Studies of Third-Order Optical Nonlinearity, Nonlinear Absorption and Excited State Dynamics in Tetra Tolyl Porphyrins using Degenerate Four Wave Mixing and Z-Scan

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Abstract

We present our experimental results on the third-order optical nonlinearity, nonlinear absorption and excited state dynamics measurements in tetratolyl porphyrins using DFWM and Z-scan with incoherent light and 35 ps pulses.

Introduction

The last decade has received tremendous interest and witnessed extensive research activity in the nonlinear optical, photophysical and photochemical properties of organic materials in general and metalloporphyrins/related compounds in particular [1]. They are found to possess strong nonlinearity and fast response time, the desired criteria for making photonic devices. Recently we synthesized Tetra Tolyl Porphyins (TTP) with sixteen different metal ions in the ring and studied the third order optical nonlinearity, nonlinear absorption and excited state dynamics using Degenerate Four Wave Mixing (DFWM) and Z-Scan techniques.

Degenerate Four Wave Mixing and Z-scan

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 ~ 200 cm lens to avoid large power densities inside the sample. The angle between the pump and probe beams is ~ 5^0. 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. For the Z-scan studies, dye laser pulses centered at 600 nm wavelength and 6 ns duration also were used for excitation, in addition to the others. The sample is scanned across the focus using a micrometer translation stage, which is controlled by a PC. The transmitted light is collected using a large area lens of f ~ 100 mm and focused on to a photodiode for open aperture data.

Results and Discussion

During the DFWM experiments, the cubic dependence of the phase conjugate signal with the input intensity and linear dependence with concentration has been verified for all the samples. It is seen that for ns pulses SnTTP has the largest value of F (~ 323 x 10^{-13} cm.esu) whereas for ps pulses H_2TTP has the largest value (~ 7.24 x 10^{-13} cm.esu). 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 and occurrence of excited-state absorption require special mention**.** On comparing the $\langle\gamma\rangle$ values of our compounds with other porphyrins, 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 and thermal effects are not dominant. However, there should be a significant contribution to this large value of $\langle\gamma\rangle$ from the excited singlet and triplet states, since we observe very strong ESA in all the open aperture Z-scan data. 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 at different input intensity levels whereby we observe an enhancement by a factor of three to four in its value. Furthermore, the intensity dependence of PC signal shows a different behavior at high intensities. A log-log plot of input energy versus PC signal gives a slope of < 3 at lower intensities and a slope of ~ 5 at higher intensities suggesting nonlinearity contributions from higher excited states. We observe the two-peak structure for FWM signals in all the porphyrins viz. a sharp, intense peak and a broad, weak peak. The widths of the peaks and the ratio of the peaks give information on the dephasing of the S_n, S_1 states and the population relaxation time (lifetime) of the S_1 state [2,3]. The dephasing time (T_2) for all the samples are < 170 fs, the vibrational relaxation times ($S_{1v} - S_{10}$) are ~ 3-6 ps, the population relaxation time (T_1) values are in the range of ~ 20 - 70 psec. Figures 2(b) show the PC signal obtained for samples NiTTP as a function of the beam 2 delay using ps 35 pulses. For cross polarization of the probe beam (beam 2) the signal dropped down to ~ 3-4 times but the structure remained the same. Solid dots are the experimental data for the sample and the solid line is for the sample CS_2 (to show the auto-correlation function). The results of $\chi^{(3)}$ measurements, excited state dynamics for different samples will be discussed in detail.

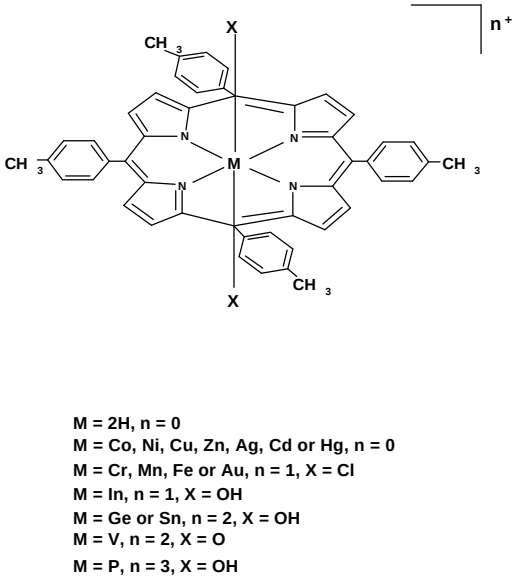

Fig. 1 Structure of the compounds used in the study

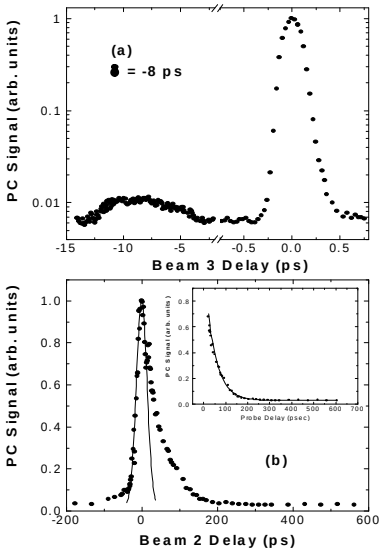

Fig. 2 PC signal in CoTTP ($ChCl_3$) **(a)** using Incoherent light and **(b)** 35 ps pulses

References

[1] H.S. Nalwa and S. Miyata, Ed.s, Nonlinear Optics of Organic Molecules and Polymers, CRC Press Inc., USA, (1997).

[2] D.V.G.L.N. Rao, F.J. Aranda, D.E. Remy, J.F. Roach, Int. J. Nonlinear Opt. Phys. **3** (1994) 511.

[3] S.V. Rao, N.K.M.N.Srinivas, L.Giribabu, B.G.Maiya, R. Philip, G.R. Kumar, and D.N. Rao, Submitted to Optics Communications; *ibid.* submitted to JOSA B