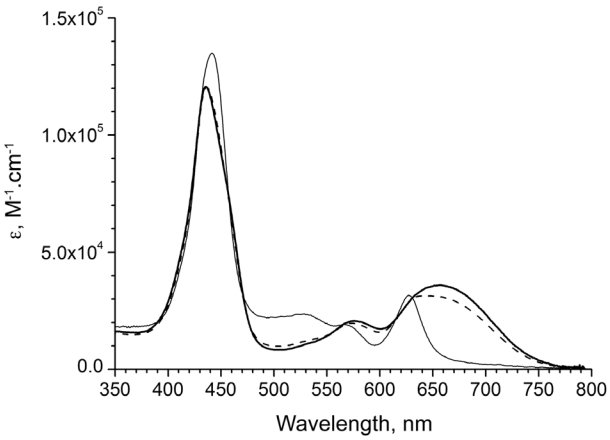


Fig. 5. UV-vis absorption spectra of pure $\mathbf{1}_{trans}$ (bold line), $\mathbf{1}_{cis}$ (thin line), and photostationary state (dashed line) of **1** in THF

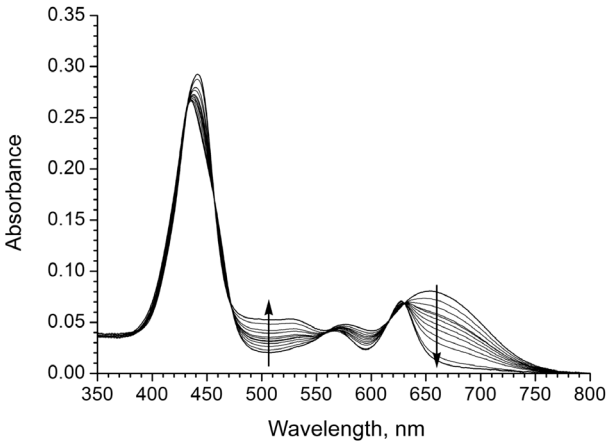


Fig. 6. Photoisomerization of the completely *trans* compound $\mathbf{1}_{trans}$ to the completely *cis* compound $\mathbf{1}_{cis}$ in THF by photoirradiation at >700 nm

2PA was measured using an open-aperture Z-scan technique with 130 fs pulses at a repetition rate of 1 kHz from an optical parametric amplifier (output wavelength was varied for 848–975 nm, incident power <0.35 mW, see Supporting information). A THF solution of a $\mathbf{1}_{trans}$-rich mixture (~80%) in a 2 mm quartz cell with rapid stirring was irradiated. After the measurements of *trans*-rich compound, a solution of $\mathbf{1}_{cis}$ was prepared by irradiation at >700 nm. The $\sigma^{(2)}$ values were calculated using the same method as previously reported [13, 24]. The $\sigma^{(2)}$ values of $\mathbf{1}_{trans}$ were extracted from those of the $\mathbf{1}_{trans}$-rich mixture by subtracting the contribution of $\mathbf{1}_{cis}$. 2PA spectra of $\mathbf{1}_{trans}$ and $\mathbf{1}_{cis}$ are shown in Fig. 10. The 2PA cross-section maxima for both isomers appeared around 850 nm, which was almost twice of wavelength of the Soret band, with values of 2,000 GM for $\mathbf{1}_{trans}$ and 700 GM for $\mathbf{1}_{cis}$. 2PA measurements were also conducted for trimethylsilyl-protected ethynylporphyrin (**12**-TMS) and **13** instead of **11** due to its low solubility in any organic solvent. The Z-scan signal for **12**-TMS was too weak to be observed. From the measurement conditions and concentration of the sample solution, the $\sigma^{(2)}$ value of **12**-TMS was estimated to be less than 20 GM, which was two orders of magnitude smaller than that of $\mathbf{1}_{trans}$. The maximum $\sigma^{(2)}$ value for $\mathbf{13}_{trans}$ and $\mathbf{13}_{cis}$ obtained in a similar manner to those of $\mathbf{1}_{trans}$ and $\mathbf{1}_{cis}$ were 580 GM at 870 nm and 180 GM at 840 nm, respectively. The enhancement factors by the connection of porphyrin to PNT are 3.5–3.9. As observed in the absorption spectra, strong electronic communication between porphyrin and PNT led to a significant enhancement in the 2PA of **1**.

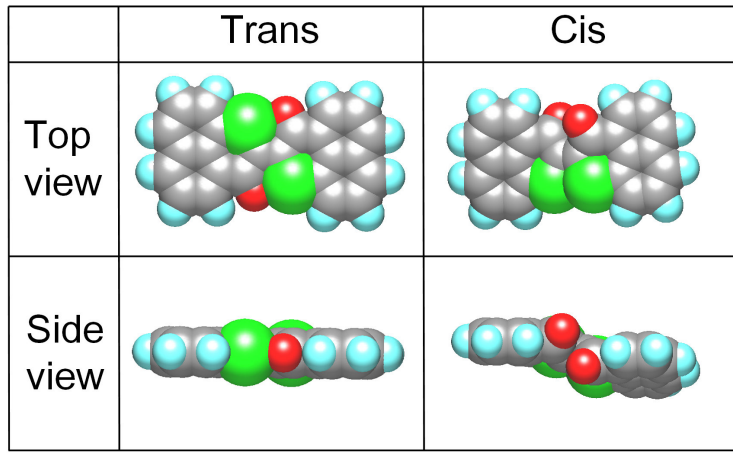


Fig. 7. Optimized structures of *trans*- and *cis*-PNT calculated by an AM1 method

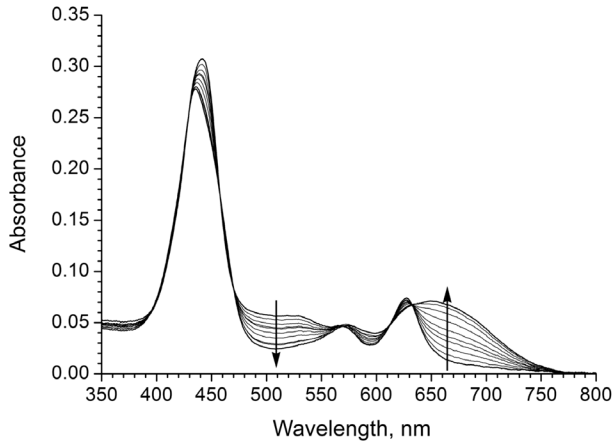


Fig. 8. Photoisomerization of the completely *cis* compound $\mathbf{1}_{cis}$ to the *trans* compound $\mathbf{1}_{trans}$ in THF by photoirradiation at 500 nm

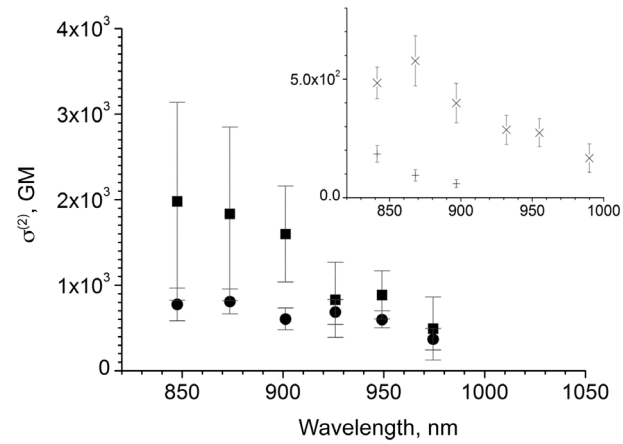


Fig. 10. Two-photon absorption spectra of $\mathbf{1}_{trans}$ (square), $\mathbf{1}_{cis}$ (circle), $\mathbf{13}_{trans}$, (inset; ×), and $\mathbf{13}_{cis}$ (inset; +) in THF

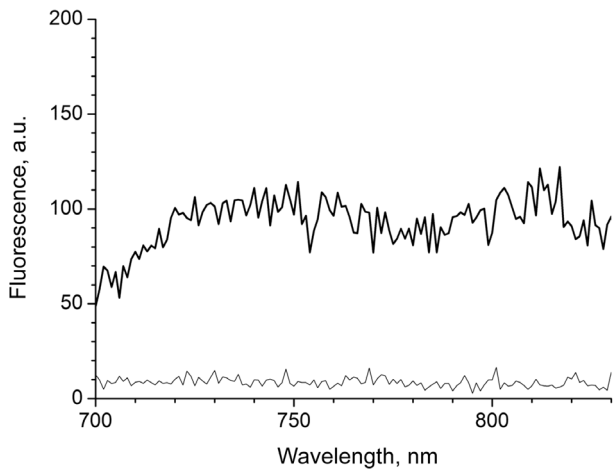


Fig. 9. Fluorescence spectra of $\mathbf{1}_{trans}$ (bold line) and $\mathbf{1}_{cis}$ (thin line) after 680 nm excitation

Although the value of 2,000 GM obtained for $\mathbf{1}_{trans}$ is not so large compared to other porphyrin systems [12, 13], this is of the largest class among the values reported for photochromic compounds.

Finally, we investigated the two-photon isomerization of $\mathbf{1}_{trans}$. $\mathbf{1}_{trans}$ was dissolved in THF (2.8 μM) and was placed in a 1.0 cm cell and degassed by N_2 bubbling. The volume of the sample was set to 1.0 mL and continuously stirred during measurements. The sample was irradiated with a Coherent MIRA 900 Ti:Sapphire laser + focusing lens at 890 nm with pulse width of 200 fs and peak power of 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. The progress of the isomerization of $\mathbf{1}_{trans}$ to $\mathbf{1}_{cis}$ is shown in Fig. 11. After irradiating 4.6×10^{10} shots for 10 min, around 1.2×10^{14} molecules of $\mathbf{1}_{trans}$ were converted to $\mathbf{1}_{cis}$ corresponding to 7% conversion,

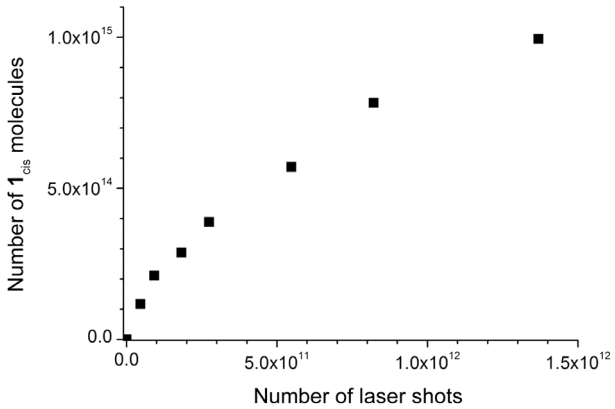


Fig. 11. Time courses of the photoisomerization of $\mathbf{1}_{trans}$ to $\mathbf{1}_{cis}$ (1 mL of 2.8 μM THF solution in a 1 cm cell) using two-photon excitation with 200 fs pulses at 890 nm. The progress of isomerization was monitored at 505 nm

which was estimated from the change in the absorption spectra. This may take around 0.2 ms using the same experimental conditions to isomerize all the $\mathbf{1}_{trans}$ molecules within a spherical volume of a diameter of 40 μm. This corresponds to a writing frequency of around 5 kHz, which depends on the peak power and molecular density.

EXPERIMENTAL

General procedures

THF used for 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 standard and recorded on either JEOL JNM EX270, JEOL ECP 500, or JEOL ECP 600. UV-vis spectra were measured 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 or 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 40–50 μm (Flash). The alumina used for column chromatography was purchased from Merck: aluminum oxide 90 active basic.

Synthesis

Preparation of O-(hydroxymercuri)-1-naphtoic acid anhydride 4 [17]. Naphtoic acid anhydride (0.991 g, 5 mmol) was added into aqueous NaOH solution (0.7 g, 17.5 mmol in 0 mL) and refluxed for 1 h. After neutralization with 0.5 mL of acetic acid, a solution of mercury acetate, which was prepared by dissolving HgO (1.1 g, 5.1 mmol) into boiling acetic acid (2.5 mL) followed by dilution with 18 mL of water, was added. After reflux for 30 min, further acetic acid (0.9 mL) was added and refluxed for 48 h. The precipitate formed was separated by filtration and washed with methanol and water. After drying *in vacuo*, brownish yellow powder was obtained (99.9%). This compound was insoluble in either water or any organic solvents.

Preparation of 8-iodo-1-naphthoic acid 5 [18]. Iodine (1.2 g, 4.7 mmol) and **4** (1.16 g, 3.13 mmol) was added into an aqueous solution of KI (2.23 g, 13.5 mmol in 12 mL). After reflux for 15 h, the reaction mixture was filtered. The filtrate was acidified using hydrochloric acid until pH = 1. Yellow precipitate formed was separated by filtration and dissolved in 100 mL of chloroform. The solution was washed with saturated aqueous sodium thiosulfate and then water. After evaporation of solvent, yellow solid was obtained (79.6%). ^{1}H NMR (270 MHz, $CDCl_3$): δ, ppm 8.27 (dd, 1H, J = 1.1 Hz), 7.92 (m, 3H), 7.52 (dd, 1H, J = 7.3, 8.1 Hz), 7.22 (dd, 1H, J = 7.3, 8.1 Hz).

Preparation of naphtho[1,8-bc]thiophen-2-one 6 [19]. 5 (743.4 mg, 2.49 mmol) was dissolved in 7 M KOH (4 mL). Copper powder (25.3 mg, 0.40 mmol) and 3-mercaptopropionic acid (642 mL, 6.23 mmol) were added into the above solution. After refluxing for 5 h under a nitrogen atmosphere, further 2 mL of 7 M KOH were added and refluxed for 2 h. The reaction solution was diluted with water and filtrated. The filtrate was acidified using 6 M HCl until pH = 1. Yellow precipitate formed was separated by filtration and dissolved in 100 mL of chloroform. The solution was washed with aqueous sodium hydrogencarbonate and then water. After evaporation of solvent, yellow solid was obtained (83.9%). ^{1}H NMR (270 MHz; $CDCl_3$): δ, ppm 8.19 (d, 1H, J = 7.0 Hz), 8.16 (d, 1H, J = 7.1 Hz), 7.85 (dd, 1H, J = 3.5, 7.1 Hz), 7.78 (dd, 1H, J = 3.5, 7.0 Hz), 7.64 (d, 1H, J = 3.5 Hz), 7.63 (d, 1H, J = 7.0 Hz).

Preparation of 6-iodonaptho[1,8-bc]thiophen-2-one 7 [20]. 6 (242.1 mg, 1.30 mmol) and ICl (1.05 g, 65 mmol) were added into 5 mL of acetic acid. After reflux for 12 h, 30 mL of water were added into the reaction solution. The precipitate formed was separated by filtration and dissolved in 100 mL of chloroform. The solution was washed with saturated aqueous sodium thiosulfate and then water. After silica gel chromatography, yellow solid was obtained (50.3%). ^{1}H NMR (600 MHz; $CDCl_3$): δ, ppm 8.240 (d, 1H, J = 8.1 Hz), 8.212 (d, 1H, J = 7.3 Hz), 8.128 (d, 1H, J = 7.6 Hz), 7.845 (dd, 1H, J = 8.4 Hz), 7.344 (d, 1H, J = 7.6 Hz).

Preparation of 8-carboxymethylsulfany-5-iodo-naphthalene-1-carboxylic acid 8 [21]. **7** (89.6 mg, 0.29 mmol) was added into 10 mL of 5% aqueous NaOH and stirred for 1 h at 80 °C. Then chloroacetic acid (110.2 mg, 1.16 mmol) was added and stirred further for 1 h at 80 °C. The reaction solution was acidified using hydrochloric acid until pH = 1. Yellow precipitate formed was separated by filtration and washed with chloroform. After drying, yellow solid was obtained (90.5%). This compound was insoluble in either water or any organic solvents.

Preparation of acetic acid 7-iodo-benzo[de]thio-chromen-3-yl ester 9 [21]. **8** (79.4 mg, 0.20 mmol) and sodium acetate (24.6 mg, 0.30 mmol) was added into 5 mL of acetic anhydride and refluxed for 4 h. After cooling to rt, 50 mL of chloroform were added and aqueous sodium hydrogencarbonate was slowly added to neutralize. After silica gel chromatography, yellow solid was obtained (83.2%). ^{1}H NMR (600 MHz; $CDCl_3$): δ, ppm 7.744 (d, 1H, J = 8.1 Hz), 7.727 (d, 1H, J = 7.8 Hz), 7.303 (t, 1H, J = 7.8 Hz), 6.942 (d, 1H, J = 7.8 Hz), 6.795 (d, 1H, J = 8.1 Hz), 2.342 (s, 3H).

Preparation of 7-iodo-benzo-[de]thiochromen-3-one 10 [21]. **9** (60.7 mg, 0.17 mmol) was suspended in 10 mL of acetic acid using sonicator. Them, 1 mL of 35% HCl was added and stirred for 5 h at 40 °C under a nitrogen atmosphere. The reaction solution was poured into ice and the precipitate formed was separated by filtration, then washed with water. After silica gel chromatography, yellow solid was obtained (69.7%). ^{1}H NMR (600 MHz; $CDCl_3$): δ, ppm 8.397 (dd, 1H, J = 1.1 7.8 Hz), 8.251 (dd, 1H, J = 1.1 7.3 Hz), 8.003 (d, 1H, J = 7.3 Hz), 7.682 (dd, 1H, J = 7.3 Hz), 7.298 (d, 1H, J = 7.8 Hz).

Preparation of diiodo-perinaphthothioindigo 11 [21]. **10** (111.2 mg, 0.34 mmol) was suspended in 10 mL of ethanol using sonicator. After addition of 10% aqueous NaOH (15 mL), air was bubbled for 8 h at 70 °C. The precipitate formed was separated by filtration, then washed with chloroform, methanol, and water to give **11** as blue solid (35.9%). This compound was insoluble in water and most organic solvents, but slightly soluble in THF. MS (MALDI-TOF; dithranol): m/z = 648.77 $[M + H]^+$, calcd. for $C_{38}H_{30}N_4O_4$, 647.82.

Preparation of $\mathbf{1}_{trans}$. Under argon atmosphere, **11** (21 mg, 32.4 μmol) in 135 mL THF was sonicated for 10 min. Triethylamine (15 mL), $Pd_2(dba)_3$ (1.8 mg, 1.7 μmol), and triphenylarsine (6 mg, 19.5 μmol) were added and the reaction mixture was degassed by three freeze thaw cycles. **12** (10 mg, 14.4 μmol) in THF (10 mL) was added dropwise during 2 min. After stirring for 6 h at 35 °C, half of the solvent was evaporated and the mixture was washed with water and extracted with chloroform. Remaining **11** was removed from the crude by passing through a silica gel column. The crude material was purified by preparative GPC (TSK-GEL G2500HHE, eluent: pyridine) to give pure $\mathbf{1}_{trans}$ (20%). ^{1}H NMR (500 MHz; $C_2D_2Cl_4$/pyridine-d_5): δ, ppm 10.07 (s, 1H, Por *meso*), 9.81 (d, 2H, J = 4.5 Hz, Por β), 9.31 (d, 1H, J = 8 Hz, H_1), 9.23 (d, 2H, J = 4.5 Hz, Por β), 8.92 (d, 2H, J = 4.5 Hz, Por β), 8.83 (d, 2H, J = 4.5 Hz, Por β), 8.69 (d, 1H, J = 8 Hz, H_3), 8.54 (d, 1H, J = 8 Hz, H_{11}), 8.37 (d, 4H, J = 8 Hz, ph), 8.24 (d, 4H, J = 8 Hz, ph), 8.20 (d, 1H, J = 8 Hz, H_4), 8.08 (d, 1H, J = 8 Hz, H_9), 7.98 (t, 1H, J = 8 Hz, H_2), 7.77 (d, 1H, J = 8 Hz, H_5), 7.70 (d, 1H, J = 8 Hz, H_6), 7.68 (t, 1H, J = 8 Hz, H_{10}), 7.62 (H_8, overlaps with pyridine peak), 7.46 (t, 1H, J = 8 Hz, H_7), 4.49 (q, 4H, J = 7.5 Hz, methylene), 1.48 (t, 6H, J = 7.5 Hz, methyl). MS (MALDI-TOF; dithranol): m/z 1086.33 $[M]^+$, calcd. for $C_{64}H_{38}N_4O_6S_2Zn$, 1086.20. UV-vis ($CHCl_3$): λ_{abs}, nm 435, 575, 655.

Preparation of $\mathbf{1}_{cis}$. Pure $\mathbf{1}_{cis}$ 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, ppm 10.08 (s, 1H, Por *meso*), 9.81 (d, 2H, J = 4.5 Hz, Por β), 9.34 (d, 1H, J = 8 Hz, H_1), 9.23 (d, 2H, J = 4.5 Hz, Por β), 8.92 (d, 2H, J = 4.5 Hz, Por β), 8.83 (d, 2H, J = 4.5 Hz, Por β), 8.55 (d, 1H, J = 8 Hz, H_3), 8.41 (d, 1H, J = 8 Hz, H_{11}), 8.37 (d, 4H, J = 8 Hz, ph), 8.24 (d, 4H, J = 8 Hz, ph), 8.21 (d, 1H, J = 8 Hz, H_4), 8.11 (d, 1H, J = 8 Hz, H_9), 7.98 (t, 1H, J = 8 Hz, H_2), 7.78 (d, 1H, J = 8 Hz, H_5), 7.76 (d, 1H, J = 8 Hz, H_6), 7.68 (t, 1H, J = 8 Hz, H_{10}), 7.62 (H_8, overlaps with pyridine peak), 7.49 (t, 1H, J = 8 Hz, H_7), 4.49 (q, 4H, J = 7.5 Hz, methylene), 1.48 (t, 6H, J = 7.5 Hz, methyl). UV-vis (THF): λ_{abs}, nm 441, 527, 572, 625.

Preparation of $\mathbf{13}_{trans}$. Under argon atmosphere, **11** (45.8 mg, 70.6 μmol) in THF (10 mL) and triethylamine (1.0 mL) was sonicated for 10 min. To this solution, trimethylsilylacetylene (34.7 mg, 210 μmol CuI (1.00 mg, 4.23 μmol) and $Pd(PPh_3)_2Cl_2$ (6.0 mg, 8.50 μmol) were added and stirred for 2 h at rt. The solvent was evaporated and the mixture was dissolved in chloroform and washed with saturated aqueous NH_4Cl solution and then water. Almost pure $\mathbf{13}_{trans}$ (purity 99.9%) could be obtained by silica gel chromatography ($CHCl_3$/Hex = 1/1) in 57.4% yield. ^{1}H NMR (600 MHz; $CDCl_3$): δ, ppm 8.63 (m, 4H), 7.80 (t, 2H, J = 7.8 Hz), 7.67 (d, 2H, J = 7.8 Hz), 7.57 (d, 2H, J = 7.8 Hz), 0.342 (s, 18H). MS (MALDI-TOF; dithranol): m/z 588.11 $[M]^+$, calcd. for $C_{34}H_{28}O_2S_2Si_2$, 588.11. UV-vis (toluene): λ_{abs}, nm 652.

Preparation of $\mathbf{13}_{cis}$. Pure $\mathbf{13}_{cis}$ was obtained in the same way with $\mathbf{1}_{cis}$. ^{1}H NMR (600 MHz; $CDCl_3$): δ, ppm 8.65 (d, 4H), 8.51 (d, 4H, J = 7.8 Hz), 7.804 (t, 2H, J = 7.8 Hz), 7.69 (d, 2H, J = 7.8 Hz), 7.54 (d, 2H, J = 7.8 Hz), 0.34 (s, 18H). UV-vis (toluene): λ_{abs}, nm 519.

Preparation of 15. Under argon atmosphere, **10** (4.3 mg, 13.2 μmol) , **12** (10 mg, 14.4 μmol), $Pd_2(dba)_3$ (7.0 mg, 6.6 μmol), $AsPh_3$ (8.1 mg, 26.4 μmol), and triethylamine (0.5 mL) were dissolved in 5 mL of THF and stirred for 1 h at rt. After evaporation, the crude was dissolved in 50 mL of chloroform and washed with NH_4Cl solution, and then water. After silica gel chromatography, green solid was obtained (96.2%). ^{1}H NMR (600 MHz; $CDCl_3$): δ, ppm 10.14 (s, 1H),

9.89 (d, 2H, J = 4.2 Hz), 9.35 (d, 1H, J = 7.8 Hz), 8.90 (d, 2H, J = 4.2 Hz), 8.86 (d, 2H, J = 4.2 Hz), 8.46 (d, 4H, J = 7.8 Hz), 8.36 (d, 1H, J = 7.8 Hz), 8.35 (d, 4H, J = 7.8 Hz), 8.16 (d, 1H, J = 7.8 Hz), 7.88 (t, 1H, J = 7.8 Hz), 7.74 (d, 4H, J = 7.8 Hz), 3.88 (s, 2H). MS (MALDI-TOF; dithranol): m/z = 890.15 $[M]^+$, calcd. for $C_{52}H_{34}N_4O_5SZn$, 890.15.

CONCLUSION

We have successfully prepared a perinaphthothioindigo-porphyrin conjugate **1** with an ethynyl linkage using a Sonogashira coupling reaction of Znethynylporphyrin **12** and diiodo-PNT **11** in 20%. $\mathbf{1}_{trans}$ and $\mathbf{1}_{cis}$ isomers displayed distinct UV-vis absorption spectra and ^{1}H-NMR spectra reflecting stereochemical changes. $\mathbf{1}_{trans}$ yielded a maximum 2PA cross-section value of 2,000 GM at 850 nm measured by femtosecond pulses while $\mathbf{1}_{cis}$ yielded a maximum of 700 GM at the same wavelength. This enhancement is attributed to the more planar structure of $\mathbf{1}_{trans}$ as compared to the slightly twisted structure of $\mathbf{1}_{cis}$. On the other hand, the enhancement factors by the connection of porphyrin to perinaphthothioindigo were found to be 3.5–3.9 by measuring cross-section values of bis(TMS-ethynyl)perinaphthothioindigo as the reference compound. $\mathbf{1}_{trans}$ also successfully isomerized to $\mathbf{1}_{cis}$ upon two-photon excitation at 890 nm employing femtosecond pulses. This suggests that $\mathbf{1}_{trans}$ is a potential material for future 3D optical data storage applications.

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Supporting information

Figures S1–S6 are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

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