Design of two-photon absorbing materials for molecular optical memory and photodynamic therapy

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Molecular design of two-photon absorption materials toward three dimensional high-density optical memory and highly selective photodynamic therapy at deep tissue sites is introduced. Functionality such as photochromism was attached to highly efficient 2PA materials. In the case of PDT, solubilization of the 2PA agents in water without any aggregation is important.

Introduction

Two-photon absorption (2PA) involves excitation of a molecule promoted by the simultaneous absorption of two photons at the same or different wavelength. Since 2PA is quadratically proportional to the incident light intensity, the maximum absorption occurs at the focal point of the laser beam allowing localized excitation of a small volume at the deep site of materials. This characteristic feature opens the way for a variety of optical applications such as photodynamic therapy (PDT),[1–3] three dimensional (3D) optical data storage,[4–7] and optical limiting.[8]

The search for molecules exhibiting large 2PA cross-section values ($\sigma^{(2)}$) has been of interest since the first prediction was made by Göppert-Mayer[9] and the experimental proof was done by Kaiser and Garrett.[10] In 1990s, new classes of molecules with $\sigma^{(2)}$ values were reported and strategies employing donor/acceptor sets with a π-conjugation system in a symmetric (D-π-D or A-π-A)[11] or asymmetric (D–π–A) arrangement[12] have been proposed. It is known that monomeric porphyrins show only small $\sigma^{(2)}$ values (less than 100 GM where 1 GM = 10^{-50} cm^4 s molecule^{-1} photon^{-1}) when measured using femtosecond pulse lasers.[13] Recently, several π-conjugated porphyrins and related compounds including phthalocyanines having large $\sigma^{(2)}$ values have been vigorously synthesized.[14–20] Other amazing compounds exhibiting strong 2PA such as macrocyclic thiophenes,[21] nanoparticles,[22] and others[23] have been also reported as potential 2PA materials.

In 2003, we found that the self-assembled conjugated porphyrin **1** (Scheme 1) exhibited a large $\sigma^{(2)}$ value of 7600 GM measured by the femtosecond Z-scan method, which was the largest among the reported values measured using femtosecond pulses.[18] The large 2PA enhancement is attributed to three factors; (1) extension of π-conjugation over two porphyrins using the acetylene bridge, (2) molecular polarization induced by the asymmetric

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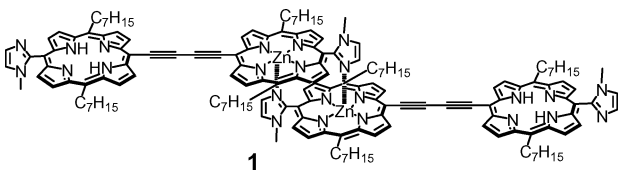

Scheme 1 Structure of acetylene-bridged porphyrin **1** exhibiting a large $\sigma^{(2)}$ value of 7600 GM.

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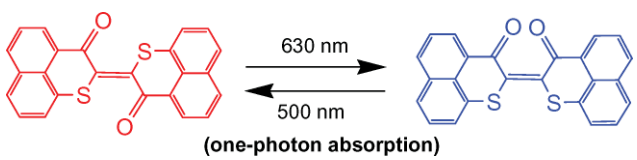
arrangement of zinc- and freebase porphyrins as donor and acceptor, respectively, and (3) complementary coordination of imidazolyl to zinc. Pioneering studies on the development of acetylene-connected conjugated porphyrins have been reported by Therien's and Anderson's groups.[24]

Since this discovery, we have studied not only 2PA materials with larger $\sigma^{(2)}$ values but also 2PA PDT for deep cancer treatment and the design of a two-photon photochromic molecule for 3D optical data storage. This article briefly reviews our recent studies on the design of two-photon absorbing materials for 3D molecular optical memory and PDT.

Design of photochromic molecule with high 2PA efficiency

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.[25] This change of the property can be used to record information as the photon-mode optical memory. Although several studies on 3D optical memory using photochromic compounds have been reported, 2PA efficiencies of these molecules are still low. The maximum $\sigma^{(2)}$ values were ~44 GM[26] and 1030 GM[27] for diarylethene derivatives and indolylfulgide, respectively. It is necessary to improve the 2PA efficiency because a smaller size and lower power laser system is desired for practical use.

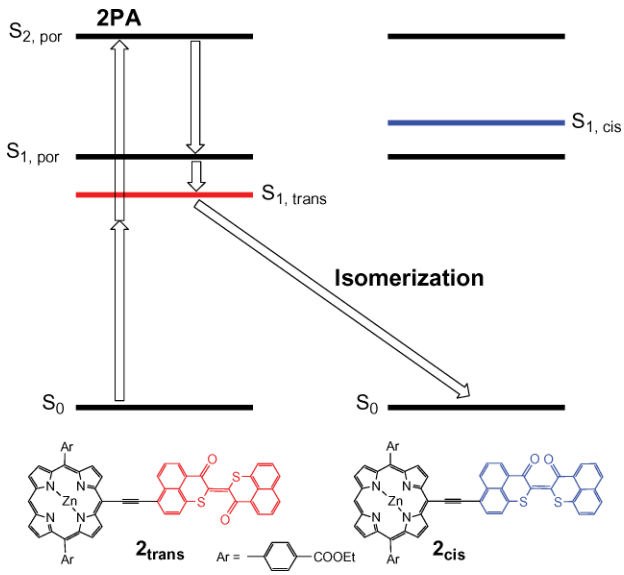
As mentioned above, we previously found that an acetylene linkage between porphyrins[18,28] enhanced significantly the 2PA efficiency. Following a similar line, we designed a new photochromic molecule having a high 2PA efficiency by linking porphyrin and photochromic π-systems using an acetylene bridge. In the molecular design, it should be remembered that the energy level of the photochromic moiety should be lower than the S_1 state of the zinc porphyrin part because this excitation energy, which is generated by rapid relaxation after the two-photon excitation to the porphyrin S_2 state, 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)[29] is lower than that of zinc porphyrin, transformation of the PNT part is expected after two-photon excitation of the zinc porphyrin moiety (Scheme 2). In this way, PNT attached to zinc porphyrin using an acetylene bond was obtained as a more efficient two-photon absorbing photochromic compound **2**.[30]



Scheme 2 Photoisomerization of PNT.

Optical properties of compound 2[30]

The *trans* compound $\mathbf{2}_{trans}$ exhibited a strong Soret band at 435 nm and a broad absorption at 655 nm originating from porphyrin and *trans*-PNT units, respectively. Pure $\mathbf{2}_{cis}$ can be generated from its *trans*-stereoisomer by one-photon irradiation at > 700 nm with a quantum yield of 5% (Scheme 3). As shown in Fig. 1, the broad *trans*-PNT band at around 655 nm gradually reduces in its intensity, and a sharp porphyrin Q-band appears at 625 nm, whereas the absorption in the region of 500 nm that corresponds to the absorption of the *cis*-unit[29] increases in its intensity. $\mathbf{2}_{trans}$ can be generated from its *cis*-isomer by irradiation at 500 nm with a quantum yield of 15%. Fig. 2 shows colour images of $\mathbf{2}_{trans}$ and



Scheme 3 Two-photon photoisomerization of **2**.

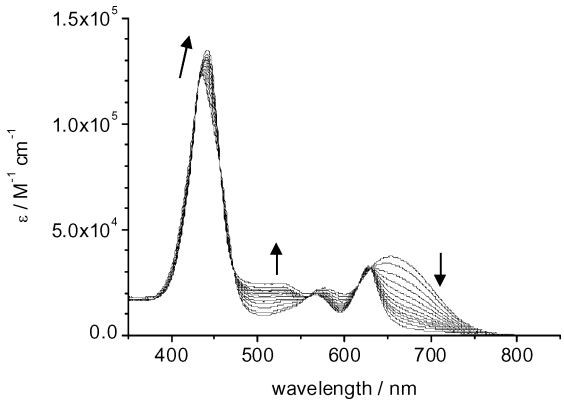


Fig. 1 Photoisomerization of the completely *trans* form, $\mathbf{2}_{trans}$, to the completely *cis* form, $\mathbf{2}_{cis}$, in THF by photoirradiation at >700 nm.

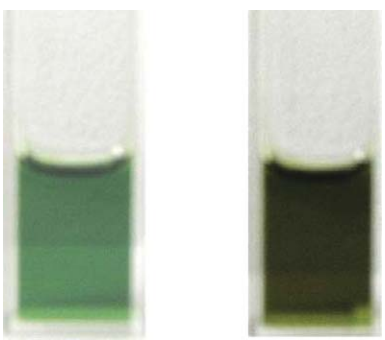


Fig. 2 Colour images of $\mathbf{2}_{trans}$ (left) and $\mathbf{2}_{cis}$ (right) in THF.

$\mathbf{2}_{cis}$ in THF. When the $\mathbf{2}_{cis}$ solution is kept in the dark at rt for a period of 7 d, no change was observed in the UV-vis spectrum, showing that it is relatively thermally stable. On the other hand, $\mathbf{1}_{trans}$ exhibited no change in the UV-vis spectrum when kept in the dark for several months.

The $\sigma^{(2)}$ values of **2** were determined by a femtosecond open-aperture Z-scan method. The 2PA maxima for both isomers appeared around at 850 nm with a value of 2000 GM for $\mathbf{2}_{trans}$ and 700 GM for $\mathbf{2}_{cis}$ (Fig. 3). The value for $\mathbf{2}_{trans}$ is two orders of magnitude larger than that of the ethynylporphyrin monomer (> 20 GM). The strong electronic communication between porphyrin and PNT probably leads to a significant enhancement of 2PA in **2**.

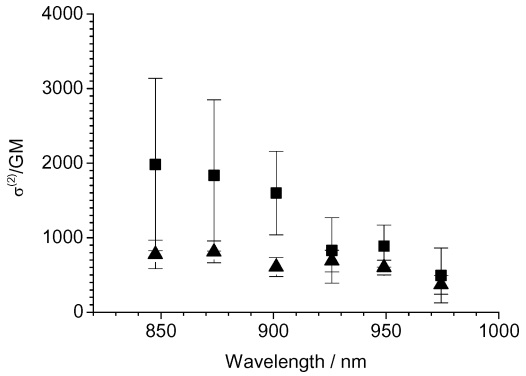


Fig. 3 2PA spectra of $\mathbf{2}_{trans}$ (squares) and $\mathbf{2}_{cis}$ (triangles) in THF.

Finally, photoisomerization by the two-photon irradiation was investigated. Fig. 4 shows the progress of the isomerization of $\mathbf{2}_{trans}$ into $\mathbf{2}_{cis}$ on two-photon irradiation using 200 fs pulses with a peak intensity of 0.53 GW/cm^2 and a beam waist around 40 μm at 890 nm, where no one-photon absorption exists. After irradiating 4.6×10^{10} shots for a period of 10 min, around 2×10^{-11} moles of $\mathbf{2}_{trans}$ were converted to $\mathbf{2}_{cis}$ (7% conversion). This result shows that it might take around 0.2 ms to isomerize the $\mathbf{2}_{trans}$ molecules within a spherical volume with a diameter of 40 μm using the same experimental conditions. In other words, the writing frequency is around 5 kHz, although this strongly depends on the peak power and molecular density. No decomposition was observed for a long time under the laser experiments both in Z-scan and two-photon photoisomerization as well as one-photon photoisomerization. The compound in the solid state is also stable without photobleaching.

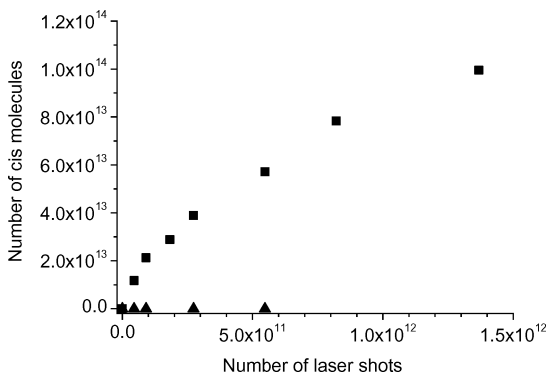


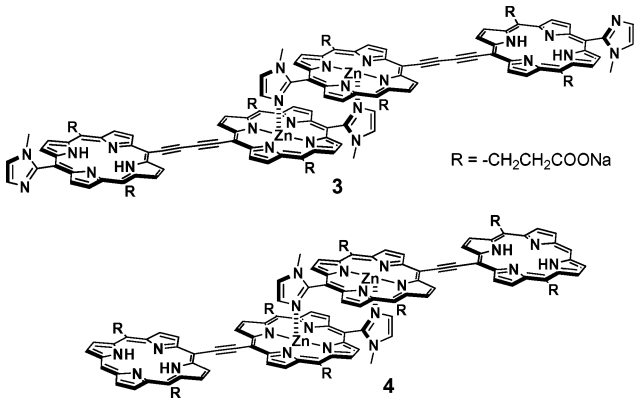
Fig. 4 Time courses of the photoisomerization of $\mathbf{2}_{trans}$ to $\mathbf{2}_{cis}$ (squares; 1 mL of 2.5 μm THF solution in a 1 cm cell) and diode PNT (triangles; 0.4 μm THF solution) using two-photon excitation with 200 fs pulses at 890 nm. The progress of isomerization was monitored at 505 nm.

Application to photodyanamic therapy

Photodynamic therapy (PDT)[31] is a local light-activated treatment of tumors, particularly skin, esophageal, and lung cancers. In the photodynamic reaction, a photosensitizer promoted to the excited singlet state upon photoirradiation decays to the triplet state and generates singlet oxygen through intermolecular triplet-triplet energy transfer to ground state oxygen. The photosensitizer, which is usually porphyrinoid, localizes to cancer parts with relatively high selectivity (in the case of Photofrin, which is one of the currently available photosentitizer composed of hematoporphyrin, the difference in photosentitizer concentration between healthy cells and cancers becomes largest around 48 hours after the injection) and PDT provides a gentle treatment method for patients without surgery. However, the penetration depth of visible light used in currently available PDT is limited to surface due to absorption and scattering by biological tissue, meaning that this method cannot be applied to the treatment of deep cancers. However, the penetration depth can be improved by shifting the excitation wavelength to longer wavelength and the light in the range of near-infrared (NIR) region provides better penetration into the tissue. In this respect, 2PA is suitable because porphyrin compounds have strong one-photon absorption bands called Soret bands between 400 and 500 nm, corresponding to the combined energy of two photons in the wavelength range from 800 to 1000 nm, which is just laid in the optical window for biological tissue.[32] Another advantage of the use of 2PA is its quadratic dependence on the laser intensity allowing high spatial selectivity by focusing the laser beam at the target point. This high selectivity prevents damages to healthy tissue. However, 2PA efficiencies of the photosensitisers used for PDT are too low to apply for two-photon PDT. For example, the $\sigma^{(2)}$ value of Photofrin was determined as 7.4 GM at 850 nm and low two-photon PDT effect was reported.[33] Recently, some groups have reported two-photon PDT using photosensitisers with high $\sigma^{(2)}$ values.[34–38] *In vivo* as well as *in vitro* two-photon PDT studies using butadiyne-bridged hydrophilic porphyrin dimers with large $\sigma^{(2)}$ values were reported.[37] On the other hand, singlet oxygen generation *via* two-photon excitation of the two-photon absorbing part connected to porphyrin has been investigated.[38]

We first reported that conjugated porphyrin array **1** exhibited a very large $\sigma^{(2)}$ of 7600 GM at around 870 to 890 nm measured using femtosecond pulses. So, we decided to apply this compound to 2PA-PDT and water-soluble compound **3** having a carboxylic group instead of heptyl at each *meso*-position was designed and synthesized (Scheme 4).[34] Monoacetylene-linked compound **4**, obtained from a direct hetero-coupling reaction between donor zinc porphyrin and acceptor freebase porphyrin, was also synthesized to improve the total yield.

The $\sigma^{(2)}$ values of **3** and **4** in water were measured by a femtosecond open aperture Z-scan method (150 fs) at 850 nm to be 7500 and 7900 GM, respectively, which were almost same as the value of **1** in chloroform, indicating no solvent effect on the $\sigma^{(2)}$ value.



Scheme 4 Structures of water-soluble porphyrin arrays **3** and **4**.

The singlet oxygen generations in H_2O were confirmed by measuring its emission spectrum around 1270 nm. The time-resolved profiles under one-photon irradiation conditions with non-focused 5 ns pulses at around 550 nm are shown in Fig. 5,[34] where the fast rise components were observed and decayed single exponentially with a life time of ~2 μs.[39]

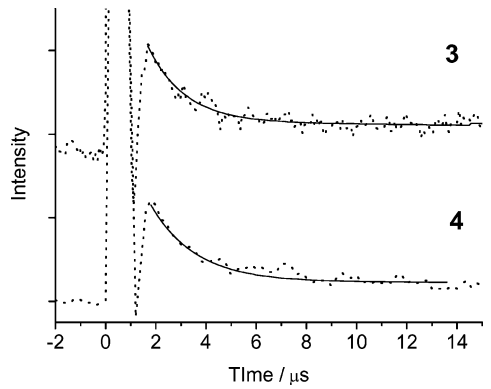


Fig. 5 Time-resolved emission profiles at 1270 nm in H_2O.

To examine the photocytotoxicity of **3**, *in vitro* experiments with Hela cells were performed under one-photon excitation conditions with a 500 W halogen lamp over 500 nm with a power density of 50 mW cm^{-2} as the light source.[34] Cell survivals after photoirradiation with **3** and hematoporphyrin (Hp) as the reference decreased with increasing the reagent concentration (Fig. 6). No PDT effect was observed at concentrations lower than 10^{-8} M and in the control experiment without the reagent. No significant difference in the photocytotoxicity between **3** and Hp was observed, indicating that **3** has a photodynamic efficiency equivalent to Hp. The photocytotoxicity of **4** for Hela cells was also examined by microscopic observation of the cell dying upon one-photon excitation with a CW diode laser (671 nm) with a power density of 1.8 W cm^{-2}.[34] As shown in Fig. 7, the leakage of cytoplasm and the formation of blebs on the cell surface were observed. The exposure time until cell death, which was judged by the trypan blue staining method, was reduced with increasing the concentration of **4**. No cell death was observed without **4**, even after 2 hours irradiation (total irradiation energy >12 960 J cm^{-2}).

Further, we reported a different approach to building a water-soluble two-photon-absorbing photosensitizer **5** that was composed of one bisacetylene-linked bisporphyrin as a 2PA

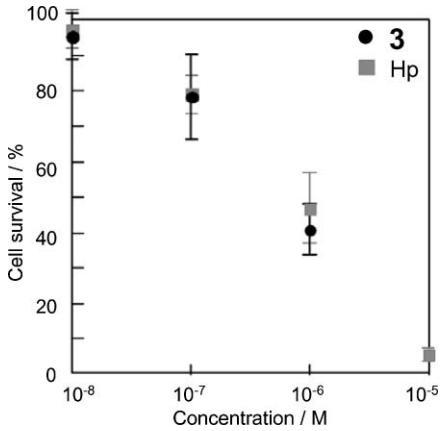


Fig. 6 Photocytotoxicity of **3** and hematoporphyrin (Hp) for Hela cells. Cell survival percentages are plotted *versus* concentration.

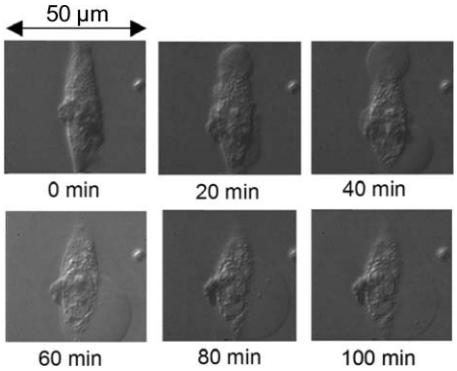
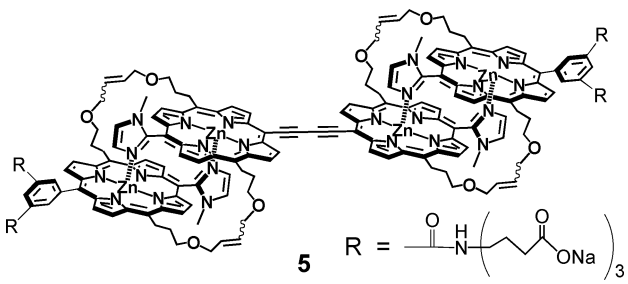


Fig. 7 Time course of cell dying for Hela cell upon photoirradiation with **4**.

component connected by two monomeric porphyrins having total twelve carboxylate groups as water-solubilizing parts through zinc-imidazolyl coordination (Scheme 5).[35,36] To prevent aggregations in water, a dendritic-type substituent was attached. In contrast to the previous compounds, the hydrophilic groups in **5** are larger in number and located only at both ends of the array. These factors will control the drug delivery property.



Scheme 5 Structure of water-soluble porphyrin array **5**.

The effective 2PA cross section value $^{eff}\sigma^{(2)}$, which contains the contribution of excited state absorption (ESA) using an open-aperture Z-scan technique with 5 ns laser pulses, was measured at non-resonant wavelengths from 780 to 920 nm in water.[35] Fig. 8 shows the 2PA spectra of **5** in water. **5** yielded $^{eff}\sigma^{(2)}$ values of 28 000 GM at 780 nm and 33 000 GM at 890 nm. Although the values obtained using nanosecond pulses are usually larger than

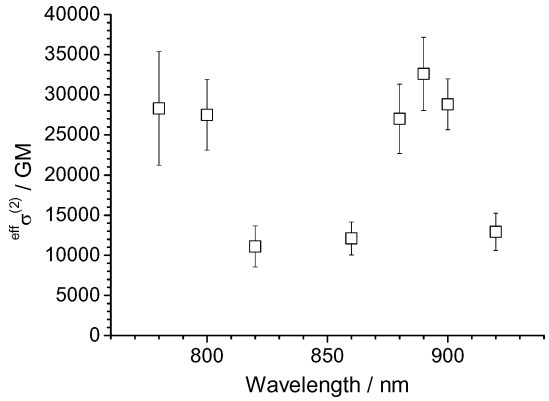


Fig. 8 2PA spectra of **5** in water.

the femtosecond data due to the ESA, the values obtained for **5** are obviously larger than those of related compounds employing the same nanosecond system. The $^{eff}\sigma^{(2)}$ value of **5** is almost three orders of magnitude larger than H_2TPP (29 GM), 150-fold that of zinc-imidazolyl-coordinated porphyrin dimer (190 GM), and twice that of an alkyl *meso*-substituted bisporphyrinatozinc (14 000 GM).[40]

The amount of singlet oxygen generated upon two-photon irradiation of **5** was determined[35] using ADPA (anthracene-9,10-dipropionic acid), which reacts with singlet oxygen to give an endoperoxide. A solution of **5** with ADPA in D_2O was irradiated with focused 5 ns pulses at 780 nm (3.0 mJ). As shown in Fig. 9, photobleaching of anthracene absorption from 350 to 400 nm was observed. Each D_2O solution of **5** with ADPA, TPPS (tetrasulfonatophenylporphyrin) with ADPA, and ADPA alone was irradiated with focused 5 ns pulses at 780 and 890 nm with pulse energies of 3.0 and 2.5 mJ, respectively. Figs. 10 and 11 show the changes in the ADPA absorption peak at 379 nm upon two-photon irradiation for both wavelengths at 780 nm and 890 nm, respectively. Almost no change was observed in the solutions without **5**.

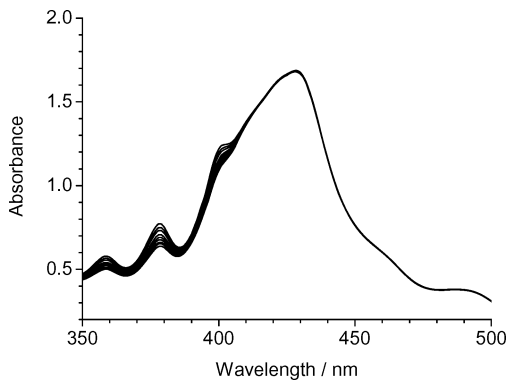


Fig. 9 Photobleaching experiments of ADPA with **5** after two-photon excitation at 780 nm in D_2O.

Finally, the femtosecond PDT experiment using Hela cells with two-photon irradiation was conducted.[36] Hela cells incubated with **6** on a glass slide were irradiated for 5 min with 100 fs focused-pulses at 780 nm with a repetition rate of 76 MHz and an average power of 2 mW corresponding to an average of 600 mJ/cell. Fig. 12 shows photographs of Hela cells. A Hela cell at the center in

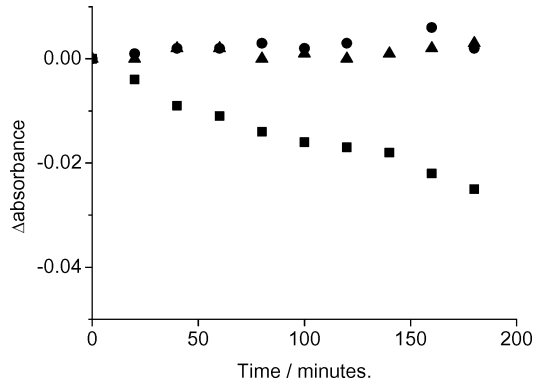


Fig. 10 Photobleaching of the ADPA peak at 379 nm after two-photon excited singlet oxygen photosensitization at 780 nm: no photosensitizer (triangles), TPPS (circles), and **5** (squares) in D_2O.

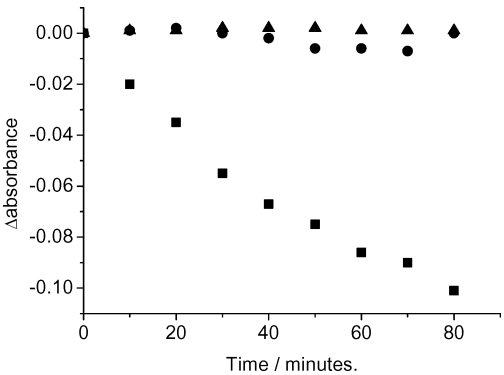


Fig. 11 Photobleaching of the ADPA peak at 379 nm after two-photon excited singlet oxygen photosensitization at 890 nm: no photosensitizer (triangles), TPPS (circles), and **5** (squares) in D_2O.

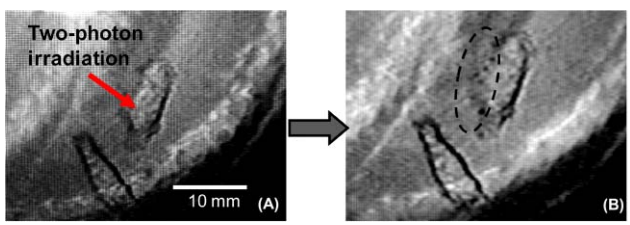


Fig. 12 Photographs of Hela cells incubated with **5** before (A) and after (B) two-photon excitation with 100 fs pulses at 780 nm.

Fig. 12(A) was selectively irradiated on the position marked by an arrow. After the irradiation, the degradation of the cell membrane was observed (Fig. 12(B)). The non-irradiated cell at lower site was intact. Control experiments without **5** and with Hp also showed no PDT effect.

All the photosensitizers used in the PDT studies could be handled as usual porphyrins without light shielding in solid and solution states and recognizable photobleaching was not observed as seen in Fig. 9, where almost no decrease in the porphyrin Soret band was observed.

Conclusions

In order to apply 2PA materials to practical use, functionality such as photochromism should be given to highly efficient 2PA materials or, in the case of PDT, water-solubilization of the 2PA

agents is needed. In the former case, 2PA is enhanced not only by the expansion of π-conjugation but also a donor/acceptor relation induced by the connection of porphyrin and the functional chromophore through ethynyl bonds. In the latter case, one of the most important points in a molecular design may be to prevent aggregation of the agent in water by attaching bulky substituents. In both cases, it is most important that the 2PA wavelength must not overlap with the red-shifted one-photon absorption of the HOMO-LUMO by enlarging the π-conjugation system too much. This is the point to be reminded in improving the 2PA efficiency by controlling the effect of the resonance enhancement.

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