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Studies of third-order optical nonlinearity and nonlinear absorption in tetra tolyl porphyrins using degenerate four wave mixing and Z-scan

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Abstract

We present our experimental results on the measurement of third-order optical nonlinearity in the ns and ps domain, in several Tetra Tolyl Porphyrin molecules (TTP), using degenerate four wave mixing (DFWM) and Z-Scan techniques. Our results indicate a very high value of nonlinearity for these molecules in the ns domain and reasonably high values in the ps domain. They are found to exhibit a strong nonlinear absorption at both 532 nm and 600 nm. The high value of nonlinearity for ns pulses is attributed to higher excited singlet and triplet states. Time-resolved studies indicate an ultra-fast temporal evolution of the nonlinearity in these molecules. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The last two decades have witnessed a phenomenal growth of research in nonlinear optical properties of various conjugated polymers, molecular solids, organic/organo-metallic composites and compounds [1–4]. A collective effort from physicists, chemists and material scientists is in progress to

understand the basic processes responsible for the nonlinearity. Current emphasis is on the synthesis of novel chemical structures that can be tailored to optimize the nonlinear response while preserving their chemical, mechanical, optical and thermal stability. Among the various organic materials porphyrins, metalloporphyrins and their derivatives are one of the most studied group of molecules [5–9]. Porphyrins are a ubiquitous class of naturally occurring compounds having important biological representatives including hemes, chlorophyll and vitamin

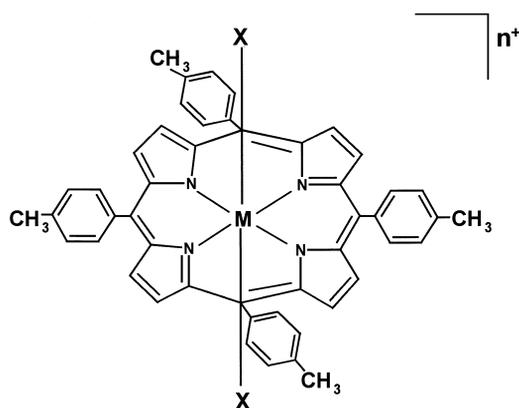
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B₁₂ among several others. They are also involved in oxygen binding, electron transfer, catalysis, light harvesting, magnetic resonance imaging and photodynamic therapy. In addition there is a multitude of synthetic porphyrinoid molecules that have been prepared and studied for purposes ranging from basic research to functional applications. All these molecules share the porphyrin macrocyclic substructure in common. The basic structure of the porphyrin macrocycle consists of four pyrrolic subunits linked by four methine bridges.

Although the porphyrin ring is a macromolecule, it is highly flexible and a number of structural changes involving different central metal ions and peripheral substituents can be introduced without compromising its excellent chemical and thermal stability. This architectural aspect is relevant to nonlinear optics in developing materials with optimum nonlinearity and response times. The high π electron density, resulting in an extended electron de-localization makes porphyrins useful for observing a variety of nonlinear optical effects. Their sharp absorption bands in the visible and NIR can be used for reso-

nance enhancement of $\chi^{(3)}$ as well. They have enormous potential for applications on the technological front, which include optical limiting [10–18], optical switching, optical data processing and optoelectronic device fabrication [19–24]. They have also been used as organic semiconductor [25] and bistable devices [26].

The nonlinear optical properties of porphyrins and their derivatives have been previously studied in solution [27–39], spin-coated thin films and polymer hosts [40–43], sol-gels [44,45] and glass [46]. In this communication, we report the measurement of the third-order optical nonlinearity and nonlinear absorption studies in Tetra Tollyl Porphyrins (TTP) synthesized with sixteen different central metal ions in the porphyrin ring. Fig. 1 shows the structure of the compounds used, where M denotes the substituent metal ion. The techniques of Degenerate Four Wave Mixing (DFWM) [47,48] and Z-Scan [49] have been employed. Preliminary studies on the excited state dynamics also have been carried out and through these studies we estimate the phase and population relaxation times.



- M = 2H, n = 0**
M = Co, Ni, Cu, Zn, Ag, Cd or Hg, n = 0
M = Cr, Mn, Fe or Au, n = 1, X = Cl
M = In, n = 1, X = OH
M = Ge or Sn, n = 2, X = OH
M = V, n = 2, X = O
M = P, n = 3, X = OH

Fig. 1. The chemical structure of the seventeen compounds used in the study.

2. Experimental details

The samples are synthesized and purified according to the reported procedures in literature [50–54]. Each sample is subjected to a column chromatographic purification process just prior to the measurements. The samples are dissolved in highly purified, spectroscopic grade chloroform and the absorption spectra are recorded using an UV-visible recording spectrophotometer (model UV-160A, Shimadzu). In all experiments, sample solutions are taken in 1-mm quartz cuvettes.

2.1. Degenerate four wave mixing

The source for ns $\chi^{(3)}$ measurements is a frequency-doubled Nd:YAG laser (6 ns, 532 nm, 10 Hz, ~ 80 mJ). A glass plate ($R \sim 8\%$) is used to reflect a part of the beam which is used as the input for the degenerate four wave mixing (DFWM) setup. We employ the standard backward DFWM geometry. Using appropriate beam splitters, the three beams

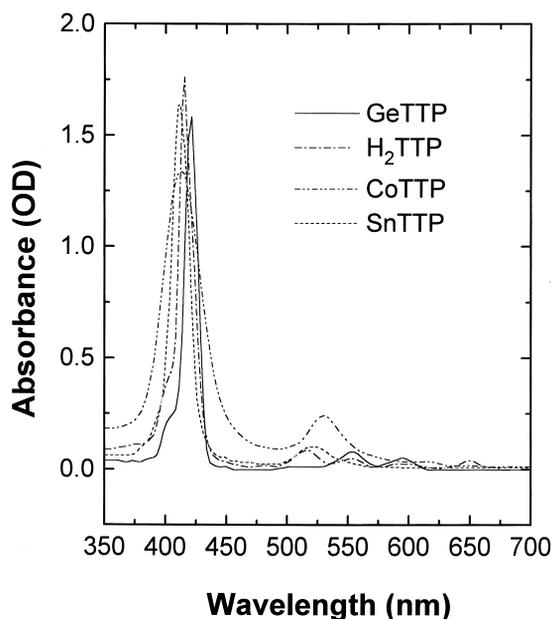


Fig. 2. The absorption spectra of representative compounds (H_2TTP , $GeTTP$, $CoTTP$ and $SnTTP$) dissolved in chloroform.

(forward pump, backward pump, and the probe) are derived with almost the same intensity. All the three input beams are focused on to the sample solution using a lens of $f \sim 15$ cm. The angular separation is

about 10° between the forward pump and the probe beam. The phase conjugate (PC) signal counter-propagating to the probe is split using a beam splitter, attenuated using a variable neutral density filter and focused onto a fast photodiode. The photodiode signal is fed to a digital oscilloscope and readings are taken after several successive signals are averaged.

The source for ps $\chi^{(3)}$ measurements is a hybrid mode-locked Nd:YAG laser (35 ps, 532 nm, 10 Hz). The experimental set-up is similar to the above, except that the beams are loosely focused by an $f \sim 200$ cm lens to avoid large power densities inside the sample. The angle between the pump and probe beams is $\sim 5^\circ$. A part of the forward pump is picked up by a fast photodiode to monitor the pulse-to-pulse fluctuations. For time-resolved measurements, the backward pump is delayed with respect to the temporally coincident forward pump and probe. The intensity ratio of beams 1, 2 and 3 approximately is 1:1:0.2 for nonlinearity measurements and 1:0.2:1 for time-resolved measurements. Polarization state of each beam is varied using a Half Wave Plate (HWP).

2.2. Z-scan

For the Z-scan [49] studies, dye laser pulses centered at 600 nm wavelength and 6 ns duration also

Table 1
UV-visible data^a of the compounds used in the study

Compound	Soret band λ_{max} , nm (log ϵ)	Q bands λ_{max} , nm (log ϵ)			
H_2TTP	418 (5.55)	516 (4.24)	551 (3.98)	592 (3.73)	648 (3.8)
$[P(TTP)(OH)_2]^+$	432 (5.35)	522 (3.48)	560 (4.20)	603 (3.79)	
$V(O)TTP$	424 (5.42)	547 (4.17)	584 (3.37)		
$Cr(TTP)Cl$	435 (5.26)	520 (4.12)	566 (4.17)	603 (4.12)	
$Mn(TTP)Cl$	478 (4.91)	526 (3.78)	577 (4.00)	613 (4.03)	
$Fe(TTP)Cl$	416 (5.01)	508 (4.11)	575 (3.52)	691 (3.50)	
$CoTTP$	411 (5.23)	529 (4.10)			
$NiTTP$	415 (5.27)	527 (3.98)	615 (3.15)		
$CuTTP$	415 (5.48)	538 (4.26)	570 (3.47)		
$ZnTTP$	419 (5.62)	549 (4.34)	588 (3.78)		
$Ge(TTP)(OH)_2$	421 (5.50)	517 (3.40)	555 (4.12)	594 (3.92)	
$Ag(TTP)Cl$	425 (5.17)	541 (3.99)	575 (3.47)		
$CdTTP$	429 (5.31)	526 (3.49)	564 (4.03)	605 (3.90)	
$In(TTP)(OH)$	426 (5.46)	522 (3.47)	561 (4.16)	602 (3.99)	
$Sn(TTP)(OH)_2$	426 (5.47)	523 (3.50)	562 (4.16)	603 (4.15)	
$Au(TTP)Cl$	412 (5.35)	522 (4.12)			
$HgTTP$	426 (5.17)	542 (3.92)	575 (3.47)		

^aSpectra were taken in $CHCl_3$. Error limits: λ_{max} , ± 1 nm; ϵ , $\pm 7\%$.

were used for excitation, in addition to the others. The input beam in each case is appropriately focused using different lenses to ensure the thin sample regime. The sample is scanned across the focus using a micrometer translation stage, which is controlled by a PC. A small part of the input beam is split using a glass plate to monitor the pulse-to-pulse energy fluctuation. The transmitted light is collected using a large area lens of $f \sim 100$ mm and focused on to a photodiode for open aperture data. A fraction of the transmitted beam is split and passed through a variable aperture before focusing on to another photodiode to obtain the closed aperture data.

3. Results and discussion

All samples used in this study show the linear absorption features typical of metalloporphyrins, namely the high energy B (Soret) band and the low energy Q band(s). Fig. 2 illustrates the UV-visible spectra obtained for some representative samples, and Table 1 summarizes the λ_{\max} and $\log \varepsilon$ ($\varepsilon =$ molar extinction coefficient) values for each porphyrin investigated. The compounds remain stable even after exposure to laser pulses for a long period of time, which is confirmed from absorption spectra recorded before and after the measurements. All the experiments are carried out with samples having a concentration in the range of 10^{-4} to 10^{-5} M corresponding to an absorbance of less than 0.3. During the DFWM experiments, the cubic dependence of the phase conjugate signal to the input intensity has been verified for all the samples. A typical plot of the phase conjugate signal versus input intensity is shown in Fig. 3(a) for the sample SnTTP and the data is fitted to a cubic function. Fig. 3(b) shows the linear dependence of $\chi^{(3)}$ to the sample concentration for SnTTP. The other samples also show a similar behavior. The calculated values of the cubic hyperpolarizability $\langle \gamma \rangle$ and the figure of merit F are given in Table 2. These are calculated using the equations

$$\chi_s^{(3)} = \left(\frac{n_0}{n_{\text{ref}}} \right)^2 \left(\frac{l_{\text{ref}}}{l} \right) \left(\frac{A}{A_{\text{ref}}} \right)^{1/2} \times \left(\frac{\alpha l \exp(\alpha l/2)}{1 - \exp(-\alpha l)} \right) \chi_{\text{ref}}^{(3)} \quad (1)$$

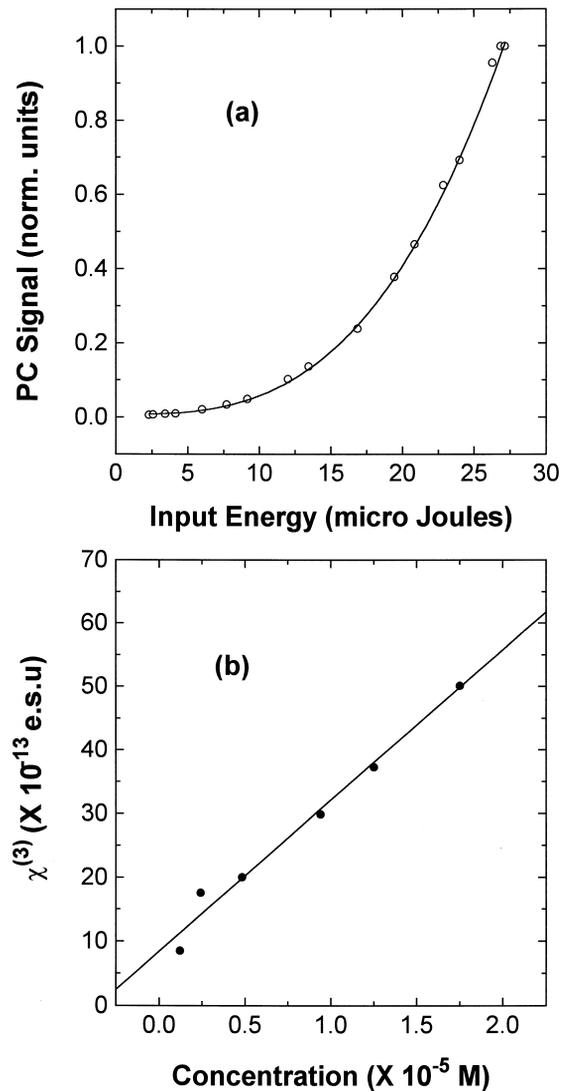


Fig. 3. (a) Intensity dependence of the PC signal in $\chi^{(3)}$ measurements for AuTTP. (b) Concentration dependence of the PC signal for the same sample.

and

$$\langle \gamma \rangle = \frac{\chi^{(3)}}{L^4 N} \quad \text{in which } L = \frac{n^2 + 2}{3}, \quad (2)$$

where n is the refractive index, l is the length of the sample, A is the coefficient of the cubic term of a least squares fit to the plot of PC signal versus input

Table 2
Calculated values of γ and figure of merit F using 6 ns and 35 ps pulses

Compound	(Redox potential)	$\langle\gamma\rangle$ (6 ns) (10^{-30} esu)	$F = \chi^{(3)}/\alpha$ (10^{-13} cm esu)	$\langle\gamma\rangle$ (35 ps) (10^{-30} esu)	$F = \chi^{(3)}/\alpha$ (10^{-13} cm esu)
H ₂ TTP	(2.18 V)	111.40	91.50	1.240	7.24
[P(TTP)(OH) ₂] ⁺	(2.13 V)	325.50	289.33	0.286	2.62
V(O)TTP	(2.30 V)	375.00	121.13	0.442	2.39
Cr(TTP)Cl	(1.93 V)	166.25	45.93	0.403	1.04
Mn(TTP)Cl	(2.88 V)	289.5	158.01	0.674	3.21
Fe(TTP)Cl	(2.23 V)	96.25	48.78	0.437	1.82
CoTTP	(1.58 V)	146.75	42.65	1.432	3.23
NiTTP	(2.36 V)	177.25	69.95	0.193	0.62
CuTTP	(2.28 V)	154.25	37.05	0.541	0.11
ZnTTP	(2.12 V)	289.75	158.83	0.442	1.73
Ge(TTP)(OH) ₂	(2.34 V)	302.00	297.5	0.988	1.06
Ag(TTP)Cl	(–)	226.50	94.58	0.170	0.69
CdTTP	(1.88 V)	162.50	148.53	0.079	0.70
In(TTP)(OH)	(2.17 V)	111.25	142.00	0.380	3.69
Sn(TTP)(OH) ₂	(2.27 V)	346.25	322.75	0.368	3.26
Au(TTP)Cl	(–)	725.00	198.93	0.088	2.10
HgTTP	(–)	45.25	20.65	0.106	0.42

intensity, and α is the absorption coefficient; F is given as $\chi^{(3)}/\alpha$; $\chi^{(3)}$ for the reference sample CS₂ is taken to be 1.7×10^{-12} esu for ns pulses and 4.0×10^{-13} esu for ps pulses [30,55]; L is the local field correction factor, and N is the number density of the solute molecules in solution. The $\chi^{(3)}$ contribution from solvent is taken to be zero, as it is negligibly small in comparison to the solute.

Obviously, structural modifications to the porphyrin ring can be expected to result in molecules with diverse photophysical and photochemical properties that will in turn affect their optical nonlinearity. Among the various factors involved, the atomic number of the central metal atom, redox potential of the ring [56–58] and occurrence of excited-state absorption require special mention. It is seen that for ns pulses SnTTP has the largest value of F ($\sim 323 \times 10^{-13}$ cm esu) whereas for ps pulses H₂TTP has the largest value ($\sim 7.24 \times 10^{-13}$ cm esu). The variation of $\langle\gamma\rangle$ and F as a function of the atomic number does not reveal any heavy atom effect, and no obvious relationship can be established between the measured $\langle\gamma\rangle$ value and the atomic number of the corresponding metal ion. Similarly the variation of $\langle\gamma\rangle$ and F with redox potentials (which is a

measure of the extent of delocalization of π electron cloud) of the corresponding molecules also does not indicate an immediate relationship. We, thus, infer that no simple relationship exists between the physical structure and the macroscopic nonlinearity in these molecules. It is too early to comment on the exact structure–property relationship and more detailed studies are required for a better understanding of the nonlinearity in these samples.

Open aperture Z-scans with ns pulses show deeper valleys for those samples which are found to have higher $\langle\gamma\rangle$ values as measured from the DFWM experiments. Fig. 4(a) shows a typical closed aperture Z-scan, for NiTTP. All the samples are found to exhibit similar behavior, indicating a negative nonlinearity as evidenced by the peak occurring at negative Z values in the scan. Because of the near-resonant excitation this negative nonlinearity, in the ns time scales, could be due to the thermal excitation of the medium. Fig. 4(b) shows the open aperture Z-scan for the sample NiTTP. Depending on the pulse duration, pump intensity and wavelength, nonlinear absorption can be from (a) the ground state S₀ to higher excited singlet states S_n (two-photon or multi-photon excitation), (b) the first excited singlet

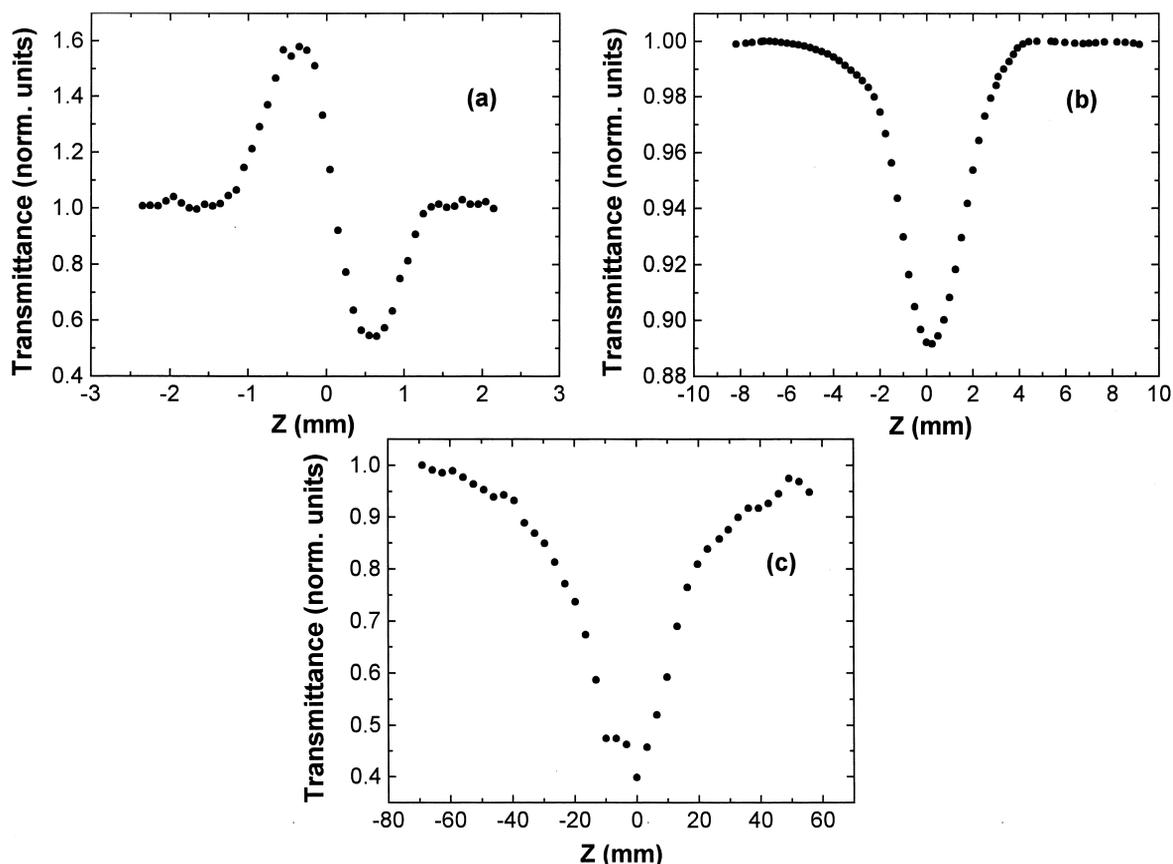


Fig. 4. (a) Closed aperture Z-scan curve for the sample NiTTP using ns pulses. (b) Open aperture Z-scan curve for NiTTP using ns pulses (c) Open aperture Z-scan curve for InTTP using ps pulses.

state S_1 to higher excited states S_n , or from (c) the T_1 to T_n states in the triplet manifold. The last two processes are known as excited state absorption (ESA), and if their cross-sections are larger than that of the ground state linear absorption, then these are referred to as reverse saturable absorption (RSA). We attribute the observed nonlinear absorption to strong ESA or RSA. Typical peak intensities at the focus are in the range of 10^8 to 10^9 W/cm². Fig. 4(c) shows the open aperture Z-scan for InTTP using 35 ps pulses. In this case, however, the triplet contribution to the nonlinear absorption can be much less due to the decreased intersystem crossing (which is \sim few hundred ps) as compared to ns excitation [59–62].

We have carried out the ns time scale studies of the susceptibilities in order to see the effect of the triplet states contribution to the signal, though it is expected that during these time scales part of the contribution would be of thermal origin. On comparing the $\langle \gamma \rangle$ values of our compounds with other porphyrins [26–45], the ns values are found to be three orders of magnitude larger than any of them. When the probe polarization is made normal to the pump beams, the PC signal gets reduced by only one-third of the original value (when all beams are co-polarized) indicating that the nonlinearity is predominantly electronic in origin [63] and thermal effects are not dominant in our case. Reports show an excited state enhancement of the nonlinearity in

linear conjugated molecule [66] and a square planar complex [67], where the experiments were performed in the presence of a strong pump beam. In polyphenyls [68], the enhancement was due to strong Two-Photon Absorption (TPA). In a porphyrin heterodimer [69] and in an azo-benzene material [70], the enhancement was due to the presence of highly populated excited states. We observe very strong ESA, due to fast intersystem crossing rate compared to the pulse width, in all the open aperture Z-scan data recorded with the ns pulses. Porphyrins are therefore ideal candidates to probe the nonlinearity due to the excited states, S_n and T_n apart from S_1 and T_1 . A significant contribution to this large value of $\langle \gamma \rangle$, therefore, comes from the long-lived and excited triplet states in addition to the excited singlet states. It is well established that ESA is an intensity dependent process and will dominate at higher intensity levels. This is well supported by our $\chi^{(3)}$ measurements, using ns pulses, at different input intensity levels whereby we observe an enhancement by a factor of three to four in its value. $\chi^{(3)}$ measurements on the sample AuTTP give a value of 10×10^{-12} esu at an input of ~ 2 mW (corresponding peak intensity at focus is ~ 100 MW/cm²) and a value of $\sim 30 \times 10^{-12}$ esu at an input of ~ 6 mW (corresponding peak intensity at focus is ~ 300 MW/cm²) for the same sample concentration. A log–log plot of input energy versus PC signal, shown in Fig. 5, gives a slope of < 3 at lower intensities and a slope of ~ 5 at higher intensities suggesting nonlinearity contributions from higher excited states. Equally large γ values have been observed using dye laser pumping also, when excited at 595 nm. At this wavelength these compounds have a stronger two-photon absorption [64,65] as compared to 532 nm.

Rao et al. [26,28] report the largest γ values for some of the Tetrabenzporphyrins [10×10^{-30} esu for Zinc meso-tetra-(*p*-dimethylaminophenyl) tetrabenzporphyrin] using 30 ps pulses. Our results on Tetra Toly Porphyrins using 35 ps pulses show a value of 2.4×10^{-30} esu for CoTTP (assuming a $\chi^{(3)}$ value of 6.8×10^{-13} esu for CS₂) which is comparable to the TBP. Advantages of tetraarylporphyrins over tetrabenzporphyrins are that they are easy to synthesize, have a high thermal and chemical stability, and have a longer shelf life. We can also

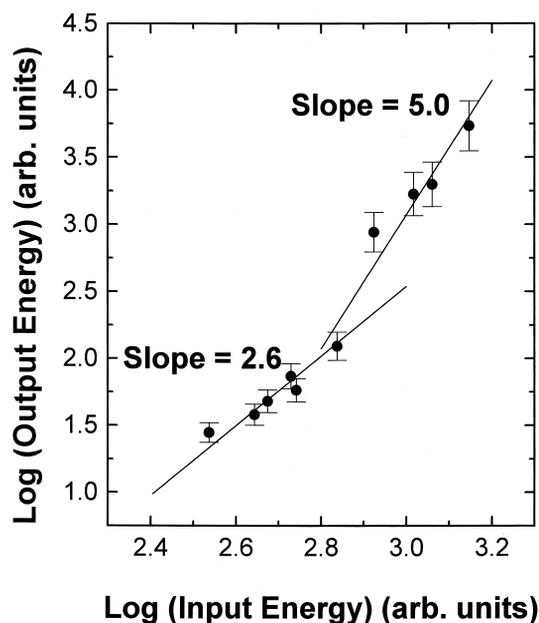


Fig. 5. Logarithmic plot of the input intensity versus the PC signal for the sample AuTTP indicating different slopes at different input intensities.

compare the ps nonlinearity magnitudes with that observed in other kind of porphyrins – for example those reported for basket handle porphyrins by Kumar et al. [36]. We find that the present molecules have larger nonlinearity in comparison to those porphyrins. The difference could be attributed to the higher electron delocalization in the present set of molecules.

The temporal evolution of the nonlinearity has been investigated using 35 ps pulses where the backward pump is delayed with respect to the forward pump and probe beams. Fig. 6 shows one such curve for CoTTP with the inset showing the fitting to the decay part of the curve. From the fit, a population relaxation time (T_1) of ~ 100 ps is estimated for this sample. Our preliminary studies indicate fast population relaxation times for the other molecules as well, falling in the approximate range of 30–200 ps. These observations are further corroborated by our earlier incoherent DFWM studies on some of these molecules [64] which showed fast dephasing (< 170 fs) and population relaxation (~ 30 – 50 ps) times.

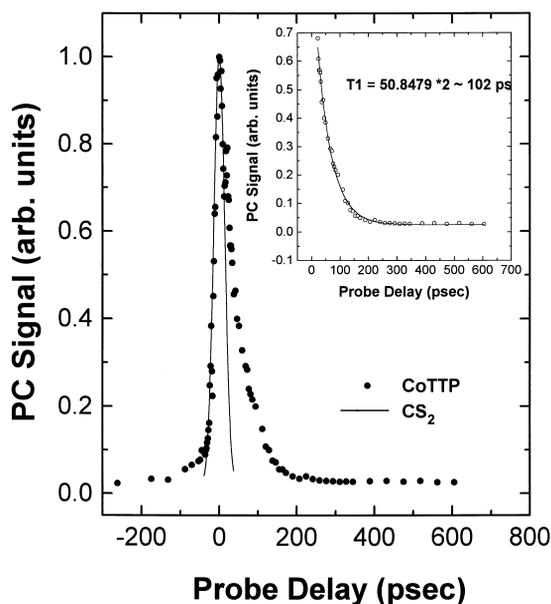


Fig. 6. Time-resolved PC signal in the sample CoTTP using 35 ps pulses with backward pump delayed and forward pump kept at zero delay. Inset shows the fit to the decay part.

In general, it is very difficult to quantify the individual contributions of various channels (real and imaginary parts, thermal part, due to excited states etc.) to a nonlinear signal. To the extent possible, we have tried to separate the thermal and electronic nonlinear mechanisms. This has been achieved by using cross polarizing the grating forming (write) beams in FWM, whereby the thermal mechanism is suppressed and we measured only the electronic nonlinearity. Even this, however, is not a complete solution because the ‘*electronic*’ susceptibility components measured in the two cases are different. Also the determination of the contributions of excited states demands knowledge of excited state cross-sections and lifetimes. We are in the process of doing the spectroscopy of these states using ps and fs time-resolved pump–probe, Four Wave Mixing and Z-scan experiments and will publish the results and their implications on nonlinearity in the near future. Considering that the subject of structure–property relationships pertaining to third-order nonlinearity is still in its infancy, we feel that these experimental results would be of interest in furthering research in this area.

4. Conclusions

In conclusion, we have synthesized a set of Tetra Tollyl Porphyrins with sixteen different metal ions in the ring, and studied their third-order nonlinear optical properties with ns and ps laser excitation. The large negative nonlinearity exhibited by these molecules when pumped by ns pulses is attributed to strong ESA/RSA and partly due to thermal excitation. The strong nonlinear absorption at both 532 nm and 595 nm show that these molecules are promising candidates for efficient optical limiting at these and a nearby range of wavelengths. From the time-resolved DFWM data the nonlinearity is found to have an ultrafast response time in the order of fs to ps. These values are in good agreement with our results previously obtained using DFWM with incoherent light. Thus these molecules, with their large nonlinearity properly combined with ultra-fast response times, can become potential candidates for various photonic applications.

Acknowledgements

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