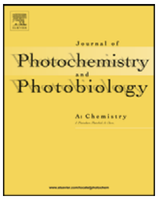
Journal of Photochemistry and Photobiology A: Chemistry 206 (2009) 213–219

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Photoswitching of the third-order nonlinear optical properties of azobenzene-containing phthalocyanines based on reversible host–guest interactions

Zihui Chen[a,*], Sida Dong[a], Cheng Zhong[a], Zhi Zhang[a], Lihong Niu[a], Zhongyu Li[b,*], Fushi Zhang[a,*]

[a] *The Key Lab of Organic Photoelectrons & Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University, Shuang Qing Street, Beijing 100084, PR China*

[b] *Department of Chemical Engineering, Jilin Institute of Chemical Technology, Jilin 132022, PR China*

ARTICLE INFO

Article history:
Received 6 December 2008
Received in revised form 1 July 2009
Accepted 3 July 2009

Keywords:
Phthalocyanine
Azobenzene
Host–guest interaction
Third-order optical nonlinearity
Z-scan technique

ABSTRACT

Two water soluble azobenzene and phthalocyanine dyads with D–π–A alignment were synthesized. It was found that both compounds showed very large molecular cubic hyperpolarizabilities which are at the order of 10^{-30} esu as the result of their unique chemical structure. The azobenzene moieties of these compounds, upon alternating illumination of UV and visible light, could reversibly associate with α-CD to form inclusion complexes through host–guest interaction in aqueous media, resulting in apparent influences to the 3rd NLO properties of these compounds. This influence is especially significant for the phthalocyanine whose central metal atom is copper (II). The molecular cubic hyperpolarizability γ of the inclusion complex for the copper phthalocyanine is 2.1×10^{-30} esu. When the inclusion complex dissociated under the illumination of 365 nm light, γ value increased to 4.2×10^{-30} esu, which is a 100% enhancement. Taking account of the large molecular cubic hyperpolarizabilities of these compounds, the present materials are potential as ideal 3rd NLO photoswitching systems.

1. Introduction

Materials with third-order nonlinear optical (3rd NLO) properties have attracted extensive attentions for their potential applications in various photonic technologies such as optical signals, optical data storage and optical computing [1–7]. Although the focus was initially on the preparation of compounds with large nonlinearities, there has been significant interest in the possibilities for reversibly switching NLO systems [8–14]. Powell et al. [12] reported the first electrochromic switching of molecular nonlinear absorption and refraction. The electrochemical switching of these complexes resulted in a change of the cubic hyperpolarizability γ from a minimum of 0 to a maximum of 3.1×10^{-33} esu. Bertarelli et al. [14] studied the photoreversible 3rd optical nonlinearities of some photochromic dithienylethenes. It was found that conjugated closed form of dithienylethenes showed γ values ($\sim 10^{-34}$ esu) 5–30 times larger than that of the open-ring counterparts ($\sim 10^{-35}$ esu).

For an ideal practical 3rd NLO switch, however, apparent difference in cubic hyperpolarizability between "on" and "off" states is not enough. In order to detect this difference readily and reliably, at least one state's cubic hyperpolarizability should be sufficiently large.

Phthalocyanines are one of the major types of tetrapyrrole derivatives with an extensive two-dimensional 18π electron system [15]. Over the past two decades, phthalocyanines have been widely studied as an important class of 3rd nonlinear optical material [16–18]. The 3rd NLO properties of phthalocyanines depend not only on the chemical structure of component monomers, but also on their packing arrangements. For example, the edge-to-edge aggregates of phthalocyanines (namely J-aggregates) show optical nonlinearities 3–5 times larger than their corresponding monomers [19]. Recently, our group [20] reported a novel zinc phthalocyanine which showed photo-responsive J-aggregate behavior, and consequently the NLO properties of this system were photo-modulated. It was found that this dye showed very large cubic hyperpolarizabilities at the order of 10^{-30} esu both before and after UV illumination. Also, the change of γ after UV irradiation is large. The γ value after irradiation is 1.25 times larger than that before illumination. This study enlightened us that reversibly control either the chemical structure or the molecular packing arrangement of excellent 3rd NLO materials maybe a promising way to make ideal 3rd NLO switches.

It has been well established [21,22] that azobenzene could reversibly assemble with α-cyclodextrin (α-CD) through host–guest interaction under suitable external photo-stimuli.

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[*] Corresponding authors. Tel.: +86 10 62782596; fax: +86 10 62770304.
E-mail addresses: chenzihui04@mails.tsinghua.edu.cn (Z. Chen), zhongyuli70@hotmail.com (Z. Li), zhangfs@mail.tsinghua.edu (F. Zhang).

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doi:10.1016/j.jphotochem.2009.07.005

This phenomenon has been exploited as the basis of some molecular shuttles [23–26] and motors [27]. However, their applications in phthalocyanine chemistry have rarely been studied yet. We believe that this reversible host–guest interaction can be used to modulate the NLO properties of phthalocyanines if phthalocyanines were carefully designed. In the present work, we prepared for the first time two azobenzene-containing water soluble unsymmetrical metal phthalocyanines. Their reversible host–guest interaction with α-cyclodextrin in aqueous media and the resulting effects on the NLO properties of such molecules were investigated.

2. Experimental

2.1. General experiments

Absorption spectra were measured by using diode array spectrophotometer HP8452A. IR spectra were performed on a Nicolet Avatar 360 FT-IR spectrometer. NMR spectrum was recorded on JOEL JNM-ECA300 Spectrometer with TMS as an internal reference. Mass spectroscopy was recorded on Bruker LC–MS/MS (ESQUIRE-LC) 1100 series. Element analyses were performed on a Carlo-Erba-1106 element analyzer. The fluorescence spectra were recorded with a Hitachi F-4500 Fluorescence Spectrophotometer. Photo-illumination was carried out using a high pressure mercury lamp (mejiro precision, SHG-200, 1000W, made in Japan) with suitable filters.

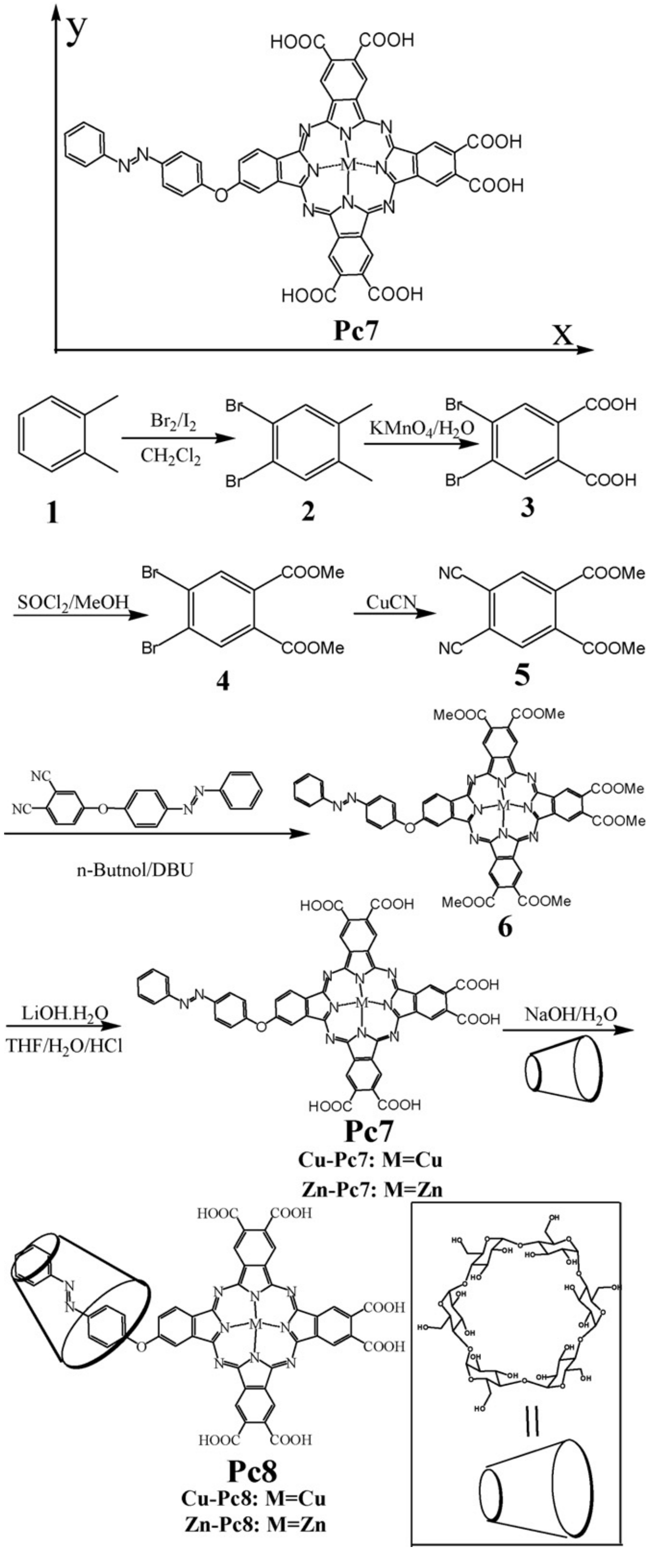
The third-order optical nonlinearities of samples were determined by standard Z-scan technique [28]. This technique, known for its simplicity and sensitivity, relies on the distortions induced in the spatial and temporal profile of the input beam on passing through the sample. It is used widely in material 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 beam waist of 25 μm and the pulse energy of 3.0 μJ at the focus. The on-axis transmitted beam energy, the reference beam energy, and the ratios of them were measured using 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 detector using another lens (120 mm). The Z-scan measurements were performed with samples placed in a standard 1-mm quartz cuvette. Each point is the average of 5 pulses.

2.2. Synthesis

The structures and the synthesis of target azobenzene-containing water soluble unsymmetrical zinc (II) and copper (II) phthalocyanines (abbreviated as Zn-Pc7 and Cu-Pc7, respectively) and their inclusion complexes with α-cyclodextrin (Zn-Pc8, Cu-Pc8) were depicted in Scheme 1.

*2.2.1. 1,2-Dimethyl-4,5-dibromobenzene (**2**) [29]*

To the mixture of I_2 (0.4 g) and o-xylene (20.5 mL), Br_2 (24 mL) was slowly added in 2 h at 0 °C. The resultant solid cake was left at room temperature for 24 h before dissolved in Et_2O (200 mL), washed with sufficient saturated $NaHCO_3$ aqueous solution and water, the organic phase was collected and dried with $MgSO_4$ overnight. Filtered and the organic phase was concentrated to afford a faintly pink colored oil which solidification upon standing. Recrystallization from MeOH gave white crystallized solid in 70% yield.



Scheme 1. Synthetic route of phthalocyanines (Pc7) and their inclusion complex (Pc8) with α-cyclodextrin.

*2.2.2. 4,5-Dibromo-o-phthalic acid (**3**) [30]*

A mixture of 1,2- dimethyl-4,5-dibromobenzene (8.5 g) and $KMnO_4$ (20.5 g) in water (200 mL) was reacted under refluxed for 6 h and then cooled to temperature. After got rid of the unreacted $KMnO_4$ with $NaHSO_3$, the pH value of this mixture was adjusted to greater than 12 using NaOH. The mixture was then filtered, and the filtrate was then slowly acidified using concentrated HCl. The resultant white precipitate (5.0 g) was obtained by filtration and washed with pure water. This product was carried into next stop without further purification.

2.2.3. 4,5-Dibromophthalic acid dimethyl ester (**4**)

To the suspension of 4,5-dibromo-o-phthalic acid (5.0 g) in MeOH (50 mL) was treated with thionyl chloride (6 mL) dropwise over 2 h under argon flux. The resulting solution was then stirred for 72 h and followed by concentration under reduced pressure. The resulting white solid was purified by column chromatography on silica gel, with 1:1 petroleum/ethyl acetate as the eluent (white solid 4.2 g). ^{1}H NMR($CDCl_3$) ppm: 3.90(s, 6H), 7.96(s, 2H); ^{13}C NMR: 51.12, 71.01, 128.32, 131.96, 134.01, 166.06; ESI-MS(M+Na$^+$): 373.0, 374.9, 376.8.

2.2.4. 4,5-Di(methyloxycarbonyl) phthalonitrile (**5**)

A mixture of 4,5-dibromophthalic acid dimethyl ester (4.2 g) and CuCN (3.4 g) was added into new distilled DMF (50 mL) under argon reflux. After being stirred for 20 min under room temperature, the mixture was heat to reflux for 2 h. After being cooled to room temperature, the mixture was poured in to toluene (200 mL). This is followed by stirring for 15 min and then filtered. The filtrate was washed with water, dried with $MgSO_4$ overnight. Filtered and the solvent was removed under reduced pressure. The resultant green solid was purified by chromatography on silica gel with 1:1 petroleum/ethyl acetate as eluent (colorless solid, 1.32 g, yield 44%). ^{1}H NMR(DMSO-d_6) ppm: 6.82(s, 6H), 8.56(s, 2H); ^{13}C NMR: 54.06, 115.38, 118.52, 134.52, 135.70, 165.24; ESI-MS: 245.5(M+H$^+$) (Calc. 244.2); IR: 3042(Ph-H), 2957(CH_3), 2236(–CN), 1720(CO), 1437, 1319, 1255, 1220.

2.2.5. 4-(Phenylazophenoxy)-phthalonitrile

4-Phenylazophenol (1.5 g) and 4-nitrophthalonitrile (1.2 g) were dissolved in N, N-dimethylformamide (15 mL). After being stirred for 15 min at room temperature, dry finely powdered potassium carbonate (2.0 g) was added. The mixture was kept stirring for 24 h at room temperature and poured into 60 mL ice water. After precipitated, the solid was filtered off and washed with water. Recrystallization from EtOH gave needle-like yellow crystal 1.75 g in yield of 78%. ^{1}H NMR (DMSO-d_6) δ ppm: 7.30–7.40(d, 2H), 7.51–7.61(m, 4H), 7.85–7.89(q, 2H), 7.92–7.94(d, 1H), 7.97–8.10(d, 2H), 8.11–8.15(d, 1H). ^{13}C NMR(DMSO-d_6) δ ppm: 121.29, 123.08, 123.69, 124.06, 125.48, 130.05, 132.16, 136.97, 149.66, 152.43, 157.13, and 160.70. MS: M+Na$^+$: 347.2

2.2.6. Pc6

A mixture of 4,5-di(methyloxycarbonyl) phthalonitrile (0.80 g), 4-(phenylazophenoxy)-phthalonitrile (0.12 g), anhydrous $Zn(OAc)_2$ (0.32 g) and DBU (0.31 g) was added to 1-pentanol (10 mL). After being stirred for 10 min, the mixture was heat to reflux for 3 h under argon. The mixture was cooled to room temperature and 100 mL methanol was then added. The dark-green precipitate was collect while the impurities were left in filtrate. Then the crude product was purified by column chromatography on silica gel with 50:1 $CHCl_2$/methanol mixture as eluent. The first band was collect as crude product carried to next step (MS: 1117.3(M+H$^+$)).

2.2.7. Zn-Pc7

The product of above step was dissolved in THF (10 mL) and slowly added to a NaOH saturated mixed solvents of water (10 mL) and MeOH (45 mL). The mixture was stirred for 5 h in room temperature, then the precipitate was filter off and washed with MeOH. The resulting blue solid was added to pure water. Filtered, the filtrate was acidified by diluted HCl to about pH = 6, the precipitate was collected and then redissolved by NaOH aqueous solution, filtered, the filtrate was acidified by diluted HCl again. The green precipitate (32 mg) was collected as target product.

^{1}H NMR(DMSO-d_6) ppm: 6.63(s, 6H), 6.87(s, 6H), 7.10–7.42(m, 4H), 7.53–7.68(q, 4H), 7.78–7.91(d, 2H), 7.92–8.07(m, 2H). ^{1}H NMR(D_2O solution with NaOH in it) 6.10–7.38(12H), 9.21(s, 6H). IR (cm^{-1}): 3000(Ph-H), 1701(CO), 1588(N=N), 1499, 1483, 1266, 1231, and 1091. ESI-MS: M+Na$^+$: 1056.3. Elementary analysis: Calc. for $C_{54}H_{28}N_6O_{13}Zn$: C, 62.71%; H, 2.73%; N, 8.13%; Found: 61.43%; H, 2.65%; N, 7.71%.

2.2.8. Cu-Pc7

The synthesis of Cu-Pc7 is similar to that of Zn-Pc7, only the metal salt is CuCl instead of $Zn(OAc)_2$.

ESI-Ms: M+Na$^+$: 1055.2. IR (cm^{-1}): 3120(Ph-H), 1643(CO), 1589(N=N), 1483, 1232 and 766. Elementary analysis: Calc. for $C_{54}H_{28}CuN_6O_{13}$: C, 62.82%; H, 2.73%; N, 8.14%; Found: 62.41%; H, 2.66%; N, 7.63%.

3. Results and discussions

Both Zn-Pc7 and Cu-Pc7 consist of an electron donating phenylazophenoxy group (D) and six electron withdrawing carboxyl groups (A), forming a D–π–A alignment along the *x*-axis. The conformations of Zn-Pc7 were optimized by quantum chemistry calculation in energy minimization mode. When azobenzene moiety is in *trans*-configuration (abbreviated as *trans*-azo-Zn-Pc7), as shown in Fig. 1(a), the intersecting line between the plane of azobenzene and phthalocyanine ring is the C_2 symmetrical axis of azobenzene moiety. That is to say, the azobenzene moiety of Zn-Pc7 was sticking outward in the plane of phthalocyanine ring. In this conformation, it is easy for α-CD to associate with the azobenzene moiety of Zn-Pc7. When azobenzene moiety isomerizes to *cis*-configuration (abbreviated as *cis*-azo-Zn-Pc7), as shown in Fig. 1(b), the azobenzene moiety is apparently not planar any more. Due to steric hindrance, such conformation is not favorable for the host–guest interaction between the azobenzene moiety and α-CD. Illumination with visible light can shift azo back to transformation, and the planarity is restored. Based on the conformational analysis of Zn-Pc7, it is predicted that the azobenzene moiety of Pc7 could reversibly assemble with α-CD. We expect that the host–guest interaction between azobenzene moiety of Pc7 and α-CD would disrupt the electron donating ability of phenylazophenoxy group or influence the packing style of these compounds, thereby affect the dipole moment of Pc7 and consequently its NLO properties.

Pc7 can be dissolved in water to form corresponding deprotonated compound under alkaline conditions. Fig. 2(a) shows the absorption spectra of Zn-Pc7 in alkali aqueous solution. Unexpectedly, the spectrum of Zn-Pc7 was well defined, suggesting that this compound was essentially dispersed in the solvent. The sharp, intense Q-band at 696 nm indicated monomeric behavior in solution which was further correlated with the strong fluorescence emission at 700 nm. The dispersion of Zn-Pc7 in water was extremely important for its applications as a photosensitizer, as aggregation usually quenches the excited states effectively and decreases the singlet oxygen quantum yield. Yet, aggregation is very common for phthalocyanines in water due to their large hydrophobic π systems [31]. The dispersion properties of Zn-Pc7 in alkali aqueous solution can be attributed to the effect of electrostatic repulsion between the negatively charged carboxylate moieties upon deprotonation [32,33]. The characteristic absorption of π–π* transition of azobenzene moiety in Pc7 was overlapped with the B-band of phthalocyanine. Therefore, the molar extinction coefficient of Zn-Pc7 at 350 nm is remarkably high. Upon irradiation at 365 nm, the azobenzene moiety underwent *trans*–*cis* isomerization. The absorption band at around 350 nm decreased remarkably,

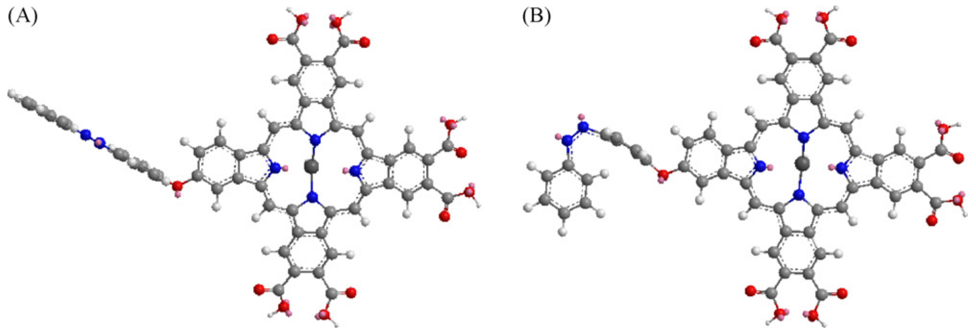


Fig. 1. Computer-optimized conformations of Zn-Pc7 by energy minimization method. (a) *trans*-azo-ZnPc-7; (b) *cis*-azo-Zn-Pc7.

and simultaneously the band between 400 and 450 nm increased slightly. The change of the absorption band induced by UV light is a persuasive evidence of such photo-isomerization of azobenzene moiety. When irradiated by 450 nm visible light, the UV–vis spectra of Zn-Pc7 regenerated. This photoreaction could be cycled several times without apparent degradation and the UV–vis behaviors of Cu-Pc7 are quite similar to those of Zn-Pc7.

Pc7 could form 1:1 stable inclusion complexes (Pc8) with α-CD in alkali aqueous solution through host–guest reaction between the azobenzene moiety of Pc7 and the hydrophobic cavity of α-CD.

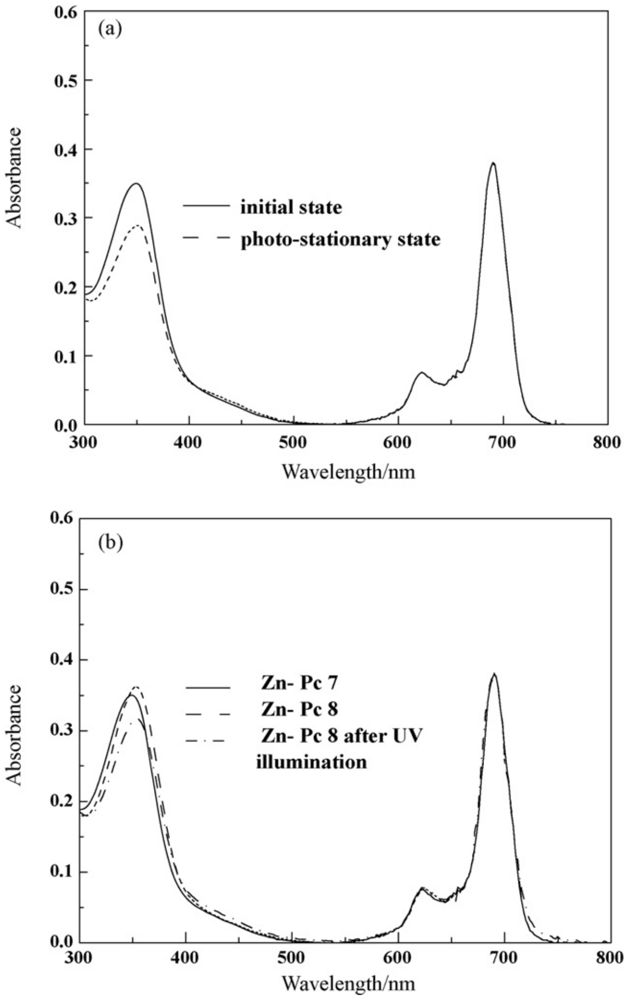


Fig. 2. (a) UV–vis spectra of Pc7 in alkali aqueous solution (pH = 8, [Zn-Pc7] = 5×10^{-6} M) when irradiated by 365 nm UV light; (b) the spectral changes of Zn-Pc7 upon the addition of α-CD (Zn-Pc8) and photo-stationary of Zn-Pc8 upon the UV light irradiation.

However, when azobenzene moiety photo-isomerized from *trans* to *cis* state, the sizes of host and guest do not match any more. As a result, the inclusion complex was dissociated. The formation of Pc8 was first demonstrated by the UV–vis spectral changes of Pc7 upon the addition of α-CD. As shown in Fig. 2(b), the characteristic absorption of the azobenzene moiety red-shifted after the addition of α-CD. Meanwhile, the molar extinction coefficient in this region was slightly enhanced. According to the modified Benesi–Hildebrand equation [34], the association constant $K_{\mathrm{Pc7}/\alpha\text{-CD}}$ for the 1:1 inclusion complex of α-CD with Pc7 is 1.57×10^5 M^{-1}. It was noticed that Pc8 showed similar photo-responsive characters with that of Pc7 in alkali aqueous media. However, the spectra of Pc7 and Pc8 at their photo-stationary states under the illumination of 365 nm UV light were not completely overlapped, indicating the presence of α-CD exerted an influence on the photo-behavior of Pc7 in a certain way.

^{1}H NMR is a useful method to monitor these processes. As shown in Fig. 3(a), Zn-Pc7 in alkali aqueous solution showed three broad peaks at around 6.25, 6.75 and 7.30 ppm, respectively, suggesting the formation of H-aggregated azobenzenes instead of phthalocyanine based on hydrophobic effect [35]. In the presence of α-CD (Fig. 3(b)), because of the formation of Zn-Pc8, H-aggregates of azobenzene were dissociated, the peaks of azobenzene moiety down-shifted and the splits became clear. After the *trans*–*cis* isomerization of azobenzene under the illumination of 365 nm UV light, as mentioned above, the inclusion complexes (Zn-Pc8) dissociated. Driven by the hydrophobic effect, azobenzene in Zn-Pc7 re-aggregated. The broad ^{1}H NMR peaks showed again (Fig. 3(c)). Then, with the 450 nm light on, azobenzene underwent *cis*–*trans* isomerization and re-formed the inclusion complexes with α-CD (Fig. 3(d)). The fact that Fig. 3(b) and (d) is quite similar meant this reaction was completely reversible.

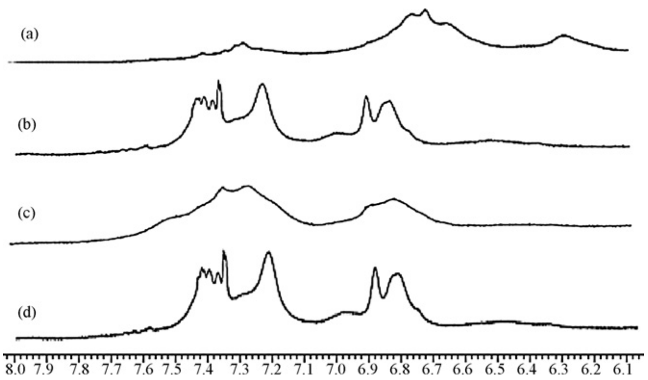


Fig. 3. ^{1}H NMR spectra of (a) Zn-Pc7, (b) Zn-Pc7 in the presence of α-CD, (c) after irradiation at 365 nm for 2 min, and (d) irradiation at 450 nm light for 10 min and then kept in darkness for 2 days. The solvent is D_2O with NaOH in it.

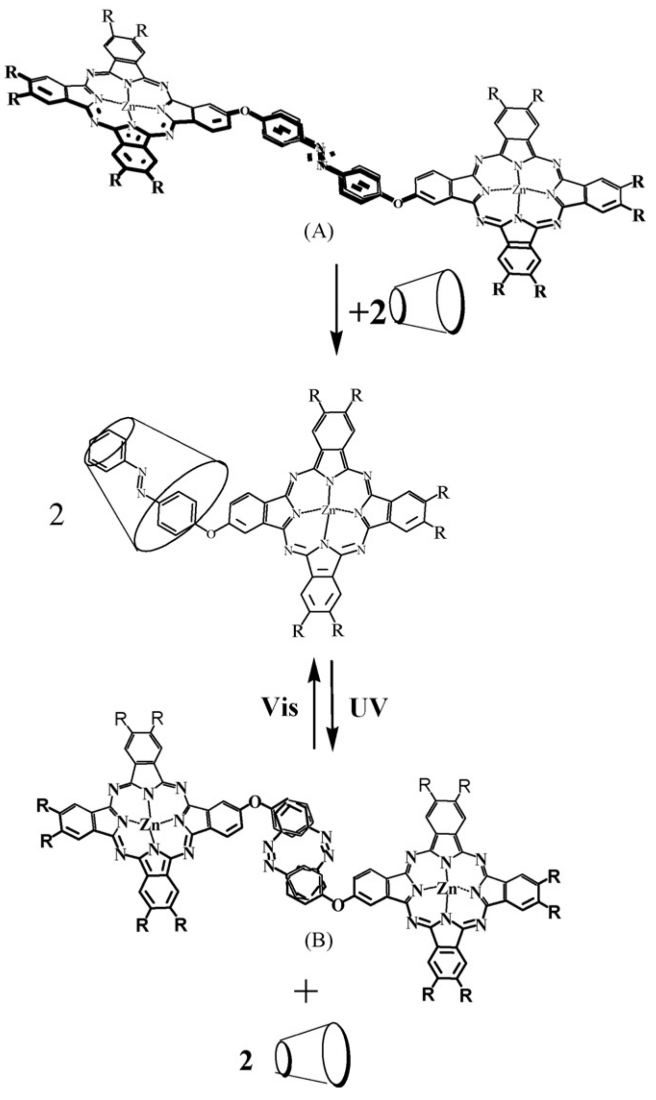


Fig. 4. The changes of the existing form of Zn-Pc7 in alkali aqueous solution upon the following treatment: (1) added α-CD; (2) upon the illumination of 365 nm UV light; (3) upon the illumination of 450 nm light.

Considering the ^{1}H NMR spectra and the conformation analysis of Zn-Pc7, together with the UV–vis spectra of Pc7 in alkali aqueous solution, it is concluded that, during the process from Zn-Pc7 converting to Zn-Pc8 upon the addition of α-CD, and further to Zn-Pc8 dissociation under the illumination of UV light, the existing form of Zn-Pc7 in alkali aqueous solution underwent remarkable changes which could be depicted in Fig. 4. The UV–vis studies (Fig. 2) have shown that the phthalocyanine moiety of Zn-Pc7 was well dispersed in solution. However, the ^{1}H NMR studies also showed that the azobenzene moieties were H-aggregated in alkali aqueous solution before α-CD was added. This means that Zn-Pc7 could only be existed as dimmer A, as shown in Fig. 4, in which the two azobenzene moieties form H-type aggregations. In the presence of α-CD, accompany the host–guest interaction between azobenzene moiety and α-CD, dimmer A converted to two inclusion complexes of Zn-Pc8. The electronic structure of Zn-Pc7 also changed at the same time. Upon illumination of 365 nm UV light, Zn-Pc8 dissociated. The resulting *cis*-azo-Zn-Pc7 formed the supramolecular dimmer B that is somewhat similar to A, which will converted to Zn-Pc8 again under the illumination of 450 nm visible light.

The structure of Cu-Pc7 is similar to Zn-Pc7. Therefore, it is reasonable to deduce that the packing arrangement of Cu-Pc7 undergo similar conversion with above treatments. Such changes of existing forms and electronic structures of Pc7, caused by the reversible host–guest interaction between azobenzene moiety and α-CD, will inevitably affect the optical properties of these materials.

The 3rd NLO properties of Pc7 and their inclusion complexes Pc8 in alkali aqueous solution (pH = 8) were investigated using a Z-scan method. Since the samples were prepared in solutions, the measured data were the combination of the response from both Pc7 and water molecules. However, it should be noted that the contribution from water is negligible. Fig. 5 shows the normalized transmission without aperture at 532 nm (open aperture, OA) as a function of distance along the lens axis. Each point is corresponding to the average of 5 pulses. The OA curves exhibit the normalized valleys, indicating the presence of reverse saturable absorption with a positive coefficient β. The nonlinear absorption coefficient β (m/W) can be obtained from a best fitting performed on the experimental data of the OA measurement with Eq. (1) [28]:

$$T_{\mathrm{OA}} = \sum_{m=0}^{\infty} \frac{[-\beta I_0 L_{\mathrm{eff}}/(1+z^2/z_0^2)]^m}{(m+1)^{3/2}} \qquad (1)$$

where T_{OA} is the normalized transmittance for OA, L_{eff} (equals $1-\exp(-\alpha L)/\alpha$) 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 (equals $\pi\omega_0^2/\lambda$) is the Rayleigh range, ω_0 is the beam waist at local point ($z = 0$), and λ is the laser wavelength.

Fig. 6 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 by [28]

$$T(z) = 1 - \frac{4x}{(x^2+9)(x^2+1)}\Delta\phi_0 \qquad (2)$$

and

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}|\Delta\phi_0| \quad \text{for } |\Delta\phi_0| \le \pi \qquad (3)$$

$$n_2 = \frac{\Delta\phi_0\lambda}{2\pi I_0 L_{\mathrm{eff}}} \qquad (4)$$

where $\Delta\phi_0$ the on-axis phase is 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.

Eqs. (3) and (4) are valid for non-resonant nonlinearity. Our samples have no absorption at 532 nm. Therefore, we can use the above mentioned equations to calculate the effective nonlinear refractive index.

Accordingly, the real and imaginary parts of $\chi^{(3)}$, abbreviated as $\chi_R^{(3)}$ and $\chi_I^{(3)}$ respectively, can also be calculated by the following equations [28]:

$$\chi_R^{(3)} = 2n_0^2\varepsilon_0 c n_2 \qquad (5)$$

$$\chi_I^{(3)} = \frac{c^2\varepsilon_0 n_0^2}{\omega}\beta \qquad (6)$$

$$\chi^{(3)} = \chi_R^{(3)} + i\chi_I^{(3)} \qquad (7)$$

The molecular cubic hyperpolarizability γ of sample can be estimated through the following equation [36]:

$$\gamma = \frac{\chi^{(3)}}{N_c L} \qquad (8)$$

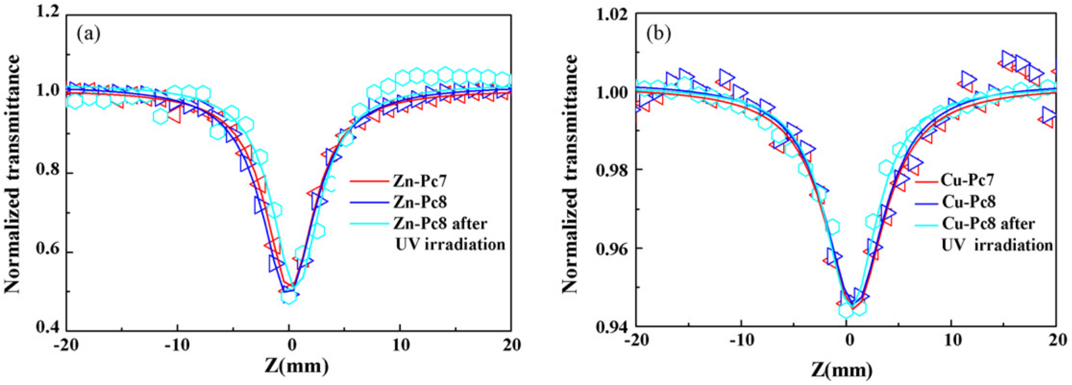


Fig. 5. Normalized transmission without aperture at 532 nm (open aperture, OA) of Pc7, Pc8 and Pc8 after UV irradiation as a function of distance along the lens axis.

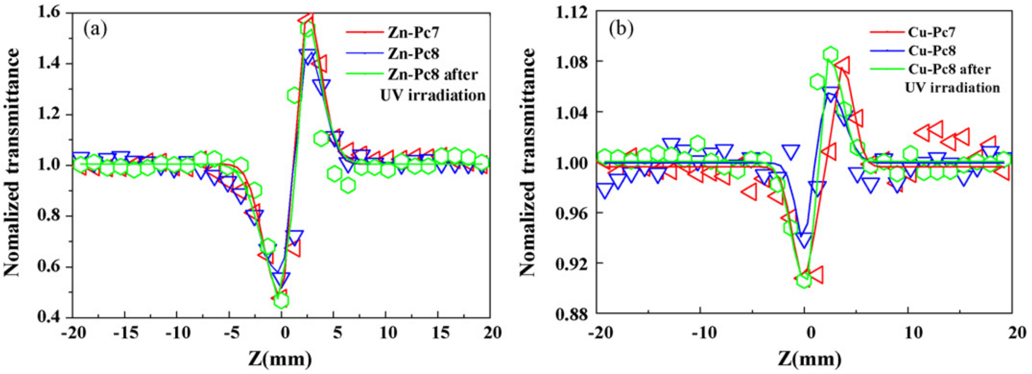


Fig. 6. Normalized transmission for the closed aperture (CA) of Pc7, Pc8 and Pc8 after UV irradiation.

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 in cm^{-3} and L is the local-field correction factor which may be approximated by $[(n_0^2+2)/3]^4$.

The nonlinear absorption coefficient (β, m/W), the nonlinear refraction coefficient (n_2, m^2/W), the third-order nonlinear susceptibility ($\chi^{(3)}$, esu) and the molecular cubic hyperpolarizability (γ, esu) are calculated and listed in Table 1.

From Table 1, it was found that all the studied samples showed large molecular cubic hyperpolarizabilities which were of the order of 10^{-30} esu. Shirk et al. [37] have studied the 3rd NLO properties of scandium, yttrium, and several lanthanide bis-phthalocyanines by DFWM technique at 1064 nm. The γ values of these compounds varied from 1.5×10^{-31} to 4.8×10^{-31} esu and the fluctuation of the γ were attributed to the intervalence-transition-induced resonance enhancement. Unnikrishnan et al. [38] reported γ values at 532 nm from the DFWM measurements for several peripheral-free mono-phthalocyanines (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 mono-phthalocyanines were attributed to the presence of a higher π–electron conjugation in these sandwich type molecules. Recently, Derkowska et al. [39] reported the γ values of metallo-phthalocyanines (MPcs, M = Co, Cu, Zn, Mg) which was studied by standard backward DFWM method at 532 nm with 30 ps pulses from a Nd:YAG laser. Due to resonance contribution, these metallo-phthalocyanines showed large γ values of $(0.56–3.38) \times 10^{-44}$ m^5/V^2 ($\sim 4.0 \times 10^{-31}$–2.4×10^{-30} esu). In the present study, the γ values of Pc7 and Pc8 are large, which probably is due to the D–π–A structures in these compounds.

The formation of inclusion complex Pc8 decreased the γ values of Pc7. For Zn-Pc7, the γ value was changed from 3.6×10^{-30} to 2.9×10^{-30} esu, which is a 24% decrease as Zn-Pc8 formed. Upon the illumination of 365 nm UV light, azobenzene moiety in Zn-Pc7 underwent photoisomerization from *trans* to *cis* isomers. As a result of such photoreaction, the sizes of host and guest do not match any more and the inclusion complex is dissociated. Accordingly, the γ value of this sample increased to 3.5×10^{-30} esu, which is almost as same as that of Zn-Pc7. It was observed that the reversible host–guest interaction between the azobenzene unit of Cu-Pc7 and α-CD exerted a much larger influence on the NLO properties of Cu-Pc7 than those of Zn-Pc7. The γ value of Cu-Pc8 is 2.1×10^{-30} esu. While the inclusion complex of Cu-Pc8 disassociated under the illu-

Table 1
Values of the nonlinear refraction coefficient, the nonlinear absorption coefficient, the third-order nonlinear susceptibility and the molecular cubic hyperpolarizability of Pc7 and Pc8.

Physical value	Zn-Pc7	Zn-Pc8[a]	Zn-Pc8[b]	Cu-Pc7	Cu-Pc8[a]	Cu-Pc8[b]
$n_2/\times 10^{-19}$ $m^2\,W^{-1}$	9.5	7.5	9.3	1.5	0.8	1.6
$\beta/\times 10^{-9}$ $m\,W^{-1}$	49.0	49.9	50.3	4.8	5.0	5.0
$\chi_R^{(3)}/\times 10^{-13}$ esu	42.7	33.7	41.8	6.6	3.4	7.0
$\chi_I^{(3)}/\times 10^{-14}$ esu	94.2	95.8	96.6	9.2	9.6	9.6
$\chi^{(3)}/\times 10^{-13}$ esu	43.7	35. 1	42.9	6.7	3.5	7.1
γ /$\times 10^{-30}$ esu	3.6	2.9	3.5	3.9	2.1	4.2

Notes: Zn-Pc8[a] and Cu-Pc8[a] are the samples before UV irradiation. Zn-Pc8[b] and Cu-Pc8[b] are the samples after UV irradiation. $c_{Zn\text{-}Pc7} = 2.03 \times 10^{-3}$ M, $c_{Cu\text{-}Pc7} = 2.83 \times 10^{-4}$ M. After equal molar of α-CD was added, considering the association constant $K_{Pc7/\alpha\text{-}CD}$, it was found that about 94% of Zn-Pc7 converted to Zn-Pc8. Also, 87% of Cu-Pc7 converted to Cu-Pc8 when the equilibrium is attained. Therefore, the NLO data of Pc8 can be calculated from the equation: $N_{solution} = cN_{Pc8} + (1 - c)N_{Pc7}$, where $N_{solution}$ is the measured NLO result of the solutions after equal molar of α-CD was added, N_{Pc7} and N_{Pc8} represent the NLO coefficients of Pc7 and Pc8, respectively. And c is the conversion ratio of Pc7 to Pc8.

mination of 365 nm light, γ value increased to 4.2×10^{-30} esu, a 100% improvement.

Interestingly, it was found that the fluctuation of γ values of Pc7 mainly is resulted from the changes of molecular third-order nonlinear refraction coefficient. As shown in Table 1, during the whole processes, the $\chi_I^{(3)}$ of investigated solutions remained approximately the same while the $\chi_R^{(3)}$ changed obviously. This phenomenon can be explained as follows: The reversible recognition between Pc7 and α-CD, on the one hand, exerted negligible influence to the Q-band absorption of Pc7, as shown in Fig. 1. On the other hand, the packing style of Pc7 in alkali aqueous solutions was changed with addition of α-CD, so was the molecular rotation ability of Pc7 in strong electro-magnetic field. For anisotropic molecules, with pico-second and femto-second pulses, the electron distortion effect and molecular reorientational Kerr effect are the dominant contributors to their 3rd NLO properties. The latter affects only the nonlinear refraction of materials. Therefore, the reversible recognition between Pc7 and α-CD had made significant impact on the 3rd nonlinear refraction coefficients of Pc7 while the 3rd nonlinear absorption coefficients were basically unchanged.

4. Conclusion

Novel 3rd NLO photoswitching systems of phthalocyanine have been successfully constructed based on the reversible host–guest supramolecular approach. A novel family of azobenzene-containing water soluble unsymmetrical phthalocyanines was synthesized. Each phthalocyanine presented in these study consists of an electron donating phenylazophenoxy group (D) and six electron withdrawing carboxyl groups (A) forming a D–π–A structure along the x-axis. As a result of such unique chemical structure, all the samples showed very large molecular cubic hyperpolarizabilities which were at the order of 10^{-30} esu. The azobenzene moieties of these compounds could reversibly associate with α-CD to form inclusion complexes through host–guest interaction in aqueous media upon alternating illumination of UV and visible light, resulting in apparent influences to the 3rd NLO properties of these phthalocyanines. This influence was especially striking for the phthalocyanine whose central metal atom was copper (II). The molecular cubic hyperpolarizability γ of the inclusion complex of the copper phthalocyanine was 2.1×10^{-30} esu. When the inclusion complex disassociated under the illumination of 365 nm light, the γ value was 4.2×10^{-30} esu, which is a 100% increase. Taking account of the large molecular cubic hyperpolarizabilities of these compounds, our endeavors toward ideal 3rd NLO photoswitching systems is very promising, with sufficient room for improvement. This work suggested that reversible control of either the chemical structure or the molecular packing arrangement of excellent 3rd NLO materials is an attractive strategy for constructing ideal 3rd NLO photoswitching systems. Moreover, the present study emphasized the effect of the reversible host–guest interaction between azobenzene and α-CD on the packing style of phthalocyanines, which may provide new insights to the host–guest chemistry.

Acknowledgements

This work was supported by National Natural Science General Foundation of China (20773077), the Postdoctoral Science Funding (023260069) and the National Key Fundamental Research Program (2007CB808000).

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