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Nonlinear Absorption by Porphyrin Supramolecules

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1. Introduction

Two-photon absorption (2PA) is a nonlinear optical process in which two photons are simultaneously absorbed to promote a molecule to the excited state by combination of their energy. 2PA can occur even at wavelengths where one-photon absorption does not take place. Because of quadratic dependence of 2PA on the incident light intensity, the maximum absorption occurs at the focal point of laser allowing high spatial selectivity. These features can find a variety of optical applications such as photodynamic therapy (PDT) (Bhawalkar et al., 1997; E.A. Wachter et al., 1998), 3D optical data storage (Parthenopoulos & Rentzepis, 1989; Strickler & Webb, 1991), and optical limiting (Sutherland, 2003). 2PA was first predicted by Maria Göppert-Mayer in 1931 (Göppert-Mayer, 1931) and was demonstrated experimentally by Kaiser and Garrett using Ruby laser (Kaiser & Garrett, 1961). However, the study on 2PA materials had been inactive until 1990's. After that, new classes of organic molecules exhibiting large 2PA cross section values ($\sigma^{(2)}$) have been reported and the strategies employing donor/acceptor sets with a π-conjugation system in a symmetric (D-π-D or A-π-A) (Albota et al., 1998) or asymmetric (D-π-A) arrangement (Reinhardt et al., 1998) have been proposed.

Porphyrins are attractive target materials for 2PA applications because they have a highly conjugated 18π-electron system leading to a small HOMO-LUMO energy difference. Further, it is interesting in view of visible-light (the Soret band around 400 nm and Q band around 500-700 nm) absorbing and emitting materials as candidates for opto-electronics application as well as nonlinear optics (NLO) including 2PA materials. Novel NLO materials may not be obtained from simple monomeric porphyrins, but be produced when strong electronic interactions between porphyrins are induced by self-assembly to bring porphyrins close together or connecting their π-conjugation systems.

A lot of multiporphyrin systems have been reported either by covalent or noncovalent approaches (Chambron et al., 1999; Chou et al., 1999; Ogawa & Kobuke, 2004) and some of them showed such the strong electronic interactions between porphyrins. In most of covalent approaches, strong interactions have been found in linear porphyrin arrays by

connecting porphyrins at *meso*-positions (Osuka & Shimidzu, 1997; Aratani et al., 2005; Tsuda & Osuka, 2001; Anderson, 1994; Anderson, 1999; Lin et al., 1994).

In contrast to the covalent approaches, noncovalent approaches allow easy construction of multiporphyrin arrays. However, studies on self-assembled porphyrin arrays exhibiting strong excitonic and electronic interactions are limited because it is hard to arrange porphyrins in an appropriate position to invoke strong excitonic interaction between porphyrins.

We have reported that zinc imidazolylporphyrin **1** (Fig. 1) allows formation of stable slipped cofacial dimer **2D** through complementary coordination of the imidazolyl to zinc in another porphyrin with a stability constant over 10^{11} M^{-1} (Kobuke & Miyaji, 1994). Then, we challenged to construct one-dimensional supramolecular linear porphyrin arrays by connecting the complementary coordination dimer units in a linear fashion. As a result, a giant supramolecular porphyrin array **3P** of over 800 porphyrin units could be obtained by linking two imidazolylporphyrin units directly at the *meso* positions (Ogawa & Kobuke, 2000). The polymeric structure can easily be cleaved by adding coordinating solvents such as MeOH or pyridine, and reorganized again by removing the solvents. When this reorganization was performed in the presence of **3P** and another imidazolylporphyrinatozinc dimer **4D**, oligomer **5n** having terminal units of **4M** was obtained. Thus, the reorganization can serve an efficient method for introducing appropriate donor and/or acceptor groups at the molecular terminals of the array as a substituent R_2. For example, when freebase porphyrin was used as an acceptor, large enhancements of the real part of the molecular second hyperpolarizability were observed (Ogawa et al., 2002). However, almost no nonlinear absorption was observed in femtosecond optical Kerr effect (OKE) measurements at the off-resonant wavelength of 800 nm.

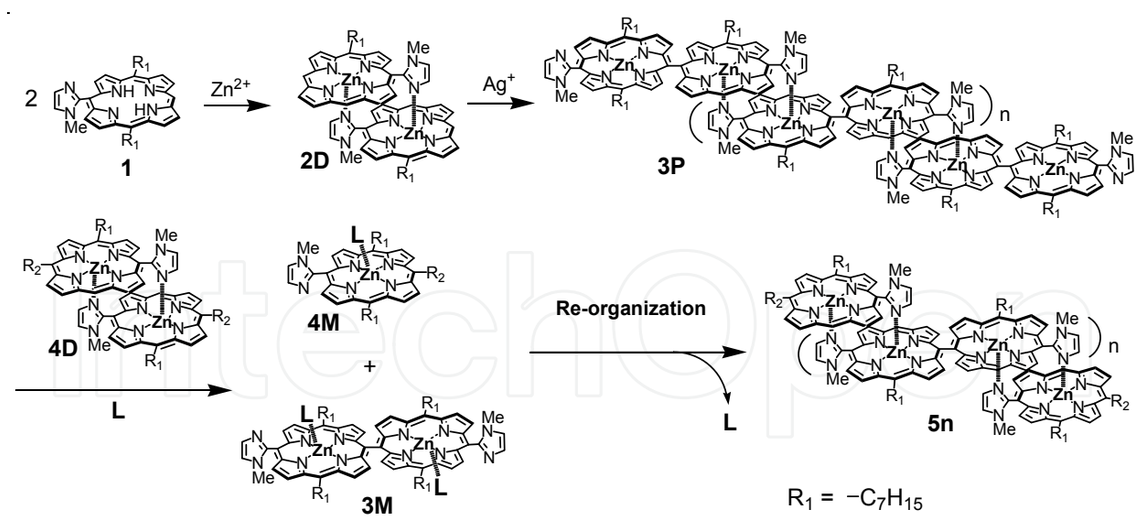

Fig. 1. Formation of self-assembled porphyrin dimer and giant porphyrin array by complementary coordination of imidazolyl to zinc.

2. Strong 2PA of conjugated porphyrins by self-coordination

In order to extend the use of this supramolecular porphyrin system to 2PA materials (i.e. to obtain a large 2PA cross section) we designed a novel porphyrin assembly **7D** (Fig. 2)

(Ogawa et al., 2003) according to the general strategy as mentioned above. At first, two porphyrins were connected by butadiynylene to allow π-conjugation by taking a coplanar orientation of two porphyrins. In the case of *meso-meso* linked bisporphyrins shown in Fig. 1, orthogonal orientation between porphyrins prevents the desired porphyrin-porphyrin π-conjugation. The conjugated porphyrin arrays, covalently linked by butadiynylene and ethynylene linkages (Piet et al., 1997; Anderson, 1994; Anderson, 1999; Thorne et al., 1999; Screen et al., 2002; Karotki et al., 2004; Drobizhev et al., 2004; Lin et al., 1994; Lin et al., 1995; Angiolilloet al., 2004), are assumed to be converted to cumulenic structures upon photoexcitation. This may make the absorption of the second photon favorable and enhance their nonlinear optical properties. Next, free base porphyrins as electron acceptors were introduced at both terminals of the array to induce molecular polarization.

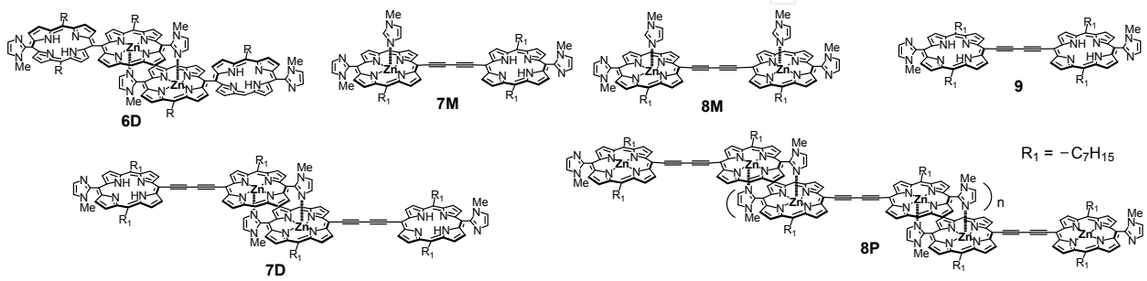

Fig. 2. Structures of compounds investigated.

2.1 Effect of the expansion of π -conjugation between porphyrins on 2PA

The butadiynylene linkage in **7D** allows a coplanar orientation between bisporphyrins, leading to the expansion of π-conjugation. On the other hand, in the case of **6D**, two porphyrins directly connected at *meso*-positions are almost orthogonal to each other, preventing π-conjugation between two porphyrins. Fig. 3 shows one-photon absorption spectra of **6D** (dotted line) and **7D** (bold solid line) in $CHCl_3$. Both self-assemblies show strong one-photon absorption in the range of 400 nm to 500 nm, which corresponds to the S2 state (the Soret band). On the other hand, only very weak absorptions are observed over 800 nm. These observations suggest that two photons at the wavelength over 800 nm will be absorbed simultaneously to promote the molecules to the S2 state. The Q-band (the S1 state) of **7D** was red-shifted to 740 nm compared to that of **6D** (660 nm), and was also significantly intensified suggesting the expansion of the porphryin-porphyrin π-conjugation due to the butadiynylene linkage.

The 2PA cross sections were measured using an open aperture Z-scan method (Sheik-Bahae et al., 1990) at wavelengths from 810 to 1300 nm, with a femtosecond optical parametric amplifier. This technique detects nonlinear absorption, i.e. two- or multi-photon absorption, by scanning the sample around the focal point along the direction of laser beam (Z-axis). The nonlinear absorption is observed most strongly at the focal point, where the peak intensity of the incident light becomes maximum. The $\sigma^{(2)}$ value can be estimated by curve fitting using theoretical equations.

2PA spectra of **6D** and **7D** measured in $CHCl_3$ are shown in Fig. 4. The maximum $\sigma^{(2)}$ values were obtained as 370 GM at 964 nm for **6D** and 7,600 GM at 887 nm for **7D**, respectively. The maximum value obtained for **7D** is almost 20 times larger than that for **6D**, showing that the

expansion of π-conjugation between porphyrins by introducing the butadiynylene linkage is the most important factor to enhance the $\sigma^{(2)}$ value. The value of 7,600 GM was the largest class among reported organic compounds measured in femtosecond time scale at that time.

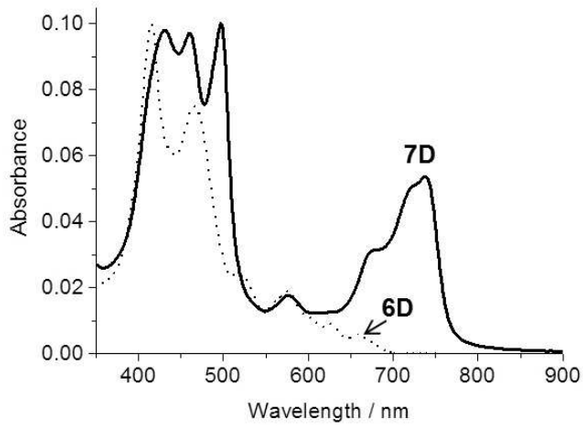

Fig. 3. One-photon absorption spectra of **6D** (dotted line) and **7D** (bold solid line) in $CHCl_3$.

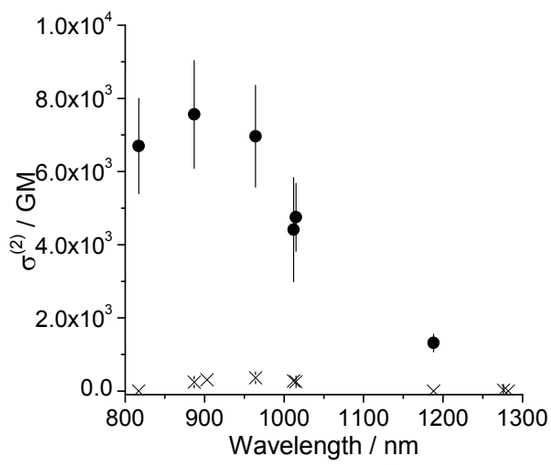

Fig. 4. 2PA spectra of **6D** (cross) and **7D** (circle) measured using femtosecond pulses in $CHCl_3$.

2.2 Effects of complementary coordination and monozinc metalation on the enhancement of the 2PA cross section

As described in the above section, the expansion of π-conjugation between two porphyrins is one of the significant reasons for the enhancement of the $\sigma^{(2)}$ value. From a viewpoint of the relationship between structure and 2PA property, it is interesting to examine the effect of the complementary coordination of imidazolyl to zinc and the monozinc metalation, which induces the molecular polarization. Therefore, we examined the 2PA properties of bisporphyrins in the forms of monozinc complex **7M**, di-zinc complex **8M**, and free base **9** in $CHCl_3$ solution containing 3,000 equivalents of 1-methylimidazole, which acted as a competing ligand to lead the cleavage of the complementary coordination. The 2PA absorption spectra of **7M**, **8M**, and **9** are shown in Fig. 5. These compounds without the complementary coordination also exhibited relatively large $\sigma^{(2)}$ values of 1,800, 1,200, and 1,000 GM,

respectively. The $\sigma^{(2)}$ value of **7M** was almost twice of those obtained for **8M** and **9**, suggesting that monozinc metalation is effective for 2PA enhancement. Since free base porphyrin works as an electron acceptor against zinc porphyrin, the monozinc metalation induces the molecular polarization which may cause intramolecular charge transfer in the 2PA transition process. On the other hand, the $\sigma^{(2)}$ value of 1,800 GM obtained for **7M** was four times smaller than that for **7D**. This indicates that the complementary coordination is another effective enhancement factor. In **7D**, the complementary coordination brings in the extended electronic communication through the coordination bonds. Further, the complementary coordination may also contribute to the larger $\sigma^{(2)}$ value of **7D** by the enhancement of the transition dipole moments as a result of the excitonic coupling (McRae & Kasha, 1958).

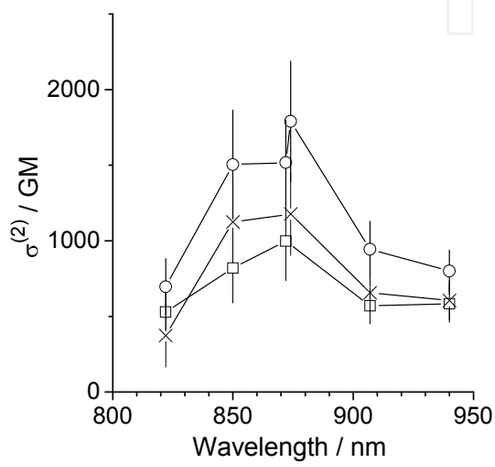

Fig. 5. 2PA spectra of **7M** (circle), **8M** (cross), and **9** (square) in $CHCl_3$ with 1-methylimidazole (1.5 M).

2.3 Effect of polymerization on the enhancement of the 2PA cross section

Reaction of free base **9** with excess amount of zinc acetate give di-zinc complex, which allows the formation of one-dimensionally propagated polymer **8P** by the successive complementary coordination of imidazolyl to zinc. Molecular weight of **8P** was analyzed by using gel permeation chromatography (GPC) with a column having an exclusion limit of 500,000 Dalton eluted by $CHCl_3$. The mean molecular weights, M_w and M_n of **8P** were estimated by comparing the data with those of polystyrene standards as 200,000 and 150,000, respectively.

The 2PA cross section of **8P** was measured in $CHCl_3$. Strong two-photon absorption was also observed in the Z-scan experiment and the $\sigma^{(2)}$ value per biszinc unit was estimated to be 4,000 GM at 873 nm. The enhancement factor for polymerization is 3.3 compared with the value obtained for **8M**. The mean $\sigma^{(2)}$ value of polymer **8P** was estimated to be ~400,000 GM, using the M_n value of 150,000 corresponding to 110 bisporphyrin units. The two-photon absorption spectra of **8P** are shown in Fig. 6. This value is extremely large compared with the value for **8M** with an enhancement factor of 360. Although the $\sigma^{(2)}$ value per dimer unit of **8P** shows the enhancement factor of 3.3 compared with that of **8M**, the value of 4,000 GM is almost the same as that of **7D** (3,800 GM), suggesting that the elongation effect more than three dimer units is not so significant for the 2PA enhancement.

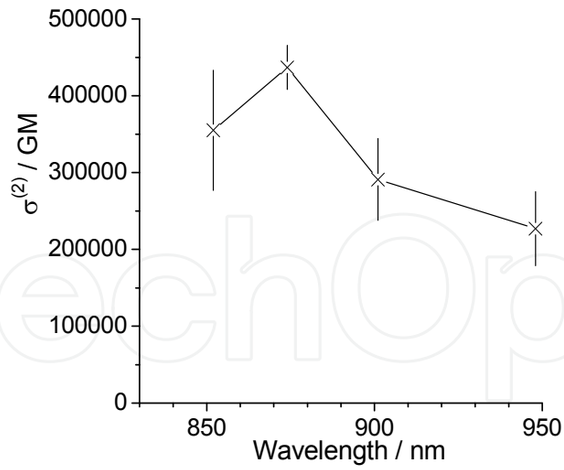

Fig. 6. 2PA spectra of **8P** in $CHCl_3$.

2.4 Nonlinear absorption measured with nanosecond pulses

Generally, the $\sigma^{(2)}$ value obtained with nanosecond laser pulses is 2 or 3 orders of magnitude larger than that measured using femtosecond pulses due to the excited state absorption (ESA) (Swiatkiewicz et al., 1998; Kim et al., 2000; Lei et al., 2001). This contribution is difficult to remove from the Z-scan data. However, on considering application of 2PA materials such as 2PA-PDT or 3-D optical memory, the nanosecond pulse system may be more appropriate because of availability and the easiness of operation. Therefore, we examined nonlinear absorption properties of nanosecond region for **7D** and **8P** by Z-scan measurements with a nanosecond optical parametric oscillator (OPO) pumped by a Nd:YAG laser. Fig. 7 shows plots of two-photon absorbance q_0 (Ogawa et al., 2005) against incident light intensity I_0 for **8P** at 850 nm. The pulse energy was varied between 1.0 mJ and 2.1 mJ. The value of q_0 was almost proportional up to I_0 of 1.1×10^{14} W/m^2, corresponding to

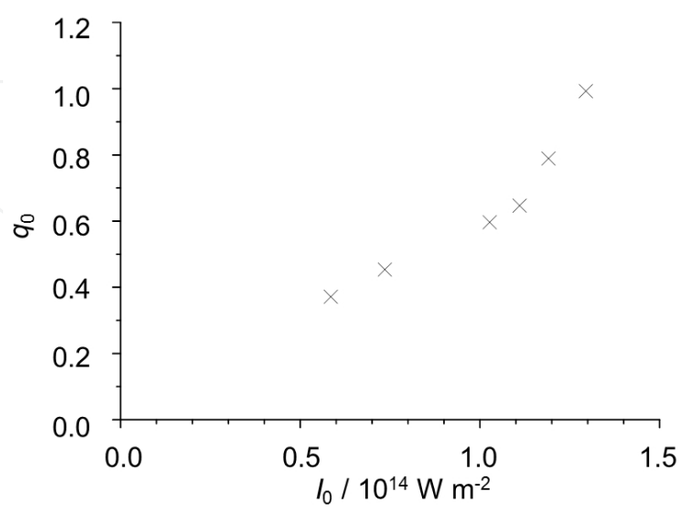

Fig. 7. Plots of the two-photon absorbance q_0 against peak intensity I_0 for **8P** at 850 nm with nanosecond pulses.

I_0 = 15 mW. This result shows that the ESA is significant at the high intensity region over 15 mW. Therefore, the effective $\sigma^{(2)}$ ($^{eff}\sigma^{(2)}$) spectrum was measured at the lowest intensity of 1.0 mJ as shown in Fig. 8. These spectra were similar to those obtained using femtosecond measurements and absorption maxima were observed at 890 nm in both compounds. The maximum $^{eff}\sigma^{(2)}$ values for **7D** and **8P** were estimated as 210,000 and ~22,000,000, respectively, which were 30 to 50 times larger than those observed by femtosecond pulses, indicating the presence of the ESA contribution.

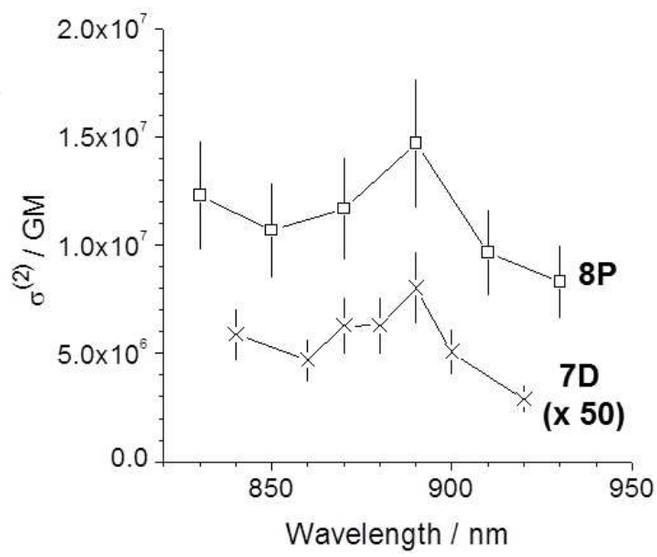

Fig. 8. 2PA spectra of **7D** and **8P** measured with nanosecond pulses. The pulse energy was 1.0 mJ for all the measurements.

2.5 Three-photon absorption

The higher-order nonlinear absorption than 2PA was found for **7D** at wavelengths longer than 1180 nm. The most probable higher-order nonlinear absorption process observed on using the femtosecond pulses originates from three-photon absorption (3PA). Furthermore, the wavelengths were almost three times long as that of the Soret band, suggesting 3PA. 2PA and 3PA can occur simultaneously in this wavelength range. When the observed data were analyzed as only 3PA was taken into account, a linear relationship between 3PA parameter p_0 (Tykwinski et al., 2002; Ogawa et al., 2005) and I_0 was obtained. This linear relationship does not necessarily mean the observation of the intrinsic 3PA (i.e. the simultaneous absorption of three photons), since two-step 3PA (e.g. 2PA followed by an excited state absorption process) also shows the same linear relationship. Although the possibility of two-step 3PA process cannot be completely ruled out, the observation may originate from the intrinsic 3PA process because the $\sigma^{(2)}$ values decreased as the irradiation wavelength approached the wavelength range in which 3PA was observed, and furthermore this range corresponds to three times the wavelength of the Soret band. The 3PA cross sections were estimated to be 7.1×10^{-77} m^6s^2 and 1.8×10^{-77} m^6s^2 at 1190 and 1280 nm, respectively. Materials exhibiting 3PA may be interesting for further high-resolution 3D optical memory, 3D fabrication, and PDT applications with merit of using longer NIR wavelength light.

2.6 Effects of water-solubilization and ethynylene connection on 2PA

Photodynamic therapy (PDT) is a medical treatment of cancers, which uses a photosensitizer without surgery, and is a one of the possible 2PA applications as described in Introduction. The penetration depth of visible light used in currently available PDT (630 nm) is limited only to reach tissue surface due to absorption and scattering by biological tissue, indicating that this method cannot be applied to the treatment of deep cancers. However, the penetration depth can be improved by using longer wavelength range of 700-1500 nm which is relatively transparent for biological tissue and called as the optical window. Since porphyrin compounds have strong one-photon absorption bands between 400 and 500 nm (the Soret band) 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, 2PA using porphyrins is suitable for PDT for deep cancers. Quadratic dependence on the laser intensity is another advantage of the use of 2PA. This allows high spatial selectivity by focusing the laser beam at the target point and prevents damages to healthy tissue. So, we have studied 2PA-PDT using conjugated porphyrins having high 2PA efficiency. First, compound **7D** was modified to be solubilized in water. Because porphyrins are tend to stack in water and this may affect optical properties of compounds, effect of water-solubilization on 2PA was examined. The water-solubility was obtained by introducing a carboxylic group instead of heptyl at each *meso*-position (**10D** (Fig. 9)) (Ogawa et al., 2006). Further, ethynylene-linked compound **11D**, obtained from a direct hetero-coupling reaction between donor zincporphyrin and acceptor freebase porphyrin, was also synthesized.

The $\sigma^{(2)}$ values in water were measured by a femtosecond open aperture Z-scan method at 850 nm. Strong nonlinear absorption was also observed at the focal point even in a dilute solution of 0.37 mM. The $\sigma^{(2)}$ value of **10D** was determined as 7,500 GM. This value is almost same as that of **7D** in chloroform, indicating no water-solubilization effect on 2PA. The $\sigma^{(2)}$ value of ethynylene compound **11D** was also measured as 7,900 GM, being almost equivalent to that of **10D**. These results show that the water-soluble porphyrin assemblies **10D** and **11D**, exhibiting strong two-photon absorption, are possible candidates for the 2PA-PDT agent.

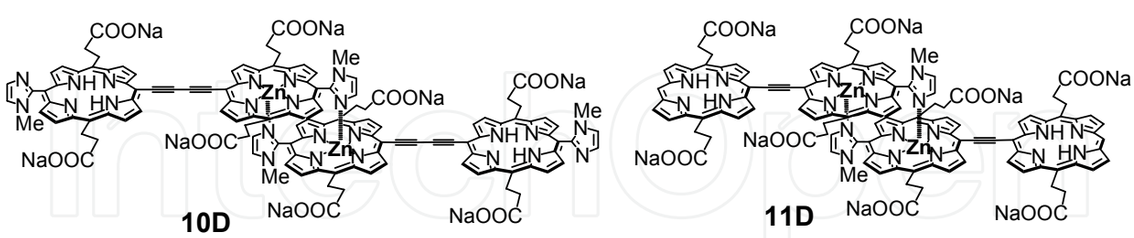

Fig. 9. Structures of water-soluble self-assembled porphyrins **10D** and **11D**.

2.7 Effect of elongation of conjugated bisporphyrin on 2PA

Bis(imidazolylporphyrin) generates not only polymers but also discrete shorter porphyrin arrays by the addition of monomeric imidazolylporphyrins as terminators through the complementary coordination of imidazolyl to zinc (Ogawa & Kobuke, 2000; Kobuke & Ogawa, 2003; Ogawa & Kobuke, 2006). The conjugated bisporphyrins also gives regulated porphyrin arrays by the self-assembly. Consequently, we synthesized a butadiynylene-bridged bisporphyrin monomer **12** and dimer **13** terminated with monomeric porphyrins on

both ends and examined the effect of incremental elongation of butadiynylene-linked porphyrin arrays on 2PA (Dy et al., 2008).

Absorption spectra are illustrated in Fig. 11. Zinc-imidazolyl coordinated dimer **14** shows characteristic splitting of the Soret band at 415 and 438 nm. On the other hand, the Soret band of **12** having one butadiynylene-linked bisporphyrin unit exhibits broader and red-shifted peaks at 434, 461, and 495 nm due to not only larger head-to-tail interaction between chromophores but also the expansion of π-conjugation. Furthermore, strong Q-bands corresponding to HOMO-LUMO absorption were observed at longer wavelengths of 666 and 728 nm, also indicating the expansion of π-conjugation. Q-bands of **13** which consists of two butadiynylene-linked bisporphyrin units appeared at 670 and 733 nm which are slightly red-shifted and amplified compared to **12**. The amplification of Q-bands is not two times but almost three times the intensity, indicating stronger dipole moments caused by excitonic interaction between the two bisporphyrins, and may contribute to larger resonance enhancement for **13**.

The 2PA spectra were measured using the open-aperture z-scan method with 120 fs pulses at off-resonant wavelengths from 820 to 940 nm, as described above. Compounds **12** and **13** exhibited maximum $\sigma^{(2)}$ values of 10,000 and 61,000 GM at 870 nm, respectively (Fig. 12), showing a six times enhancement of $\sigma^{(2)}$. Self-assembled porphyrin dimer **14** was not measured due to its too weak 2PA (less than 20 GM). The large $\sigma^{(2)}$ value observed for **12** is mainly due to the expansion of π-conjugation by the butadiynylene linkage as evidenced by the large and red-shifted Q-band (Fig. 11).

The insertion of another butadiynylene-linked bisporphyrin unit by complementary coordination resulted in a further enhanced $\sigma^{(2)}$ value. As described in the one-photon absorption spectra, the amplification of the Q-band of **13** is almost three times the value of **12** due to the larger transition dipole moments caused by the excitonic interaction between two butadiynylene-linked bisporphyrins. Since the $\sigma^{(2)}$ value is proportional to the square of the transition dipole moment of the one-photon absorption (Birge & Pierce, 1979), the amplification of the Q-band may contribute to larger enhancement for **13**.

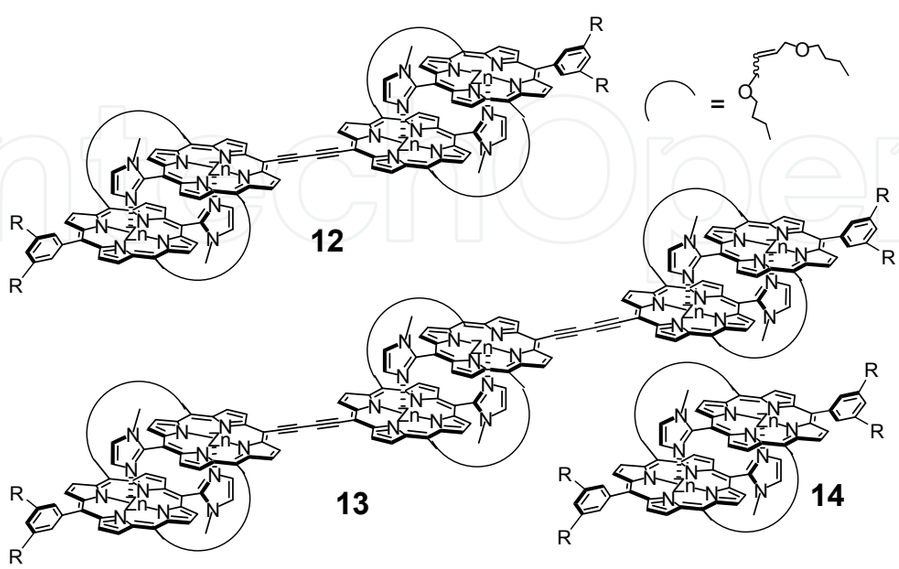

Fig. 10. Structures of compounds **12**, **13**, and **14**.

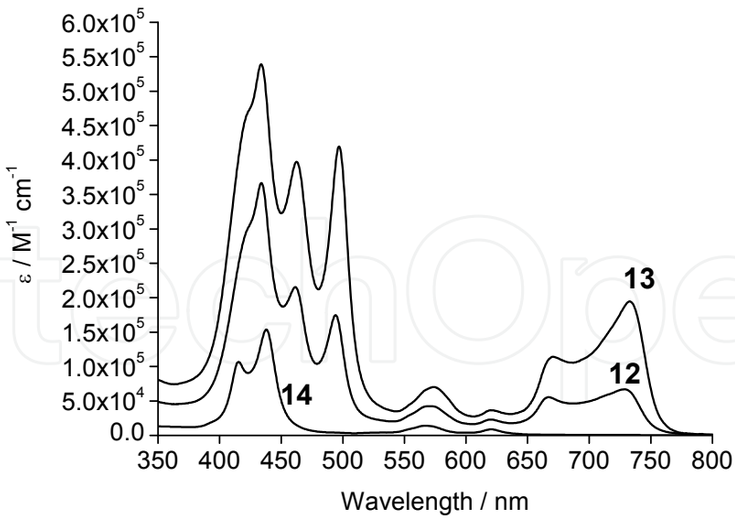

Fig. 11. One-photon absorption spectra of compounds **12**, **13**, and **14**.

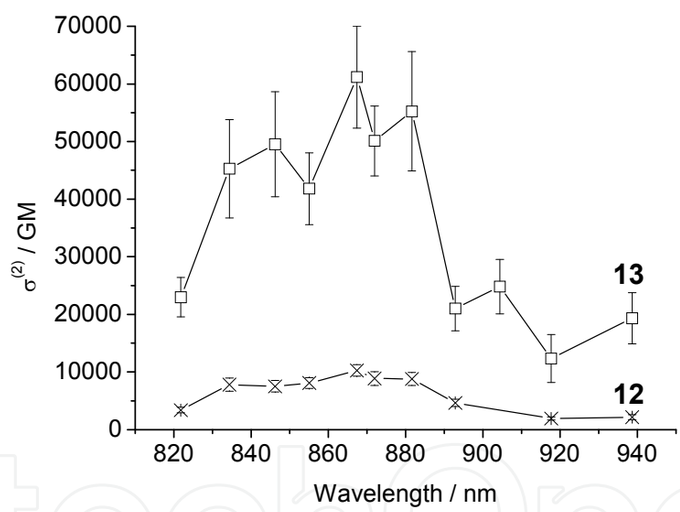

Fig. 12. 2PA spectra of **12** and **13**.

2.8 Nonlinear absorption by self-assembled porphyrin-phthalocyanine conjugates

As discussed above, we have developed supramolecular conjugated porphyrins linked with a ethynylene or butadiynylene bond exhibiting the largest class of $\sigma^{(2)}$ values reaching an order of 10^4 GM and relatively strong 3PA, too. Then, we have developed further multichromophore systems, in which porphyrin and other chromophores are connected using an ethynylene inducing a molecular polarity. Phthalocyanines are of attractive interest because they have an 18π conjugation system as large as porphyrins and are chemically stable. In this respect, it is interesting to construct a porphyrin-phthalocyanine conjugate using the ethynylene bridge. Here, we introduce large multiphoton absorption, 2PA and 3PA, behavior of self-organized dimers of imidazolylporphyrin-zincphthalocyanine **15**

(H$_2$(ImPor)-Zn(Pc)) and **16** (Zn(ImPor)-Zn(Pc)) in the antiparallel fashion (Fig 13) (Morisue and Kobuke, 2008; Morisue et al., 2010). A high association constant of complementary coordination of imidazolyl to zinc (~10^{14} M^{-1}) allows organization of M(ImPor)-Zn(Pc) into the dimer. The dimer composed of porphyrin and phthalocyanine tetrad gives following advantages for exhibiting strong multiphoton absorption. One is the coplanar π-conjugation between porphyrin and phthalocyanine through the ethynylene bond. The other is the possibility of the resonance enhancement of 2PA transition, because the Q band of phthalocyanine would give a small detuning energy for a 2PA transition in the near-IR range. Furthermore, the dimer may form a 2D quadrupolar structure different from the 1D ones, for example D–π–A–π–D or A–π–D–π–A. In addition, electron-withdrawing nature of porphyrin can be tuned further by metalation of the porphyrin center, for example, **15** having free base porphyrin gives higher charge-transfer ability than **15** having zincporphyrin.

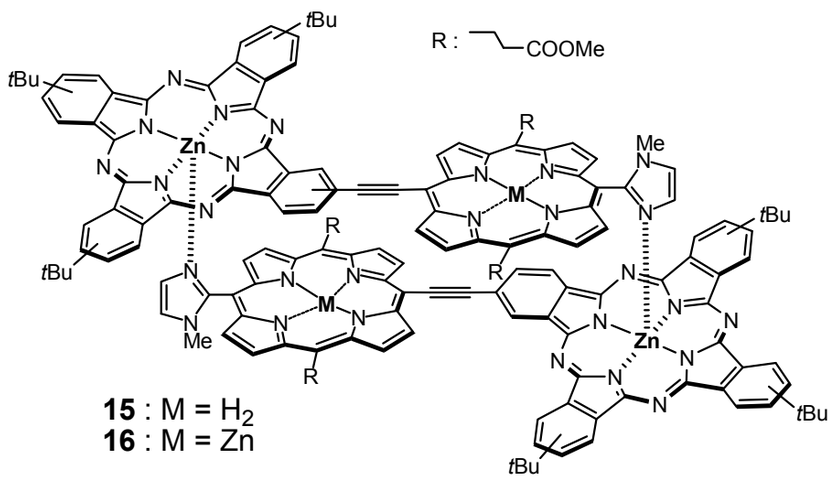

Fig. 13. Structures of the antiparallel dimers **15** (M=H$_2$) and **16** (M=Zn). The dimer is a regioisomeric mixture due to the presence of the regioisomeric mixtures of ethynylene linker and *tert*-butyl groups at the β-position of phthalocyanine.

Nonlinear absorption (NLA) was measured with the same femtosecond Z-scan system as above Chapters varying the incident laser wavelength from 800 to 1550 nm. The NLA behavior depended on the wavelength range. At a wavelength shorter than 996 nm, the simultaneous 2PA process was dominant. In the wavelength region shorter than 900 nm where the edge of one-photon absorption remains, the saturable absorption (SA) of one-photon absorption was observed. The Z-scan data was analyzed by considering the SA process (Morisue et al., 2010). As shown in 2PA spectra (Fig. 14), $\sigma^{(2)}$ value increased with decreasing the incident wavelength and no peak top was observed. The maximum $\sigma^{(2)}$ values in the wavelength region where SA and 3PA are negligible (900–996 nm) were 16,000 and 7,000 GM at 900 nm for **15** and **16**, respectively. These $\sigma^{(2)}$ values are relatively large compared to those of related compounds as discussed in above Chapters. The $\sigma^{(2)}$ value of **15** having free base porphyrin is twice larger than that of **16** having zincporphyrin, suggesting that larger molecular polarity amplified the $\sigma^{(2)}$ value for **15**. The obtained large values suggest considerable π-delocalization over tetrad through complementary coordination between imidazolylporphyrin–zincphthalocyanine dimers. Unfortunately, the

comparable value of the dissociated dimer could not be obtained due to its extremely large association constant of 10^{14} M^{-1}.

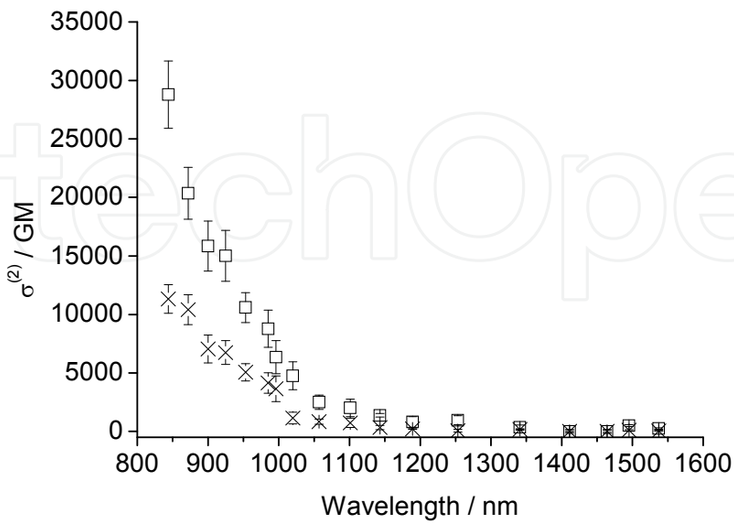

Fig. 14. 2PA spectra of **15** (square) and **16** (cross).

On the other hand, in the wavelength region longer than 996 nm, the higher-order NLA other than 2PA was observed for all the samples. When the observed data were analyzed as 3PA, a good linear relationship between 3PA parameter p_0 and I_0 was obtained. The 3PA spectra are shown in Fig 15. 3PA were observed around 1000–1100 nm, which corresponds to three times the wavelength of the Soret band of phthalocyanine part (around 350 nm). Since 3PA has the same parity selection rule with one-photon absorption, a one-photon-allowed excited state is always 3PA-allowed even for the centrosymmetric system unlike the case of 2PA. Therefore, the final state of the 3PA transition is considered to be the Soret band of phthalocyanine part. The maximum $\sigma^{(3)}$ values were estimated as 7.6×10^{-76} cm^6 s^2 at 1020

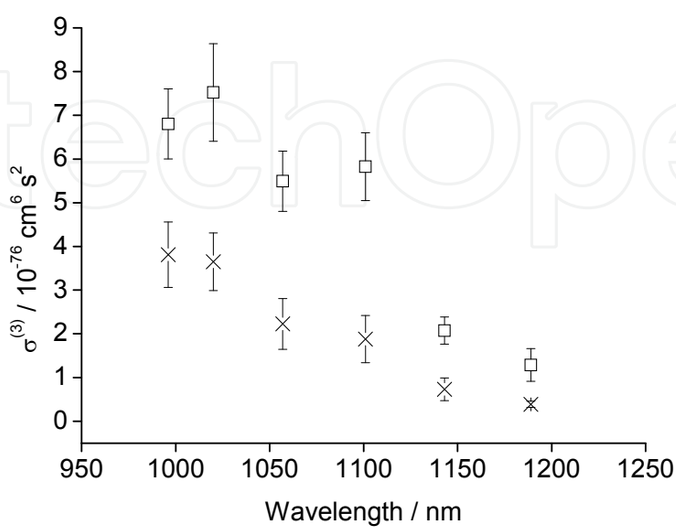

Fig. 15. 3PA spectra of **15** (square) and **16** (cross).

nm and 3.8 × 10^{-76} cm^6 s^2 at 996 nm for **15** and **16**, respectively. The values are almost 10 times larger than those obtained for **7D**. This large $\sigma^{(3)}$ values may arise from the resonance enhancement of the 2PA state or the two-step 3PA process: i.e., the 2PA followed by the excited state absorption (ESA).

3. Conclusion

Recent progress in the nonlinear absorption (2PA and 3PA) properties of self-assembled porphyrin arrays has been reviewed. These studies demonstrate that self-coordination for constructing porphyrin arrays based on complementary coordination of imidazolyl to zinc is a convenient and powerful tool enhancing the nonlinear absorption. We believe that these investigations open the way for further exploration of new types of nonlinear absorption materials. Moreover, the enhancement of the cross-sections will make possible the production of future 2PA applications.

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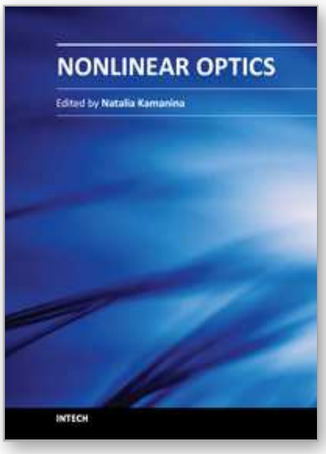

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Rapid development of optoelectronic devices and laser techniques poses an important task of creating and studying, from one side, the structures capable of effectively converting, modulating, and recording optical data in a wide range of radiation energy densities and frequencies, from another side, the new schemes and approaches capable to activate and simulate the modern features. It is well known that nonlinear optical phenomena and nonlinear optical materials have the promising place to resolve these complicated technical tasks. The advanced idea, approach, and information described in this book will be fruitful for the readers to find a sustainable solution in a fundamental study and in the industry approach. The book can be useful for the students, post-graduate students, engineers, researchers and technical officers of optoelectronic universities and companies.

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