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Self-Aggregation Enhanced Third-Order Optical Nonlinearities of Aryloxy Substituted Zinc Phthalocyanines *

LI Zhong-Yu(李忠玉)[1**], WU Chun-Hui(吴春晖)[1], HUANG Xin(黄新)[2], XU Song(徐松)[1]

[1]*Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Department of Petrochemical Engineering, Changzhou University, Changzhou 213164*

[2]*Institute of Animal and Plant Quarantine of Chinese Academy of Inspection and Quarantine, Beijing 100029*

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Third-order optical nonlinearities of three aryloxy substituted phthalocyanines are measured by femtosecond forward degenerate four-wave mixing technique at 800 nm. Ultrafast optical responses are observed and the magnitude of the second-order hyperpolarizabilities γ of the phthalocyanines is measured to be as large as 10^{-31} esu. Due to the enhancement of J-aggregates, the γ value of an aryloxy substituted zinc phthalocyanine in chloroform is approximately 2.2 times larger than that of the dye in methanol. Moreover, the morphologies of aryloxy substituted zinc phthalocyanine in chloroform exhibit that the nanowires with a diameter of 50–100 nm are connected to each other to form an indefinite network structure, while no aggregates are detected when the samples are prepared from a solution in the methanol.

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Research of third-order optical nonlinearities of materials in applications to develop optical devices for the control of light has been of great interest so far.[1−6] Among nonlinear optical materials, J-aggregates of dye molecules are attractive from a spectroscopic viewpoint because the systems are expected to show the crossover between the macroscopic properties of bulk materials and microscopic ones of isolated molecules. The experimental and theoretical works have shown that molecular J-aggregates are self-organized quasi-one-dimensional systems of cyanine dyes that combine large third-order susceptibility in the J-band with a fast response time.[7,8] The enhancement of the nonlinear optical properties results from the exciton delocalization over the aggregates.[9]

Owing to the extended π system, it is well-known that phthalocyanines exhibit a high aggregation tendency forming dimeric and oligomeric species in solutions.[10] It has been shown that this molecular association greatly influences the intrinsic nature of macrocycles including their spectroscopic, photophysical, electrochemical and nonlinear optical properties.[11] Therefore, much effort has been taken over assembling J-aggregates. For example, Li and Ng[12] have demonstrated that phthalocyaninenucleobase conjugates such as phthalocyanineadenine derivatives in dichloromethane can form J-aggregates due to a variety of intermolecular interactions. Watarai *et al.*[13] have observed that the two-dimensional high-ordered J-aggregates of thioether-substituted phthalocyanine and subphthalocyanine derivatives were formed at the toluene/water interface upon addition of Pd(II) into the system. Recently, our group has provided another facile strategy to construct phthalocyanine J-aggregates based on Zn^{2+}-O coordination.[14,15] In the present Letter, we report the third-order nonlinear optical properties of three aryloxy substituted phthalocyanines measuring by femtosecond forward degenerate four-wave mixing (DFWM) technique at 800 nm. The J-aggregation enhancement of the third-order nonlinear optical property for an aryloxy substituted zinc phthalocyanine in chloroform is also discussed.

The three tetrakis(aryloxy)phthalocyanines, tetra-R-(4-tert-butylphenoxy)phthalocyanine (Pc1), tetra-R-(4-tert-butylphenoxy)phthalocyaninatonickel (Pc2) and tetra-R-(4-tert-butylphenoxy)phthalocyaninatozinc (Pc3) were synthesized as a described procedure,[14] and characterized by IR, MS, ^{1}H NMR and elemental analysis. Their structures are shown in Fig. 1. The phthalocyanines Pc1–Pc3 were dissolved in chloroform at the concentration of $\sim 3.0 \times 10^{-5}$ M, and the Pc3 was dissolved in methanol at a concentration of 4.0×10^{-5} M for experiments.

The absorption spectrum of each sample solution was recorded at room temperature on a UV/visible spectrophotometer (UV-759, Shanghai Precision & Scientific Instrument Co., Ltd., China). Morphologies of the samples were observed on a JEM-2100 transmission electron microscope (TEM) and SUPRA 55 Field emission scanning electron microscope (FESEM, Germany).

The measurements of time-resolved DFWM were performed at a wavelength of 800 nm with 50 fs

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**Corresponding author. Email: zhongyuli@mail.tsinghua.edu.cn

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pulses from a Ti:sapphire regenerative amplifier laser (Spectra-Physics, Spitfire, 1 kHz, 1 W) in a two-beam configuration.[16] Samples were collected in quartz cuvette with a path length of 1 mm. The two incident light beams with nearly equal intensities were split off the same laser pulse, and were impinging on the sample with a variable optical delay between them. Setting up a polarization grating is an example of a technique that can achieve the interaction. The nonlinear DFWM signal results in self-diffraction of the second pulse in the grating setup through coherent overlap between the polarizations from the first and second pulses. The generated DFWM signal emitted in the direction $2\boldsymbol{k}_2$–$\boldsymbol{k}_1$ was detected by a photodiode, and subsequently analyzed by a boxcar and computer.

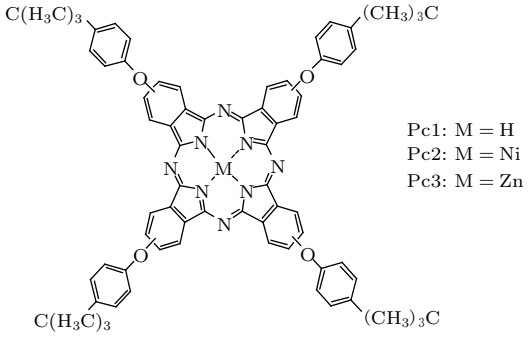


Fig. 1. Structural formulae of the three aryloxy substituted phthalocyanines Pc1–Pc3.

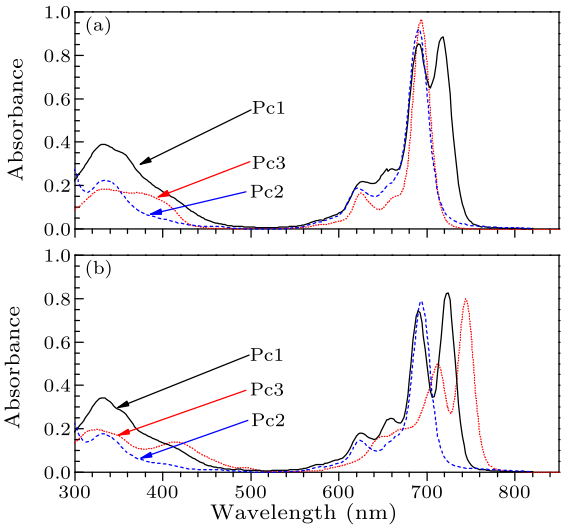


Fig. 2. Absorption spectra of the phthalocyanines Pc1–Pc3 in methanol (a) and chloroform (b).

Figure 2 shows the absorption spectra of the phthalocyanines Pc1–Pc3 in methanol and chloroform. The metal-free Pc1 in methanol exhibits split Q-bands with absorption maxima ($\lambda_{\max}$) at 690 and 718 nm, while the metalled Pc2 and Pc3 show a single Q-band absorption centered at 693 and 690 nm, respectively (Fig. 2(a)). All these absorption spectra are typically of monomeric phthalocyanines and metallophthalocyanines.[17] However, in chloroform, the absorption behavior of Pc3 is significantly changed. As shown in Fig. 2(b), while Pc1 and Pc2 in chloroform still exhibit monomeric absorption (split Q-bands with $\lambda_{\max}$ at 690 and 724 nm for Pc1 and a single Q-band at 694 nm for Pc2), the Q-band for Pc3 is distinctly red-shifted and split. The $\lambda_{\max}$ of the split bands for Pc3 is at 713 and 744 nm. With reference to previous spectroscopic work on metalled Pc's,[13,18] this absorption spectrum change is attributed to the aggregation of Pc3. As mentioned previously, the J-aggregates of Pc's and their metalled congeners show sharp and red-shifted Q-bands relative to their monomer bands. Thus, the red-shifted and split Q-band of Pc3 in chloroform solvent suggests the formation of J-aggregates.

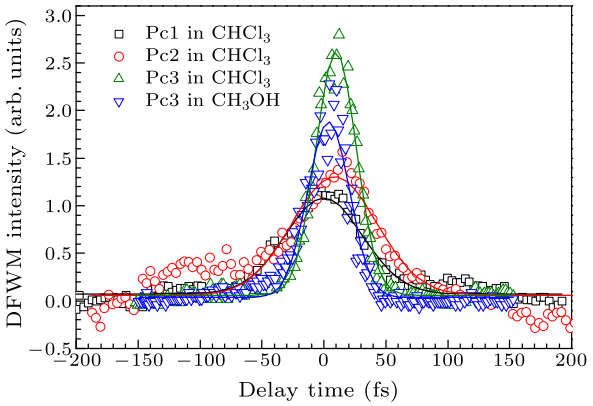


Fig. 3. Temporal response of the DFWM signal as a function of the probe delay for the samples (Pc1–Pc3 in chloroform and Pc3 in methanol).

Figure 3 shows the temporal response of the DFWM signal as a function of the probe delay for the samples (Pc1–Pc3 in chloroform and Pc3 in methanol). The DFWM signal of each sample is well-fitted by a Gaussian function (solid curve), and the half width of fitting curve is similar to the autocorrelated pulse duration. All the signal profiles almost exhibit symmetry about the maximum signal (the zero time delay), which indicate that the response times of the third-order optical nonlinearities are shorter than the experimental time resolution (50 fs). Such instantaneous response means that the Kerr effect (electronic component) from the distortion of the large π-conjugated electron charge distribution of phthalocyanine molecules is the main reason for generating the DFWM signal.

The third-order nonlinear susceptibility $\chi^{(3)}$ is obtained according to the following relationship

$$\chi^{(3)}_{\text{sample}} = \left(\frac{n_{\text{sample}}}{n_{\text{ref}}}\right)^2 \left(\frac{I_{\text{sample}}}{I_{\text{ref}}}\right)^{1/2} \left(\frac{L_{\text{ref}}}{L_{\text{sample}}}\right) \times \alpha L_{\text{sample}} \exp\left(\frac{\alpha L_{\text{sample}}}{2}\right) \left[1 - \exp(-\alpha L_{\text{sample}})\right]^{-1} \chi^{(3)}_{\text{ref}}, \quad (1)$$

where I is the DFWM signal intensity, α is the linear

absorption coefficient, L is the sample path length, and n is the refractive index. The subscript ref refers to the reference CS_2 and the $\chi^{(3)}$ value of CS_2 is estimated to be 1×10^{-13} esu in femtosecond timescale.[19]

Then the second-order molecular hyperpolarizability γ of the sample may be estimated by the equation

$$\gamma = \frac{\chi^{(3)}}{T^4 N_0}, \tag{2}$$

where N_0 is the number density of the dye molecules per milliliter, and T is the local field factor. For the calculation, the formula for the spherical molecules $T = (n^2_{\text{sample}} + 2)/3$ is used.

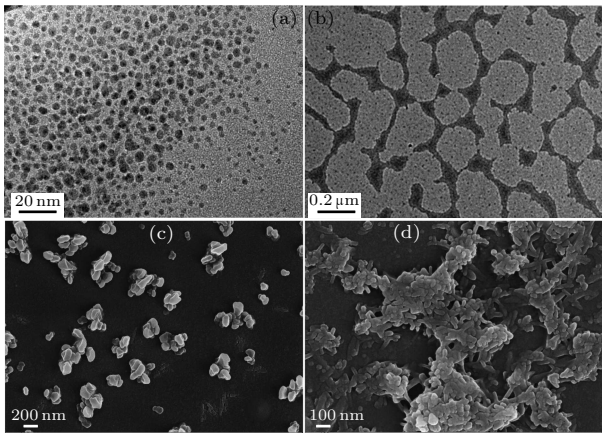


Fig. 4. TEM and FETEM images of Pc3 samples prepared from the methanol solution [(a) and (c)], from chloroform solution [(b) and (d)].

Therefore, the evaluated values of γ for the studied phthalocyanines (Pc1–Pc3) in chloroform solution and Pc3 in methanol solution are 3.41×10^{-31}, 3.91×10^{-31}, 10.1×10^{-31} and 4.6×10^{-31} esu, respectively. The values of the second-order molecular hyperpolarizabilities of the Pc2 and Pc3 are larger than that of metal-free phthalocyanine Pc1. This enhancement of γ mainly comes from the d valence orbital contribution of central metal atoms (Zn and Ni) of the Pc2 and Pc3. The γ value of Pc3 is slightly larger than that of Pc2, which can explain the electronic structures of the upper occupied and lower vacant molecular orbitals for the ground states of metal substituted phthalocyanines (MPcs).[20] Moreover, the γ value of Pc3 in chloroform is approximately 2.2 times larger than that of the dye in methanol. This can be ascribed to the formation of J-aggregates for the Pc3 in chloroform solution, resulting in enhancement of the third-order optical nonlinearities of molecules.

In order to correctly interpret the enhancement of third-order optical nonlinearity for the J-aggregates of Pc3, the morphologies of Pc3 in chloroform and methanol are studied by TEM and FESEM. Figures 4(b) and 4(d) show the TEM and FESEM images of the Pc3 sample prepared from the chloroform solution, respectively. It is found that the nanowires with a diameter of 50–100 nm are connected with each other to form an indefinite network structure. In contrast and as expected, no aggregates are detected when the samples are prepared from a solution in the methanol (Fig. 4(a) and 4(c)). Recently, Li *et al.*[21,22] reported an ordered nanosphere alignment of porphyrin (TEOP) for the improvement of nonlinear optical properties. They studied the nonlinear absorption and nonlinear refraction of the TEOP solution and the film with an ordered pattern by using the Z-scan technique. The TEOP film with the well-ordered uniform pattern possesses strong nonlinearities compared to the TEOP solution. The values of the nonlinear absorption coefficient of the well-ordered TEOP film and the solution are different up to three orders of magnitude.

We reported a proposed mode of J-aggregation of analogous Pc3 phthalocyanines in previous studies,[14,15] which is illustrated in Fig. 5, wherein the J-type aggregates are stabilized by axial coordination of oxygen from the side chain to the zinc(Ⅱ) center between the phthalocyanine macrocycles. Therefore, because of dipole-dipole interaction between adjacent molecules, absorption of a photon produces a coherent delocalized excitation or exciton. The exciton involves a collective oscillation of N adjacent dipoles in a chain or in a lattice of molecules, leading to an N-fold enhancement of the transition oscillator strength.[23] The large oscillator strength provides for an increased value of nonlinear optical property of Pc3 J-aggregates.

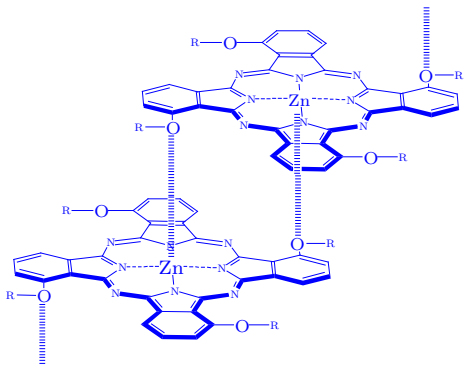


Fig. 5. Proposed mode of J-aggregation of Pc3 in chloroform solution.

In summary, third-order optical nonlinearities of three aryloxy substituted phthalocyanines were measured by DFWM technique at 800 nm. The magnitude of the second-order hyperpolarizabilities (γ) of the phthalocyanines has been measured to be as large as 10^{-31} esu. Their response times are also obtained and no more than 50 fs, which are commonly accepted to the contribution from the transient motion of the conjugate electron distribution. Due to the enhancement of J-aggregates, the γ value of an aryloxy substituted zinc phthalocyanine in chloroform is approximately 2.2 times larger than that of the dye in methanol. These features indicate that the studied phthalocya-

nines have potential applications in nonlinear optics.

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