Two-Photon Sensitized Polymerization of Vinyl Ethers via Electron Transfer of ZnTTBP

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Zinc 9,18,27,36-tetrakis(p-tolyl)tetrabenzoporphyrin (ZnTTBP) was synthesized. The photo-physical process was determined by absorption and fluorescence spectra, fluorescence lifetime measurements, and transient absorption measurements. ZnTTBP has absorption of Q-band at 620nm, Soret at 420nm, and the fluorescence emission and T-T absorption were observed at 630nm and 480nm, respectively. Sensitization to a photo acid generator (PAG) does not occur from one-photon excited S1 or T1 states, while irradiation of the mixture of ZnTTBP and the PAG by 635nm and 490nm light changes the absorption spectrum due to the generation of ZnTTBP cation. This result suggests electron transfer from ZnTTBP to PAG occurred. Isobutyl vinyl ether was polymerized by the acid generated via ZnTTBP sensitization.

Keywords: Two-photon sensitization, Porphyrin, Electron transfer, Photo acid generator

1. Introduction

Photochemical process via two-photon excitation have been attracting much attention because they are applicable to three-dimensional imaging, three-dimensional optical memory and three-dimensional lithographic microfabrication due to high three-dimensional spatial resolution and tight volume confinement in materials.

Two-photon irradiation can locally induce polymerization or cross-linking in a resin. Applicable to three-dimensional lithographic micro-fabrication where the non-irradiated portions of a resin were removed by dissolution in a solvent and microstructure was left behind. Two-photon excitation polymerization has advantage relative to other microfabrication, because it can generate complex three-dimensional structure in a single exposure/development cycle.[1]

The density of stored optical information depends upon the wavelength. For example, the information density which can be stored in one-dimensional space is proportional to 1/λ. This relation suggests that wavelength must be shorter in order to increase information density but there is a limitation for this method. However, three-dimensional optical memory makes it capacities and requests shorter access time. Writing has been three-dimensional optical memory is demonstrated in photopolymer, photorefractive and photochromic materials.[2-4]

Two-photon excitation used in these techniques was basically non-linear system two-photon absorption in these systems depends on the square of the input light density and so they this two-photon absorption requires very large absorption cross-section and high-power beam. However, two-photon absorption via step-by-step transition requires only small power density of light, because they have enough long lifetimes with this technique, Xe-Lamp or low-power CW laser are enough to use as light source. Therefore, this step-by-step two-photon process was more useful than using non-linear absorption carried out only by high-power pulse laser, for example, a Nd:YAG laser or a Ti:sapphire laser.

In this work, we used sensitization from two-photon excited state of a dye, and
generating acid from sensitization to a photo acid generator (PAG). We attempted to polymerize vinyl ethers by this acid. We prepared porphyrin called ZnTTBP as the dye. Porphyrins generally has long lifetime of exited triplet state, which enough to carry out two-color, two-photon excitation.

2. Experiment

2.1. Materials

Chemical structure of ZnTTBP is shown in Fig. 1. This compound was prepared by heating the mixing of sodium (p-tolyl) acetate, potassium phthalimide and zinc acetate for four hours at 370°C. Product was purified by Soxhlet extraction followed by column chromatography. The structure of the products was characterized by UV absorption spectra, \(^1\)H-NMR and FAB-Mass. [5-6]

![Chemical structure of ZnTTBP](image)

Triphenyl sulfonium trifluoromethanesulfate used as a photo acid generator (PAG), was used as supplied from Midori Kagaku. Isobutyl vinyl ether (IBVE) was obtained from Tokyo Chemical Industry, and was distilled before the use for polymerization.

2.2. Measurements

2.2.1. Spectroscopic measurements

Absorption spectra were measured using a JASCO UV-560 spectrophotometer. Fluorescence emission spectra were measured with a JASCO FL-6200 spectrophotometer. The absorbance of all sample solutions was kept constant to be 0.25 at the excitation wavelength during the fluorescence measurements.

2.2.2. Fluorescence lifetime measurement

Fluorescence lifetime measurements were carried out by the single-photon-counting method. ZnTTBP was excited at 420nm by a dye laser pumped by a nitrogen laser (Nihon Laser LN-100 pulsewidth of 300ps). The laser dye, LD-423, was obtained from Exiton Co. Sample solutions for the fluorescence lifetime measurements were argon purged just before use.

2.2.3. Laser flash photolysis

For laser flash photolysis, sample solutions were excited by third harmonics (355nm) of a Nd:YAG laser(HOYA Continuum 10Hz, 10ns). Monitoring light from a Xe-lamp (HAMAMATSU photonics C7535) through the sample cell, was cut below 430nm off with an Asahi Techno Glass Y-43 cut filter. The monitoring light through passing cut filter was monochromated and detected by a photomultiplier, whose output signal was recorded on a digitizing oscilloscope (SONY Tektronix TDS 3012). All sample solutions were degassed by a freeze-pump-thaw cycle for 5 times and sealed in quartz cells.

2.2.4. Gel permeation chromatography of poly IBVE

Molecular weight of poly IBVE was measured by gel permeation chromatography (TOSOH GPC8020) with GPC column (TOSOH TSK-GL 2500 and 3000) using Tetrahydrofuran as an eluent. Calibration for the molecular weight was carried out by using monodisperse polystyrene as standard.

2.3. Reaction

2.3.1. Two-photon irradiation

The sample solution in a quartz cell was photoirradiated with the same apparatus as the laser flash photolysis system but using a dye laser (DCM 635nm) pumped with the second harmonics of a Nd:YAG laser(HOYA Continuum 10Hz, 10ns). The laser dye, DCM, was obtained from Exiton Co. The Xe-lamp light below 470nm was cut by an Asahi Techno Glass Y-47 cut filter.

2.3.2. Two-photon sensitized polymerization of iso-Butyl vinyl ether

A sample solution of isobutyl vinyl ether (IBVE) (2ml), PAG (0.0071g) was added 2ml of ZnTTBP in CH\(_2\)Cl\(_2\) such that the absorbance at Q-band was as large as 1.0. The PAG content was 1/1000 to the IBVE. The sample solution
in a quartz cell was argon purged before use and then photo irradiated with the same apparatus as described above.

3. Results and discussion

3.1. Photophysical process of ZnTTBP

Absorption spectrum of ZnTTBP in acetone (10⁻⁵mol/l) was shown in Fig.2. Q-band at 620nm and the Soret band at 420nm are observed. Those absorption corresponds to the transition of S₀-S₁, S₀-S₂, respectively.

Fig.3 shows the fluorescence spectra of the ZnTTBP. A fluorescence band at 630nm corresponds to the transition from S₁ to S₀, which is the mirror image of the Q-band absorption. In addition to the emission at 630nm, a weak emission was observed at 430nm, due to the transitional from S₂ to S₀ radiational transition.

Decay of the fluorescence of the ZnTTBP at the 630nm excited by 300ps pulse of 423nm light is shown in Fig.4. The fluorescence lifetime was determined by deconvolution to be 1.2ns.

Decay of the transient absorption from T₁ to Tₙ state and its spectrum was shown in Fig.5 and Fig.6 respectively. The absorption maxima is observed at 480nm in Fig.6, and the transient absorption ranges from 440nm to 560nm. Lifetime of the transient absorption of ZnTTBP was determined to be 4.8µs.

According to the spectral and transient measurements, the photophysical process of
ZnTTBP determined from these results was shown in Fig.7.

![Diagram of Photophysical process of ZnTTBP]

**Fig.7** Photophysical process of ZnTTBP

3.2. One-photon sensitized reaction

Table 1 shows the fluorescence lifetimes and transient absorption lifetimes of ZnTTBP solution in the presence of various concentrations of PAG from 0 to \(10^{-2}\) mol/l. Stern-Volmer plots for the fluorescence lifetimes and the T-T absorption lifetimes were shown in Fig.8. The lifetime of ZnTTBP does not change so much even in the PAG concentration of up to \(10^{-2}\) mol/l, suggesting that the electron transfer did not occur from singlet nor triplet excited state of ZnTTBP to the PAG.

<table>
<thead>
<tr>
<th>[PAG] / mol(^{-1})</th>
<th>(\tau_f/) ns</th>
<th>(\tau_T/) μs</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.17</td>
<td>4.97</td>
</tr>
<tr>
<td>(10^{-4})</td>
<td>1.25</td>
<td>4.73</td>
</tr>
<tr>
<td>(10^{-3})</td>
<td>1.26</td>
<td>5.47</td>
</tr>
<tr>
<td>(10^{-2})</td>
<td>1.20</td>
<td>4.80</td>
</tr>
</tbody>
</table>

ZnTTBP concentration was \(10^{-5}\) mol/l.

![Stern-Volmer plots of fluorescence lifetime (•) and transient absorption lifetime (■)]

**Fig.8** Stern-Volmer plots of fluorescence lifetime (•) and transient absorption lifetime (■)

3.3. Two-photon sensitized reaction

Sample solution of ZnTTBP (\(10^{-5}\) mol/l) and PAG (\(10^{-5}\) mol/l) was prepared, and both 630nm and 470nm-light was irradiated. Fig.9 shows the change in the absorption spectrum of ZnTTBP during two-photon irradiation. The absorbance of Q-band decreased upon the two-photon irradiation. This decrease in the absorption suggests that the photochemical reaction of ZnTTBP occurs during the two-photon irradiation, however, no new absorption expected for a product is not seen clearly in this Figure.

![Absorption spectrum change of ZnTTBP solution by two-photon irradiation](image)

**Fig.9** Absorption spectrum change of \(10^{-5}\) mol/l ZnTTBP solution by two-photon irradiation.

In order to detect the absorption change in detail, ten times concentrated sample solution was prepared and two-photon excitation experiment was performed again. In Fig.10, grow of a new absorption band is observed during the two-photon irradiation of ZnTTBP as the Q-band decrease, suggesting the occurrence of electron transfer from the two-photon exited state (\(T_a\)) of ZnTTBP, and the generation of radical cation by the electron transfer. Electron transfer is often quenched by back electron transfer, whereas, in this process the contribution of back electron transfer is quite small because the transferred electron is rapidly consumed by the decomposition of PAG. [7-8]

![Absorption spectrum change of ZnTTBP solution](image)

**Fig.10** Absorption spectrum change of \(10^{-4}\) mol/l ZnTTBP solution.
3.4 Two-photon polymerization of iso-Butyl vinyl ether

When a mixture of ZnTTBP/PAG in THF solution was two-color photoirradiated, the sample became viscous, suggesting that polymerization occurred by tw-color sensitized initiation. Fig. 11 shows the GPC of the two-photon irradiated isobutyl vinyl ether in the presence of ZnTTBP and PAG. Number-average molecular weight ($M_n$), and weight-average molecular weight ($M_w$) of the poly isobutyl vinyl ether were $2.3 \times 10^4$, and $4.1 \times 10^4$ according to the GPC, respectively.

![Fig.11 GPC chart of poly IBVE prepared by two-photon sensitization](image)

The mechanism of acid generation of PAG is reported to involve complexed intermediate including some radicals. However, vinyl ethers are known to be polymerized only by the cationic mechanism but not by radical mechanism, showing the polymerization was initiated by the acid which is produced by the decomposition of PAG via two-photon sensitization of ZnTTBP. [9]

**Conclusion**

ZnTTBP was synthesized and its photophysical process was determined. PAG couldn't sensitized via one-photon excited states ($S_1$ and $T_1$) of ZnTTBP, while electron transfer occurred via two-photon excited state ($T_n$) of ZnTTBP. PAG were sensitized by two-photon excitation of ZnTTBP and generated acid. The generated acid were confirmed by to be potential to polymerization of isobutyl vinyl ether.

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**Reference**