

# Picosecond and femtosecond nonlinear optical studies of Corroles

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## ABSTRACT

We present our results of nonlinear optical properties of Tritolyl Corrole (TTC) and Triphenyl Corrole (TPC) studied in the form of solution using Z-scan technique with 660 nm, ~2 picosecond (ps) pulses and 800 nm, ~40 femtosecond (fs) pulses excitation. Picosecond open-aperture Z-scan data revealed these molecules exhibited strong saturable absorption. These molecules possessed negative nonlinear refractive index ( $n_2$ ). The estimated value of  $n_2$  was  $6 \times 10^{-15}$  cm<sup>2</sup>/W and  $8 \times 10^{-15}$  cm<sup>2</sup>/W for TPC and TTC, respectively. We have recently reported NLO properties of Corroles with 800 nm excitation where they exhibited strong two-photon absorption (2PA) at higher intensities and effective two-photon absorption at lower intensities in the ps regime. Femtosecond open aperture Z-scan studies indicated the presence of strong saturable absorption with effective nonlinear absorption coefficients ( $\beta$ ) of  $\sim 0.8 \times 10^{-13}$  cm/W and  $\sim 2.7 \times 10^{-13}$  cm/W for TPC and TTC, respectively. We have also estimated the sign and magnitude of real part of third order nonlinearity through the closed aperture scans. We discuss the nonlinear optical performance of these organic molecules.

**Keywords** Z-scan, Corroles, picosecond, femtosecond, nonlinear absorption, saturable absorption

## 1. INTRODUCTION

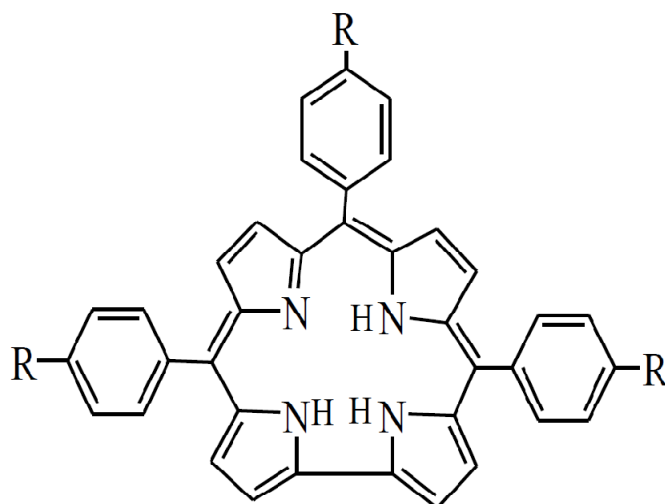
Novel moieties with strong two-photon (2PA) and three-photon absorption (3PA) cross-sections/coefficients are attractive for potential applications in the fields of photonics and bio-medicine.<sup>1-4</sup> Studies on a variety of molecules with strong 2PA/3PA have been established to be relevant in fluorescence spectroscopy, 3D imaging, and lithography because of high spatial resolution achieved through intensity dependent processes.<sup>3-7</sup> Additionally, they can be used for optical data storage and optical limiting purposes. Several materials such as porphyrins and phthalocyanines that possess such properties have been investigated extensively in recent times by several groups including our group.<sup>8-26</sup> Porphyrins, Phthalocyanines, and Porphycenes are macromolecules with huge number of delocalized  $\pi$  electrons resulting in interesting third order nonlinear optical (NLO) properties leading to extensive applications in optical limiting, all-optical switching, and optical signal processing.<sup>27-38</sup> 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<sup>33-38</sup>. Corroles generally show porphyrin type spectra, with strong absorptions in the visible range associated with very highly colored compounds. Furthermore, among the interesting attributes of Corroles are their photo-physical properties. 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 applications, including diverse areas such as cancer diagnosis, treatment, and solar cell research. Rebane et al.<sup>39-40</sup> studied the NLO properties and reported two-photon absorption (2PA) cross sections and spectra of Corroles in the spectral range of 800–1400 nm. They also observed that the strength of 2PA peak in the Soret region strongly decreased with the electron-withdrawing ability of the side substituents. Cho et al.<sup>41</sup> studied Corrole dimers and obtained superior values of two-photon cross-section compared to the values obtained by Rebane et al.<sup>39-40</sup> A molecule could be useful for optical limiting applications when studies with ns/ps pulses while its utility for signal processing or all-optical switching is decided by the femtosecond NLO properties and dynamics. A molecule might be applied for broadband optical limiting or could

possess interesting NLO properties at different wavelengths and input intensities. Therefore, for identification of the complete potential of any new molecule, studies at different input conditions (wavelengths, pulse duration, input intensity, surrounding matrix etc.) are indispensable.

In this paper we present the results from our studies on the NLO properties of Triphenyl Corrole (TPC) and Tritolyl Corrole (TTC) with Z-scan technique with 660 nm, ~2 ps and 800 nm, ~40 fs laser pulses excitation at the same concentration of  $5 \times 10^{-4}$  M. The sign and magnitude of nonlinear refractive index were derived from the closed aperture Z-scan in both ps & fs domains. From the nonlinear absorption data, achieved through the open aperture Z-scans, we observed strong saturable absorption in both ps and fs domains. We have recently reported<sup>42</sup> our results from the NLO studies of Corroles using ps and fs [Triphenyl Corrole and Tritolyl Corrole, herewith represented as TPC and TTC, throughout this manuscript] obtained at same wavelength of 800 nm and picosecond spectral dependent studies at the wavelengths of 680 nm, 700 nm, and 740 nm using the standard Z-scan technique.

## 2. EXPERIMENTAL DETAILS

Corroles were synthesized according to the procedures reported in literature<sup>42</sup> and were purified before use. Each sample was subjected to a column chromatographic purification process prior to the nonlinear optical measurements. The details of molecular structures have been detailed in figure 1.



**Figure 1** Structures of Corroles used (a) R = H, Triphenyl Corrole (TPC), Molecular Formula =  $C_{37}H_{26}N_4$ ; (b) R =  $-CH_3$ , Tritolyl Corrole(TTC), Molecular Formula =  $C_{40}H_{32}N_4$ .

Z-scan measurements were performed using an amplified Ti:sapphire laser system (LEGEND, Coherent) delivering nearly transform-limited pulses of ~2 ps at 800 nm. Wavelength 660 nm has been generated from OPA (TOPAZ) ranging from 200 nm to 2  $\mu$ m with pulse duration of ~60 fs and a same repetition rate of 1 kHz. The amplifier was seeded with ~15 fs pulses from an oscillator (MICRA, Coherent, 1 W average power, 80 MHz repetition rate, 800 nm). The beam was focused using 200 mm focal length lens into the sample. The beam waist ( $\omega_0$ ) estimated was about ~30  $\mu$ m with a Raleigh range of ~3.5 mm. The transmittance changes of the sample placed on the translation stage (Newport, ILS250PP), which was controlled by an ESP motion controller, was measured with a sensitive photodiode (Si photodiode, SM1PD2A, Thorlabs) in the far-field and output was connected to a lock-in amplifier. An aperture is placed in front of detector and the lock-in-amplifier and stage were interfaced to the computer. The picosecond studies were performed with solutions having the concentration of 0.5 mM providing ~55% (for TPC) and ~50% (for TTC) linear transmittance at 660 nm. Femtosecond studies were performed with solutions having the same concentration providing 90% linear transmittance at 800 nm. We established that the pulse energies remained low to avoid contribution from higher order nonlinearities. The experiments were repeated more than once and the best data were used for obtaining the

nonlinear optical coefficients from the best fits. These molecules are highly soluble in chloroform. Full details this experiment has been reported earlier.<sup>42</sup> Typical Z-scan experimental schematic is shown in figure 2. Closed aperture scans were performed at intensities where the contribution from the higher order nonlinear effects is negligible (the value of  $\Delta\phi$  estimated in all the cases was  $<\pi$ ). The complete nomenclature of these compounds is presented in table 1.

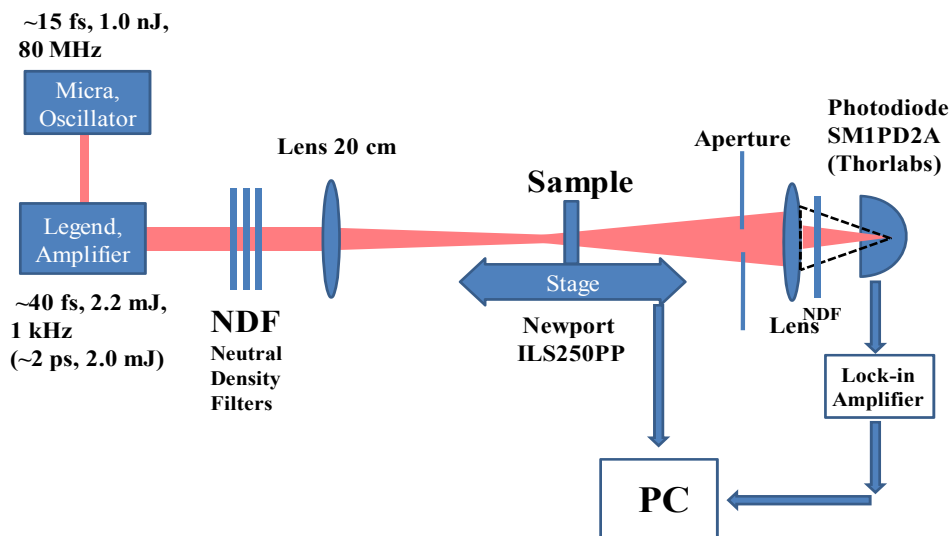
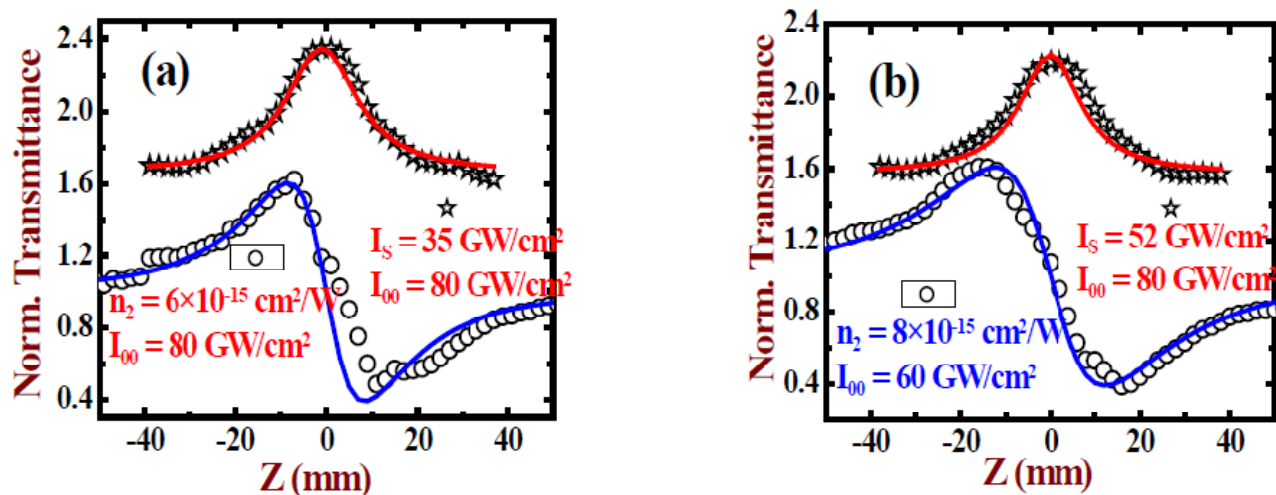


Figure 2 Experimental schematic of Z-Scan

### 3. RESULTS AND DISCUSSION

#### Picosecond pulse domain studies at 660 nm

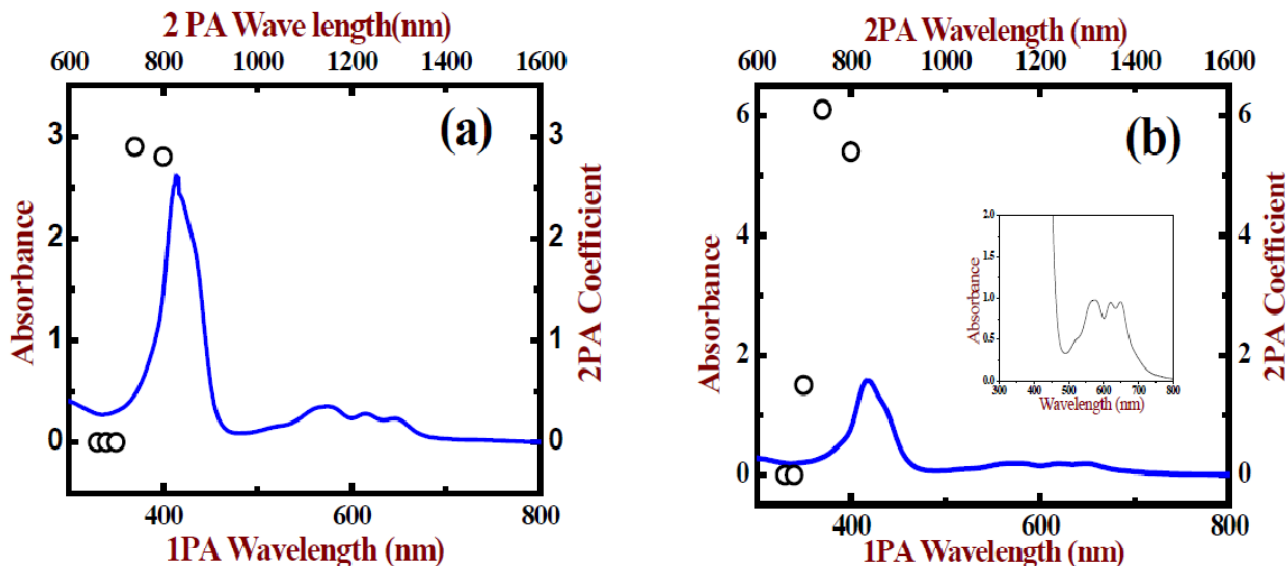
Open aperture scans for TPC and TTC recorded at 660 nm using  $\sim 2$  ps pulses indicated SA apparent from the changes in transmittance values. The concentrations of solutions used were 0.5 mM. Figures 3(a) and 3(b) illustrate the open aperture data (stars) and closed aperture data (open circles) obtained with a peak intensity of  $80 \text{ GW/cm}^2$ . The data was recorded for TPC and TTC well below the peak intensity levels where the contribution from solvent is significant. Obtained experimental data was fitted using the standard equations (2) and (3). We found the best fit was obtained with transmittance equation for SA. The linear absorption is high at 660 nm and therefore we can expect only saturation from the singlet state  $S_1$ . For lower peak intensities the population in the ground state is bleached initially ( $S_0$  states to  $S_1$  states). In this case, the excited absorption cross-section ( $\sigma_{ex}$ ) is usually lesser than the ground state absorption cross-section ( $\sigma_0$ ). The energy level diagram was reported in earlier article.<sup>42</sup> In this domain, saturation intensity  $I_S$  ( $35 \text{ W/cm}^2$  for TPC and  $52 \text{ W/cm}^2$  for TTC) are less than peak intensity and therefore we cannot calculate  $\beta$  using eqn. (4). Both the samples exhibited negative nonlinearity as discovered by the peak-valley signature in the ps domain. Closed aperture data was fitted using the eqn. (5). The magnitudes of the nonlinear refractive indices ( $n_2$ ) evaluated, using the standard procedure, were  $6 \times 10^{-15} \text{ cm}^2/\text{W}$  for the TPC and  $8 \times 10^{-15} \text{ cm}^2/\text{W}$  for TTC. The summary of NLO coefficients is presented in table 2. The solvent nonlinearity was positive suggesting the final values of  $n_2$  calculated for the pure solute will be higher than the calculated. The spectral dependent studies were performed at 680 nm, 700 nm, 740 nm and 800 nm with same concentration and the data was reported earlier.<sup>42</sup>



**Figure 3** Picosecond open aperture (open stars) and closed (open circles) of (a) TPC and (b) TTC with intensity of  $I_{00} = 80 \text{ GW/cm}^2$  obtained at 800 nm for a concentration of  $0.5 \times 10^{-3} \text{ M}$ .

### Picosecond spectral dependent studies within 660 nm – 800 nm

The 2PA spectra of Corroles (TPC & TTC) were measured in  $\text{CHCl}_3$  over a range of laser wavelengths, 660 nm (no 2PA), 680 nm (no 2PA), 700 nm (no 2PA for TPC & effective 2PA for TTC), 740 nm (2PA for both) and 800 nm (pure 2PA for TPC & effective 2PA for TTC) (transition wavelengths, 400–800 nm) and the data is shown in figure 4 together with the corresponding 1PA spectra. The lower X-axis presents the transition wavelength which is common for both of excitations. 1PA spectra of all molecules show a distinct and strong band in the wavelength region 400–450 nm, and a progression of three or four weaker bands in the region, 520–680 nm.



**Figure 4** One-photon (line) absorption spectra and two-photon absorption coefficients (symbols) of Corroles (a) TPC and (b) TTC (inset shows the expanded view of 1PA spectra). Bottom X-axis presents 1PA wavelength and top X-axis presents 2PA wavelength. Left Y-axis presents Absorbance, right Y-axis presents 2PA coefficients.

In analogy to porphyrins, one usually keeps the notations Soret and Q for the short and long-wavelength bands, respectively. In both Soret- and Q-region, the 2PA transition wavelengths roughly coincide with the corresponding one-photon transition wavelengths.<sup>39</sup> This indicates that, contrary to centro-symmetric porphyrins,<sup>43-45</sup> in non-centro-symmetric Corroles with contracted macro cycle, the 1PA and 2PA transitions take place into the same final state because the parity selection rules are relaxed. The most pronounced 2PA bands of Corroles are found in the short wavelength region near 860 nm (transition wavelength 430 nm) with maximum cross sections<sup>39</sup>, but our results suggests that all the 2PA wavelengths are below 800 nm. However, we could not perform studies beyond the 800 nm wavelength. In our case the most pronounced 2PA bands of Corroles were close to the 800 nm wavelength. We observed the high 2PA coefficient values in case of TTC rather than TPC and we did not find the presence of instantaneous/pure two photon absorption below the 800 nm wave length.

### Theoretical Considerations

To fit the data for the flip of saturable absorption around the beam waist, we combined saturable absorption coefficient and two photon absorption (TPA,  $\beta$ ) coefficients yielding the total absorption coefficient<sup>46</sup> as

$$\alpha(I) = \alpha_0 \frac{1}{1 + \frac{I}{I_s}} + \beta I \quad (1)$$

where the first term describes the negative nonlinear absorption and the second term describes positive nonlinear absorption such as reverse saturable absorption and/or two photon absorption  $\alpha_0$  is the linear absorption coefficient.  $I$  and  $I_s$  are laser peak intensity and saturation intensity, respectively.  $\beta$  is the nonlinear absorption coefficient. In presence of saturable absorption only the intensity dependent nonlinear absorption is given by the equation.<sup>47, 48</sup>

$$\alpha(I) = \alpha_0 \frac{1}{1 + \frac{I}{I_s}} \quad (2)$$

Using equations (1) and (2),  $I_s$  and  $\beta$  can be obtained from the open aperture Z-scan data by fitting it to the following equation

$$\frac{dI}{dz} = -\alpha(I)I \quad (3)$$

where  $z$  corresponds to sample length. If the excitation intensity  $I$  is lesser than  $I_s$ , we can consider SA as a third order process and in such cases  $-(\alpha_0/I_s)$  is the equivalent of nonlinear absorption coefficient  $\beta$  (negative nonlinear absorption), to a good approximation.  $\text{Im}[\chi^{(3)}]$  can be evaluated from  $\beta$ <sup>48</sup>.

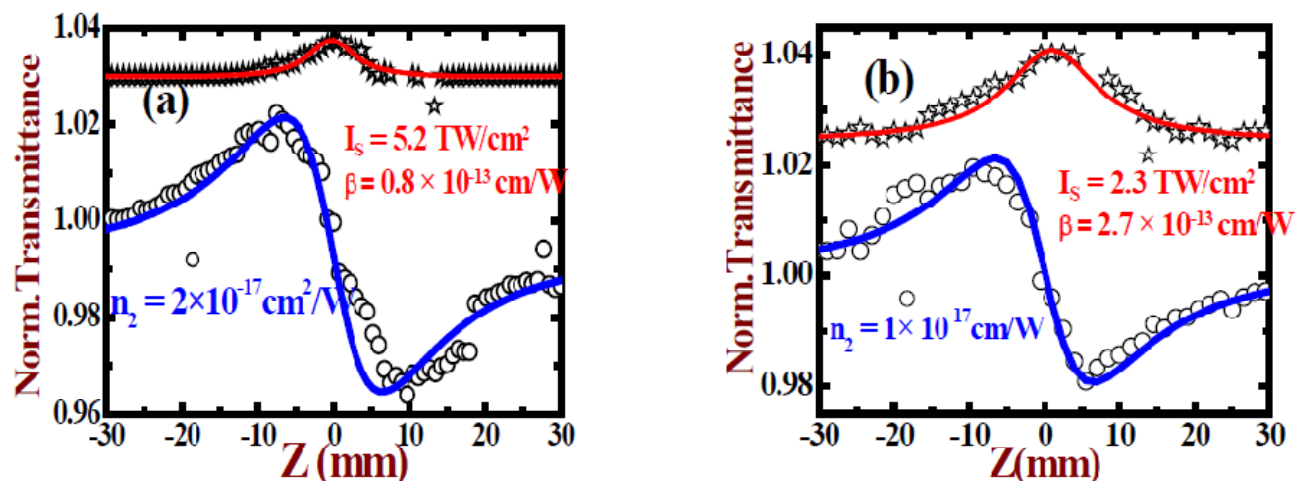
$$\beta = -(\alpha_0/I_s) \quad (4)$$

CA data were fitted using following equations<sup>49</sup>:

$$T_{CA} = 1 + \frac{4\Delta\phi\left(\frac{z}{z_0}\right)}{\left(\left(\frac{z}{z_0}\right)^2 + 9\right)\left(\left(\frac{z}{z_0}\right)^2 + 1\right)} \quad (5)$$

## Femtosecond NLO properties at 800 nm

Open aperture scans for TPC and TTC recorded at 800 nm using  $\sim 40$  fs pulses indicated SA apparent from the changes in transmittance values. The concentrations of solutions used were  $\sim 1$  mM (to achieve appreciable changes in transmittance). Figures 5(a) and 5(b) illustrate the open aperture data (stars) and closed aperture data (open circles) obtained with an intensity of  $0.9 \text{ TW/cm}^2$ . The peak intensities were calculated considering the pulse duration to be  $\sim 70$  fs due to broadening from the optical components (neutral density filters and lenses). An independent experiment performed for measuring the pulse duration indeed confirmed the value to be 70-75 fs. The experiment was performed using Silhouette (Coherent, USA) with optical components in the path. The data was recorded for TPC and TTC well below the intensity levels where the contribution from solvent is significant. Obtained experimental data was fitted using eqns. (2) and (3). We found the best fit was obtained with transmittance equation for SA. The fs pulses possess large bandwidth ( $\sim 26$  nm) and in combination with linear absorption at 800 nm we can only expect saturation of the  $S_1$  state. For pumping with higher peak intensities we observed Supercontinuum generation from the solvent. Both the samples exhibited negative nonlinearity as discovered by the peak-valley signature in the fs domain also. The magnitudes of the nonlinear refractive indices ( $n_2$ ) evaluated, using the standard procedure, were  $2 \times 10^{-17} \text{ cm}^2/\text{W}$  for the TPC and  $1 \times 10^{-17} \text{ cm}^2/\text{W}$  for TTC. In this domain, we calculated the nonlinear absorption coefficients ( $0.8 \times 10^{-13} \text{ cm/W}$  for TPC and  $2.7 \times 10^{-13} \text{ cm/W}$  for TTC) for both the cases, because the saturation intensity  $I_s$  greater than the peak intensity.



**Figure 5** Fs open aperture (open stars) and closed (open circles) of (a) TPC and (b) TTC with intensity of  $I_{00} = 0.9 \text{ TW/cm}^2$  obtained at 800 nm for a concentration of  $0.5 \times 10^{-3} \text{ M}$ .

The summary of all the NLO coefficients measured for both Corroles is presented in table 3. The solvent nonlinearity was positive suggesting the final values of  $n_2$  calculated for the pure solute will be higher than the calculated. Some of the data of these samples with same concentration were reported in our earlier articles<sup>42, 50</sup> in the fs domain. Our future endeavor is to study the (1) fs NLO properties of these molecules at different wavelengths in the visible and NIR (2) excited state dynamics of both the molecules using ultrafast pump-probe techniques (3) incorporate these molecules in suitable polymer/glass matrix and later evaluate their NLO properties and dynamics.

## 4. ACKNOWLEDGMENTS

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## 5. CONCLUSIONS

We have investigated the nonlinear optical properties of two different Corroles at 660 nm in 2 ps domain and at 800 nm in 40 fs. Both the samples were found to possess good  $n_2$  values comparing to some of the recently reported values for the same molecules. The sign of the nonlinearity was confirmed to be negative. Open aperture studies demonstrated saturable absorption to be responsible for nonlinear absorption in fs domain and ps domain. In this work, we have also compared the 1PA spectra (linear absorption spectra) with the spectra two photon absorption coefficients. 2PA transition frequencies roughly coincide with the corresponding one-photon absorption frequencies. In fs domain, we observed peak intensity was lesser than the saturation intensity and we calculated nonlinear absorption coefficients. We measured the values of  $I_s$ ,  $\beta$ ,  $n_2$ ,  $\text{Im}[\chi^{(3)}]$ ,  $\text{Re}[\chi^{(3)}]$  and  $|\chi^{(3)}|$  for all wavelengths.

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Sample	Nomenclature
TPC	5,10,15-tri phenyl Corrole
TTC	5,10,15-tri-(4-methyl phenyl) Corrole

**Table 1** Nomenclature of compounds used in the present study.

Wavelength	Sample	$\beta$ $\times 10^{-11}$ cm/W	$n_2$ $\times 10^{-14}$ cm <sup>2</sup> /W	$ \chi^{(3)} $ $\times 10^{-21}$ m <sup>2</sup> /V <sup>2</sup>	$ \chi^{(3)} $ $\times 10^{-12}$ (e.s.u.)	References
800 nm	TPC	2.8 (2PA)	1.0	11.31	5.3	[42]
	TTC	5.4 ( $I_S = 31$ GW/cm <sup>2</sup> )	0.6	7.65	3.6	
740 nm	TPC	-2.9 ( $I_S = 200$ GW/cm <sup>2</sup> )	1.0	11.26	5.3	[42]
	TTC	-6.1 ( $I_S = 150$ GW/cm <sup>2</sup> )	2.0	22.55	10.6	
700 nm	TPC	0 ( $I_S = 28$ GW/cm <sup>2</sup> )	0.8	.....	.....	[42]
	TTC	1.5 ( $I_S = 8$ GW/cm <sup>2</sup> )	1.0	10.14	5.25	
680 nm	TPC	0 ( $I_S = 16$ GW/cm <sup>2</sup> )	0.5	.....	.....	[42]
	TTC	0 ( $I_S = 35$ GW/cm <sup>2</sup> )	0.7	.....	.....	
660 nm	TPC	0 ( $I_S = 35$ GW/cm <sup>2</sup> )	0.6	.....	.....	Present study
	TTC	0 ( $I_S = 52$ GW/cm <sup>2</sup> )	0.8	.....	.....	

**Table 2** Summary of the nonlinear coefficients of Corroles extracted from the previous and present studies in the ps domain.

Sample	Conc. (mM)	$\beta$ (fs) $\times 10^{-13}$ cm/W	$n_2$ (fs) $\times 10^{-17}$ cm <sup>2</sup> /W	$\text{Im}[\chi^{(3)}]$ $\times 10^{-23}$ m <sup>2</sup> /V <sup>2</sup>	$\text{Re}[\chi^{(3)}]$ $\times 10^{-23}$ m <sup>2</sup> /V <sup>2</sup>	$ \chi^{(3)} $ $\times 10^{-23}$ m <sup>2</sup> /V <sup>2</sup>	$ \chi^{(3)} $ $\times 10^{-14}$ (e.s.u.)	References
TPC	1	-1.6	3.4	-1.12	3.77	3.94	1.9	[42]
	0.5	-0.8	2	0.57	2.26	2.33	1.1	Present study
TTC	1	-3.6	2.5	-2.51	2.78	3.74	1.8	[42]
	0.5	-2.7	1	1.92	1.13	2.22	1.05	Present study

**Table 3** Summary of the nonlinear coefficients of Corroles extracted from the previous and present studies in the fs domain.