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# Third-Order Optical Nonlinearity in Novel Porphyrin Dimers

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*We investigate the third-order optical nonlinearities in four novel porphyrin dimers (dimers A to D) and a monomeric porphyrin $H_2$CPTPP measured by using the single-beam z-scan technique with a pulsed Q-switched Nd:YAG nanosecond laser at 532nm. All the samples show strong excited state absorption (ESA) and high value of $\chi^{(3)}$ in the ns domain at this wavelength. We perform a comparison between dimer A and its monomer $H_2$CPTPP in their third-order optical nonlinearity, and discuss the relationships between the values of $\chi^{(3)}$ and the different bridging groups for all the dimers.*

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Porphyrins are macrocyclic aromatic molecules having four pyrrole rings connected by four unsaturated methine bridges to complete the macrocycle. Because of the delocalization of their $\pi$-electrons throughout the macrocyclic ring and the quality of easy to be tailored, porphyrins are interesting chromophores for investigating their nonlinear optical (NLO) properties. In recent 20 years, the NLO response of porphyrins has been studied extensively, starting from simple symmetric porphyrins[1,2] to asymmetrically substituted porphyrins,[3,4] porphyrin oligomers and polymers.[5,6] It is now known that the electronic nonlinearity can be significantly enhanced by using conjugated porphyrin polymers.[7] To obtain larger nonlinearity in porphyrins, the complete understanding of the relationships that exist between the molecular structure and the resulting third-order nonlinearities has become more and more important. Many structure-related research works have focused on different substituents on the periphery[8] or different metals at the centre.[9] However, there have been few studies on how the bridging groups affect the third-order nonlinearity.[5,10] In this Letter, we report the third-order optical nonlinearities in four novel porphyrin dimers (dimers A–D) with different bridging groups and a monomeric porphyrin $H_2$CPTPP. The values of $\chi^{(3)}$ are derived from the experiments conducted by using single-beam z-scan technique developed by Sheik–Bahae *et al.*[11] a well known method for the measurements of the third-order optical nonlinearities, particularly nonlinear refraction and nonlinear absorption. The influence of structure of the bridging groups on the values of $\chi^{(3)}$ is also discussed. Our results show that the more conjugated the bridging groups of the porphyrin dimers, the better the nonlinear properties of the materials. To the best of our knowledge, the compounds studied here are novel porphyrin-like function materials and for the first time we report on their third-order nonlinear optical properties.

The total absorption coefficient of a material $\alpha$ can be written as

$$\alpha = \alpha_0 + \beta I, \tag{1}$$

where $\alpha_0$ is the linear absorption coefficient and $\beta$ is the nonlinear absorption coefficient which can be estimated from the open aperture z-scan data. The normalized transmittance for the open aperture condition is given by[11]

$$T(z, s = 1) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}}, \tag{2}$$

for $|q_0(0)| < 1$, where $q_0(z) = \dfrac{\beta I_0(1 - \exp(-\alpha_0 L))}{(1 + z^2/z_0^2)\alpha_0}$, $L$ is the thickness of the sample, $I_0$ is the on-axis peak irradiance at the focus, and $z_0$ is the Rayleigh length given by the formula $z_0 = k\omega_0^2/2$ with $k$ being the wave vector.

The total refractive index $n$ is given by

$$n = n_0 + \frac{n_2}{2}|E|^2 = n_0 + \gamma I, \tag{3}$$

where $n_0$ is the linear index of refraction, $E$ is the peak electric field (cgs) and I denotes the irradiance (MSK) of the laser beam within the sample, $n_2$ and $\gamma$ are related by the conversion formula $n_2(\text{esu}) = cn_0\gamma/40\pi$. The nonlinear refractive index can be calculated by[11]

$$T(z, \Delta\Phi_0) = 1 - \frac{4\Delta\Phi_0 x}{(x^2+9)(x^2+1)}, \tag{4}$$

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where $x = z/z_0$, and $\Delta\Phi_0 = k\gamma I_0 \dfrac{1-\exp(-\alpha_0 L)}{\alpha_0}$ is the on-axis phase shift at the focus.

The real part of the third-order nonlinear susceptibility is related to $\gamma$ by[11] $\mathrm{Re}\chi^{(3)} = 2n_0^2\varepsilon_0 c\gamma$ and the imaginary part is related to the nonlinear absorption by $\mathrm{Im}\chi^{(3)} = n_0^2\varepsilon_0 c\lambda\beta/2\pi$, where $\varepsilon_0$ is the permittivity of free space, and $c$ is the velocity of light in vacuum.

The UV-visible absorption spectra of all compounds in solution were recorded at room temperature using a UV-3100 UV-VIS-NIR recording spectrophotometer (SHIMADZU). The solutions were prepared with a concentration of $10^{-4}$ mol/L in dimethyl formamide (DMF) and placed in 2 mm cuvettes as samples. The structures and absorption spectra of all the samples are shown in Fig. 1.

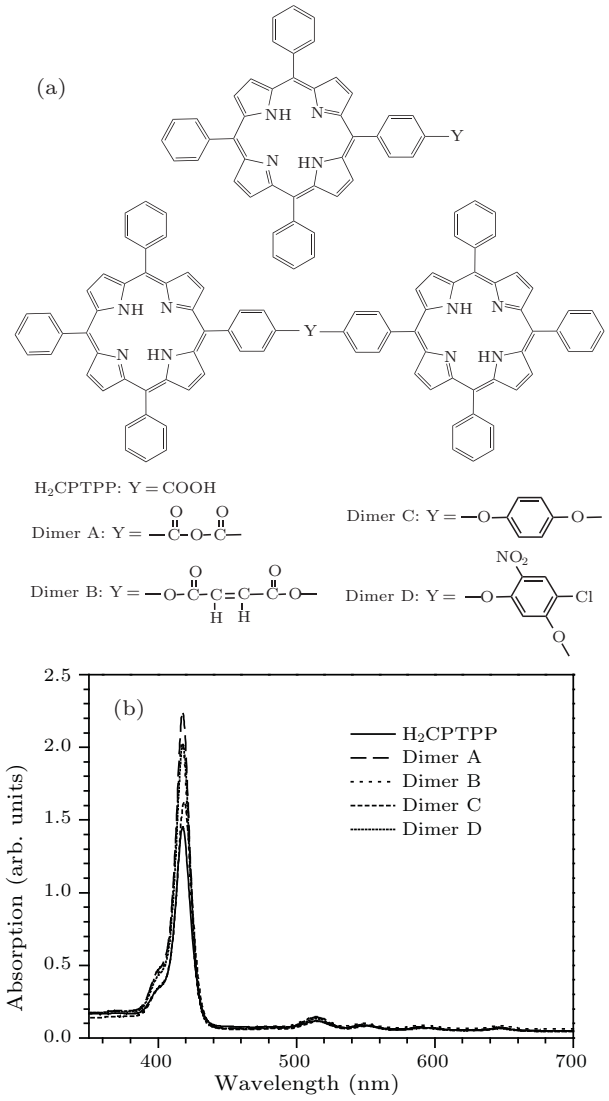



**Fig. 1.** Molecular structures (a) and absorption spectra (b) of $H_2$CPTPP and dimers A, B, C and D

The schematic diagram of the z-scan setup used is shown in Fig. 2. Nonlinear refraction in the sample manifests itself as a beam narrowing ($n_2 > 0$) or broadening ($n_2 < 0$) in the far field thus changing, together with nonlinear absorption, the fraction of light passing through the aperture as the sample moves along the $z$-direction. The measured curves have a valley-to-peak or peak-to-valley shape depending on $n_2$ sign. In particular, if $n_2$ is positive (negative) the curve shows a valley (peak) followed by a peak (valley) going from negative to positive $z$ positions.

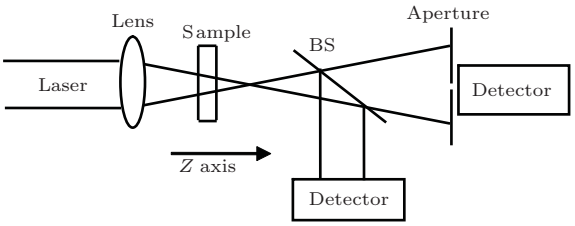



**Fig. 2.** Experimental setup for the $z$-scan measurement.

In our $z$-scan experiment, a cuvette with sample was placed on a translation stage moving along the $z$-axis through the focus of a Gaussian laser beam, a small aperture was placed in the far field, while the energy transmitted through the aperture in far field was recorded as a function of sample position. A Q-switched Nd:YAG pulsed laser (continuum) with pulsed length of 4.5 ns at 532 nm was used as the irradiation light beam. The laser beam was focused on the sample solution by a 40 cm focal length lens. The beam waist radius at the focus was 26 μm with the corresponding Rayleigh range of 3.99 mm and therefore the sample can be treated as thin medium.[12] In order to avoid cumulative thermal effects, the laser was working at 1 Hz.[13] The laser pulse energy at the focus point was 21.4 μJ. A small aperture ($S = 0.13$) was placed in the far field. A dual-channel laser power/energy meter (Laserprobe) was used to synchronously detect the change of the transmittance through the sample both open aperture and closed aperture.

The synthesizing procedures of dimer A and its monomeric derivative $H_2$CPTPP were reported in detail in Ref. [14]. From the absorption spectra we know that they both show the typical absorption bands as regular porphyrins, the Soret band around 418 nm corresponds to the transition from $a_{1\mu}(\pi)$ to $e_g^*(\pi)$ and four Q bands in the region 500–650 nm correspond to the transitions from $a_{2\mu}(\pi)$ to $e_g^*(\pi)$. Since the absorption spectrum of dimer A is almost identical to that of $H_2$CPTPP, the formation of dimer did not change the electronic transitions in the monomer.

Figure 3 shows the $z$-scan results and their theoretical fittings of these two compounds with Eqs. (2) and (4). The deep valleys from the results of the open aperture show the nonlinear absorption of the samples. Depending on the laser parameters, for example,

pulse duration, pump intensity and wavelength, nonlinear absorption can be taken from (a) the ground state $S_0$ to higher excited singlet $S_n$ (two-photon or multi-photon excitation), (b) the first excited singlet state $S_1$ to higher excited states $S_n$, or (c) the $T_1$ to $T_n$ states in the triplet manifold.[15] We attribute the observed nonlinear absorption to strong excited state absorption (ESA), which occurs when the excited state has an absorption cross section $\sigma_T$ higher than that of the ground state $\sigma_0$.[16] The peak-valley configuration of the pure nonlinear refraction curves, which were obtained by dividing the closed aperture data by respective open aperture data, demonstrates that the refraction index change is negative.

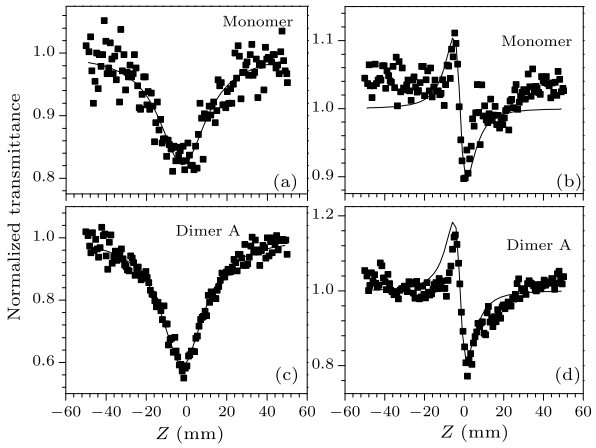



**Fig. 3.** Open aperture curves and pure refraction curves for $H_2$CPTPP and dimer A. Scatter points are experimental data, and solid curves are theoretical fitting results.

Table 1. Values of $\beta$, $n_2$ and $\chi^{(3)}$ determined experimentally for different compounds.

| Samples | $\beta$(MSK) $\times10^{-11}$ | $n_2$(esu) $\times10^{-11}$ | Re$\chi^{(3)}$(esu) $\times10^{-13}$ | Im$\chi^{(3)}$(esu) $\times10^{-13}$ |
|---|---|---|---|---|
| $H_2$CPTPP | 11 | −3.33 | −70.6 | 31.3 |
| Dimer A | 28.5 | −5.91 | −125 | 81.5 |
| Dimer B | 25.6 | −5.34 | −113 | 73.3 |
| Dimer C | 47.5 | −13 | −276 | 136 |
| Dimer D | 34.8 | −8.65 | −184 | 99.4 |

Values $\beta$, $n_2$, Re$\chi^{(3)}$ and Im$\chi^{(3)}$ were derived from the experimental data according to Eqs. (1)–(4), as shown in Table 1. The structure of dimer A is that two porphyrin monomers linked by two acid anhydrides, which means that the electrons can transfer from one monomer to another through the bridging group. Compared to the monomer, dimer A has the longer conjugated length and the enhanced $\pi$-electron density in the molecules. As a result, the value Re$\chi^{(3)}$ for dimer A is nearly doubled as compared to that of monomer.

To investigate the structure-dependence between the different bridging groups and the values of $\chi^{(3)}$, a series of porphyrin dimers were studied. Still, the absorption spectra of these dimers all show intense absorption at around 418 nm, followed by four weaker absorptions at higher wavelength (500–650 nm). The synthesizing procedures were described in Refs. [17–19].

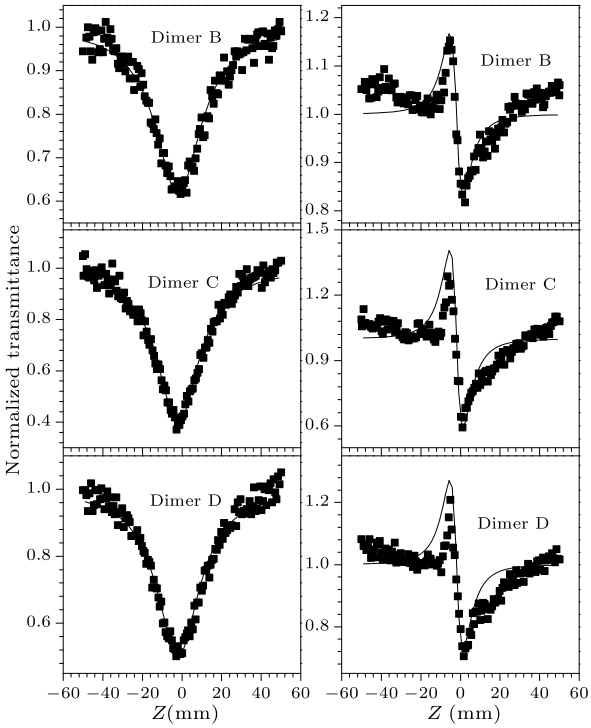



**Fig. 4.** Open aperture curves and pure refraction curves for dimers B, C and D. Scatter points are the experimental data, and solid curves are the theoretical fitting results.

Figure 4 shows the z-scan results and their theoretical fittings of these dimers. From Table 1 we find that the Re$\chi^{(3)}$ values follow the trend of dimer C > dimer D > dimer A > dimer B. For dimer A, the bridging groups are two carboxyls, which are electron-withdrawing groups. Dimer B is linked by an ethylene bond and two carboxyls, which are also electron-withdrawing groups. Compared to dimer B, dimer A has a shorter electron transfer pathway, so the electrons can travel through it a little faster and resulting in the increase in the electron donating abilities of the bridging group in dimer A. The bridging group of dimer C is a phenyl, which makes the whole dimer is composed by three conjugated systems. Dimer D is linked by a phenyl with two electron-withdrawing groups, which reduce the electron density of the benzene ring and make the electron transfer slow. Thus we can make the conclusion that the trend of Re$\chi^{(3)}$ is dimer C > dimer D and dimer A > dimer B. For dimer A, the electron density of two porphyrin rings is reduced, while for dimer D only the density of the benzene ring on the bridging group is reduced. Thus the value of Re$\chi^{(3)}$ for dimer D is larger than that of dimer A, which consists of the trend listed in Table 1.

In our experiment, the laser was working at 1 Hz,

which could avoid cumulative thermal effects. However, on a nanosecond time scale, a laser pulse can also induce temperature and density gradients that change the refractive-index profile. Thus we need to estimate the thermal effects.

The thermal effect in our experiment is in the transient regime instead of quasi-steady-state regime, since the condition

$$\tau_p \leq \tau_{ac} < \tau_D, \tag{5}$$

is satisfied,[20] where $\tau_p$ is the pulse duration time, $\tau_{ac}$ is the buildup time of the thermal nonlinearity given by the time required for a sound wave to propagate across the beam ($\tau_{ac} \approx \omega_0/v_s$, where $\omega_0$ is the beam radius and $v_s$ is the velocity of sound) and $\tau_D$ is the relaxation time related to the thermal diffusive coefficient $D$ ($\tau_D = \omega_0^2/4D$). The velocity of sound in DMF is 1439 m/s, then we can obtain $\tau_{ac}$ in our experiment to be 18 ns and $\tau_{ac}/\tau_p = 4$. As the transient thermal nonlinear refraction decreases exponentially with the increase of $\tau_{ac}/\tau_p$,[21] we can estimate that the thermal effect in our experiment does not play the main role of the nonlinearity.

Yet, we can use the theoretical treatment given in Ref. [21] and obtain the on-axis time-averaged effective index variation induced by the thermal mechanism during the Gaussian temporal pulse duration $\langle \Delta n_0 \rangle = 0.2\langle \Delta n_{0qss} \rangle$, where $\langle \Delta n_{0qss} \rangle$ is the on-axis time-averaged index change under quasi-steady-state approximation. Then we could find that though the thermal effect is not too great in our experiment, it did affect our results a little. Detailed research on these thermal effects in the experiment will be our next work.

The third-order nonlinear optical properties of four novel porphyrin dimers and $H_2$CPTPP have been probed using z-scan technique. The experimental results showed some structure-dependent nonlinear response for the four dimers with different bridging groups. We conclude that the variation in $\pi$-electron density caused by the incorporation of the bridging groups in these materials is responsible for the variation in their third order nonlinear response. Therefore, the nonlinear optical properties of the compounds can be tuned by the structural design with alternating bridging groups. Our results suggest that bridging groups with more large conjugation should be employed for further designing of such a kind of nonlinear optical materials at molecular levels and hence in finely tuning $\chi^{(3)}$ for future potential applications in photonics.

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