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The third-order optical nonlinearities of thiophene-bearing phthalocyanines studied by Z-scan technique

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ABSTRACT

The third-order optical nonlinearities of thiophene-bearing phthalocyanines (Ni-TPc and Cu-TPc) measured using Z-scan technique at 532 nm have three features: firstly, both Ni-TPc and Cu-TPc showed large molecular cubic hyperpolarizabilities γ whose values were of the order of 10^{-30} esu; secondly, the nonlinear absorption and the nonlinear refraction contribute almost equally to their molecular cubic hyperpolarizabilities, while for our previous studied phthalocyanines, the contribution from nonlinear refraction was always overwhelming; thirdly, the γ value of Cu-TPc is 1.5 times larger than that of Ni-TPc, which is mainly due to their different nonlinear absorptions. This study may indicate that the incorporation of thiophene rings into phthalocyanines could notably increase the multi-photon absorption cross-section of Pc.

1. Introduction

Materials with large third-order nonlinear optical (3rd NLO) properties, low optical losses and ultrafast response time have stimulated considerable researches for their potential in optical communication, data storage, optical computing, dynamic holography, harmonic generators, frequency mixing, and optical switching [1–5]. Among various organics [6], phthalocyanines (Pcs) and their analogues have emerged as one of the most promising candidates for third-order nonlinear optics because of their high degree of aromaticity, unique electronic spectra, architectural flexibility, ease of processing and fabrication into films, as well as their exceptionally high thermal and chemical stability [7–9]. The 18-π electrons conjugated macrocycle of Pc is recognized as the provider of large nonlinearities with fast response times, which can further be tailored by either metal substitution at the central core or by introducing peripheral and axial functionalities. For instance, the insertion of transition metals with unfilled d orbitals into the central core of Pc can strongly enhance the off-resonant 3rd nonlinear susceptibility $\chi^{(3)}$ [10]. Particularly, a clear enhancement of the molecular cubic hyperpolarizability has been observed for Pcs containing cobalt [11].

Sulfur-rich compounds such as tetrathiafulvalene (TTF) derivatives and polythiophene composed another class of important NLO materials [6,12–16]. The high polarizability of sulfur atoms and non-bonding sulfur–sulfur interaction of neighboring molecules [17] assist the generation of large NLO effects. As a notable example, carbon disulfide, which can be regarded as a prototypical sulfur-rich molecule, has been used as a standard in 3rd NLO studies for a long time [12].

We are interested in the NLO behaviors of sulfur-rich Pcs, which are rarely reported yet. Tian and his co-workers designed a series of bisthieynylethene-based tetraazoporphyrin and Pc hybrids as photo-switching molecules [18–20]. Bryce et al. prepared two phthalocyanines bearing TTF substituents in order to search novel optoelectronic materials [21,22]. Muto et al. synthesized a Pc derivative bearing eight 2-thienyl substituents for preparing novel π-conjugated polymers [23]. Recently, we synthesized a series of symmetrical thiophene-bearing Pcs [24]. In the present paper, we report the 3rd NLO properties of these compounds measured by Z-scan technique at 532 nm.

2. Experimental

The structures of Cu-TPc and Ni-TPc were shown in Fig. 1(A). Each Pc was dissolved in tetrahydrofuran (THF) at a concentration of 1×10^{-4} mol L^{-1} and then placed in 1-mm quartz cuvette for

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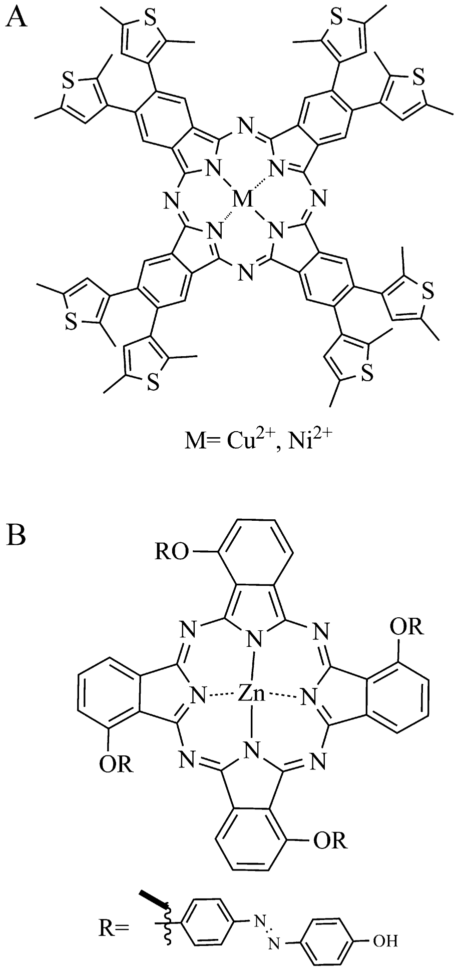

Fig. 1. The chemical structure of (A) Ni-TPc, Cu-TPc and (B) azo-ZnPc.

experiments. The absorption spectra were measured using diode array spectrophotometer HP8452A at 20 °C.

The 3rd NLO properties of these samples were determined by standard Z-scan technique. In the present study, a Nd:YAG laser (Model PL2143B, EKSPLA) with a 25-ps pulse width at 532 nm was employed 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). Each point is the average of 5 pulses.

In order to make comparison, the 3rd optical nonlinearity of a tetra-azobenzene derivatives substituted zinc Pc (abbreviated as azo-ZnPc) [25], which has been measured at the same condition by Z-scan method, were also presented. The structure of azo-ZnPc was shown in Fig. 1(B).

3. Results and discussions

Fig. 2 shows the UV–vis spectra of 1×10^{-4} mol L^{-1} THF solutions of Ni-TPc, Cu-TPc and azo-ZnPc in 1-mm quartz cuvette. It can be seen that all of the three Pcs in THF showed well-defined spectra with sharp, intense Q-band absorption at 690 nm, 692 nm and 692 nm, respectively. These absorptions were found to follow the Beer–Lambert's law range from 0 to 1×10^{-4} mol L^{-1}, suggesting that these compounds are essentially dispersed in THF. However, azo-ZnPc has less than half of the Q-absorptions of the Cu-TPc and Ni-TPc. According to our experiences, there is little dependence on central mental for the Q-band of molecularly dispersed Pcs. Therefore, this phenomenon can only be understood from polar and steric substituents effects.

Generally, Pcs have high tendency to interact with each other by attractive π–π stacking interactions, leading to aggregation in solution because of their extended flat aromatic surface. In order to explore the reasons for the excellent dispersion behaviors of Ni-TPc and Cu-TPc, molecular geometry optimization was carried out by energy minimization method. As shown in Fig. 3, thiophene rings are tilted from the Pc plane of Ni-TPc and the dihedral

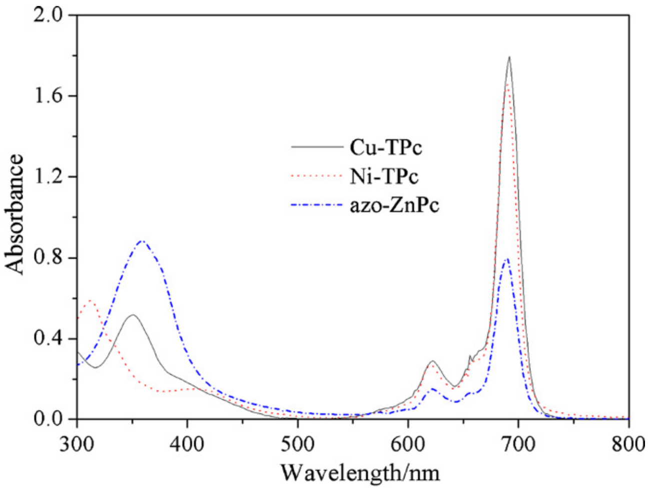

Fig. 2. The UV–vis spectra of Ni-TPc, Cu-TPc and azo-ZnPc in THF ($c = 1\times10^{-4}$ mol L^{-1}).

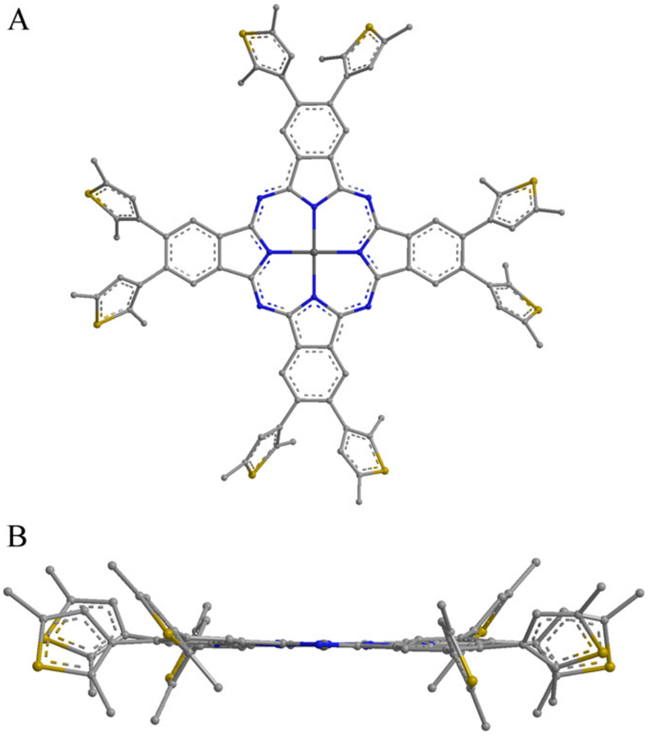

Fig. 3. Computer-optimized conformation of Ni-TPc by energy minimization method. (A) Top view and (B) side view.

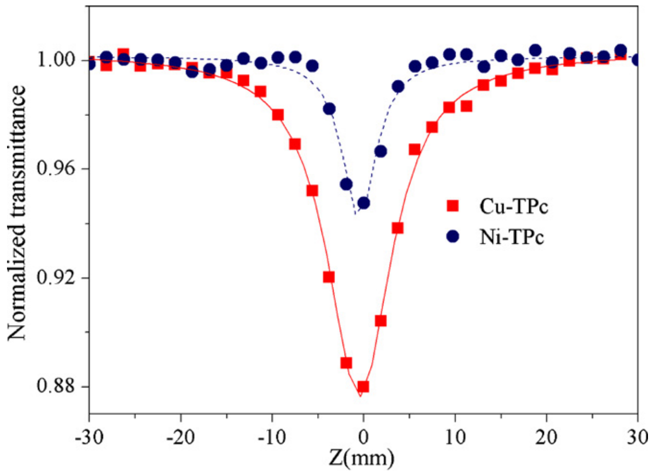

Fig. 4. Normalized transmission for the open aperture at 532 nm.

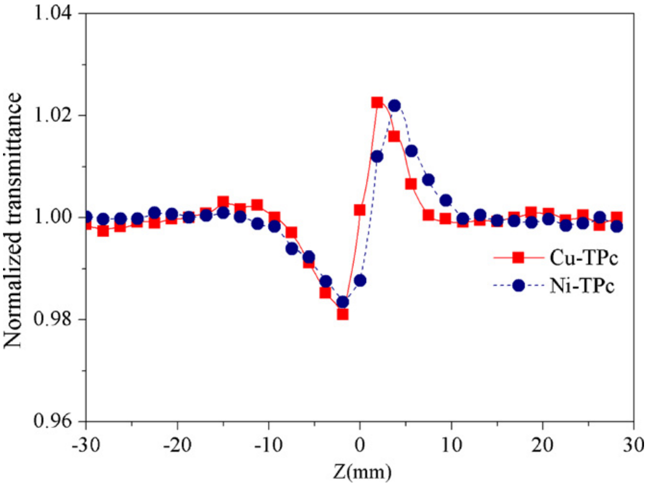

Fig. 5. Normalized transmission for the closed aperture at 532 nm.

angles between each thiophene ring and the Pc plane are about 60°, forming a "picket-fence" conformation which will prevent the macrocycles from getting close to each other through mutual steric hindrance. Pcs in such conformation is very unfavorable for aggregation [26]. It was noting that central metal is also important. Studies on porphyrins have revealed the greater the intramolecular polarization between the porphyrins and the metal, the stronger is the π–π interaction between two porphyrins [27]. Indeed, when the central metal in Ni-TPc was altered by zinc, the solution above 2×10^{-5} mol L^{-1} in THF showed slight J-aggregation [24].

The 3rd NLO properties of Ni-TPc and Cu-TPc were measured by Z-scan. 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 provides not only the magnitudes but also the sign of real and imaginary parts of third-order nonlinear susceptibility ($\chi^{(3)}$) [28]. Since the samples were prepared in solutions, the measured data were the combination of the response from both Pc and THF molecules. However, it should be noted that the contribution from THF is negligible.

Fig. 4 shows the normalized transmissions of Ni-TPc and Cu-TPc without aperture (OA) at 532 nm as a function of distance along the lens axis. The transmittance of each sample decreased with increasing intensity of the exiting radiation, suggesting a typical reverse saturable absorption with a positive coefficient. However, the transmittance of Cu-TPC at focal point ($z = 0$) is 0.87, whereas that of Ni-TPc is 0.94, which means the nonlinear absorption coefficient of Cu-TPc will be 2 times higher than that of Ni-TPc. The nonlinear absorption coefficient β (m/W) was obtained from a best fitting performed on the experimental data of the OA measurement with Eq. (1) [28].

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

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 focal point ($z = 0$), and λ is the laser wavelength.

Fig. 5 illustrated the typical closed aperture Z-scan curve (CA) of Ni-TPc and Cu-TPc. These curves represent normalized data obtained after division of the closed aperture with the open aperture data in order to eliminate the contribution of nonlinear absorption. It is apparent that both Ni-TPc and Cu-TPc showed positive refractive index changes as indicated by the large valley-to-peak configurations of CA curves. 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]

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

and

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

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

where $\Delta\phi_0$ the on-axis phase is shift at the focus; 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 tiny absorption at 532 nm (the molar extinction coefficients for Cu-TPc and Ni-TPc are 320 and 711 M^{-1} cm^{-1}, respectively). 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 Re $\chi^{(3)}$ and Im $\chi^{(3)}$, respectively, can also be calculated by the following equations [28]

$$Re\,\chi^{(3)} = 2n_0^2 \varepsilon_0 c n_2 \tag{5}$$

$$Im\,\chi^{(3)} = \frac{c^2 \varepsilon_0 n_0^2}{\omega} \beta \tag{6}$$

$$\chi^{(3)} = Re\,\chi^{(3)} + i Im\,\chi^{(3)} \tag{7}$$

The molecular cubic hyperpolarizability γ of sample can be estimated through the following equation [29]

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

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 $\left[(n_0^2+2)/3\right]^4$.

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 molecularcubic hyperpolarizability

Table 1
Values of the nonlinear refraction coefficient, the nonlinear absorption coefficient, the third-order nonlinear susceptibility and the molecular cubic hyperpolarizability of Cu-TPc, Ni-TPc and azo-ZnPc.

Physicalvalue	Cu-TPc	Ni-TPc	Ratio	Azo-ZnPc [25]
n_2 ($\times 10^{-20}$ m^2 W^{-1})	3.7	3.4	1.1	3.3
β ($\times 10^{-8}$ m W^{-1})	1.2	0.6	2.0	1.8
Re $\chi^{(3)}$ ($\times 10^{-13}$ esu)	1.9	1.7	1.1	5.1
Im $\chi^{(3)}$ ($\times 10^{-13}$ esu)	2.6	1.2	2.2	0.2
$\chi^{(3)}$ ($\times 10^{-13}$ esu)	3.2	2.1	1.5	5.1
γ ($\times 10^{-30}$ esu)	1.7	1.1	1.5	2.6

Note: the ratio is the corresponding NLO coefficients of Cu-TPc to those of Ni-TPc.

(γ, esu) are calculated and listed in Table 1. For comparison, the 3rd NLO properties of azo-ZnPc measured at the same condition by Z-scan technique were also presented [25].

As shown in Table 1, both Ni-TPc and Cu-TPc showed large molecular cubic hyperpolarizabilities γ whose values were of the order of 10^{-30} esu. The γ value of Cu-TPc ($\gamma = 1.7 \times 10^{-30}$ esu) is 1.5 times larger than that of Ni-TPc ($\gamma = 1.1 \times 10^{-30}$ esu), indicating that the diversity of central metal atom helps in tailoring the NLO properties of Pcs. Nalwa et al. studied the 3rd NLO susceptibilities $\chi^{(3)}$ of naphthalocyanines (Ncs) containing various central metals by THG, and the $\chi^{(3)}$ values are found to decrease in the order VONc > CuNc > ZnNc > NiNc > PdNc [30,31]. Li et al. have investigated the 3rd NLO properties of four diarylethene-substituted metal Pcs, and found that the γ value of Cu–DE–Pcs are larger than those of corresponding Zn–DE–Pcs [32]. These behaviors can be explained from the electronic structures of the upper occupied and lower vacant molecular orbitals for the ground states of metal Pcs [33]. In the case of metal Pcs, the unfilled d valence orbital can be split into serials level due to the interaction between the d electrons of metal and π-conjugation electrons of Pc ring. This result will lower the transition energy in low-lying d orbital-ligand or d–d transition. As one progresses from Ni to Cu, the 3d orbitals of metal are lowered. Consequently, the energy gap between HOMO and LUMO decreases, which has been revealed in UV–vis absorption measurements: the maximum Q-band absorption of Cu-TPc is 2 nm red-shifted from that of Ni-TPc. The existence of excited state with low transition energy will enhance the nonlinear optical susceptibilities of materials. As a result, Cu-TPc shows larger optical nonlinearity than Ni-TPc.

Compared with azo-ZnPc, the γ values of Cu-TPc and Ni-TPc are relatively small, suggesting the incorporation of thiophene rings into the periphery of metal Pc has no obvious advantages in this regard. However, on closer inspection of Table 1, it was found that the Im $\chi^{(3)}$/Re $\chi^{(3)}$ ratios for Cu-TPc and Ni-TPc were 1.37, 0.71, respectively, which means both the nonlinear absorption and the nonlinear refraction played important roles to the large γ values of Cu-TPc and Ni-TPc. This observation is unprecedented to us. For the molecular cubic hyperpolarizabilities of our previous studied phthalocyanines, whether published [25,34,35] or not [data did not shown], the contribution from nonlinear refraction was always absolutely overwhelming. As an example, the Im $\chi^{(3)}$/Re $\chi^{(3)}$ ratio for azo-ZnPc was only 0.04. The nonlinear absorption contributed no more than 1/1000 to the γ value of azo-ZnPc. Although Cu-TPc and Ni-TPc showed tiny absorptions at 532 nm ($\varepsilon_{\text{Cu-TPc}}$ and $\varepsilon_{\text{Ni-TPc}}$ at 532 nm are 320 and 711 M^{-1} cm^{-1}, respectively), they are much weaker than that of azo-ZnPc at this wavelength ($\varepsilon_{\text{azo-ZnPc}}$ at 532 nm is 2500 M^{-1} cm^{-1}). Therefore, one-photo resonance cannot explain why the nonlinear absorptions of Cu-TPc and Ni-TPc contributed so significantly to their molecular cubic hyperpolarizabilities. Instead, this study may indicate that the introduction of thiophene rings could remarkably increase the multi-photon absorption cross-section of Pc.

4. Conclusion

The third-order optical nonlinearities of two thiophene-bearing phthalocyanines (Ni-TPc and Cu-TPc) have been measured using Z-scan technique at 532 nm. Both Ni-TPc and Cu-TPc are found to show large molecular cubic hyperpolarizabilities γ whose values are of the order of 10^{-30} esu. The γ value of Cu-TPc is 1.5 times larger than that of Ni-TPc, mainly as a result of their notably different nonlinear absorptions. Most notably, the nonlinear absorption and the nonlinear refraction contribute almost equally to their molecular cubic hyperpolarizabilities, while for our previous studied Pcs, the nonlinear refraction always plays an absolutely predominant role. It is assumed that the incorporation of thiophene rings into phthalocyanines could notably increase the multi-photo absorption cross-section of Pc. However, for unraveling the real effects of thiophene substituents, further investigations, both theoretical and experimental, are still needed.

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