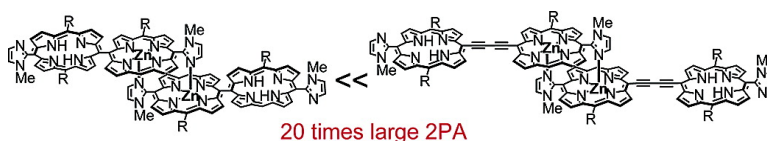


Strong Two-Photon Absorption of Self-Assembled Butadiyne-Linked Bisporphyrin

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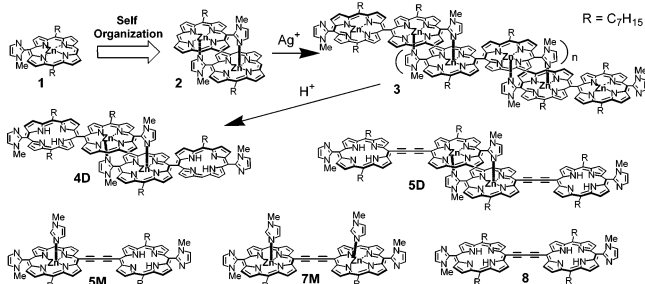
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We have developed a unique supramolecular porphyrin system¹ by using the complementary coordination of imidazolyl to the zinc of imidazolylporphyrinatozinc(II) such as in **1** to provide an extremely stable dimer **2** (Scheme 1).^{1a} A one-dimensional giant porphyrin array **3** consisting of up to 800 porphyrin units was obtained by the coupling of coordination units of **2**.^{1b} The terminals of the multiporphyrin array **3** can be exchanged to porphyrins having donor or acceptor groups through a reorganization process. Therefore, porphyrin oligomers were prepared by introducing free base porphyrin as an energy acceptor as compared to zinc porphyrin at both terminal positions, and large enhancements of the real part of molecular second hyperpolarizability were observed under one-photon off-resonant conditions.^{1c}

Scheme 1. Self-Assembled Porphyrin System



Our current interest is focused on two-photon absorption (2PA)² materials with a view to potential optical applications such as 3-D optical memory,³ photodynamic therapy (PDT),⁴ optical power limiting,⁵ 3-D microfabrication,⁶ and fluorescence microscopy.⁷ To enhance the 2PA cross section, $\sigma^{(2)}$, molecular designs involving donor/acceptor sets intervened with a π -conjugation system in a symmetrical (D- π -D or A- π -A)⁸ or asymmetrical (D- π -A)⁹ arrangement have been proposed. Porphyrin has a highly conjugated π -system exhibiting large real parts of the third-order susceptibility, $\text{Re}[\chi^{(3)}]$,^{1c,10} but only a limited number of reports of the $\sigma^{(2)}$ value of porphyrin are available.^{10,11} For a large $\sigma^{(2)}$ value, here we introduced two factors to design a conjugated self-assembled porphyrin tetramer **5D**. First, to expand the π -conjugation between two porphyrin units, two imidazolylporphyrins were connected by a butadiyne unit to allow a coplanar orientation, whereas two porphyrins directly linked at meso-positions in the self-assembly **4D** are almost orthogonal. The covalently linked conjugated porphyrin arrays by ethyne¹² and butadiyne linkages,¹³ forming cumulenyl structures with largely separated charges upon photoexcitation, have been investigated. Additionally, free base porphy-

rins were introduced at both terminals to promote the polarization and so to form the A- π -A structure. Very recently, it was found that a small organic molecule with a similar A- π -A structure linked by a butadiyne moiety exhibits a very large $\sigma^{(2)}$ value.¹⁴ In this paper, we report that **5D** has excellent 2PA properties as compared to the meso-linked self-assembled porphyrin tetramer **4D** as well as other conjugated porphyrins as determined by a femtosecond open aperture Z-scan method.

Conjugated bis(imidazolylporphyrin) **8** bridged by a butadiyne linkage was synthesized by oxidative coupling of ethynylporphyrinatozinc(II) **6**¹⁵ followed by demetalation for purification. Reaction of **8** with 1 equiv of zinc acetate gave a complementary dimer of mono-metallated-bis(imidazolylporphyrin) **5D**, which could be isolated through gel permeation chromatography (GPC). The reference porphyrins **5M** and **7M** were prepared by adding 1-methylimidazole as a ligand to cleave the complementary coordination.¹⁵ Figure 1 shows the absorption spectra of **4D**^{1c} (broken line) and **5D** (solid line) in CHCl_3 . The one-photon absorption in the Q-band region of **5D** was red-shifted to ~ 740 nm, and its intensity became larger than that of **4D** due to expansion of the porphyrin-porphyrin conjugation.¹³

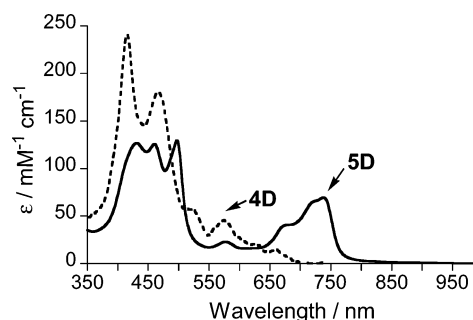


Figure 1. One-photon absorption spectra of **4D** and **5D** in CHCl_3 .

The 2PA spectra were measured by an open aperture Z-scan method at wavelengths from 817 to 1282 nm using a femtosecond optical parametric amplifier.¹⁵ No signs of higher-order effects, such as the three-photon absorption (3PA) and 2PA-induced excited-state absorption (ESA), were observed at wavelengths shorter than 1180 nm.¹⁵ Figure 2 shows the obtained $\sigma^{(2)}$ spectra of **4D** and **5D** in CHCl_3 . The largest $\sigma^{(2)}$ values of **4D** and **5D** were 370 ± 80 GM (93 ± 20 per porphyrin unit) at 964 nm and 7600 ± 1500 GM (1900 ± 370 per porphyrin unit) at 887 nm ($1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s molecule}^{-1} \text{ photon}^{-1}$). Recently, a double-strand conjugated porphyrin polymer linked by butadiyne bonds exhibiting large $\sigma^{(2)}$ values of $\sim 5 \times 10^4$ GM, as measured by a DFWM method with a picosecond pulse laser, was reported.¹⁰ However, it should be noted here that the direct comparison among the cross-section data

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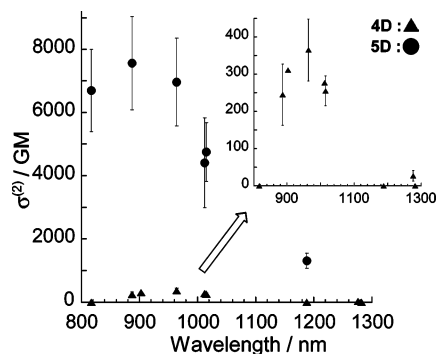


Figure 2. Two-photon absorption spectra of **4D** and **5D** in CHCl_3 .

measured with different pulse widths is very difficult because the $\sigma^{(2)}$ values measured with picosecond and nanosecond pulses are known to be 2 or 3 orders of magnitude larger than those measured with femtosecond pulses.¹⁶ Thus, we compared the $\sigma^{(2)}$ value of **5D** to those of other porphyrins and tetraazaporphyrins (TAP) measured with femtosecond pulses¹¹ (Table 1). The conjugated self-assembly **5D** exhibited one of the largest $\sigma^{(2)}$ values among these compounds. Most of the reported values of other organic compounds on the femtosecond time scale have not exceeded 1000 GM.¹⁷ The compounds **5M**, **7M**, and **8** also showed larger $\sigma^{(2)}$ values of 900 ± 200 , 590 ± 140 , and 500 ± 130 GM per porphyrin, respectively, as compared to **4D** (93 GM). This comparison demonstrates that the expansion of the π -conjugation between porphyrin units by introducing a butadiyne linkage is the overriding factor to increase the $\sigma^{(2)}$ value. The $\sigma^{(2)}$ value of unit **5D** was twice compared to that observed in **5M** per porphyrin unit, corresponding to 4 times enhancement per molecule. This result indicates that the complementary coordination is also an effective factor for 2PA enhancement. The values of **7M** and **8** were almost one-half that of **5M**, suggesting that the increase of polarization by monometalation was another effective factor for 2PA enhancement. Furthermore, the nonlinear absorption that was of higher order than 2PA was found for **5D** at wavelengths longer than 1180 nm. The wavelengths were almost 3 times as long as the wavelength of the Soret band, so the higher-order absorption probably originates from 3PA. The observed data were reanalyzed as 3PA¹⁵ and gave the 3PA cross-section values of 7.1×10^{-89} and 1.8×10^{-89} m⁶ s² at 1188 and 1282 nm, respectively. Although these data are not large in comparison with the reported values¹⁸ for small organic compounds (10^{-92} – 10^{-86} m⁶ s²), to our knowledge, this is the first observation of the 3PA process in porphyrin compounds.

Table 1. 2PA Cross-Section Values ($\sigma^{(2)}$) of Porphyrins and Tetraazaporphyrins (TAP) Measured by Femtosecond Laser Pulses

sample	$\sigma^{(2)}$ /GM (per porphyrin unit)	pulse width/fs	wavelength/nm
4D	370 (93)	120	964
5D	7600 (1900)	120	887
5M	1800 (900)	120	873
7M	1200 (600)	120	873
8	1000 (500)	120	873
ZnOEP ^{11a}	4.4	150	780
H ₂ TPP ^{11a}	15	150	780
Bu ₄ TAP ^{11b}	70	150	780
(BrPh) ₈ TAP ^{11b}	380	150	800
(NO ₂ Ph) ₈ TAP ^{11b}	900	150	800
(NO ₂ Ph) ₈ TAP ^{11b}	1600	150	770

Free base and zinc porphyrins are well-known to generate the excited triplet state from the S₁ state with a high quantum yield, producing singlet oxygen efficiently.¹⁹ Thus, the self-assembled

porphyrin array **5D** may be extremely interesting for PDT application. Furthermore, the self-assembled system presented here allows facile modification of the unit molecular length and introduction of donor/acceptor groups to obtain far-enhanced $\sigma^{(2)}$ values. The extremely large $\sigma^{(2)}$ values of self-assembled porphyrins are the subject of further investigation.

Supporting Information Available: Preparation of compounds, experimental details, and analytical methods for TPA measurements (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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