Multiphoton Absorption Studies in Porphycenes Using Picosecond and Femtosecond Pulses

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Abstract. We present our results obtained from the Z-scan measurements in porphycenes performed using ~2 picosecond (ps) and ~40 femtosecond (fs), 800 nm pulses with a repetition rate of 1 kHz delivered by amplified Ti:sapphire laser systems. Open aperture Z-scan data demonstrated interesting multi-photon absorption properties for these molecules. In the ps regime these compounds exhibited two-photon absorption (2PA) at lower peak intensities whereas three-photon absorption (3PA) was dominant mechanism observed at higher peak intensities. In the fs regime saturable absorption was the mechanism detected. Closed aperture data was collected to evaluate the nonlinear refractive indices of these molecules in both the time domains. The magnitude of n_2 was ~10^{-17} cm^2/W in the fs regime and ~10^{-15} cm^2/W in the ps regime.

Keywords: Z-scan, two-photon absorption (2PA), three-photon absorption (3PA), porphycenes, picosecond, femtosecond
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INTRODUCTION

Porphycene is the first constitutional isomer of porphyrin [1]. It is a structural isomer of porphyrin that acts as a photosensitizer. Porphycene and its derivatives display unique physical and optical properties, including strong absorptions in the red region of the UV-visible spectrum. These features have made porphycene and porphycene derivatives appealing molecules for use in biomedical applications and in the design of new materials. Porphycene is a suitable candidate for the photodynamic therapy of tumors. Third-order nonlinear optical (NLO) materials possess tremendous potential in applications such as two-photon PDT, optical limiting, 3D-optical memory [2, 3]. We have performed both open aperture Z-Scan which gives information about 2PA and 3PA and saturable absorption with ps and fs pulses, respectively. Closed aperture Z-scan provides sign and magnitude of refractive index. We have studied the response of different dinaphthoporphycenes, both metal free Porphycene and Ni(II) complexes.

EXPERIMENTAL DETAILS

Different porphycenes were synthesized and purified using the methods recently reported [2]. The compounds were dissolved in chloroform to obtain solutions of typically 0.25 mM concentration providing a linear transmittance of ~70% near 800 nm. The Z-scan [3, 4] measurements were performed using ~2 ps/~40 fs, 800 nm, 1 kHz pulses. The amplifiers were seeded with pulses of duration ~15 fs (spectral bandwidth of 55-60 nm) from the oscillator (Micra, Coherent Inc.). A quartz cuvette (1-mm thick) containing the sample solution was traversed in the focusing geometry enabled by an achromat lens of 200 mm focal length.

The beam waist at focal plane was estimated to be ~80 μm and ~60 μm with corresponding Rayleigh ranges (Z_r) of ~6.0 mm and ~3.5 mm, respectively, for ps and fs pulses. The experiments were performed with peak intensities of 50–400 GW/cm^2 in the ps case while it was in the range of 0.1-1.0 TW/cm^2 in the fs case. The closed aperture scans were performed at low peak intensities (<50 GW/cm^2 in ps case and <0.5

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TW/cm^2 in fs case) to ensure that higher order nonlinear effects are minimized. Fig. 1 shows the schematic of fs Z-scan experimental set up. Table 1 illustrates the nomenclature of all the compounds studies. The solvent used in all the studies was chloroform and Z-scan studies were performed on pure solvent using both ps and fs pulses to identify their contribution. In the ps domain the solvent contribution was insignificant while in the fs domain it was significant.

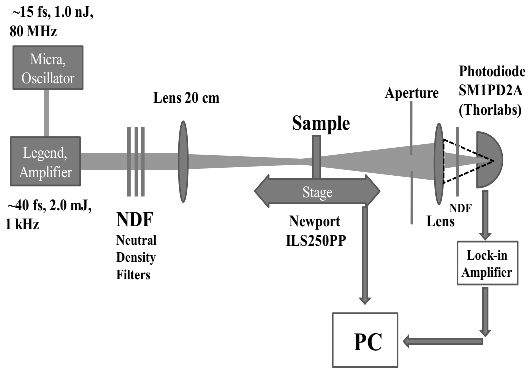

FIGURE 1. Typical experimental Z-Scan set up.

RESULTS AND DISCUSSION

Figure 2 shows the absorption spectra of all the samples studied. Fig. 3 shows the open aperture data for all the samples collected at two different peak intensities. At lower peak intensities (typically <100 GW/cm^2), the data is best fitted to 2PA formula [4, 5] indicating that 2PA is the dominant mechanism. At higher incident intensities (typically >100 GW/cm^2), the data is best fitted to 3PA formula indicating its dominance in this regime. The presence of two resonances in the absorption spectra of these molecules at 400 nm (Porphycene core) and 270 nm (Naphthalene moiety) explains the unusual nonlinear absorption behavior of the molecules. For the 800 nm photon, these two resonances are the 2PA and 3PA states respectively. 3PA is observed at higher intensities because of its weaker absorption cross-section. Since both these processes are intensity dependent, it is possible that there is contribution (or competition) from both these processes.

Table 1. Nomenclature of the compounds

Sample	IUPAC Name
Po1	2,7,12,17-Tetra-(*n*-propyl)-3,6,-13,16-dinaphtho[cde;mno]porphycene
Po2	2,7,12,17-Tetra-(*iso*-propyl)-3,6,-13,16-dinaphtho[cde;mno]porphycene
Po3	2,7,12,17-Tetra-(*n*-pentyl)-3,6,-13,16-dinaphtho[cde;mno]porphycene
Po4	[2,7,12,17-Tetra-(*iso*-propyl)-3,6,-13,16-dinaphtho[cde;mno]porphycenato]Nickel(II)
Po5	[2,7,12,17-Tetra-(*n*-pentyl)-3,6,-13,16-dinaphtho[cde;mno]porphycenato]Nickel(II)

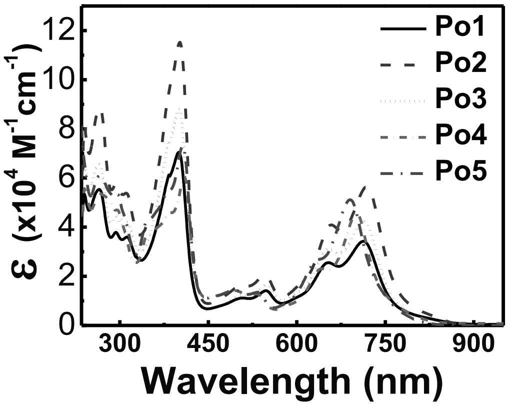

FIGURE 2. Absorption spectra of different porphycenes.

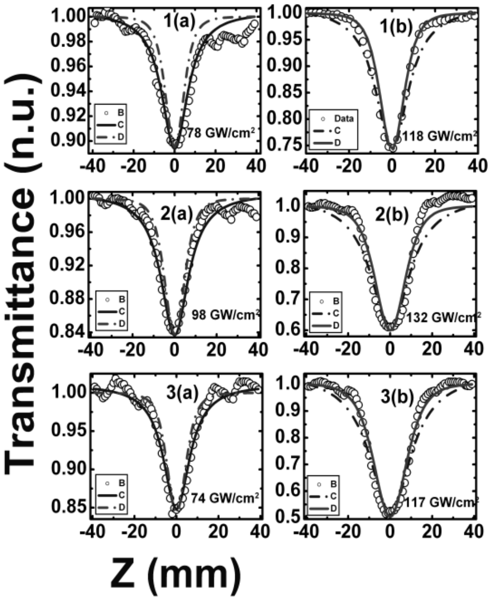

FIGURE 3. Open aperture ps-Z-scans for metal free dinaphthoporphycenes (Po1, Po2and Po3) (a) Best fits with 2PA (solid lines) and 3PA (dash-dot lines) at lower peak intensities (b) Best fits with 3PA (solid lines) and 2PA (dash-dot lines) at higher peak intensities.

However, our intensity dependent studies clearly confirm 2PA at lower peak intensities and 3PA at higher peak intensities. Table 2 gives the two photon absorption and three photon absorption coefficients, extracted from fits, for different incident intensities and for all the samples. The magnitude of 2PA coefficient was typically 10^{-11} cm/W whereas the magnitude of 3PA coefficient was typically 10^{-20} cm^3/W^2. The values of n_2 were ~10^{-17} cm^2/W. The random experimental errors (arising from concentration measurement, input power measurement, data fitting, and estimation of spot size and peak intensities at focus) result in an overall error of ±20% in all of our calculations.

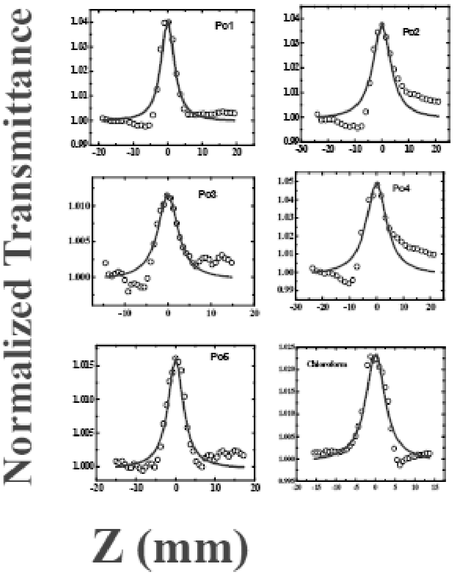

FIGURE 4. Saturable absorption demonstrated by fs Z-scan in Porphycenes (Po1, Po2, Po3, Po4 and Po5) with typical peak intensities of 0.6-0.8 TW/cm^2.

TABLE 2. Nonlinear coefficients of porphycenes extracted from the Z-scan studies using ps and fs pulses.

Sample	β (fs) (cm/W) × 10^{-13}	n_2 (fs) (cm^2/W) ×10^{-17}	β (ps) (cm/W) × 10^{-11}	n_2 (ps) (cm^2/W) ×10^{-15}	γ (ps) (cm^3/W^2) × 10^{-21}
Chloroform	0.5	0.5	0.6	0.6	-
Po1	6.0	3.0	5.0	3.8	3.5
Po2	3.1	3.0	7.0	2.6	9.0
Po3	0.95	2.0	8.0	2.7	25.0
Po4	6.0	5.0	13.0	3.7	19.5
Po5	1.15	0.9	4.8	3.5	11.0

Figure 4 depicts the open aperture data of all samples, including the solvent, obtained with fs pulses. Evidently, saturable absorption (SA) is the mechanism observed. Since the peak intensities associated with fs pulses are extremely large there could be saturation of the single photon or two-photon states and further detailed pump-probe studies using sub-ps pulses are essential to determine the exact states involved in saturation. The magnitude of the nonlinear coefficient extracted was ~ 10^{-13} cm/W for all the molecules. The values of n_2 were ~10^{-17} cm^2/W.

CONCLUSIONS

From ps Z-scan investigations we have evaluated the nonlinear absorption coefficients along with nonlinear refractive indices of five novel dinaphthoporphycenes. The singular nonlinear absorption behavior is explicated through the presence of two strong resonances in the absorption spectrum which allowed the 800 nm photons to access both the two-photon and three-photon states with different peak intensities. From fs Z-scan experiments nonlinear absorption was found to be saturable type and the magnitude of coefficients were ~10^{-13}cm/W recorded at peak intensities <1 TW/cm^2.

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REFERENCES

1. E. Vogel, M. Kocher, H. Schmickler, J. Lex, *Angew. Chem., Int. Ed. Engl.* **25,** 257–259 (1986).
2. T. Sarma, Pradeepta K. Panda, P.T. Anusha, S. Venugopal Rao, *Org. Lett.* **13,** 188-191, (2011).
3. R.S.S. Kumar, S. Venugopal Rao, L. Giribabu, D.N. Rao, *Chem. Phys. Lett.* **447,** 274–278 (2007).
4. K. Venkata Saravanan, K.C. James Raju, M. Ghanashyam Krishna, Surya P. Tewari, S. Venugopal Rao, *Appl. Phys. Lett.* **96,** 232905 (2010).
5. M. Sheik-Bahae, A.A. Said, T.-H. Wei, D.J. Hagan, E.W. Van Stryland, *IEEE Journal of Quantum Electronics* **26(4),** 760-769 (1990).