

Short Communication
 Ethynylene-bridged Porphyrin Fluorene Composites

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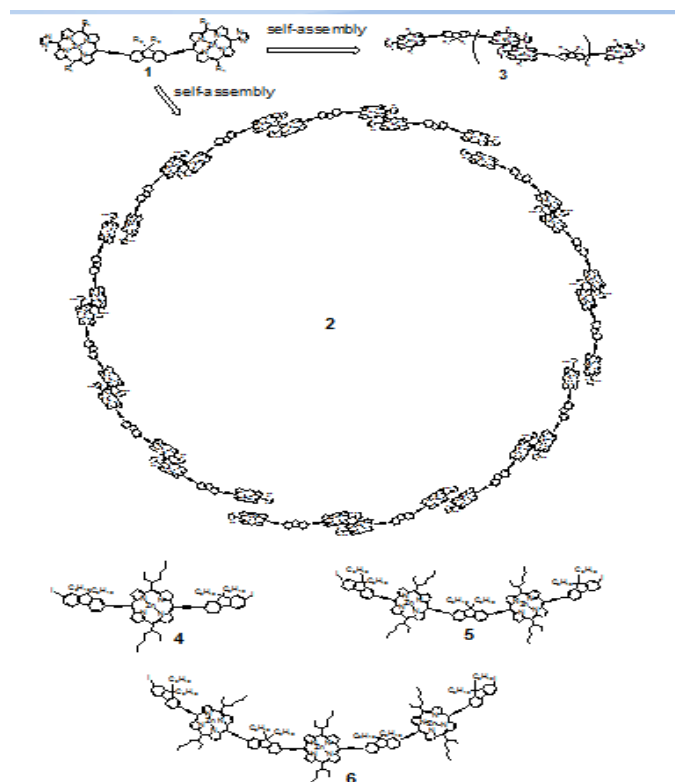
ABSTRACT:

Porphyrin-fluorene conjugates bridged by ethynylene were synthesized through Pd-catalyzed cross-coupling reaction. These molecules showed strong nonlinear absorption when measured using a nanosecond Z-scan method. The largest effective two-photon absorption cross-section was observed for trisporphyrin as 2.7×10^5 GM at 760 nm, which was 10 times larger than that obtained for monoporphyrin.

INTRODUCTION

Recently, much attention has been focused on the organic dye molecules in view of optical applications such as nonlinear optics including two-photon absorption (2PA) materials.¹ Novel functions will be expected by connecting two or more chromophores even if a monomeric dye itself does not exhibit a significant function. We have developed two-photon absorbing molecules using self-assembled multi-porphyrin arrays and found that the connection of π -conjugation between porphyrins with ethynylene bridges is the most significant for the 2PA enhancement.^{1a, 1b, 2} However, the expansion of π -conjugation raises large red-shift of one-photon absorption (1PA) up to 2PA range.^{2g} In order to prevent such the overlapping of 1PA and 2PA, it is necessary to control the position of one-photon absorption band by tuning the interaction between chromophores. Fluorene is a well-known π -spacer for two-photon absorption materials³ and provides an angle of 160° between ethynylporphyrins when these are connected at 2- and 7-positions of fluorene. Previously, we reported fluorene-bridged bisimidazolylporphyrins 1 having two allyl groups at meso-positions have been synthesized to construct macro cyclic arrays 2. The self-assembled structure in the macro cycle was fixed by the ring-closing metathesis reaction of the allyl groups to investigate the effect of cyclization on 2PA by a femtosecond fluorescence method in the range between 800 and 875 nm.^{2f} Further, linear polymers self-organized by fluorene-bridged bisimidazolylporphyrins 3, and their 2PA properties in the range from 740 to 930 nm were reported.⁴ However, the π -conjugation was

disconnected between chromophores at the self-coordination sites. So, we designed new fluorene-bridged porphyrin arrays 4 – 6 without the self-assembly.



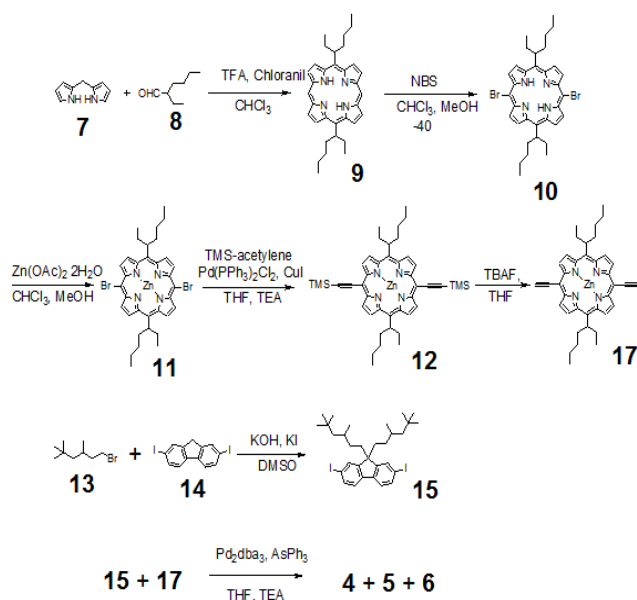
Scheme 1 Structures of fluorene-conjugated porphyrins.

RESULTS AND DISCUSSION

Synthetic routes of 4, 5, and 6 are shown in Scheme 2. Fluorene 15 and porphyrin 9 were synthesized

according to the literatures.^{2f, 5} Dibromoporphyrin 10 was prepared from 9 using *N*-bromosuccinimide (NBS) at $-40\text{ }^{\circ}\text{C}$ in 50% yield. Dibromoporphyrin 10 was metalated by zinc acetate to afford 11. Bis (TMS-ethynyl) zincporphyrin 12 was prepared from 11 with TMS-acetylene using $\text{Pd}(\text{PPh})_2\text{Cl}_2/\text{CuI}$ as a catalytic system in THF/triethylamine in a 90% yield. The cross-coupling reaction of 12 and 15 was conducted using a $\text{Pd}_2(\text{dba})_3/\text{AsPh}_3$ catalyst system at $40\text{ }^{\circ}\text{C}$ to obtain a mixture of targets. Figure 1 shows an analytical GPC chart of the mixture after 3.5 hours. Three fractions corresponding to the peaks around 14.5, 13.5, and 13 minutes were separated using preparative gel permeation chromatography (GPC) using chloroform as an eluent. The purity and identification were confirmed by analytical GPC and MALDI-TOF mass as shown in Figures 2. In each mass data, small peaks less than 10% compared with main peaks were observed. Since these molecular weights corresponded to each molecular weight minus atomic weight of iodine, these species were produced by competing reduction reaction, which is often observed in the palladium-catalyzed cross-coupling reaction.

Figure 3 shows normalized one-photon absorption spectra of 4, 5, and 6 in CHCl_3 . There is little difference in the Soret bands appeared around 450 nm among three compounds. Contrary to this, the Q-bands around 650 to 700 nm was intensified with the increasing number of porphyrin, indicating expansion of π -conjugation between chromophores. The difference in the Q-band absorption intensity between 5 and 6 is smaller than that between 4 and 5, suggesting that the effect on the expansion of π -conjugation decreases with the number of porphyrin.



Scheme 2 Synthetic route of 4, 5, and 6.

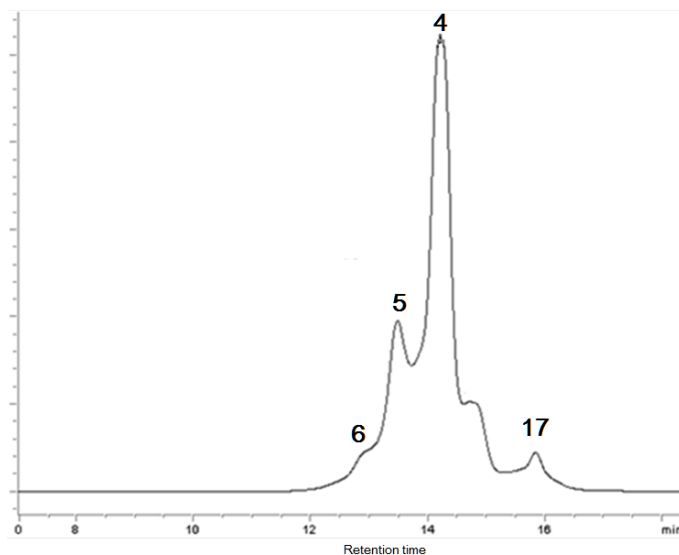


Figure 1 Analytical GPC chart of the reaction mixture.

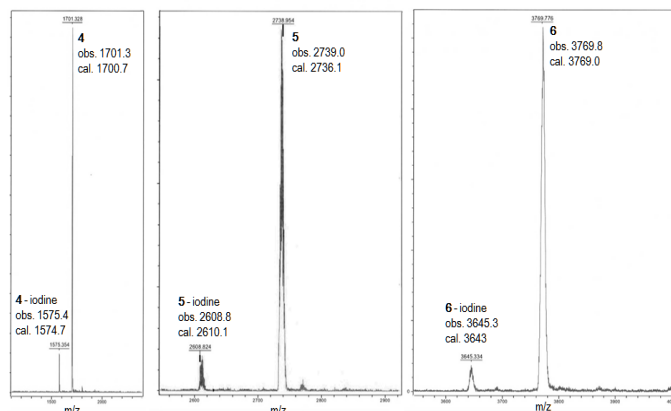


Figure-2 MALDI-TOFF mass charts of 4, 5, and 6 after isolation.

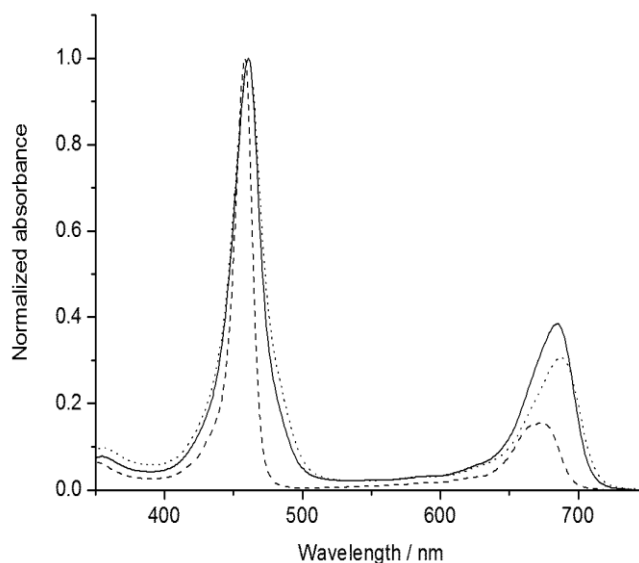


Figure-3 Normalized absorption spectra of 4 (dash), 5 (dot), and 6 (solid) in CHCl_3 .

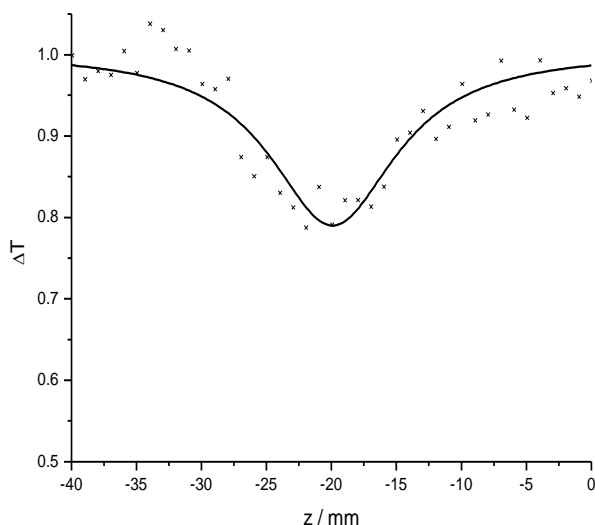


Figure-4 Typical open-aperture Z-scan traces (x) with theoretical fitted line of 6 measured using nanosecond pulses at 760 nm in CHCl_3 .

The nonlinear absorption measurements were performed using a nanosecond Z-scan method in toluene/pyridine (95:5) and pyridine, and analyzed as the effective 2PA including the excited-state absorption.^{1b} Figure 4 represents typical Z-scan trace of 6 in CHCl_3 (the concentration was 1.2×10^{-4} M) with theoretically fitted curves at 760 nm. In this figure, the normalized transmittance was plotted as a function of the sample position, z . The dip was observed around the focal position around at -20 mm in this setup. The curve fit was performed according to the theoretical equations assuming 2PA to afford the effective two-photon absorption cross-section, $\text{eff}\sigma^{(2)}$.^{1b} Figure 5 shows effective 2PA spectra of 4, 5, and 6. The maximum $\text{eff}\sigma^{(2)}$ values of 4, 5, and 6 were obtained as 2.6×10^5 , 8.5×10^5 , and 2.7×10^6 GM at 760 nm, respectively. These values are comparable to those obtained for similar porphyrin-fluorene conjugates.⁴ Interestingly, the $\text{eff}\sigma^{(2)}$ value obtained for 6 is 10 times larger than that for 4. One of the reasons is considered as the expansion of π -conjugation. Another explanation can be made by considering the resonance enhancement by the one-photon $S_1 \leftarrow S_0$ transition (Q-band), which is explained using three- or four-state model, to afford the amplification of the $\sigma^{(2)}$ value. The red-shift and the intensification of the Q-bands of 5 and 6 compared with those of 4 should increase the resonance enhancement for 5 and 6. The 2PA measurements using femtosecond pulsed laser that gives $\sigma^{(2)}$ values without the effect of the

excited state absorption are now under investigation and will be reported elsewhere.

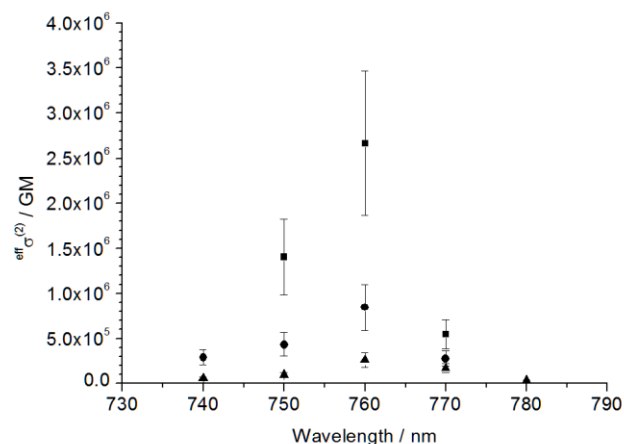


Figure-5 Effective 2PA spectra of 4 (triangle), 5 (circle), and 6 (square) measured using nanosecond pulses in CHCl_3 .

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