SDRP JOURNAL OF NANOTECHNOLOGY & MATERIAL SCIENCE
2016
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Short Communication

Synthesis and Optical Properties of Ethynylene-linked Trisporphyrins

Kazuya Ogawa[1*] and Mayuka Yoshida[2]
(1)Interdisciplinary Graduate School of Medicine and Engineering, Division of Medicine and Engineering Science, Life Environment Medical Engineering, University of Yamanashi, 4-3-11 Takeda, Kofu, Yamanashi 400-8511.
(2) Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0101, Japan

Received date: 28-12-2015; **Accepted date:** 26-02-2016; **Published date:** 03-03-2016

CORRESPONDENCE AUTHOR: Kazuya Ogawa
E-mail: kogawa@yamanashi.ac.jp

CONFLICTS OF INTEREST
There are no conflicts of interest for any of the authors.

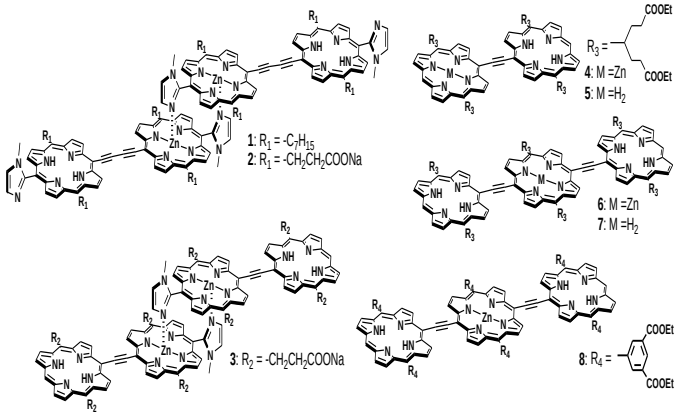
ABSTRACT:
Ethynylene-linked trisporphyrin having aryl substituents was synthesized using Pd-catalyzed cross-coupling reaction. This compound exhibited a large effective two-photon absorption cross section value of 2.2 × 10^4 GM at 890 nm measured by using a nanosecond Z-scan method, which was almost twice as long as those of the Soret band. The value was 3 times larger than that obtained for trisporphyrin having alkyl groups.

INTRODUCTION

Two-photon absorption (TPA) is one of the nonlinear optical effects, in which two photons are simultaneously absorbed by a molecule. In this phenomena, the excitation is proportional to the square of the incident light intensity, allowing a spatial selectivity, allowing photonic applications promising, e.g. two-photon photodynamic therapy (PDT), [1] three-dimensional optical storage,[2] and optical limiting.[3] Porphyrin is a potential candidate for TPA materials because of its highly conjugated π-electron system. But simple porphyrins have only small $\sigma^{(2)}$ values less than a few tens of GM (1 GM = 10^{-50} cm^4 s $molecule^{-1}$ $photon^{-1}$).[4]

We reported that bisporphyrin linked by triple bonds 1 as shown Scheme 1, which constructed by self-assembling through zinc-imidazolyl coordination, [5] showed a large TPA cross section value ($\sigma^{(2)}$) of 7,600 GM (1 GM = 10^{-50} cm^4 s $molecule^{-1}$ $photon^{-1}$).[6] The large enhancement is mainly achieved by the expansion of π-conjugation between porphyrins by linking with triple bonds. In order to apply this compound to TPA-PDT, water-solubilized derivatives 2 and 3 were synthesized.[7] Since many steps are requested in synthesizing these compounds with the supramolecular system, we designed simple bis- and trisporphyrins 4, 5, 6, and 7 linked by ethynylene.[7] In this molecular design, an ethynylene bond instead of butadiyne was chosen to connect porphyrins, since the ethynylene bridging allows a facile synthesis of the asymmetric bis- or trisporphyrin through a one-step hetero-coupling reaction between zinc- and free base porphyrins unlike. Trisporphyrins exhibited larger effective TPA

cross section values ($^{eff}\sigma^{(2)}$), which were obtained using nanosecond pulsed laser, than those of bisporphyrins. TPA properties of some porphyrin derivatives having expanded π-conjugation have been investigated to date. [8] [9] [10] [11] [12] [13] Here, we report synthesis and preliminary optical properties of new ethylene-linked trisporphyrin 8 employing aryl groups.

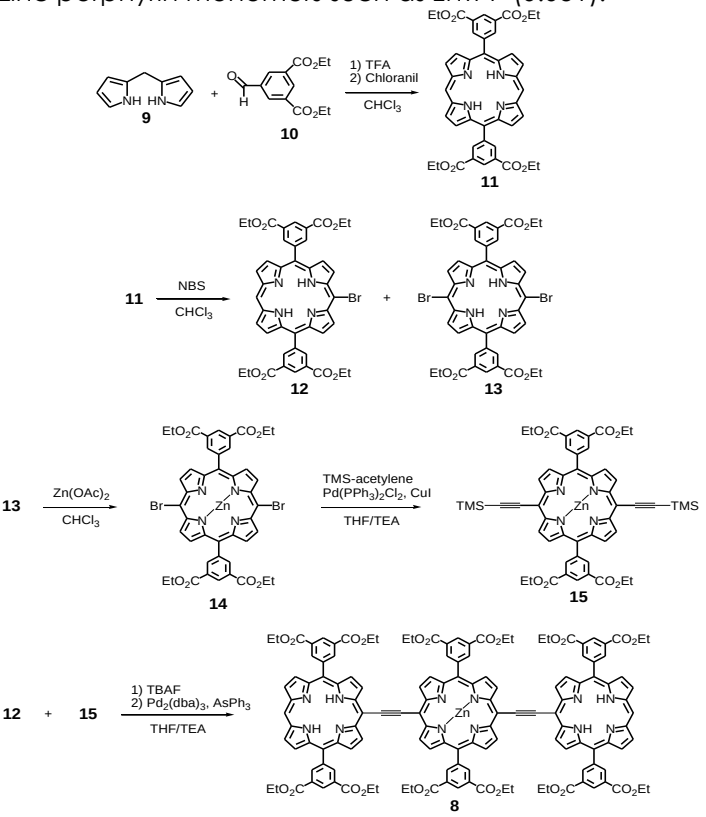


Scheme 1 Structures of conjugated porphyrins 1 – 8.

RESULTS AND DISCUSSION

Synthetic routes for the target 8 are shown in Scheme 2. Ester groups, which allow a water-soluble agent when these will be hydrolyzed, are introduced for future PDT application. Dipyrromethane 9 and aldehyde 10 were synthesized according to the literatures.[14] Porphyrin 11 was synthesized from 9 and 10 using 1 equivalent of trifluoroacetic acid (TFA) followed by chloranil oxidation in a 16% yield. Monobromoporphyrin 12 and dibromoporphyrin 13 were prepared from 11 using 1.1 equivalents of *N*-bromosuccinimide (NBS) at –40 ˚C in 40 and 24% yields, respectively. Dibromoporphyrin 13 was metalated by zinc acetate to give 14. Bis(TMS-ethynyl)zincporphyrin 15 was obtained from 14 by the reaction with TMS-acetylene using a $Pd(PPh)_2Cl_2$/CuI catalytic system in THF/triethylamine (TEA) in a 99% yield. The hetero-coupling reaction of 12 and 15 was conducted by using $Pd_2(dba)_3$/$AsPh_3$ as a catalyst system at relatively high temperature of 60 ˚C to obtain the target 8. In this one-pot reaction, the TMS group in 15 was first deprotected using tetrabutylammonium fluoride (TBAF) at 60 ˚C because of the low solubility of deprotected-bisethynylzincporphyrin. The target 8 was isolated using preparative gel permeation chromatography (GPC) using pyridine as an eluent. The yield of the target was only 14% because precipitates including the target and intermediate of bisporphyrin were formed during the coupling reaction. The purity and identification were confirmed by analytical GPC and MALDI-TOF mass, as shown in Figures 1 and 2, respectively. Unfortunately, clear ^{1}H NMR could not be obtained because of the low solubility in the NMR condition.

Figure 3 shows one-photon absorption spectrum of 8 in $CHCl_3$. The Soret band was split into two peaks at 410 and 485 nm, and the Q-band appeared around 850 nm. These spectral features indicate expansion of π-conjugation between porphyrins and are essentially similar to those of 6. Figure 4 presents fluorescence spectrum of 8 measured in $CHCl_3$ with excitation wavelength at 567 nm. The fluorescence was observed almost in near-IR region. The quantum yield was estimated as 0.05, which was relatively large compared to that of zinc porphyrin monomers such as ZnTPP (0.031).



Scheme 2 Synthetic route for 8

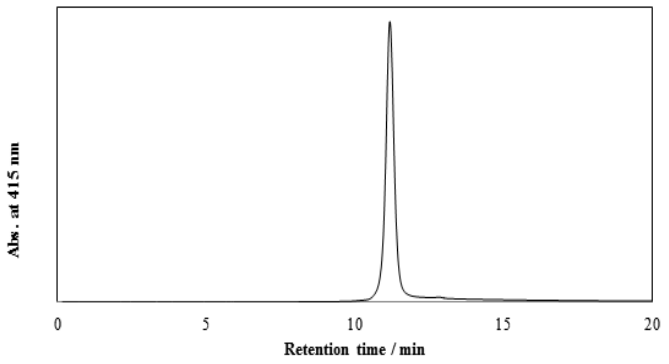


Figure 1 Analytical GPC chart of 8.

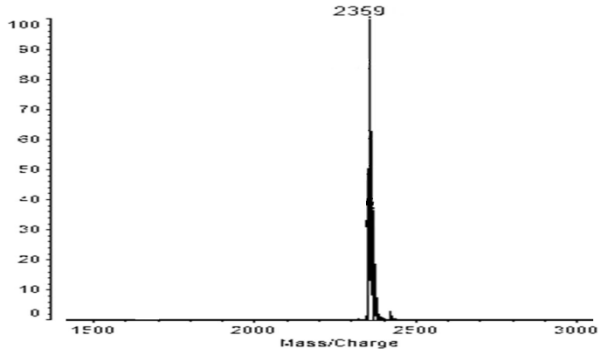


Figure 2 MALDI-TOFF mass chart of 8.

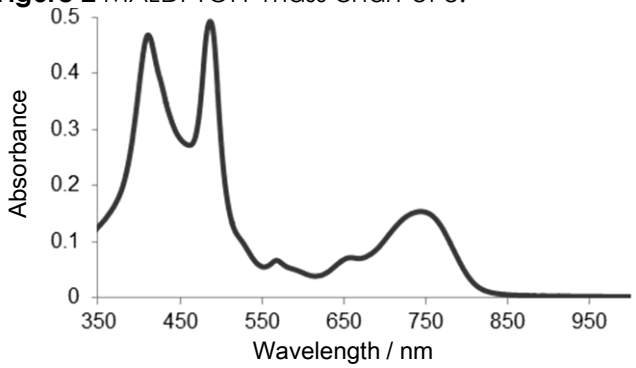


Figure 3 Absorption spectrum of 8 in $CHCl_3$.

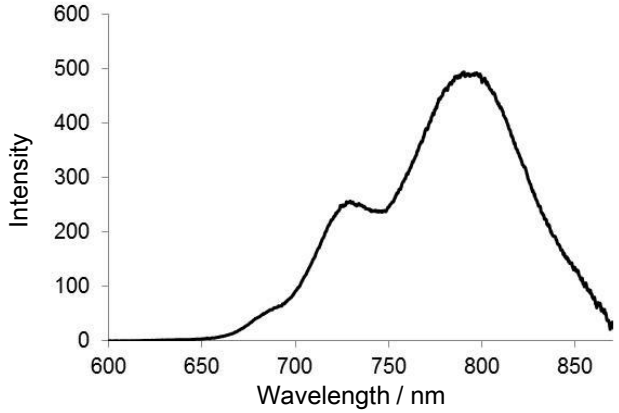


Figure 4 Fluorescence spectrum of 8 in $CHCl_3$.

The TPA measurement was performed using a nanosecond open-aperture Z-scan method at a wavelength range from 870 to 910 nm. Figure 5 shows typical Z-scan trace of 3 × 10^{-5} M 8 in $CHCl_3$ using pulse energy of 2.0 mJ at 890 nm with theoretically fitted curves according to the following equations.[6b, 15] In this figure, normalized transmittances were plotted as a function of the sample position, z, and the dip was observed around the focal position due to nonlinear absorption.

$$T(\zeta) = \frac{(1-R)^2 e^{(-\alpha^{(1)}L)}}{\sqrt{\pi} q(\zeta)} \int_{-\infty}^{\infty} \ln[1 + q(\zeta) e^{(-x^2)}] dx \qquad (1)$$

$$q(\zeta) = \frac{q_0}{1+\zeta^2} \qquad (2)$$

$$q_0 = \beta^{(2)} (1-R) I_0 L_{eff} \qquad (3)$$

$$L_{eff} = [1-\exp(-\alpha^{(1)}L)]/\alpha^{(1)} \qquad (4)$$

$$\sigma_{eff}^{(2)} = \hbar\omega\beta^{(2)} / N \qquad (5)$$

where ζ denotes the normalized z-position ($\zeta = (z-z_0)/z_R$), and z_0 and z_R mean the focal position and the Rayleigh range, respectively. $\alpha^{(1)}$ denotes a one-photon absorption coefficient and R is the Fresnel reflectance. L denotes the light path length (2 mm) and $\beta^{(2)}$ denotes the 2PA coefficient. L_{eff} is the effective path length and I_0 denotes the peak intensity at the focal position. N is the number density of the molecule and $\hbar\omega$ is the photon energy of the incident light. Finally, the effective TPA cross section value $\sigma_{eff}^{(2)}$ was calculated using equation (5). All Z-scan curves could be well fitted with the reasonable parameters such as Rayleigh range, which were consistent with those obtained for Rhodamine B.[16]

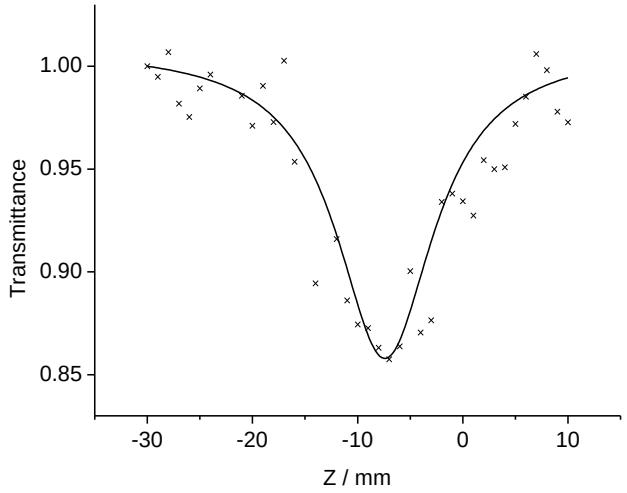


Figure 5 Typical open-aperture Z-scan traces (x) of 8 measured using nanosecond pulses at 890 nm in $CHCl_3$.

Figure 6 shows effective TPA spectra of 8. The maximum $\sigma_{eff}^{(2)}$ value was obtained as (2.2 ± 0.6) × 10^4 GM at 890 nm that was almost twice as long as those of the Soret band. Interestingly, the $\sigma_{eff}^{(2)}$ value obtained for 8 is 3 times larger than that for 6. Since the ground state absorption spectra are almost same between two compounds, excited state absorption, which is likely to be observed using nanosecond pulse and may be depend on the triplet state, is probably different. The TPA measurements using femtosecond pulsed laser that gives $\beta^{(2)}$ values without the effect of the excited

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

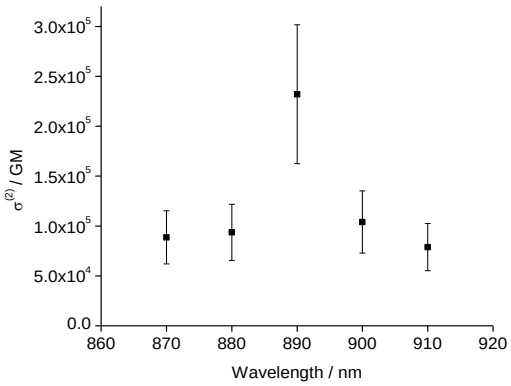


Figure 6 Effective TPA spectra of 8 measured using nanosecond pulses in $CHCl_3$.

ACKNOWLEDGMENTS

This work was supported by Grant-in-Aids for Scientific Research (C) (No. 15K05471) from Ministry of Education, Culture, Sports, Science and Technology, Japan (Monbu Kagakusho).

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