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Femtosecond, broadband nonlinear optical studies of a zinc porphyrin and zinc phthalocyanine

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ABSTRACT

Broadband (700–950 nm) third order nonlinear optical (NLO) properties of porphyrin (ZnTPP) and phthalocyanine (TPA-ZnPc) molecules in solution form have been studied using the Z-scan technique with femtosecond, MHz pulses. Two-photon, three-photon absorption coefficients along with the third-order NLO susceptibility (χ^3) and their optical limiting thresholds are estimated from the theoretical fits to experimental data. Closed aperture Z-scan data provided the information on the sign and magnitude of nonlinear refractive indices (n_2) at different wavelengths. Our results clearly suggest that these molecules possess the potential for applications such as optical limiting and biological imaging at high repetition rates.

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1. Introduction

Novel organic molecules with exceptional third-order nonlinear optical (NLO) coefficients are required for various device applications in the fields of optical communications, biomedical imaging, and photonics [1–3]. Both porphyrins and phthalocyanines are aromatic organic macromolecules with a huge number of delocalized π electrons [4–8]. Porphyrins, rigid square planar molecules made of four pyrroles, connect to form a larger ring. Porphyrin is stabilized by an aromatic character which extends over its entire structure. Phthalocyanines are a group of synthetic pigments that contain four isoindole units linked together in a large ring. A phthalocyanine is typically intensely blue-green-coloured and is widely used in dyes. Both porphyrins and phthalocyanines can carry a central metal ion in their rings which opens up lots of possibilities in tuning the NLO properties [9–13]. In fact, they can be used for tailoring the NLO coefficients to suit a specific application. For example, certain moieties depict saturable absorption (SA) and such molecules can be used in mode-locking of ultrafast lasers. A few others demonstrate strong nonlinear absorption, and these can be utilized in either bio-imaging applications [strong two-photon absorption (TPA) coefficient/cross-section] or as optical limiters. Some class of these molecules depict strong nonlinear refractive index (n_2) and such molecules have potential applications in all-optical switching provided they have ultrafast electronic response. The nonlinear absorption can be tuned in such molecules to achieve SA or reverse saturable absorption (RSA). Similarly, the n_2 of a molecule can be modified by simply changing the central metal ion or the peripheral substituents. It is observed that the NLO properties strongly depend on the excitation wavelength and the input pulse duration used. Therefore, it is imperative to scrutinize the NLO properties of any novel molecules over a wide wavelength range. In the present work we present NLO properties of a porphyrin and a phthalocyanine molecule in the 700–950 nm spectral range achieved with femtosecond pulses.

The Z-scan technique is a single-beam technique that provides both the sign and magnitude of real and imaginary parts of third order nonlinear susceptibility $\chi^{(3)}$. This method is simple to perform and gives rapid, accurate results. This technique was originally introduced by Sheik Bahae et al. [14]. According to Beer-Lamberts law the amount of light transmitted is a linear function of incident light intensity. $\alpha(I) = \alpha + \beta I$ and $dI/dZ = -\alpha(I)I$, where α is linear absorption coefficient; I is the intensity of the light and β is a nonlinear absorption coefficient. The light induced refractive index change is described by the relationship $n = n_o + n_2 I$, where n_o is the linear refractive index; I is the intensity of the light and n_2 is a nonlinear refractive index coefficient. In open aperture Z-scan the nonlinear absorption of the sample is measured. One can use the following equations $dI/dz = -\alpha I - \alpha_2 I^2$

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where α_2 is the two-photon absorption/2-photon absorption (TPA/2PA) coefficient and $dI/dz = -\alpha I - \alpha_3 I^3$ where α_3 is the 3-photon absorption (3PA) coefficient for fitting the obtained data. Assuming a spatial, temporal Gaussian profile for the input laser pulses and applying the open aperture Z-scan theory for multi-photon absorption, the normalized transmittance is evaluated by the following equations [11,15,16]

$$\text{Transmittance, } T_{OA(2PA)} = 1 \Bigg/ \left[1 + \alpha_2 L_{eff}\left(I_{00}/1 + \left(\frac{z}{z_0}\right)^2\right)\right]$$

$$\text{Transmittance, } T_{OA(3PA)} = 1 \Bigg/ \left[1 + 2\alpha_3 L_{eff}\left(I_{00}/1 + \left(\frac{z}{z_0}\right)^2\right)^2\right]^{1/2}$$

where effective path length of the sample $L_{eff}(cm^{-1}) = \frac{1-e^{-\alpha L}}{\alpha}(2PA), L_{eff}(cm^{-1}) = \frac{1-e^{-2\alpha L}}{2\alpha}(3PA)$, α absorption coefficient, I_{00} is the peak intensity, Rayleigh range, $z_0(mm) = \frac{\pi\omega_0^2}{\lambda}$, $\omega_0(\text{beam waist at focal point}) = \frac{f.\lambda}{\pi.d}$, λ is wavelength and ‘d’ is the input beam waist at focal point. The nonlinear refractive index is calculated using the relation $n_2(e.s.u) = \frac{cn_0}{4\pi} n_2(m^2/W)$. The third-order nonlinear susceptibility is a complex quantity: $\chi^{(3)} = \chi_R^{(3)} + i\chi_I^{(3)}$ where real part related to n_2 through $Re|\chi^{(3)}|\left(\frac{m^2}{V^2}\right) = 2c\epsilon_0 n_0^2 n_2\left(\frac{m^2}{W}\right)$ and imaginary part related to α_2 (absorption coefficient) through $Im|\chi^{(3)}|(m^2/V^2) = \frac{c\epsilon_0\lambda n_0^2\alpha_2(m/W)}{2\pi}$. The magnitude of the third order nonlinear susceptibility was calculated using $|\chi^{(3)}|(e.s.u) = \left(3 \times 10^4\right)^2 |\chi^{(3)}|\left(m^2/V^2\right)/4\pi$. For a Gaussian beam, each Z position corresponds to an input fluence of

$$4(\ln 2)^{\frac{1}{2}} E_{in}/\pi^{\frac{3}{2}}\omega(z)^2$$

where E_{in} is the input laser pulse energy and $\omega(z)$ is the beam radius. $\omega^2(z) = \omega_0^2\left[1 + \left(\frac{z}{z_0}\right)^2\right]$ where $\omega(z)$ is the beam waist at a particular z value while ω_0 is the beam radius at the focus.

2. Experimental details

5,10,15,20-tetraphenyl porphyrinato zinc(II) and tetrasubstituted triphenylamine zinc phthalocyanine were synthesized and purified by following the procedures listed in literature reports [17]. The Z-scan experiments were performed using a Ti:Sapphire laser (Chameleon, Coherent). The input pulses with a duration of ~150 fs, the repetition rate of 80 MHz and tunable in the 680–1080 nm spectral region was used for all the studies [18–21]. An input beam diameter of ~2 mm combined with a Plano-convex lens of focal length 100 mm was used to focus the beam onto the sample. For wavelengths ranging from 700 nm to 950 nm, the beam waist (ω_0) was estimated and found to be 23–30 μm with the corresponding Rayleigh ranges (Z_0) in the range of 2.2–3 mm. Neutral density filters were utilized for attenuating the input pulse energy. The experiments were carried out with the samples (dissolved in dichloromethane) possessing a concentration in the range of 1×10^{-4} M providing a linear transmittance of 64–88% in the 700–950 nm spectral range. A 1-mm glass/quartz cuvette was used for the sample solutions. A translation stage with a step size of 1-mm was used to manually scan the sample. The transmittance changes of the sample were measured with a sensitive power meter. The experiments were performed at 2.6–47 MW/cm^2 peak intensities. To scan the sample in closed aperture, a variable aperture was placed in front of the photo detector. The closed aperture scans were performed at low peak intensities. The experiments were repeated multiple times and best data were averaged to retrieve the NLO coefficients. The optical absorption spectra were recorded on a Shimadzu (model UV-3600) spectrophotometer. Concentrations of solutions are ca. 1×10^{-6} M for Soret band and 1×10^{-5} M for Q-band absorption in case of ZnTPP and it is 1×10^{-6} M for both Q-band and Soret band absorption in case of TPA-ZnPc. The error bars of ~10% represent the errors in analysis arising due to (a) error in the estimation of beam waist (b) fluctuations of input laser power (c) fitting errors.

3. Results and discussion

Both ZnTPP and TPA-ZnPc were synthesized as per the methods reported in the literature and characterized using standard techniques. The molecules are confirmed by ^{1}H NMR and mass spectral analysis. TPA-ZnPC (Triphenylamine Zinc Phthalocyanine, $C_{104}H_{68}N_{12}Zn$) with a molecular weight 1548.5 and ZnTPP (Zinc Tetraphenylporphyrin, $C_{44}H_{28}N_4Zn$) with a molecular weight of 678.12 were used in the present study. These samples are highly soluble in dichloromethane (DCM). The absorption spectra of these samples were recorded using an UV–VIS spectrophotometer. The absorption data of these samples are shown in Fig. 1. ZnTPP exhibited a characteristic intense Soret band at 420 nm, an $a_{1u}(\pi)/e_g(\pi^*)$ electronic transition, which is assigned to the second excited state (S_2). Whereas Q-bands in 500–650 nm region due to $a_{2u}(\pi)/e_g(\pi^*)$ electronic transitions as the first excited state (S_1) [7,13]. The absorption peak wavelength was identified at 350, 704 nm for TPA-ZnPC. Insets of Fig. 1 depict the structure of these molecules. A 1-mm quartz/glass cuvette was used for both the open and closed aperture Z-scan experiments. These molecules emit typically in the visible region with lifetimes of few nanoseconds. Fig. 2 illustrates the schematic energy level diagram of these samples for the excitation wavelengths used in this study.

Fig. 3(a)–(f) illustrate the open aperture (OA) Z-scan data while Fig. 3(g)–(l) illustrate the closed aperture (CA) Z-scan data for TPA-ZnPC obtained in the wavelengths ranging from 700 nm to 950 nm. The data obtained for all the wavelengths show a strong decrease in the transmission which is indicative of reverse saturable absorption (RSA). The obtained experimental data was best fitted for two-photon absorption (2PA) from 700 to 850 nm and the calculated 2PA coefficients (α_2) with magnitudes in the range of 0.2–9.5 × 10^{-7} cm/W shown in Fig. 3(a)–(d). It is evident that 3PA is the dominant mechanism for longer wavelengths. At 900 nm and 950 nm the best fit was obtained with transmission equation for 3PA [red color solid line, the green colored solid line represents 2PA – Fig. 3(e), (f)]. The energies corresponding to the wavelengths 900 nm and 950 nm are 11,111 cm^{-1} and 10,526 cm^{-1}, respectively. The energy of two photons combined is not sufficient to

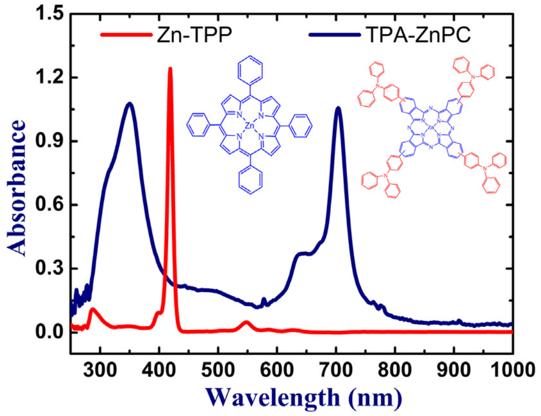

Fig. 1. The absorption spectra of representative compounds dissolved in DCM.

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