

## Two-photon Absorption Cross Sections of Phthalocyanine Nanoparticles

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Materials having large two-photon absorption cross sections have attracted considerable interest because they offer a wide range of potential applications such as 3D-microfabrication, optical power limiting, optical data storage, two-photon-excited fluorescence imaging, and two-photon photodynamic therapy. In this study, we measured two-photon absorption cross sections of nanoparticles of phthalocyanine derivatives by the open aperture Z-scan method using a femtosecond Ti: sapphire regenerative amplifier laser. Transparent phthalocyanine nanoparticles dispersed in water was prepared by a method of laser ablation in water. The values of two-photon absorption cross section per molecule of nanoparticles were ca. 48 GM ( $1 \text{ GM} = 1 \times 10^{-50} \text{ cm}^4 \text{ s/photon}$ ) at 800 nm for copper phthalocyanine, ca. 65 GM at 820 nm for nickel phthalocyanine nanoparticles, and ca. 121 GM at 820 nm for tetra-*t*-butyl-substituted copper phthalocyanine. Nanoparticles of the tetra-*t*-butyl-substituted copper phthalocyanine have a little higher two-photon absorption cross sections than the molecules in tetrahydrofuran.

Key words: nanoparticle, two-photon Absorption, optical nonlinearity, Z-scan, phthalocyanine derivative

## 1. INTRODUCTION

Materials having large two-photon absorption cross sections have attracted considerable interest because they offer a wide range of potential applications such as 3D-microfabrication [1,2], optical power limiting [3-5], optical data storage [6,7], two-photon-excited fluorescence imaging [8,9], and two-photon photodynamic therapy [10]. Therefore, compounds exhibiting large two-photon absorption cross sections ( $\sigma^{(2)}$ ) have been practically sought for such applications, resulting in a number of molecules with large  $\sigma^{(2)}$ 's have been synthesized [11-13]. However, the  $\sigma^{(2)}$ 's of compounds developed up until now still need to be improved in order to fulfill the requirement of practical applications.

Nanoparticles are also very attractive materials. Nanoparticles of metals and semiconductors have different properties from crystals or atoms. Energy of an electron in a metal or semiconductor nanoparticle depends on the particle size significantly due to quantum effects. In these twenty years, optical properties of nanoparticles of organic compounds have been studied [14-17]. Furthermore, a new method to produce nanoparticles utilizing the laser ablation has been developed recently [18-26]. This method has many advantages compared with other methods. For instance, it can be applied to materials insoluble to solvents.

In this study, we measured two-photon absorption cross sections of nanoparticles of phthalocyanine derivatives by the open aperture Z-scan method using a femtosecond Ti: sapphire regenerative amplifier laser. Two-photon absorption cross section spectra were measured in the laser wavelength range of 780-840 nm. Molecular orbital calculations were done to prove the existence of two-photon allowed high-lying excited states. Although optical limiting property of

phthalocyanine nanoparticles has been reported [27], two-photon absorption of nanoparticles has not been reported to the authors' knowledge.

## 2. EXPERIMENTAL

Copper(II) phthalocyanine (CuPc) and nickel(II) phthalocyanine (NiPc) were purchased from Tokyo Chemical Industry Co., Ltd., and Copper(II) 2,9,16,23-tetra-*tert*-butyl-29*H*,31*H*-phthalocyanine [Cu (Bu)<sub>4</sub>Pc] was purchased from Aldrich Chemical Co. They were used without further purification. The structural formulas of these dyes are shown in Fig. 1.

Transparent organic dye nanoparticles dispersed in water was prepared by a method of laser ablation in water; the 355 nm output beam of a YAG laser was irradiated a mixture of polycrystals of a dye, a surfactant, sodium dodecyl sulfate, and water for ca. 5 minutes. The surfactant was added to stabilize the colloidal solutions [17]. Typical energy density of the laser beam for laser

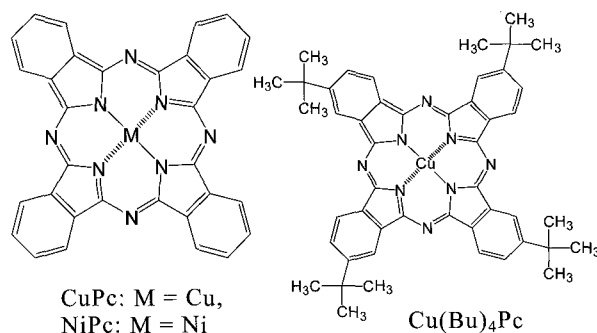


Fig. 1. Structural formulas of the studied phthalocyanines.

ablation was  $590 \text{ mJ/cm}^2$ . After irradiation of YAG laser beam, colloidal solutions were concentrated using a rotary evaporator by a factor of 4-8. Solutions were filtered using membrane filters (pore size 800 nm was used for Z-scan measurements).

One-photon absorption (UV-visible) spectra of the dyes were measured using a JASCO spectrophotometer V-550 with a 1-mm quartz cell.

Two-photon absorption cross section spectra were measured by the open-aperture Z-scan method [28]. A femtosecond regenerative amplifier (Spectra-Physics, Spitfire) was used as a wavelength-tunable light source. The typical pulse duration was ca. 300 fs with a repetition rate of 1 kHz. The incident beam was focused by a plano-convex lens ( $f = 150 \text{ mm}$ ) and the sample solutions held in a quartz cuvette was scanned along the propagation axis of the incident beam. The path length of the cuvette was chosen to be 1 or 2 mm depending on the sample concentration and the magnitude of the cross section. It was shorter than the Rayleigh range of the setup ( $z_R = 4.9 \text{ mm}$  depending on the wavelength), which fulfills the optically thin condition. The average incident power was varied from 0.4 to 1.5 mW, corresponding the on-axis peak powers ( $I_0$ ) of 90–330  $\text{GW/cm}^2$ . The concentrations of the sample were made to be as high as possible for the better signal-to-noise ratio in the Z-scan measurements. The concentrations of nanoparticles as a monomer were  $6.4 \times 10^{-4}$  -  $3.7 \times 10^{-3} \text{ mol/l}$  for CuPc,  $9.0 \times 10^{-4}$  -  $1.5 \times 10^{-3} \text{ mol/l}$  for NiPc, and  $7.0 \times 10^{-4} \text{ mol/l}$  for  $\text{Cu}(\text{Bu})_4\text{Pc}$ . Two-photon absorption spectra were taken from 780 to 840 nm. Methanol solution of rhodamine 6G or rhodamine B was used as a reference of two-photon absorption cross sections [29].

### 3. RESULTS AND DISCUSSION

#### 3.1 One-photon UV/Vis absorption spectra

The one-photon UV/Vis absorption spectra of colloidal solutions of CuPc and NiPc are shown in Fig. 2. A small peak at 686 nm can be attributed to monomer band, and a broad band around 604 nm can be attributed to H-aggregate band for CuPc nanoparticles. A similar assignment can be done for NiPc nanoparticles.

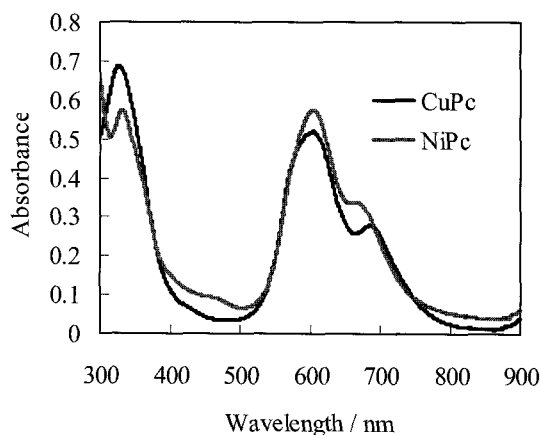


Fig. 2. UV/Vis absorption spectra of CuPc and NiPc nanoparticles.

Although their solubility was very poor, an absorption spectrum of CuPc in dimethyl sulfoxide (DMSO) was measured and is shown in Fig.3. A broad band around 680 nm can be attributed to dimer and/or H-aggregate bands. Difference between spectra of colloidal solution and DMSO solution of CuPc is little.

Figure 4 shows absorption spectra of colloidal solutions after filtration with filters of pore size 800 nm, 450 nm and 220 nm. These spectra indicate that the sizes of particles are widely distributed.

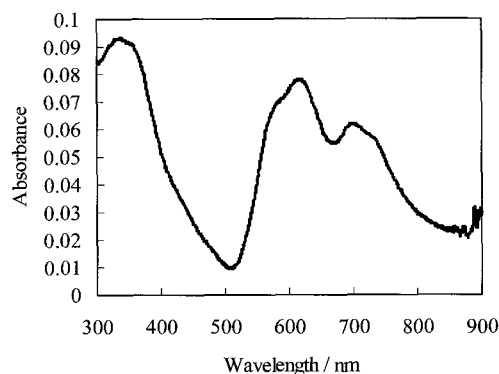


Fig. 3. UV/Vis absorption spectra of CuPc in DMSO.

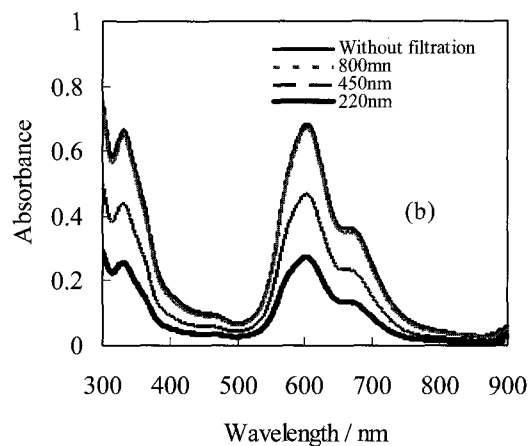
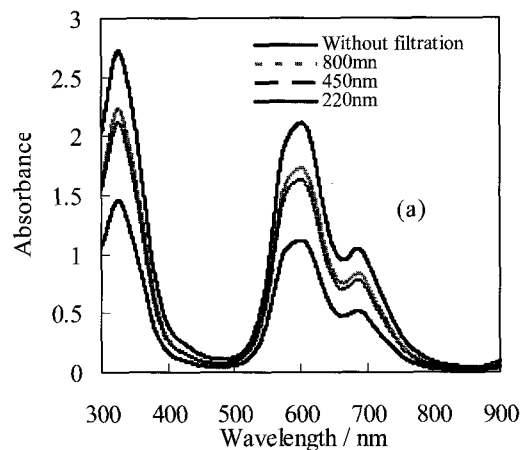


Fig. 4. UV/Vis absorption spectra of (a) CuPc nanoparticles and (b) NiPc nanoparticles.

### 3.2 Two-photon absorption cross sections and their laser wavelength dependence

Figure 5 shows a typical example of Z-scan signatures for a CuPc colloidal solution. We adjusted laser power so that the maximum absorption is less than several percents for each dye. Values of the two-photon absorption cross sections were calculated using Eq. (1). Figure 6 shows laser wavelength dependence of two-photon absorption cross sections of these compounds. The maximum values of two-photon absorption cross section per molecule were ca. 48 GM at 800 nm for CuPc nanoparticles and ca. 65 GM at 820 nm for NiPc nanoparticles.

Correa et al. measured two-photon absorption cross section of perylene tetracarboxylic derivatives [30]. Their two-photon absorption cross section spectra show strong near-resonant effect in short wavelength range. All four derivatives have cross section of greater than 4000 GM in the near-resonant region. Our compounds have a value smaller than 100 GM in the laser wavelength range of 780-840 nm. Although we expected near-resonant effect of two-photon absorption for phthalocyanines, it was not observed.

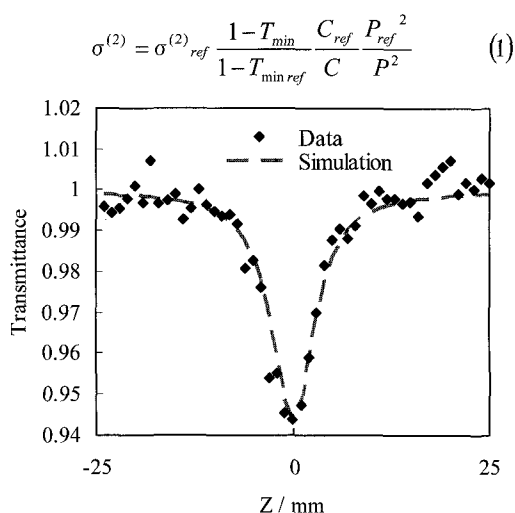


Fig. 5. Typical example of Z-scan. The concentration of colloidal CuPc is  $9.8 \times 10^{-4}$  mol/l.

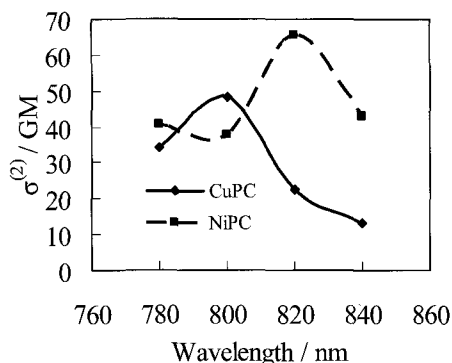


Fig. 6. Laser wavelength dependence of two-photon absorption cross sections of phthalocyanine nanoparticles.

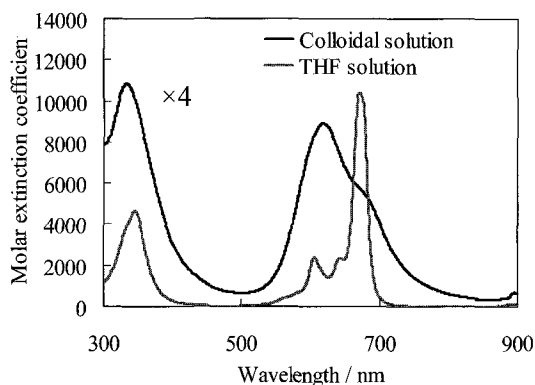


Fig. 7. UV/Vis absorption spectra of colloidal solution (solid line, concentration:  $7.0 \times 10^{-4}$  mol/l) and THF solution (broken line, concentration:  $9.5 \times 10^{-4}$  mol/l) of  $\text{Cu}(\text{Bu})_4\text{Pc}$ .

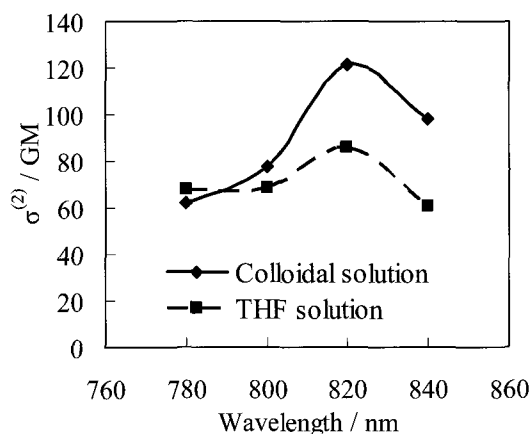


Fig. 8. laser wavelength dependence of two-photon absorption cross sections of  $\text{Cu}(\text{Bu})_4\text{Pc}$ .

### 3.3 Absorption spectra and two-photon absorption cross sections of a phthalocyanine in nanoparticles and in solution

In order to compare two-photon absorption cross sections of nanoparticles and free molecules in solution,  $\text{Cu}(\text{Bu})_4\text{Pc}$  was studied because of its solubility in organic solvents. Figure 7 shows absorption spectra of  $\text{Cu}(\text{Bu})_4\text{Pc}$  in nanoparticles and tetrahydrofuran (THF) solution. While spectrum of THF solution shows narrow bands, that of nanoparticle shows broad bands. These spectra tell that nanoparticles of  $\text{Cu}(\text{Bu})_4\text{Pc}$  has H-aggregate character. Nanoparticles of  $\text{Cu}(\text{Bu})_4\text{Pc}$  have two-photon absorption cross sections slightly higher than  $\text{Cu}(\text{Bu})_4\text{Pc}$  molecules in THF.

### 3.4 Molecular orbital calculations

In order to understand the electronic states of the studied dye molecules, *ab initio* molecular orbital (MO) calculations were done using Gaussian 03 (Gaussian Co.). The optimized structures of these dyes in the ground states and the energy levels of excited states were calculated at UHF/3-21G level.

Tables I and II summarized results of the MO calculations. One-photon transition wavelengths were underestimated by the calculations. These calculations predicted existence of two-photon allowed high-lying excited states around 25000 cm<sup>-1</sup> (energy of two-photon absorption of 800 nm).

Table I. Electronic transitions of copper phthalocyanine calculated by an *ab initio* molecular orbital method. Six excited states are listed. 1PA and 2PA mean one-photon absorption and two-photon absorption, respectively

Excited State	Transition wavelength/nm	Oscillator strength	Representation	Allowed transition
1	585.56	0.5179	E <sub>u</sub>	1PA
2	497.09	0.0669	E <sub>g</sub>	2PA
3	456.13	0.4889	E <sub>u</sub>	1PA
4	387.26	0.0949	E <sub>u</sub>	1PA
5	382.84	0.0119	B <sub>1g</sub>	2PA
6	340.25	0.0116	A <sub>1g</sub>	2PA

Table II. Electronic transitions of nickel phthalocyanine calculated by an *ab initio* molecular orbital method. Six excited states are listed

Excited State	Transition wavelength/nm	Oscillator strength	Representation	Allowed transition
1	576.08	0.5827	E <sub>u</sub>	1PA
2	500.98	0.0000	E <sub>g</sub>	2PA
3	468.55	0.6252	E <sub>u</sub>	1PA
4	395.93	0.0000	E <sub>u</sub>	1PA
5	385.62	0.0000	B <sub>1g</sub>	2PA
6	341.78	0.0000	E <sub>u</sub>	1PA

#### 4. CONCLUSIONS

Two-photon absorption cross sections of organic nanoparticles have measured for the first time using the open aperture Z-scan method. The maximum values of two-photon absorption cross section per molecule were ca. 48 GM at 800 nm for CuPc nanoparticle, ca. 65 GM at 820 nm for NiPc nanoparticles, and ca. 121 GM at 820 nm for Cu(Bu)<sub>4</sub>Pc nanoparticles.

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