

Femtosecond and Picosecond Optical Nonlinearities of Corroles Studied using Z- Scan Technique

Syed Hamad,¹ G. Krishna Podagatlapalli,² L. Giribabu,³ Surya P. Tewari,^{1,2}S. Venugopal Rao^{2,*}

¹*School of Physics* ²*Advanced Centre of Research in High Energy Materials*
University of Hyderabad, Hyderabad 500046, India.

³*Nanomaterials Laboratory, Inorganic & Physical Chemistry Division,*
IICT, Hyderabad 50007, India.

*Author for Correspondence: *svrsp@uohyd.ernet.in*

Abstract. We report our results on femtosecond (fs) and picosecond (ps) nonlinearities in two novel Corroles (a) Tritolyl Corrole (TTC) (b) Triphenyl Corrole (TPC) studied using the Z-scan technique. Both open and closure aperture Z-scan curves were recorded with ~40 fs and open Z-scan curves were recorded with ~2 ps laser pulses at same wavelength of 800 nm and nonlinear coefficients were extracted for both studies. Picosecond open aperture data clearly suggested the presence of three photon absorption (3PA) for both the molecules. One of the molecule, TPC, possessed positive refractive index with a value 2×10^{-17} cm²/W and TTC possessed negative refractive index with a value of 3×10^{-18} cm²/W in the fs domain. Solvent contribution to the nonlinearity was also identified. We discuss the nonlinear optical performance of these organic molecules.

Keywords: femtosecond, picosecond, nonlinear refractive index, saturable absorption, three photon absorption.

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INTRODUCTION

Corroles are tetrapyrrolic molecules, maintaining the skeletal structure of corrin, with its three meso carbon positions and one direct pyrrole-pyrrole linkage, and possessing the aromaticity of porphyrins [1]. Also among the interesting attributes of corroles are their photophysical properties. Corroles generally show porphyrin type spectra, with strong absorptions in the visible range associated with very highly colored compounds [1]. As well, the direct pyrrole-pyrrole linkage seems to give Corroles stronger fluorescence properties than their porphyrin counterparts. These properties open up potential for using corroles in many other applications, including such diverse areas as cancer diagnosis and treatment and solar cell research.

We present here, some of our results on the NLO measurements of two Corroles. (a) Tritolyl corrole (Molecular formula = C₄₀H₃₂N₄; Mol. Wt = 568) and (b) Triphenyl corrole (Molecular formula = C₃₇H₂₆N₄; Mol.Wt = 526) studied using femtosecond (fs) and picosecond (ps) pulses at a wavelength of 800 nm with standard Z-scan technique We derived the magnitude

of nonlinear absorption, and estimated the sign and magnitude of refractive nonlinearities.

EXPERIMENTAL DETAILS

The experiments were performed with sample solutions dissolved in chloroform. Femtosecond (fs) pulses and picosecond (ps) pulses were generated by separate Ti:sapphire lasers (Coherent, Legend amplifier) operating at a repetition rate of 1 kHz with a pulse durations ~40 fs and ~2 ps at 800 nm. The amplifier was seeded with ~15 fs pulses from the oscillator (Coherent, Micra). The input beam was spatially filtered to obtain a pure Gaussian profile in the far field. The beam was focused using 200 mm focal length lens into the sample, placed in a 1 mm path length quartz/glass cuvette. Experiments were carried out with samples possessing typical concentration of 2.5×10^{-4} mM. The beam waist (w_0) at the focal plane was estimated to be ~20 μ m with a corresponding Rayleigh range ~1.6 mm in ps domain. The beam waist was ~25 μ m with corresponding Rayleigh range ~2.5 mm in the fs domain. The solvent used was chloroform and its contribution was also

recorded. The sample was placed on a high resolution translation stage and the detector (photodiode) output was connected to a lock-in amplifier. Both the stage and lock-in were controlled by a computer program.

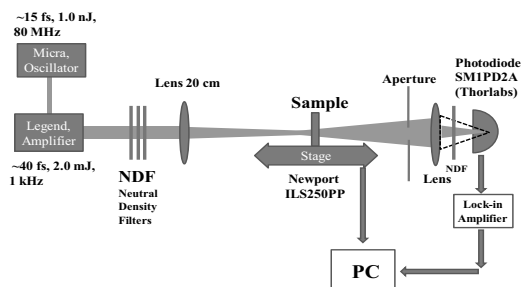


FIGURE 1. Experimental setup for fs Z-Scan

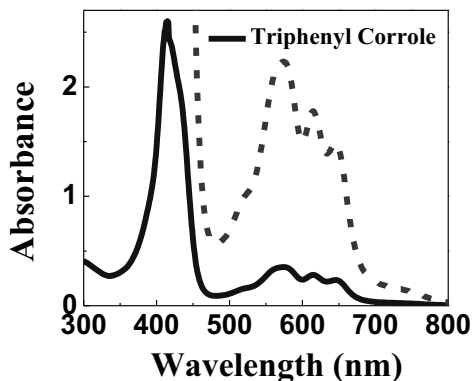


FIGURE 2. Absorption spectra of TPC in chloroform. Dotted line is the expanded view.

TPC was prepared according to the procedure described below [2]. Benzaldehyde (330 mg, 5 mmol) and pyrrole (670 mg, 10 mM) were dissolved in a mixture of methanol and water (400 ml, 1:1 of methano:H₂O). To this 4.25 ml of HCl was added for 3 h. The reaction mixture was extracted with CHCl₃, and the organic layer was washed with H₂O and dried over anhydrous Na₂SO₄. To this *p*-Chloranil (1.23 g, 5 mM) was added, and the mixture was refluxed for 1 h. The reaction mixture subjected to silica gel column chromatography and eluted with CHCl₂:hexane (1:1 v/v). The solvent front running brown color band was collected and re-crystallized from CHCl₂:hexane afforded pure corrole.

P-tolylaldehyde (600 mg, 5 mmol) and pyrrole (670 mg, 10 mM) were dissolved in a mixture of methanol and water (400 ml, 1:1 of methano:H₂O). To this 4.25 ml of HCl was added, and the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was extracted with CHCl₃, and the organic layer was washed with H₂O and dried over

anhydrous Na₂SO₄. To this *p*-Chloranil (1.23 g, 5 mM) was added, and the mixture was refluxed for 1 h. The reaction mixture subjected to silica gel column chromatography and eluted with CHCl₂:hexane (1:1 v/v). The solvent front running brown color band was collected and re-crystallized from CHCl₂:hexane afforded pure Corrole.

TABLE 1. Nomenclature of the compounds used in present studied

Sample Name	IUPAC Name
TPC	5,10,15-tri pheny corrole (for Triphenyl corrole)
TTC	5,10,15-tri-(4-methyl pheny) corrole (for Tritolyl corrole)

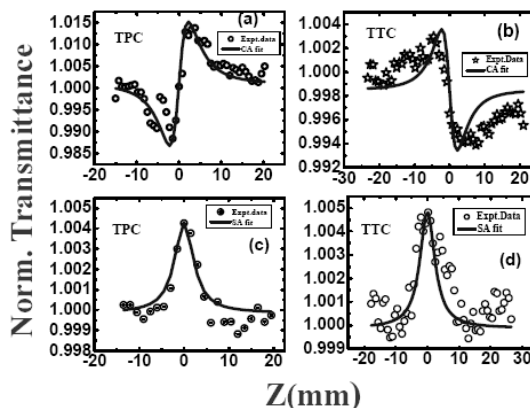


FIGURE 3. (a) and (b) represents closure aperture Z-scan data for TPC and TTC (c), (d) represents open aperture Z-scan data for TPC and TTC in Femtosecond domain

RESULTS AND DISCUSSIONS

Figures 3(a) and 3(b) show the closed aperture scans, along with the corresponding theoretical fits, for TPC and TTC and the solvent chloroform recorded with a peak intensity of 0.4 TW/cm². Open circles and stars represent the experimental data for solution while the solid lines are the theoretical fits [3-8]. In TTC the sign of nonlinear refraction n_2 was negative. The solvent nonlinearity was positive; suggesting the final value of n_2 calculated for the pure solute will be higher than the calculated. But in TPC the sign of the nonlinearity was positive like solvent. We obtain the best fit for n_2 as $\sim 2.0 \times 10^{-17}$ cm²/W and $\sim 0.6 \times 10^{-17}$ cm²/W. The value of n_2 for solvent was estimated to be $\sim 0.5 \times 10^{-18}$ cm²/W lower than that of the samples investigated here. Data recording with higher

concentrations is in progress. Fig. 3(c) shows the open aperture data for TPC and 3(d) for TTC recorded at a peak intensity of $\sim 1.3 \text{ TW/cm}^2$ and $\sim 0.8 \text{ TW/cm}^2$ with signatures in both the scans indicating simply saturable absorption. A good fit was obtained for an effective nonlinear absorption coefficient of $\beta = 8.7 \times 10^{-14} \text{ cm/W}$ for TTC and $\beta = 13.5 \times 10^{-14} \text{ cm/W}$ for TPC. The value of β for solvent was estimated to be $5.0 \times 10^{-14} \text{ cm/W}$. For higher peak intensities we observed the behavior switched from pure saturable absorption to RSA (near the focal region) in the fs domain. Fig. 4(a) and (b) show the open aperture data for both the Corroles obtained with $\sim 2 \text{ ps}$ pulses recorded at a peak intensity of $\sim 150 \text{ GW/cm}^2$. Typical concentrations of again 0.25 mM were used for the studies. It is evident from the fits that three-photon absorption (3PA) is the dominant nonlinear absorption mechanism. The best fits yielded values of $\gamma \sim 10^{-21} \text{ cm}^3/\text{W}^2$. TTC had higher 3PA coefficient compared to TPC. The solvent chloroform contribution was negligible in this case.

TABLE 2. Nonlinear coefficients obtained for Corroles using ps and fs pulses. Sign of n_2 for TPC was opposite to that of chloroform.

Sample Name	β (fs) (cm/W) $\times 10^{-14}$	n_2 (fs) (cm ² /W) $\times 10^{-17}$	γ (ps) (cm ³ /W ²) $\times 10^{-21}$
Chloroform	5.0	-0.5	-
Triphenyl Corrole (TPC)	13.5	0.3*	0.2
Tritolyl Corrole (TTC)	8.7	-2.0	8.0

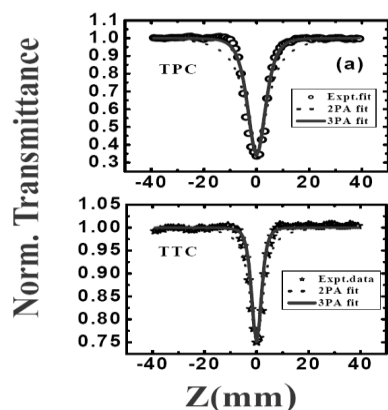


FIGURE 4. Open aperture picosecond Z-scan data for corroles (TTC and TPC) (a) Best fits with 3PA (solid line) and 2PA (dotted line) at $\sim 150 \text{ GW/cm}^2$ peak intensities (b) Best fits with 3PA (solid line) and 2PA (dotted line) at $\sim 200 \text{ GW/cm}^2$ peak intensities.

CONCLUSIONS

We have investigated the optical nonlinearities of Corroles from Z-scan studies at 800 nm using $\sim 2 \text{ ps}$ and $\sim 40 \text{ fs}$ pulses. The γ values were estimated to be $\sim 0.1 \times 10^{-21} \text{ cm}^3/\text{W}^2$ for TTC and $6.4 \times 10^{-21} \text{ cm}^3/\text{W}^2$ for TPC in the ps time domain. Both Corroles were found to be good saturable absorbers in the fs time domain.

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