Photoresponsive J-Aggregation Behavior of a Novel Azobenzene–Phthalocyanine Dyad and Its Third-Order Optical Nonlinearity

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The photoresponsive J-aggregation behaviors of a novel azobenzene-substituted zinc phthalocyanine (azo-ZnPc dyad) were studied by UV/vis, fluorescence, and ¹H NMR spectroscopy. Upon illumination with 365 nm UV light, the trans—cis isomerization of azobenzene can efficiently reduce the steric hindrance around the peripheral oxygen atom of azo-ZnPc, shortening the possible distance between two phthalocyanine molecules and, consequently, greatly improving the tendency of J-aggregation of azo-ZnPc dyad. The third-order optical nonlinearities of the photoresponsive J-aggregates (before and after illumination) were measured by a Z-scan technique at 532 nm with a pulse duration of 25 ps. The Z-scan spectra revealed that all the samples possessed large positive nonlinear refraction and positive nonlinear absorption, exhibiting a self-focusing effect and reverse saturable absorption, respectively. The second molecular hyperpolarizabilities of the dyad in two conditions were measured to be 3.87×10^{-30} and 4.82×10^{-30} esu, respectively. All the results suggest that the azo-ZnPc dyad has potential in the field of nonlinear optics applications.

Introduction

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. One of the linear spectroscopic properties of J-aggregates is a sharp excitonic absorption peak called the J-band, red-shifted from the monomer band.^{1,2} The experimental and theoretical works have shown that molecular J-aggregates are self-organized, quasi-one-dimensional systems of cyanine dyes that have large third-order susceptibility in the J-band as well as fast response times.^{3–6} Enhancement of the nonlinear optical properties is the result of the exciton delocalization over the aggregates.⁷

Over the past two decades, phthalocyanines have been extensively studied as an important class of third-order nonlinear optical materials because of their extensively delocalized twodimensional 18-electron system, their structural flexibility, their exceptionally high thermal and chemical stability, and their potential for use in photonic applications such as optical switches and optical limiting devices.^{8–13} Owing to the extended π system, it is well-known that these macrocyclic compounds exhibit a high aggregation tendency, forming dimeric and oligomeric species in solutions.^{14–16} It has been shown that this molecular association greatly influences the intrinsic nature of macrocvcles including their spectroscopic, photophysical, electrochemical, and nonlinear optical properties.¹⁷ Therefore, much effort has been put into assembling J-aggregates. For example, Li and Ng¹⁸ have demonstrated that phthalocyanine-nucleobase conjugates such as phthalocyanine-adenine derivatives in dichloromethane can form J-aggregates due to a variety of intermolecular interactions. Sessler et al.¹⁹ have reported that cytidine-phthalocyaninatozinc undergoes self-assembly to form a J-aggregate even at low concentrations in dichloromethane-toluene mixed solvents as a result of both $\pi - \pi$ interactions and cytidine macrocycle interactions. Recently, Kobuke and co-workers²⁰ have reported a methodology for supramolecular organization of imidazolylappended phthalocyanines. The complementary coordination of imidazolyl group from one phthalocyanine molecule to the central Zn^{2+} or Mg^{2+} ion in a second phthalocyanine molecule causes a "slipped cofacial dimer", with extremely large stability constants of 1011-1012 M-1. Quite recently, Watarai and coworkers²¹ have observed that two-dimensional high-ordered J-aggregates of thioether-substituted phthalocyanine and subphthalocvanine derivatives were formed at the toluene/water interface upon addition of Pd(II) into the system. Only a year ago, our group has provided another facile strategy to construct phthalocyanine J-aggregates based on Zn²⁺-O coordination.²²

According to the J-aggregates formation mechanism of α -aryl/ alkoxy-substituted zinc phthalocyanines,²² the oxygen-linked substitution in phthalocyanine rings would affect the formation of J-aggregates. The size of substitution determines the distance between two phthalocyanines due to steric hindrance. At the same time, the electronic properties of substitution will affect the polarity of adjacent oxygen atom. Therefore, peripheral substituents could influence the interaction between Zn–O atoms, which could also influence the optical nonlinearity of phthalocyanine.

It is well-known that photochromic compounds undergo reversible isomerization under the illumination of suitable lights, resulting in photoinduced changes in their molecular geometry and electronic delocalization distributions.²³ The incorporation of photochromic compounds and other functional materials has led to numerous light-responsive systems such as nano/molecular machines,²⁴ photocontrolled delivery systems,²⁵ etc. Among various photochromic compounds, azobenzene, which featured

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SCHEME 1: Synthetic Route to Azo-ZnPc



its photoinduced trans-cis isomerization, has been most widely used because of the large photoinduced changes in its geometry and physical properties.²⁶

In the present study, a novel α -aryloxy-substituted zinc phthalocyanine (azobenzene-substituted zinc phthalocyanine, hereafter, abbreviated as azo-ZnPc dyad) was prepared. This molecule was expected to form J-aggregates through Zn–O coordination. Four azobenzene units were introduced as peripheral substituents to examine whether the trans–cis isomerization of azobenzene units could exert apparent influences upon the J-aggregation behaviors and optical properties of this material. UV/vis, fluorescence, and ¹H NMR spectroscopies were applied to demonstrate that azo-ZnPc formed photoresponsive J-aggregates in noncoordinating solvents. Third-order optical nonlinearities of the photoresponsive J-aggregates of the azo-ZnPc dyad were measured by a picosecond Z-scan technique.

Experimental Section

Materials and Devices. 4-Phenylazophenol was purchased from Alfa Aesar and used without further purification. The other reagents used were commercial products from Beijing Chemical Reagent Co. Solvents for spectroscopy were refined by standard methods, while others were used as received.

Absorption spectra were measured on a HP8452A spectrophotometer. IR spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer made in America. NMR spectra were recorded on a JEOL JNM-ECA300 spectrometer with tetramethylsilane (TMS) as internal reference. Mass spectrometry was obtained on a Bruker LC-MS/MS (Esquire-LC) 1100 series; TOF-MS spectra were measured with BEFLEX III. A Carlo-Erba-1106 element analyzer was used for elemental analyses. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Melting points were determined with a XT4A microscopic melting point apparatus produced by Beijing Keyi photoelectronic corporation and were used without further calibration. Photoillumination was carried out with a high-pressure mercury lamp (mejiro precision, SHG-200; 1000 W, made in Japan) with suitable filters. Transmission electron microscopy (TEM) was performed on a model H-800 electron microscope operating at acceleration voltage of 100 kV. To prepare TEM samples for the images of the aggregation, a drop of the 8×10^{-6} M chloroform solution of azo-ZnPc before or after UV light illumination was deposited onto a microgrid, which had been coated with carbon. The excess solution was blotted away with a strip of filter paper.

Azo-ZnPc dyad was synthesized through a rather facile route as shown in Scheme 1. All products were unambiguously characterized by NMR, IR, UV-vis, MS, and elemental analysis.

Synthesis of 3-(Phenylazophenoxy)phthalonitrile (1). 4-Phenylazophenol (1.00 g) and 3-nitrophthalonitrile (0.82 g) were dissolved in N,N-dimethylformamide (DMF; 10 mL). After the mixture was stirred for 15 min at room temperature, finely grounded dry potassium carbonate powder (1.4 g) was added. The mixture was kept stirring for 24 h at room temperature and poured into 60 mL of ice-water. After precipitation was complete, the solid was filtered off and washed with water. Recrystallization from EtOH gave 1.21 g of needlelike yellow crystals with a yield of 80%. mp 161–162 °C; MS (M + Na⁺) 347.2; ¹H NMR (300 MHz, DMSO-*d*₆; ppm) 7.37–7.43 (6, 2H), 7.45-7.49 (q, 1H), 7.54-7.62 (m, 3H), 7.82-7.92 (m, 4H), 7.96-8.02 (6, 2H); ¹³C NMR (300 MHz, DMSO-*d*₆; ppm) 106.7, 113.7, 116.1, 116.7, 120.9, 123.1, 123.9, 125.4, 129.6, 130.0, 132.2, 136.7, 149.7, 152.4, 157.3, 159.4. Elemental analysis calcd for C₂₀H₁₂N₄O: C, 74.06; H, 3.73; N, 17.27. Found: C 74.06, H 3.63, N 17.02. IR (cm⁻¹) 3087, 2230, 1584, 1572, 1493, 1450, 1095, 930, 801, 727.

Synthesis of Azo-ZnPc. A mixture of 3-(phenylazophenoxy)phthalonitrile (1.00 g), zinc acetate (0.12 g), and 1,8diazabicyclo[5.4.0]undec-7-ene (DBU; 0.15 g) in 2-ethoxyethanol (30 mL) was refluxed for 2 h under argon flux. The resulting green suspension was cooled to ambient temperature and poured into 100 mL of ice-water. The precipitate was filtered off. Finally, pure azo-ZnPc (52 mg) was obtained by chromatography on silica gel with commercially available chloroform as the eluent. MALDI-TOF: calcd 1362.7, found 1362.5. ¹H NMR (300 MHz, DMSO-*d*₆; ppm) 7.2–7.6 (m, 23H), 7.6–8.2 (m, 22H), 8.4–8.5 (t, 1H), 8.5–9.0 (q, 1H, *J*³ = 0.71, *J*⁵ = 0.025), 9.1–9.2 (q, 1H). Elemental analysis calcd for C₈₀H₄₈N₁₆O₄Zn: C, 70.51; H, 3.55; N, 16.45. Found: C, 70.21; H, 3.36; N, 16.56. IR (cm⁻¹) 3060, 1577, 1480, 1413, 1278, 1115, 930, 835, 742, 685.

Third-Order Optical Nonlinearity Measurement. Thirdorder optical nonlinearity of azophthalocyanine was determined by standard Z-scan technique.²⁷ This technique, known for its simplicity and sensitivity, relies on the distortions induced in the spatial and temporal profile of the input beam on passing through the sample. It is used widely in material characterization because it provides not only the magnitudes but also the sign of real and imaginary parts of third-order nonlinear susceptibility ($\chi^{(3)}$). For the present study, a Nd:YAG laser (model PL2143B, EKSPLA) with a 25 ps pulse width at 532 nm was used as the light source. The laser beam (TEM_{0,0}) was focused onto the sample with a 150 mm focal length lens, leading to a measured

Novel Azobenzene-Phthalocyanine Dyad

beam waist of 25 μ m and the pulse energy of 3.0 μ J at the focus. The on-axis transmitted beam energy, the reference beam energy, and their ratios were measured with an energy ratiometer (Rm Laser 6600 Probe Corp.) simultaneously. In order to reduce the possible thermal accumulation effect, the laser repetition rate was set to 1 Hz. For open aperture, all the transmitted power was collected and focused onto the detector by use of another lens (120 mm). The Z-scan measurements were performed with samples dissolved in chloroform with a concentration of 2.8 × 10⁻⁵ M and placed in a standard 1-mm quartz cuvette.

Results and Discussion

C_{4h} Symmetry Configuration of Azo-ZnPc. Scheme 1 shows the synthetic route to azo-ZnPc. Nucleophilic substitution reaction between 4-phenylazophenol and 3-nitrophthalonitrile formed the 3-(phenylazophenoxy)phthalonitrile (1) in 80% yield; subsequently, 1 reacted with anhydrous zinc acetate through a template-oriented reaction in 2-ethoxyethanol to produce target compound azo-ZnPc. It is worth noting that the phthalocyanine product is obtained as a mixture of four regioisomers of C_{4h} , D_{2h} , C_{2v} , and C_s symmetry with similar physical and chemical properties, and only the C_{4h} symmetrical structure is shown in Scheme 1. While it is theoretically possible to separate these isomers due to their different geometries, it has been accomplished only for very specific phthalocyanines by use of specially designed HPLC columns.²⁸ Often, even in these cases, the best results probably give only an enriched isomeric fraction. Previous studies revealed that with appropriately large substituents or under mild reaction conditions, the 1,8,15,22-isomer with C_{4h} symmetry is selectively²⁹ or even exclusively^{28,30} produced in preference to the statistical mixture of isomers. Now that the azo-ZnPc possesses large substituents, the C_{4h} symmetrical product shown in Scheme 1 may be the dominant isomer.

UV-Vis and Fluorescence Spectra. UV-Vis spectra of compound 1 and azo-ZnPc before and after UV light illumination in chloroform are illustrated in Figure 1. Typical UV-vis spectra of phthalocyanines feature two distinct absorption bands, namely B-band and Q-band, that can be readily interpreted by use of Gouterman's highly simplified four orbital model. For azo-ZnPc, the B-band overlaps with the $\pi - \pi^*$ transition absorption band of azobenzene units at 300-400 nm. However, in addition to the normal Q-band (698 nm), an unusual redshifted sharp band at 740 nm was observed. Upon illumination with 365 nm UV light, azobenzene units underwent photoisomerization from trans to cis isomers. The decreased and blueshifted absorption peak at 340 nm, and the increased absorption peak at 400-500 nm, which is similar to spectral changes of compound 1 under UV illumination, are persuasive evidence of such photoisomerization. Accompanying such photoreaction, the absorption band at 698 nm decreased sharply and slightly red-shifted to 710 nm. Meanwhile, the absorption band at 740 nm increased from 0.2 to 0.6 after illumination for 2 min, which is a 3-fold increase.

There is the possibility that the longer wavelength band could be from either photodecomposed species or a split component of the Q-band by excitonic interaction between Pc and azobenzene chromophores. Slota and Dyrda³¹ had investigated in detail the photostability of various metal phthalocyanines (MPc) in organic solvents. They found that, regardless of the solvents, MPc (M = Li, Mg, Fe, Zn, and Pb) decomposed only under prolonged illumination of UV light without any change of λ_{max} . Azo-ZnPc was proved extremely stable under UV light. Thus it is unreasonable to attribute the spectral changes of azo-ZnPc



Figure 1. Absorption spectral changes of (a) azo-ZnPc and (b) compound **1** in chloroform under the irradiation of 365 nm UV light ($c = 1.19 \times 10^{-5}$ M).



Figure 2. Absorption spectral change of azo-ZnPc in THF ($c = 1.19 \times 10^{-5}$ M) under 365 nm UV light irradiation.

in chloroform to UV reduction. To test the latter assumption, the spectra of azo-ZnPc in other solvents were investigated.

Figure 2 shows the UV-vis spectra of azo-ZnPc in tetrahydrofuran (THF). In contrast to Figure 1 (azo-ZnPc in chloroform), azo-ZnPc in THF showed only one typical Q-absorption band at 690 nm. The longer wavelength absorption band at 740 nm was not shown any more. Upon illumination with UV light, azobenzene moieties could also isomerized to cis from the trans conformation. However, unlike in chloroform, the isomerization of azobenzene shows negligible influence upon the Q-band of azo-ZnPc. Provided the longer wavelength absorption in Figure 1 arises from the excitonic interaction between the Pc and azobenzene units, why was this phenomenon not observed in THF? Extensive investigations of the UV-vis spectra of azo-ZnPc in various solvents showed that in coordinating solvents



Figure 3. Fluorescence spectral changes of azo-ZnPc in chloroform $(c = 1.19 \times 10^{-5} \text{ M})$ upon irradiation with 365 nm UV light.

such as dimethyl sulfoxide (DMSO), ketone, pyridine, etc., azo-ZnPc behaved as it did in THF; while in noncoordinating solvents such as toluene, dichloromethane, etc., the spectral changes of azo-ZnPc were similar to those in chloroform. This means that the UV-vis spectral properties of azo-ZnPc are solvent-dependent.

J-Aggregation Behavior of Azo-ZnPc Dyad. Huang et al.²² have pointed out that α -aryloxy-substituted zinc phthalocyanine could form J-type aggregates in noncoordinating solvents through the complementary coordination of the peripheral oxygen atom of one phthalocyanine to the central Zn²⁺ in another phthalocyanine. Such J-aggregates showed a UV-vis spectrum similar at long wavelengths to that of azo-ZnPc in chloroform. If the molecule structure of azo-ZnPc is taken into account, it is rational to deduce that the unusual spectra of azo-ZnPc in chloroform also occur because of the formation of phthalocyanine J-aggregate through Zn–O coordination.

Several attempts were conducted to verify the above assumption. It was well proved that J-aggregates of organic dyes were fluorescent whereas H-aggregates were not.32 As shown in Figure 3, with the irradiation of UV light, the fluorescence spectra of azo-ZnPc in chloroform changed drastically. The intensity of fluorescence emission at 706 nm kept decreasing during the UV illumination process, and at the same time, a new peak at 743 nm came into sights, with three isobestic points at 739, 755, and 812 nm. Generally a one-step equilibrium mechanism between monomer and the aggregate ($nPc \leftrightarrow Pc_n$) was assumed. Therefore, the fluorescence peaks at 706 and 743 nm can be attributed to the monomer and the J-aggregate of azo-ZnPc, respectively. Both Figures 1 and 3 indicate the same UV light enhancement from the J-aggregation. In other words, for azo-ZnPc, there is a strong tendency to form J-aggregates when the azobenzene unit is in the cis configuration.

Another distinct behavior of α -aryloxy-substituted zinc phthalocyanine J-aggregate is that the addition of methanol could breaks the J-aggregate,²² and as a consequence, the regular Q-band shape is restored. Figure 4 shows the spectral change of initial and UV-illuminated solutions of azo-ZnPc in chloroform with addition of methanol. As methanol was titrated, absorption at 740 nm of both solutions decreased gradually and finally disappeared completely with the increase in absorption at 698 nm. This experiment together with the fluorescence spectra can roughly explain the unusual red-shifted peak at 740 nm of Figure 1, which can be attributed to J-aggregates. However, other more persuasive evidence is still required.

¹H NMR is a powerful tool to monitor molecular structure changes. If it is assumed that azo-ZnPc indeed formed J-



Figure 4. Absorption spectral changes of azo-ZnPc (a, before UV light irradiation; b, after UV light irradiation for 3 min, $c = 1.19 \times 10^{-5}$ M) in chloroform .

aggregates through Zn-O coordination in chloroform, compared with monomer, the J-aggregates would show several ¹H NMR signal changes that could be predicted. As shown in Figure 5a, the hydrogen atoms in azo-ZnPc are labeled with arabic numbers. The coordination of Zn-O would give the strongest influence on the environments of hydrogen atoms 3 and 4, therefore affecting the chemical shifts and the shape of corresponding resonances. Hydrogen atoms 2 and 5 would be less influenced, and the influence on hydrogen atoms 1, 6, 7, and 8 would be the least. Since Zn-O coordination destroyed the C_{2v} symmetry of azobenzene units, the corresponding resonance would split and make the spectrum more complex. The ¹H NMR of azo-ZnPc illustrated in Figure 5 precisely matched all above predictions. Figure 5c is the ¹H NMR spectrum of azo-ZnPc in DMSO-d₆. In DMSO, azo-ZnPc existed as monomers, as shown in the UV-vis spectrum. Therefore, it is safe to assume that Figure 5c represented the ¹H NMR spectrum of azo-ZnPc monomers. The corresponding resonance signal of each hydrogen atom in azo-ZnPc could be identified by analysis of ¹H NMR spectra in Figure 5a–c. The peaks for H_1 were at $\delta =$ 8.10-8.20 ppm; the quartet signals at 7.92-8.02 ppm belonged to H_2 ; the peaks of H_3 , H_7 , and H_8 were located at 7.40–7.54 ppm; the peaks for H_4 were observed at 7.26–7.38 ppm; and the signals of H₅ and H₆ appeared at 7.66–7.88 ppm. In CDCl₃, the position of each hydrogen peak was changed to some extent, compared with those in DMSO. As shown in Figure 5d,e, the peaks of H₂ downshifted to 7.88-8.08 ppm and the peaks of H₅ downshifted to 7.76-7.94 ppm. The signal of H₃ was upshifted. Besides those position shifts, the shapes of the peaks at 7.40-7.54 and 7.26-7.38 ppm changed as well. With UV light illumination, these changes became more apparent. However, it is worth noting that the peaks of H₁ remain unchanged in Figure 5c-e, which was consistent with theoretical prediction



Figure 5. ¹H NMR spectra of (a) 4-phenylazophenol in CDCl₃, (b) compound **1** in DMSO- d_6 , (c) azo-ZnPc in DMSO- d_6 , (d) azo-ZnPc in CDCl₃, and (e) azo-ZnPc in CDCl₃ after 15 min of UV light irradiation.

based on Zn–O coordination between two azo-ZnPc molecules. These results strongly supported the assumption of the complementary coordination structure of the peripheral oxygen atom of one azo-ZnPc molecule to the central Zn^{2+} of another azo-ZnPc molecule in chloroform. Since the J-aggregate of azo-ZnPc is the inevitable result of such Zn–O coordination, the ¹H NMR experiments provided another powerful line of evidence for the formation of Zn–O coordination-based J-aggregates of azo-ZnPc in chloroform.

Distance and steric hindrance play important roles in determining the reaction or configuration of a molecule. For phthalocyanines, the size of the peripheral substituents is essential for their aggregation ability. The introduction of bulky dendritic fragments has been exploited to generate nonaggregated phthalocyanines.33 Recently, we reported a novel family of α -aryloxy-substituted zinc phthalocyanines that are called phthalocyanine-diarylethene dyads.³⁴ Because of the big peripheral substituents, the phthalocyanine-diarylethene dyads do not form J-aggregates at all, while α -aryloxy-substituted zinc phthalocyanines with small peripheral substituents strongly favor J-aggregation. As mentioned above, azo-ZnPc with azobenzene units in the cis configuration (cis-azo-ZnPc) has a larger tendency to form J-aggregates than those with azobenzene in the trans configuration (trans-azo-ZnPc). The difference in aggregation ability may be explained by the large steric crowding changes around oxygen atom as a result of the UV light-induced trans-cis isomerization of azobenzene moieties. Figure 6 shows the optimized structure of azo-ZnPc by the semiempirical PM3 method. As we can see from Figure 6a,b, for trans-azo-ZnPc, the plane of trans-azobenzene is perpendicular to that of the phthalocyanine ring. Substituents at 1 and 15 positions are located below the plane of phthalocyanine ring, while substituents at 8 and 22 positions are above it. Four azobenzene endowed zinc phthalocyanine with the ability to alter the steric hindrance around oxygen. After the UV lightinduced trans-cis isomerization, as shown in Figure 6c,d, steric hindrance around oxygen atoms is apparently decreased. The trans-cis isomerization of azobenzene units shortened the possible distance between two macrocycles and, consequently, enhanced the aggregation ability of azo-ZnPc.

TEM studies provided direct evidence for evaluating the different aggregate abilities between *trans*- and *cis*-azo-ZnPc. Figure 7a shows the TEM image of a sample prepared from a chloroform solution of azo-ZnPc without UV light irradiation (*trans*-azo-ZnPc). Azo-ZnPc was uniformly deposited on the microgrid. However, samples prepared from UV light-illuminated solution (*cis*-azo-ZnPc) exhibited strikingly different TEM images. In Figure 7b, a lot of nanowires can be observed, which were absent in Figure 7a. This phenomenon is quite similar to our previous work.^{22b} Thus it is reasonable to attribute the nanowires to the strong J-aggregation of *cis*-azo-ZnPc.

Third-Order Optical Nonlinearity. Figure 8 shows the normalized transmission without aperture at 532 nm (open aperture, OA) as a function of distance along the lens axis. Measured data of azo-ZnPc are shown (\blacktriangle) before and (\Box) after irradiation. Each point corresponds to the average of 5 pulses. The solid line is the theoretical fit. The OA curves exhibit the normalized valleys, indicating the presence of reverse saturable absorption with a positive coefficient β . The nonlinear absorption coefficient β (meters per watt) can be obtained from a best fit performed on the experimental data of the OA measurement:²⁷

$$T_{\rm OA} = \sum_{m=0}^{\infty} \frac{\left[-\beta I_0 L_{\rm eff} / (1+z^2/z_0^2)\right]^m}{(m+1)^{32}} \tag{1}$$

where T_{OA} is the normalized transmittance for OA, $L_{\text{eff}} = [1 - \exp(-\alpha L)/\alpha]$ is the effective thickness of the sample (*L* denotes its thickness), α is the linear absorption coefficient of sample, I_0 is the on-axis illumination at the focus, *z* is the sample position, $z_0 = \pi \omega_0^{2/\lambda}$ is the Rayleigh range, ω_0 is the beam waist at local point (*z* = 0), and λ is the laser wavelength.

Figure 9 shows the normalized transmission for closed aperture (CA) of Z-scan. The large valley-to-peak configurations of CA curves suggest that the refractive index changes are positive, exhibiting a strong self-focusing effect. To extract the nonlinear refractive index n_2 from the Z-scan, pure nonlinear refraction curves were obtained from the division of CA data by OA data. Then the normalized transmittance T(z) is given by²⁷

$$T(z) = 1 - \frac{4x}{(x^2 + 9)(x^2 + 1)} \Delta \varphi_0$$
(2)

and

$$\Delta T_{\rm p-v} = 0.406(1-S)^{0.25} |\Delta \varphi_0| \quad \text{for } |\Delta \varphi_0| \le \pi \qquad (3)$$

$$n_2 = \frac{\Delta \varphi_0 \lambda}{2\pi I_0 L_{\rm eff}} \tag{4}$$

where $\Delta \varphi_0$ is the on-axis phase shift at the focus and ΔT_{p-v} is the difference of transmittance between the normalized peak and valley. The linear transmittance of far-field aperture, *S*, is defined as the ratio of the pulse energy passing through the aperture to the total energy.

Equations 3 and 4 are valid for nonresonant nonlinearity. Our samples have about 4% absorption at 532 nm, which is the excitation wavelength for the Z-scan experiment. Therefore, population of the first excited state of studied azobenzene—phthalocyanine also contributes to the nonlinear refractive index. Although Sheik-Bahae's theory must be used for nonresonant nonlinearity, we can still use the theory to calculate the effective



Figure 6. Computer-optimized structure of azo-ZnPc by semiemphirical PM3: (a) top view of *trans*-azo-ZnPc; (b) side view of *trans*-azo-ZnPc; (c) top view of *cis*-azo-ZnPc; (d) side view of *cis*-azo-ZnPc.





Figure 7. TEM images of azo-ZnPc. The samples were prepared from a chloroform solution of azo-ZnPc: (a) before UV light irradiation and (b) irradiated by UV light for 2 min. [azo-ZnPc] = 8×10^{-6} M.

nonlinear refractive index since the absorption of the studied samples are small at 532 nm.

Accordingly, the real and imaginary parts of $\chi^{(3)}$ and the molecular second hyperpolarizability γ of sample can also be calculated by³⁵

$$\operatorname{Re}\chi^{(3)}(\operatorname{esu}) = \frac{cn_0^2}{120\pi^2}n_2 \text{ (m}^2/\text{W})$$
 (5)

Im
$$\chi^{(3)}$$
 (esu) = $\frac{c^2 n_0^2}{240\pi^2 \omega} \beta$ (m/W) (6)

$$\gamma = \frac{\chi^{(3)}}{N_c L} \tag{7}$$

where n_0 is the linear refractive index of sample, ω is the angular frequency of the light-field, N_c is the molecular number density per cubic centimeter, and *L* is the local-field correction factor, which may be approximated by $[(n_0^{2}+2)/3]^4$.

The nonlinear absorption coefficient (β , meters per watt), the nonlinear refraction coefficient (n_2 , meters² per watt), the third-



Figure 8. Normalized transmission without aperture at 532 nm (open aperture, OA) as a function of distance along the lens axis. Measured data of azo-ZnPc are shown (\blacktriangle) before and (\Box) after irradiation. Each point corresponds to the average of 5 pulses. The solid line is the theoretical fit.



Figure 9. Normalized transmission for the closed aperture (CA) of Z-scan.

order nonlinear susceptibility ($\chi^{(3)}$, electrostatic units) and the molecular second hyperpolarizability (γ , electrostatic units) are calculated and listed in Table 1.

From Table 1, it is found that the studied azobenzene– phthalocyanine dyad shows large second-order molecular hyperpolarizabilities, on the order of 10^{-30} esu, both before and after UV illumination. The value of γ before irradiation is 1.25 times larger than that after illumination. This enhancement can be attributed to the increased degree of J-aggregation of the azo-ZnPc dyad after UV light irradiation.

Shirk et al.³⁶ have reported the γ values of scandium, yttrium, and several lanthanide bis(phthalocyanines) that were studied by the degenerate four-wave mixing (DFWM)

 TABLE 1: Values of Nonlinear Absorption and Refraction

 Coefficients, Third-Order Nonlinear Susceptibility, and

 Molecular Second Hyperpolarizability of Azo-ZnPc

physical values	before irradiation	after irradiation
$n_2/10^{-19} \text{ m}^2/\text{W}$	4.26	5.30
$\beta / 10^{-9} \text{ m/W}$	1.48	4.03
$\chi^{(3)}/10^{-13}$ esu	2.26	2.82
$\gamma/10^{-30}$ esu	3.87	4.82

technique at 1064 nm. The γ values varied from 1.5×10^{-31} to 4.8 \times 10–31 esu and the fluctuation of the γ value was attributed to the intervalence-transition-induced resonance enhancement. Unnikrishnan et al.³⁷ have reported γ values at 532 nm from the DFWM measurements for several peripheral free monophthalocyanines (RePc, LaPc, and MoOPc), a bis(phthalocyanine) [Sm(Pc)₂] and a bis(naphthalocyanine) [Eu(Nc)₂]. The highest value of 5.5×10^{-31} esu was observed for $Eu(Nc)_2$, followed by $Sm(Pc)_2$. The higher γ values compared with the other monophthalocyanines were attributed to the presence of a higher π -electron conjugation in these sandwich-type molecules. Recently, Derkowska et al.³⁸ have investigated the third-order optical nonlinearities of metallophthalocyanines (MPcs, M = Co, Cu, Zn, Mg) by a standard backward DFWM method at 532 nm with 30 ps pulses from a Nd:YAG laser. Due to resonance contribution, these metallophthalocyanines showed large γ values of $(0.56-3.38) \times 10^{-44} \text{ m}^{5}/\text{V}^{2} (4.0 \times 10^{-31}-2.4 \times 10^{-30} \text{ esu}).$ In the present study, values of γ of azobenzene-phthalocyanine are larger than those of the above-mentioned compounds. This probably is because the third-order nonlinear optical susceptibility was predicted theoretically to be nonlinearly scaled with the optical aggregates size; that is, the optical nonlinearity of the J-aggregates is enhanced as the exciton delocalization length compared to monomers.^{39,40}

It is known that the third-order nonlinear optical coefficient under resonant conditions will be severalfold larger than that under nonresonant conditions.⁴¹ Henari et al.⁴² have reported the third-order optical nonlinearities of some unsubstituted and peripherally substituted oxotitanium phthalocyanines by Z-scan technique at 450–650 nm with a 500 ps pulse laser, and the highest value of 7.65×10^{-29} esu was observed at 650 nm, which is the on-resonance wavelength of the oxotitanium phthalocyanine. This value is higher by an order of magnitude compared with that of our azobenzene–phthalocyanine.

Conclusion

A novel azobenzene-substituted zinc phthalocyanine (azo-ZnPc dyad) was synthesized, and its photoresponsive J-aggregation behavior was studied by UV/vis, fluorescence, and ¹H NMR spectroscopies. Third-order optical nonlinearities of the photoresponsive J-aggregates of the azo-ZnPc dyad (before and after irradiation conditions) were measured by a Z-scan technique at 532 nm with pulse duration of 25 ps. The third-order nonlinear refraction coefficient, nonlinear absorption coefficient, and molecular second hyperpolarizability values were obtained. All the results suggested that the studied azo-ZnPc dyad may be a potential candidate for applications in the nonlinear optical area.

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