A photochromic porphyrin–perinaphthothioindigo conjugate and its two-photon absorption properties†

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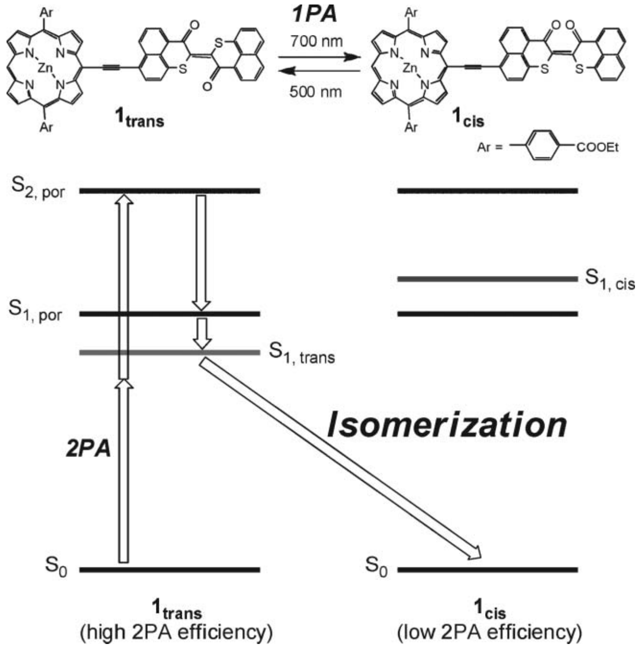
A porphyrin–perinaphthothioindigo conjugate having two-photon absorption cross-sections of ∼2000 GM and ∼700 GM for *trans*- and *cis*-isomers, respectively, was synthesized and exhibited clear photochromic behavior upon one-photon and two-photon excitation.

The search for high density storage devices with photonic capabilities has rapidly gained momentum as top-down-oriented semiconductor technology approaches its limits. So far, the most promising candidates for this purpose are photochromic compounds, which have the ability to reversibly switch structure between two different states upon photoirradiation.[1]

One of the promising approaches to producing high density memory is two-photon absorption (2PA), which has also attracted much attention because of the diverse possibilities for its application in the fields of microscopy,[2] 3D microfabrication,[3] photodynamic therapy[4] and 3D optical memory.[5] A focused laser source is used in 2PA so that a specific and minute volume can be spatially targeted, and thus provide 3D resolution. Potential candidates, such as diarylethenes,[6a,b] indolylfulgides[6c] and azobenzenes,[6d] have been investigated as two-photon photochromic storage media. However, these compounds still lack a high two-photon absorption efficiency. Diarylethene derivatives have a maximum 2PA cross-section value, $\sigma^{(2)}$, of ∼44 GM[6a] at 770 nm, while indolylfulgide has a maximum value of 1030 GM[6c] at a shorter wavelength of 775 nm.

We have previously found that acetylene-linked bis(pyridylethynylphenyl)[7] and bisporphyrins[8] are attractive for 2PA applications because they exhibit large $\sigma^{(2)}$ values. This excellent 2PA property is attributed to the combination of the acetylene π-bridge and the large π-conjugation of the porphyrin, which provides the pathway for electronic communication between the porphyrins.[8,9] However, after two-photon excitation to the zinc porphyrin's S$_2$ state (around 2.9 eV), the molecule rapidly relaxes to its S$_1$ state (2.1 eV), which is insufficient to induce the isomerization of photochromic compounds, such as diarylethenes, azobenzenes and fulgides. On the other hand, the excited state of the *trans*-isomer of a lone perinaphthothioindigo (PNT),[10] which has a HOMO–LUMO absorption band around 630 nm (2.0 eV), is lower than that of the zinc porphyrin monomer S$_1$ state (∼600 nm). This unique combination permits the switching of the PNT moiety after two-photon excitation of the zinc porphyrin, followed by the intramolecular energy transfer from the zinc porphyrin to the PNT moiety. In this work, in order to produce a more efficient two-photon-absorbing photochromic compound, a perinaphthothioindigo was attached to a zinc porphyrin using an acetylene bond to give compound **1** (Scheme 1). There have been several reports on porphyrins linked to a photochromic moiety for switching.[11] In these cases, the switching was still performed under one-photon irradiation conditions at the absorption wavelengths of the photochromic component.

Scheme 2 shows a synthetic route to compound **1**. Ethynylporphyrin **2** was synthesized according to a previous report.[12] Diiodo-PNT **3** was prepared according to the literature.[13] A palladium-catalyzed Sonogashira coupling of **3** with **2** gave compound **1** as the main product (ESI†). One of the iodines in **3** was replaced by hydrogen due to reduction, and a small amount of bisporphyrin-substituted PNT was obtained. This is currently being prepared by a different route on a larger scale, and details



Scheme 1 Photochromic properties of compound **1** *via* one-photon absorption (1PA) and 2PA.

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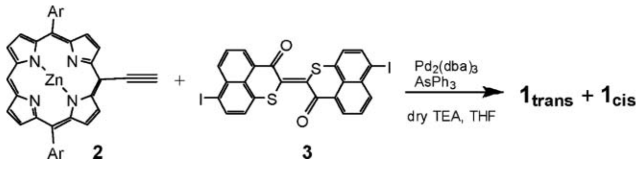

Scheme 2 Synthesis of compound **1**.

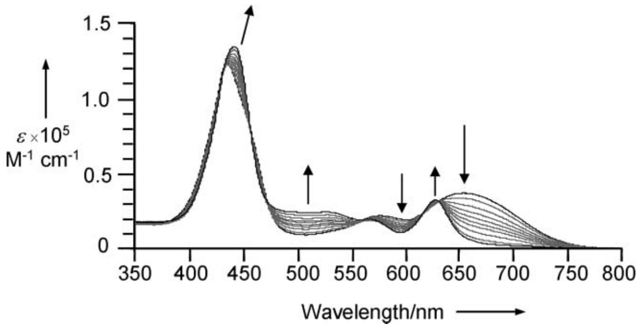

Fig. 1 Photoisomerization of completely *trans*-compound, $\mathbf{1_{trans}}$, to completely *cis*-compound, $\mathbf{1_{cis}}$, in THF by photoirradiation at >700 nm using a Xe lamp with a cut off filter.

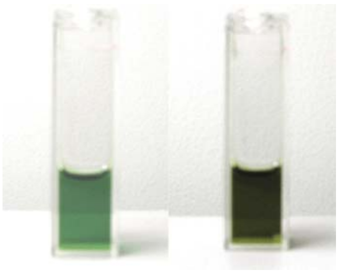

Fig. 2 Colour images of $\mathbf{1_{trans}}$ (left) and $\mathbf{1_{cis}}$ (right) (both solutions 0.04 mM in THF).

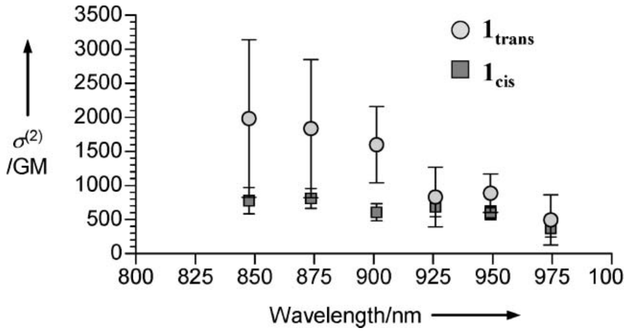

Fig. 3 2PA spectra of $\mathbf{1_{trans}}$ (○) and $\mathbf{1_{cis}}$ (■) in THF.

will be reported elsewhere. After the reaction, **1** existed as a mixture of its *trans*- ($\mathbf{1_{trans}}$) and *cis*- ($\mathbf{1_{cis}}$) stereoisomers. The completely *trans*-compound, $\mathbf{1_{trans}}$, was initially isolated from the mixture using preparative GPC in pyridine (20% yield). It exhibited a strong Soret band at 435 nm and a broad *trans*-PNT absorption at 655 nm. The peak maximum of the unsubstituted *trans*-PNT occurred around 630 nm.[2] Isomerization using one-photon irradiation was examined to investigate the photochromic properties of this compound. Pure $\mathbf{1_{cis}}$ can be generated from its *trans*-stereoisomer by irradiation at >700 nm with a quantum yield of 5%, as shown in Fig. 1. The broad *trans*-PNT band, occurring around 655 nm, gradually reduces in intensity, and a sharp porphyrin Q-band appears at 625 nm. Moreover, the Soret band is bathochromically shifted to 440 nm, and absorption in the 500 nm region, which corresponds to the absorption of the *cis*-isomer,[10] increases in intensity. $\mathbf{1_{trans}}$ can be generated from its *cis*-isomer by irradiation at 500 nm with a 78% conversion and a quantum yield of 15%. In both photoisomerization experiments, the absorption spectra changed, while also passing through clear-cut isosbestic points at 432, 457, 472, 561, 615 and 630 nm. Fig. 2 shows colour images of $\mathbf{1_{trans}}$ and $\mathbf{1_{cis}}$ in THF. $\mathbf{1_{trans}}$ was found to be more stable than $\mathbf{1_{cis}}$. When the a $\mathbf{1_{cis}}$ solution was kept in the dark at rt for a period of 7 d, no change was observed in its UV-vis spectrum, showing that it is relatively thermally stable. On the other hand, $\mathbf{1_{trans}}$ exhibited no change in its UV-vis spectrum when kept in the dark for several months. ^{1}H NMR spectra of $\mathbf{1_{trans}}$ and $\mathbf{1_{cis}}$ exhibited completely unique peaks for the naphthalene protons closest to the switching alkene bond of the PNT, which are the most sensitive to stereochemical changes during isomerization (SI).

The 2PA cross-section values of **1** in THF were determined by an open aperture Z-scan method, employing wavelength-tunable 130 fs pulses with a repetition frequency of 1 kHz.[7,8] The 2PA cross-section maxima for both isomers appeared around 850 nm, which was almost twice as long as the Soret band wavelength of the porphyrin part of the molecule, with values of 2000 GM for $\mathbf{1_{trans}}$ and 700 GM for $\mathbf{1_{cis}}$ (Fig. 3). The value for $\mathbf{1_{trans}}$ is two orders of magnitude larger than that of the ethynylporphyrin monomer ($\sigma^{(2)}$ of **2** > 20 GM). As observed in the linear absorption spectra, strong electronic communication between the individual moieties (the porphyrin and the PNT) led to a significant enhancement in the 2PA of **1**. Unfortunately, due to low solubility, the $\sigma^{(2)}$ of **3** was difficult to measure.

To the best of our knowledge, compound **1** bears the largest 2PA cross-section value reported for photochromic compounds at near-infrared (NIR) wavelengths.‡ In $\mathbf{1_{cis}}$, the PNT carbonyl units are in close proximity, resulting in a distortion of the PNT unit due to steric hindrance, thereby disrupting the electronic communication throughout the entire molecule (Fig. 4). On the other hand, in $\mathbf{1_{trans}}$, these carbonyl units are located on opposite sides of the PNT, allowing an almost planar structure. Increased conjugation enhances the $\sigma^{(2)}$ value in the *trans*-conjugate system. Encouraged by these results, we proceeded to investigate isomerization using two-photon excitation by employing a Ti:sapphire laser using 200 fs pulses with a peak intensity of 0.53 GW cm^{-2} and a beam

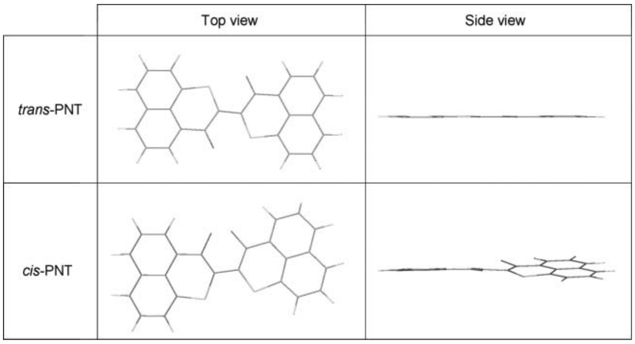

Fig. 4 Optimized structures of *trans*- and *cis*-PNT, obtained by AM1 calculations.

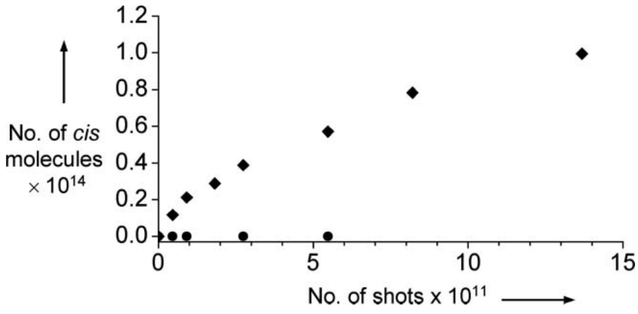

Fig. 5 Time courses in the photoisomerization of $\mathbf{1}_{\mathbf{trans}}$ to $\mathbf{1}_{\mathbf{cis}}$ (◆: 1 mL of a rapidly stirred 2.5 μM THF solution in a 1 cm cell) and **3** (●: 0.4 μM THF solution) using two-photon excitation with 200 fs pulses at 890 nm. The progress of the isomerization was monitored at 505 nm.

waist of around 40 μm at a NIR wavelength of 890 nm. Fig. 5 shows the progress of the isomerization of $\mathbf{1}_{\mathbf{trans}}$ to $\mathbf{1}_{\mathbf{cis}}$ by two-photon irradiation using the above-mentioned conditions. After irradiating 4.6 × 10^{10} shots for a period of 10 min, around 2 × 10^{-11} mol (7% conversion) of $\mathbf{1}_{\mathbf{trans}}$ had been converted to $\mathbf{1}_{\mathbf{cis}}$. Using the same experimental conditions, it would take around 0.2 ms to isomerize the $\mathbf{1}_{\mathbf{trans}}$ molecules within a spherical volume of 40 μm diameter. This would enable a writing frequency of around 5 kHz, which would strongly depend on the peak power and molecular density.

In summary, we have successfully synthesized a porphyrin–perinaphthothioindigo conjugate exhibiting an efficient two-photon absorption and demonstrated the switching of a PNT moiety *via* both two-photon excitation and one-photon irradiation. It would be interesting to observe the performance of compound **1** in a solid matrix, *e.g.* a polymer medium, to confirm its applicability to 3D optical data storage, and this project is now being actively pursued.

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Notes and references

‡ Even if we consider the experimental errors, the maximum value that can be obtained at the other wavelength of 900 nm is 1600 ± 560 GM (2160 ∼ 1040 GM), which is still larger than the 1030 GM reported for indolylfulgide.

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