Ultrafast nonlinear optical properties of alkyl phthalocyanines investigated using degenerate four-wave mixing technique

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ABSTRACT

We present our results on the investigation of ultrafast nonlinear optical properties including the time response of **2(3), 9(10), 16(17), 23(24) tetra tert-butyl phthalocyanine** (pc1) and **2(3), 9(10), 16(17), 23(24) tetra tert-butyl Zinc phthalocyanine** (pc2) studied using degenerate four-wave mixing technique at a wavelength of 800 nm with 100 fs pulses. We recorded large off-resonant second hyperpolarizabilities (γ) with estimated values of $(4.27 \pm 0.43) \times 10^{-31}$ esu and $(4.32 \pm 0.43) \times 10^{-31}$ esu for pc1 and pc2, respectively, with ultrafast nonlinear optical response in the femtosecond domain. We also estimated the figures of merit for photonic switching applications for both one-photon and three-photon loss mechanisms. The performance of these molecules vis-à-vis other molecules, in general, and phthalocyanines, in particular, is discussed.

1. Introduction

Phthalocyanines and their derivatives are a versatile class of macromolecules [1] that are extensively investigated for variety of applications in photodynamic therapy, solar cells, nanotechnology, and nonlinear optics [2–8]. The highly delocalized π-electron distribution of phthalocyanines gives rise to strong nonlinear optical (NLO) response to an external electromagnetic field of laser pulses. The high stability combined with the capability of phthalocyanines to accommodate different metallic ions in their cavity, due to their architectural flexibility, allows tailoring of their physical, chemical, and optical properties in a broad spectral range. As a consequence they result in many applications, especially, in the areas of optical limiting and all-optical switching [9–20]. Typically, the presence of nonlinear absorption in such molecules augments their capability for optical limiting applications while the presence of nonlinear refraction facilitates all-optical switching applications. Though NLO properties of variety of phthalocyanines have been investigated till date there are further opportunities and avenues to explore novel structures with superior figures of merit [5].

It is well established that for a third-order nonlinear material to be attractive for optical switching applications the nonlinear response has to be strong (a high value of the effective nonlinear refractive index n_2) and instantaneous time response of the induced refractive-index change (typical response is expected in the sub-picosecond range) along with the requirement of minuscule material losses due to one-photon, multi-photon absorption. Furthermore, scattering losses are to be minimal for any signal processing devices application [21–24]. Accurate determination of the merit factors is imperative for deciding the applicability of third-order NLO materials for optical switching and all-optical signal processing. Unfortunately many reports which dealt with the NLO properties of organic materials in general, with phthalocyanines in particular, furnish fragmentary information about these parameters. We have been recently investigating novel alkyl and alkoxy phthalocyanines in the femtosecond domain with this specific goal. In this paper we present the results of our studies on the nonlinear optical response of **2(3), 9(10), 16(17), 23(24) tetra tert-butyl phthalocyanine** (referred to as pc1) and **2(3), 9(10), 16(17), 23(24) tetra tert-butyl Zinc phthalocyanine** (referred to as pc2) in solution obtained utilizing the technique of degenerate four-wave mixing technique (DFWM) near 800 nm with ~100 fs (fs) pulses. We observed large third-order nonlinear susceptibility [$\chi^{(3)}$] and second-order molecular hyperpolarizability [γ] for these

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molecules. Time-resolved degenerate four wave mixing (DFWM) measurements in the box-car geometry revealed instantaneous response from these molecules. Our detailed FWM studies suggest that these molecules are potential candidates for photonic switching applications. We have also tried to establish the competence of these molecules, compared to some of the recently reported molecules [25–33], through their figures of merit evaluation.

2. Experimental details

Alkyl phthalocyanines were synthesized according to the procedures reported in literature [1]. Each sample was subjected to a column chromatographic purification process prior to FWM measurements. The details of molecular structures are presented in Fig. 1a. The molecular weights of pc1 and pc2 are 748 and 804 gm/M, respectively. The particulars of absorption spectra have been reported elsewhere [13]. All the experiments were performed with samples dissolved in chloroform and placed in 1-mm glass/quartz cuvettes. For DFWM measurement the ultrashort laser pulses were obtained from a conventional chirped pulse amplification system comprising of an oscillator (Maitai, Spectra-Physics Inc.) that delivered ~80 fs, 82 MHz pulse train with pulse energy of 1 nJ at 800 nm and a regenerative amplifier (Spitfire, Spectra Physics Inc.), pumped by a 150 ns, 1 kHz, Q-switched Nd:YLF laser. After regenerative amplification we obtained pulses of ~100 fs duration with output energy of up to 1 mJ delivering pulses at a repetition rate of 1 kHz with the corresponding bandwidth measured to be ~9 nm. The pulse width was determined to be ~100 fs through intensity autocorrelation measurements. The DFWM set up was configured in the standard box-car geometry [34,35]. The fundamental beam was divided into three nearly equal intensity beams (intensity ratio of 1:1.2:0.8) such that they form three corners of a square and are focused into the nonlinear medium (sample) both spatially and temporally. The resultant DFWM signal was detected at the fourth corner of the box which was generated due to the phase-matched interaction $\boldsymbol{k}_4 = \boldsymbol{k}_3 - \boldsymbol{k}_2 + \boldsymbol{k}_1$ as depicted in Fig. 1b. Sufficient care was observed to reduce the contribution of cuvette signal towards the overall DFWM signal by choosing appropriate focal conditions. The measurement of $\chi^{(3)}$ values was performed at zero time delay of all the beams. We estimated the magnitude of $\chi_{1111}^{(3)}$ by maintaining the same polarization for all the three incident beams. A half-wave plate was introduced in the path of beam 2 to control the polarization required for the estimation of $\chi_{1212}^{(3)}$. The transient DFWM profiles were obtained by delaying beam 3 with respect to the other two beams. Through nonlinear transmission measurements the input powers for three mixing pulses were chosen such that the effect of nonlinear absorption was minimal. We believe that the measured $\chi^{(3)}$ at these intensities is, therefore, purely real in nature without any contribution from the imaginary component arising from multi-photon absorption. Moreover, the choice of low input intensities allowed us to neglect the association of higher-order nonlinearities. The intensity measured at the sample due to the three input beams was ~2.7 × 10^{10} W/cm^2. Since all the samples had negligible linear absorption at the working wavelength of 800 nm we expect the measured $\chi^{(3)}$ and γ values to be off-resonant. All the studies were performed with solutions possessing concentrations of ~1 × 10^{-4} M/L.

3. Results and discussion

3.1. Third-order nonlinear optical properties by DFWM measurements

The third-order NLO susceptibility $\chi^{(3)}$ was estimated by comparing the measured DFWM signal of the sample with that of neat CCl_4 as reference [$\chi^{(3)}$ = 4.4 × 10^{-14} esu] measured with the same experimental conditions. The relationship used for $\chi_{sample}^{(3)}$ is [34]:

$$\chi_{sample}^{(3)} = \left(\frac{n_{sample}}{n_{ref}}\right)^2 \left(\frac{I_{sample}}{I_{ref}}\right)^{1/2} \left(\frac{L_{ref}}{L_{sample}}\right) \alpha L_{sample} \left(\frac{e^{\frac{\alpha L_{sample}}{2}}}{1 - e^{-\alpha L_{sample}}}\right) \chi_{ref}^{(3)}$$

(1a)
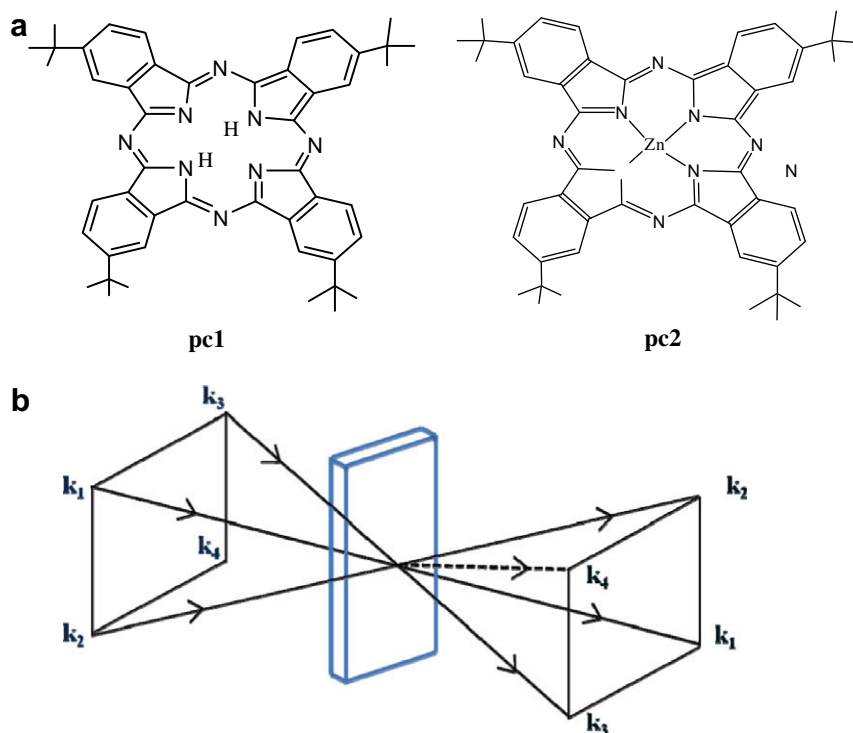
Fig. 1. (a) Structures of the phthalocyanines used pc1 and pc2; (b) Schematic of the box-car DFWM set-up. Beams 1–3 are coincident on the sample. The resultant, fourth beam (dashed line) is the DFWM signal that occurs because of the interaction $\boldsymbol{k}_4 = \boldsymbol{k}_3 - \boldsymbol{k}_2 + \boldsymbol{k}_1$.

where I is the DFWM signal intensity, α is the linear absorption coefficient, L is sample path length, and n is the refractive index. We estimated $\chi^{(3)}$ values to be $(4.26 \pm 0.43) \times 10^{-14}$ esu and $(4.31 \pm 0.43) \times 10^{-14}$ esu for pc1 and pc2, respectively, for an input intensity of $\sim 2.7 \times 10^{10}$ W/cm^2. One of the main sources of error that arises in experiments is through the intensity fluctuations of laser pulses. This problem is overcome by taking the averaged data of 1000 pulses. The second major source of error could be from the determination of solutions concentration. Considering all the unforced random experimental errors we estimate an overall error of $\sim 10\%$ in our calculations by repeating the experiment few times. In an isotropic medium $\chi^{(3)}$ has three independent components, namely, $\chi^{(3)}_{1111}$, $\chi^{(3)}_{1212}$ and $\chi^{(3)}_{1122}$. In the case of non-resonant electronic nonlinearity, $\chi^{(3)}_{1111} = 3\chi^{(3)}_{1212} = 3\chi^{(3)}_{1122}$ when the three input beams are all vertically polarized and the corresponding $\chi^{(3)}$ obtained would be $\chi^{(3)}_{1111}$. To determine $\chi^{(3)}_{1212}$, the probe beam has to be orthogonally polarized with respect to the two pump beams. We measured the values for $\chi^{(3)}_{1212}$ to be $(1.47 \pm 0.15) \times 10^{-14}$ esu and $(1.49 \pm 0.15) \times 10^{-14}$ esu for pc1 and pc2, respectively, and the obtained ratio of $\chi^{(3)}_{1111}$ to $\chi^{(3)}_{1212}$ was ~ 2.9 suggesting that there was no significant contribution arising from the coherent coupling effects [24]. We estimated the $\chi^{(3)}$ value of phthalocyanines in a solid film by assuming a density of $\sim$l g/cm^3 using the following relationship [36]

$$\chi^3_{\text{thin film}} = \frac{N}{N_{\text{solution}}} \chi^3_{\text{solution}} \tag{1b}$$

where N is the assumed density of the phthalocyanines solid and χ^3_{solution} are the value estimated from Eq. (1). The estimated values for the solid films of pc1 and pc2 were $(5.74 \pm 0.57) \times 10^{-10}$ esu and $(5.37 \pm 0.54) \times 10^{-10}$ esu, respectively, which are among the largest reported values for these types of molecules. The measured $\chi^{(3)}$ value of chloroform was insignificant compared to the $\chi^{(3)}$ value of the samples under similar experimental conditions and thus the contribution from pure solvent was neglected.

The intensity dependence of the DFWM signal amplitude in both the samples is presented in Fig. 2. At relatively low input intensities (<220 GW/cm^2) the DFWM signal amplitude followed a dependence that is essentially cubic (with a slope of ~ 2.85) clearly indicating that the nonlinearity behaves in a Kerr-like fashion and that origin of DFWM does not have contribution from any multi-photon absorption process in which case the slope of the curve would have been different from 3 [37,38]. To determine whether our molecules possessed two-photon absorption coefficient β, which corresponds to the imaginary part of $\chi^{(3)}$, we performed the nonlinear transmission measurements. For both the molecules we obtained straight lines that intercept the ordinate axis and their values were less than unity, suggesting a one-photon contribution to the absorption. This supports our argument that third-order optical susceptibility of our molecules can be attributed to the nonlinear refractive index at 800 nm. Fig. 3 shows the linearity in the transmission versus the input intensity for the range of intensities from 7×10^9 to 2.5×10^{11} W/cm^2. The DFWM signal was measured at an input intensity of $I_{\text{in}} = 2.7 \times 10^{10}$ W/cm^2 that was much lower than required for nonlinear absorption which was $\sim 2.15 \times 10^{11}$ W/cm^2.

To estimate the second-order hyperpolarizability, γ, at the molecular level we used the following relation [34]:

$$\gamma_{\text{sample}} = \chi^{(3)}/T^4 N_0, \tag{2}$$

where N_0 is the number density of the molecules per milliliter, and $T = (n^2_{\text{sample}} + 2)/3$ is the local field factor. We assume that the solvent makes negligible contribution to the signal. We estimated the γ values to be $(4.27 \pm 0.43) \times 10^{-31}$ esu and $(4.32 \pm 0.43) \times 10^{-31}$ esu for pc1 and pc2, respectively, which are reasonably large in the femtosecond regime compared to some of the phthalocyanines and their
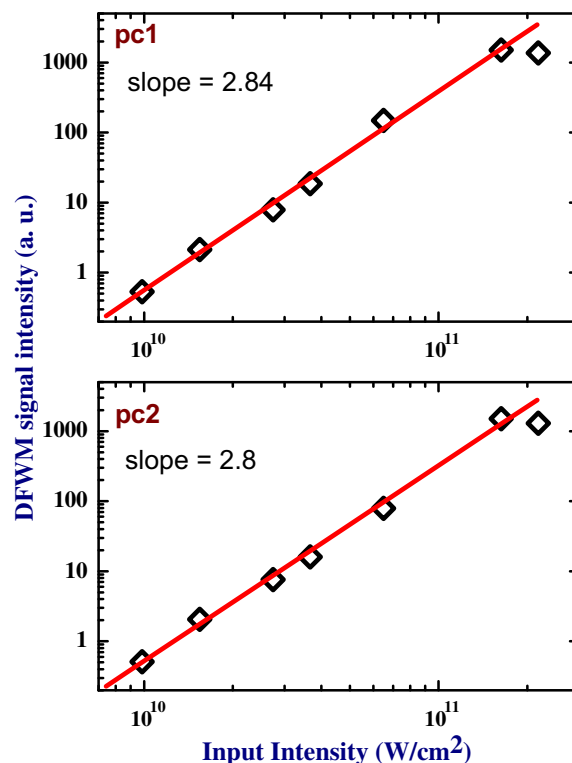

Fig. 2. Plots showing the cubic dependence of DFWM signal for pc1 and pc2 as a function of input intensity.
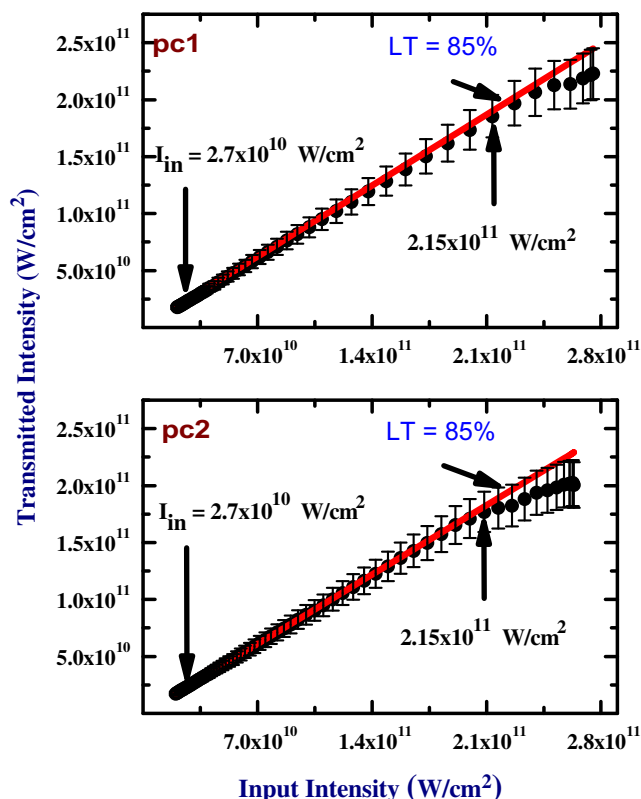

Fig. 3. Plot of output transmittance versus input power, LT represents the linear transmittance at 800 nm.

analogues reported recently [25–32]. The metallic phthalocyanine had marginally higher nonlinearity and the reason could be attributed to the presence of the metal ion.
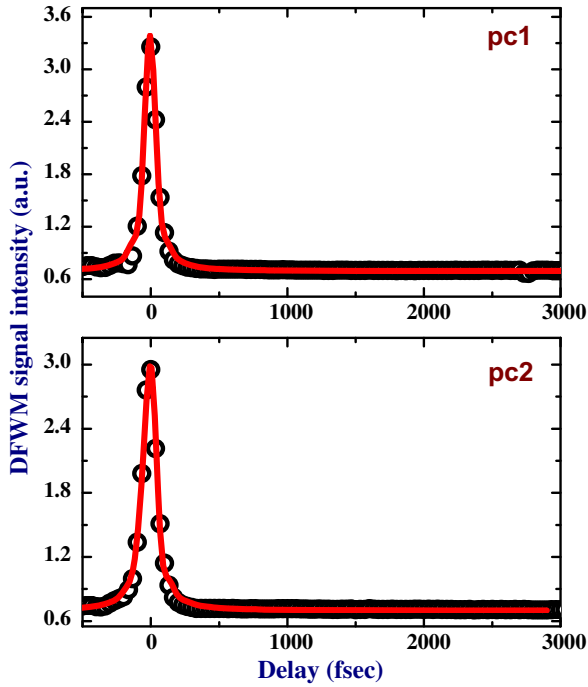
Fig. 4. Temporal profiles of DFWM signals of pc1 and pc2.

Fig. 4 shows the temporal response of the DFWM signal recorded as a function of the probe delay. The signal was fitted with a Lorenztian function (solid curve), and full width half maximum (FWHM) of the fit was similar to the response signal obtained from pure CCl$_4$. The signal profiles were nearly symmetric about the maximum (i.e. zero time delay) illustrating that the response times of the nonlinearities were much shorter than the pulse duration (100 fs). Such an instantaneous response is indicative of the Kerr effect (electronic component) from the distortion of the large π-conjugated electron charge distribution of phthalocyanine molecules. This instant response enhances their potential for photonics switching applications. Interestingly, the trapping levels originating from the multi-conformational and polaronic states situated in the HOMO-LUMO gap also play an important role in the DFWM for measurements in solutions [39].

3.2. Figures of merit (FOM) for photonic switching applications

A convenient way to quantify the losses is to consider the appropriate merit factors formulated by Stegeman for photonic switching applications [21–24]. These figure of merit (FOM) factors are related to the maximum nonlinear phase shift $\Delta\varphi$ through

$$\Delta\varphi = \frac{2\pi}{\lambda} \int_0^L n_2 I(z) \mathrm{d}z \tag{3}$$

obtained in a given material within a propagation distance L corresponding to an absorption length. $\Delta\varphi$ change of $\sim 2\pi$ is essential for switching applications. For one-photon absorption as the dominant loss mechanism, the absorption depth can be defined as α_1^{-1}, where α_1 is the absorption coefficient. We have the merit factor W defined as

$$W = \frac{n_2 I_{sat}}{\alpha_1 \lambda} \tag{4}$$

where λ is the wavelength and I_{sat} is the light intensity at which the nonlinear refractive-index change saturates. The nonlinear phase shift obtainable on the distance of α_1^{-1} is equal to 1.26 W π rad. Therefore, the pre-requisite for superior FOM is:

$$W > 1 \tag{5}$$

When the nonlinear losses prevail with materials with strong multi-photon absorption, the nonlinear phase shift will be limited, too. The absorption depth can then be defined as $(\alpha_2 I_0)^{-1}$ and $(\alpha_3 I_0^2)^{-1}$ where α_2 and α_3 are the two-photon absorption and three-photon coefficient and I_0 stands for the incident light. As the absorption depth is intensity dependant, it follows that the obtainable phase shift is now intensity independent.

The corresponding FOMs can be presented as:

$$T^{-1} = \frac{n_2}{\lambda \alpha_2} \tag{6}$$

$$V^{-1} = \frac{3 n_2}{\lambda \alpha_3 I_0} \tag{7}$$

For a successful operation of a photonics device made of such lossy materials to acquire nominal 2π phase shift the following inequalities must be satisfied

$$T < 1, \text{ and } V < 0.68 \tag{8}$$

To estimate the values of n_2 we used the data obtained from the calculation of $\chi^{(3)}$. We estimated n_2, which is related to the real part of $\chi^{(3)}$, using the relation [34]:

$$n_2 (\mathrm{cm}^2/\mathrm{W}) = \frac{0.0395}{n_0^2} \chi^{(3)} (\mathrm{esu}) \tag{9}$$

By performing intensity dependent measurements of $\chi^{(3)}$ we evaluated the corresponding n_2 and observed that n_2 was independent of the input intensity (see Fig. 5) highlighting the existence of pure nonlinearity. We achieved an average n_2 value of 9.58×10^{-16} cm^2/W and 9.72×10^{-16} cm^2/W for pc1 and pc2, respectively. For an intensity of $\sim$190 GW/cm^2, where nonlinear absorption is negligible, and α_1 for pc1 and pc2 were 0.06 cm^{-1} and 0.09 cm^{-1}, respectively,
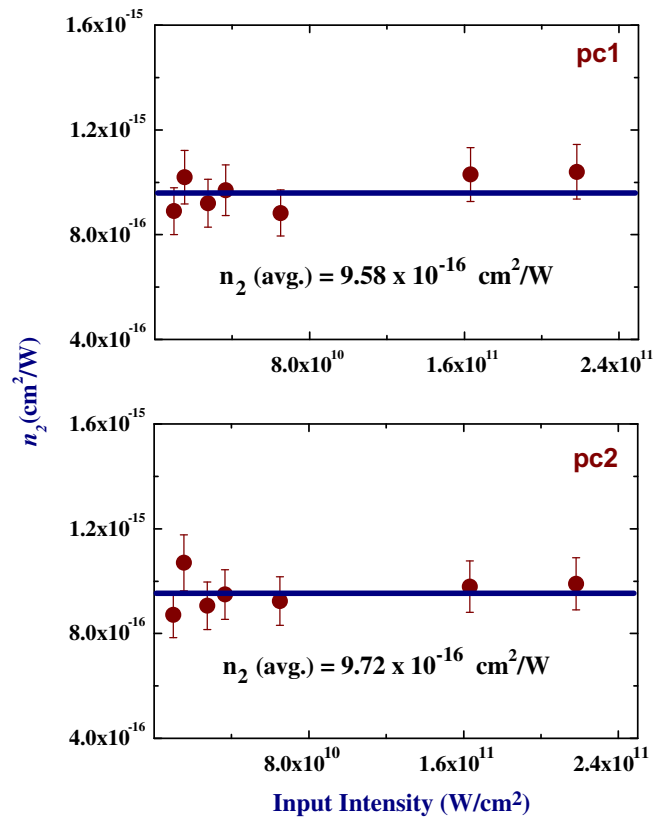

Fig. 5. Plot of n_2 as a function of input intensity.

Table 1
Summary of the nonlinear optical parameters of pc1 and pc2 studied using DFWM technique with 800 nm excitation and the corresponding one-photon and three-photon figures of merit for photonic switching applications.

Sample	$\chi^{(3)}$ (esu)[a]	γ (esu)[a]	n_2 (cm^2/W)	W[b]	V[c]
pc1	$(4.26 \pm 0.42) \times 10^{-14}$	$(4.27 \pm 0.42) \times 10^{-31}$	$(9.58 \pm 0.95) \times 10^{-16}$	37.8	0.57
pc2	$(4.31 \pm 0.43) \times 10^{-14}$	$(4.32 \pm 0.43) \times 10^{-31}$	$(9.72 \pm 0.97) \times 10^{-16}$	25.6	0.59

[a] $I = 27$ GW/cm^2.
[b] $I = 190$ GW/cm^2.
[c] $I = 230$ GW/cm^2.

we estimated W to be ~37.9 and ~25.6 for pc1 and pc2, respectively. Though the nonlinearities are higher in pc2 in contrast to pc1 higher linear absorption resulted in lower figure of merit. These are superior to the required values for photonic switching device with one-photon contribution. For input intensities >215 GW/cm^2 we expect substantial contribution from multi-photon absorption. Our earlier report [13] demonstrated and confirmed these phthalocyanines possessed strong three-photon absorption coefficient (3PA) with femtosecond pulse excitation near 800 nm. The measured 3PA coefficients (α_3) were independent of input intensity and the magnitudes were ~0.000091 cm^3/GW^2 and ~0.000095 cm^3/GW^2 for pc1 and pc2, respectively [13]. The V parameter calculated from Eq. (8) and for an input intensity of 230 GW/cm^2 was 0.57 and 0.59 for pc1 and pc2, respectively. The combination of instantaneous nonlinear response and excellent figures of merit propels pc1 and pc2 as ideal for photonic switching applications. We summarize the evaluated values of nonlinear coefficients and FOM in Table 1.

To put in perspective the merits of our molecules we have tried to compare the coefficients and FOM obtained for our phthalocyanines with some of the other molecules reported recently. Tran et al. [25] reported resonantly enhanced nonlinearities of their squaraine dyes near 700 nm with γ values of the order of 10^{-32} esu. Fu et al. [26] reported large nonlinearities in naphthalocyanine derivatives near 800 nm with value in the range of 2×10^{-29}–7×10^{-29} esu. However, the large values (two-orders of magnitude higher) obtained were again attributed to the resonance enhancement. All the molecules they investigated had strong absorption near 800 nm. Li et al. [27] presented their results on centrosymmetric squaraines possessing large nonlinearities studied using femtosecond DFWM. They achieved γ values of ~10^{-31} esu with fast response times (<100 fs). Their group [28] also reported similar studies on novel diarylethene–phthalocyanine dyads with largest γ value for one of the compounds being 10^{-30} esu. Kasatani et al. [29] also reported large resonant nonlinearities (10^{-28} esu) for cyanine dyes near 800 nm. Huang et al. [30] measured off-resonant nonlinearities of dihydroxy phosphorus (V) tetrabenzotriazacorroles, which are phthalocyanine analogues, in the range of 10^{-31} esu with sub-50 femtosecond response time. Prabhakar et al. presented their results of croconate dyes obtained with 100 fs pulses where off-resonant γ values of ~10^{-32} esu were reported [33]. It is apparent that our molecules possess better or similar values obtained for γ and the response times with exception being that reported in reference [29]. We expect further enhancement in the nonlinearities for our sample in the resonant case. In terms of FOM achieved for our molecules, Gu et al. [40] presented their measurements for chalcone derivatives with optimum values for W as 26.6, T as 0.13, and V as 0.64 which are comparable to those obtained for our phthalocyanines. Our earlier measurements [41] on the NLO properties studied using nanosecond pulse and continuous wave excitation substantiate that these molecules are prospective optical limiters with limiting threshold values as low as 0.45 J/cm^2. They also possessed high optical nonlinearities in those time scales. Based on our detailed experiments and analysis we assess that these molecules are versatile candidates for nonlinear optical device applications in all regimes of excitation.

4. Conclusions

We have investigated the ultrafast nonlinear optical properties including the time response of **2(3), 9(10), 16(17), 23(24) tetra tert-butyl phthalocyanine** and **2(3), 9(10), 16(17), 23(24) tetra tert-butyl Zinc phthalocyanine** using degenerate four-wave mixing technique at a wavelength of 800 nm with 100 fs pulses. We measured large off-resonant second hyperpolarizabilities (γ) for these molecules with ultrafast nonlinear optical response. The measured values of γ were $(4.27 \pm 0.43) \times 10^{-31}$ esu and $(4.32 \pm 0.43) \times 10^{-31}$ esu for pc1 and pc2, respectively. The merit factors for photonic switching applications were estimated. For one-photon absorption as the dominant loss mechanism we estimated W to be ~37.9 and ~25.6 for pc1 and pc2, respectively. For three-photon absorption as the dominant loss mechanism we estimated V parameter as 0.57 and 0.59 for pc1 and pc2, respectively, for an input intensity of 230 GW/cm^2. Comparing these values with other molecules from literature we conclude that these molecules are versatile candidates for nonlinear optical device applications.

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