

# Phthalocyanines, Porphycenes, and Corroles: Nonlinear optical properties and ultrafast dynamics

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## ABSTRACT

Phthalocyanines, Porphycenes, and Corroles are macromolecules with large number of delocalized  $\pi$  electrons. The magnitude of response of these loosely bound electrons to short laser pulses determines their applicability in various applications such as optical limiting, optical signal processing etc. A meticulous understanding of their performance using different pulses and at various wavelengths is indispensable to extract their accurate potential. Herein, we try to compare and contrast the nonlinear optical performance of these molecules in the ns, ps, and fs time domains. The nonlinear optical coefficients and figure of merits were estimated from the Z-scan data using different pulses over a range of input wavelengths. Ultrafast excited state dynamics of these molecules were studied using the pump-probe and degenerate four wave mixing techniques. A review of all the results obtained is presented.

**Keywords:** Phthalocyanines, Porphycenes, Corroles, femtosecond, picosecond, nanosecond, nonlinear optical, Z-scan.

## 1. INTRODUCTION

Laser-matter interaction studies over the last few decades have encompassed physical, chemical, materials science, biological and other aspects. Depending on the laser pulse duration [nanosecond (ns), picosecond (ps), or femtosecond (fs)], energy/intensity, and wavelength, the nonlinear optical interaction with materials and the mechanisms involved are completely different in different regimes [1-3]. A variety of materials have been investigated during the last two decades with an intention to identify those truly applicable for devices in the fields of ultrafast optics and photonics [1-8]. Amongst those organic materials were investigated vigorously for three main reasons: (a) ease of synthesis and modification (b) processability into thin films and (c) relatively low cost. Phthalocyanines were one of the widely studied molecules over this period [9-32]. Porphycenes [33-39] and Corroles [40-45] are some of the relatively novel molecules which have evinced interest among chemists, material scientists and physicists. The interaction of ultrashort pulses (ns, ps, fs) with such molecular liquids/thin films enabled our group to study their third order nonlinear optical (NLO) properties, figures of merit, and identify their potential for various photonic applications. Studies at a non-resonant wavelength, in general, and with fs pulses, in particular, enable us to identify pure *electronic* contribution to the nonlinearity identifying prospective molecules. The usage of longer laser pulses invokes nuclear, rotational, thermal, and other slower nonlinearities, which typically last for few nanoseconds or longer. Novel moieties with large non-resonant nonlinearities, strong two-photon (2PA)/three-photon absorption (3PA) cross-sections/coefficients are attractive for potential applications in optical lithography and bio-medical imaging. A molecule could be useful for optical limiting applications when studied with ns/ps pulses while its efficacy for signal processing or all-optical switching is determined by the fs nonlinear refractive index ( $n_2$ ). A novel molecule might 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. We could also evaluate the ultrafast time-response of optical nonlinearity. Molecules such as Phthalocyanines, Corroles, and Porphycenes were studied in solution form while some of them were investigated in thin film form [18]. Different techniques used were Z-scan [46-48], degenerate four wave mixing in the boxcar geometry [20], and degenerate pump-probe [35] etc. An overview of the complete results obtained with these samples in various time domains is presented here.

## 2. EXPERIMENTS

Details of the experiments can be found in many of our publications [xx-xx]. Z-scan experiments were performed with 6 ns pulses at 532 nm, with ps (~2 ps) pulses at 800 nm using an amplifier and in the 560-700 nm range using an optical parametric amplifier, and with fs pulses at 800 nm (~100 fs and ~40 fs). Degenerate pump-probe experiments were performed with 2 ps pulses at 800 nm and with 40 fs pulses at 600 nm. Degenerate four wave mixing experiments were performed with ~100 fs pulses at 800 nm in the boxcar geometry. Typical sample concentrations used were 0.5-1.0 mM. Samples were placed in 1-mm glass/quartz cuvettes for Z-scan experiments while 5-mm cuvettes were used for pump-probe measurements. Nearly transform limited pulses were used in each of these cases. In some cases the thin films were prepared by doping these molecules in PMMA polymer.

## 3. RESULTS & DISCUSSION

### Phthalocyanines

Most of the phthalocyanines were synthesized in-house while some of them were purchased and used as is. Depending on the pulse duration one could obtain strong 2PA [23] with ns pulses or 3PA [21] with fs pulses or mixture of saturable absorption (SA) and reverse saturable absorption (RSA) [24] as was observed by our group in different phthalocyanines. Several different phthalocyanines were investigated and most of them had impressive figures of merit combined with an ultrafast response of the nonlinearity [20]. The summary of our detailed studies on phthalocyanines include (a) Unsymmetrical phthalocyanines had better NLO properties compared to symmetrical counterparts. Nonlinearity of a molecule increases with asymmetry if the excited states transition moments dominate (b) Alkyl phthalocyanines had better NLO properties ( $n_2$  and  $\alpha_3$ ) compared to alkoxy counterparts in studies undertaken with 100 fs pulses at 800 nm whereas, interestingly, ns studies at 532 nm demonstrated vice-versa ( $n_2$  and  $\alpha_2$ ) indicating different mechanisms contributing to the nonlinearity in different time regimes (c) Thin films possessed superior NLO properties (at 800 nm). The sign of the nonlinearity was established to be negative. Open aperture studies demonstrated strong two photon absorption to be responsible for the nonlinear absorption. (d) Nanoparticles demonstrated better NLO properties compared to bulk. PcM (Nanoparticles in chloroform solution) exhibited negative nonlinearity while PcN (Nanoparticles in water) possessed positive nonlinearity. The magnitude of the  $n_2$  was  $\sim 0.92 \times 10^{-15} \text{ cm}^2 \text{ W}^{-1}$  (negative) for PcM and  $\sim 1.16 \times 10^{-15} \text{ cm}^2 \text{ W}^{-1}$  (positive) for PcN. Open aperture Z-scan data of PcM revealed saturable absorption kind of behaviour switching to RSA in SA, whereas PcN exhibited strong and pure three-photon absorption. For the case of PcM the value of three-photon absorption coefficient ( $\gamma$ ) retrieved from the fits was  $8.5 \times 10^{-23} \text{ cm}^3 \text{ GW}^{-2}$  and the two-photon absorption coefficient ( $\beta$ ) was  $3.5 \times 10^{-12} \text{ cm/W}$ . The measured three-photon absorption coefficient ( $\gamma$ ) for PcN was  $1.35 \times 10^{-22} \text{ cm}^3 \text{ GW}^{-2}$ . PcN proved to be a good optical limiter in the femtosecond domain with limiting threshold of  $\sim 0.03 \text{ J/cm}^2$ . (e) Metal phthalocyanines NLO performance was superior to free-base phthalocyanines. The non-resonant hyperpolarizability values estimated for PCH003 and PCH001 (at 800 nm) were  $\sim 10^{-31}$  e.s.u. [17]. PCH003 and PCH001 [17] were found to be good saturable absorbers. A complete summary of the NLO coefficients and cross-sections of various phthalocyanines studies are presented in table 1.

### Porphycenes

Dinaphthoporphycenes investigated by our group recently exhibited both 2PA and 3PA at the same wavelength of 800 nm due to its unique energy level structure [33, 34]. The unusual nonlinear absorption behavior was accounted by the presence of two resonances in the absorption spectrum which allowed the laser pulses to access the two-photon and three-photon states using different peak intensities. The free base porphycene, and its Ni(II) derivative, were the first annulated porphycene derivative and its metal complex, whose solid state structure has been explicitly analyzed by X-ray diffraction. The nonlinear optical coefficients and cross-sections evaluated in the ps (other than 800 nm wavelengths were also studied) and fs regimes were large compared to some of the recently reported successful molecules with similar structures. Of the five Porphycenes investigated Po2 had the strongest NLO coefficient  $n_2$  at all the wavelengths investigated [24] whereas Po4 had strong 2PA coefficient and cross-section [10, 11]. Our ps Z-scan results clearly demonstrate an effective 2PA at all wavelengths. We performed degenerate pump-probe using ~60 fs and ~2 ps laser pulses centred at 800 nm of five different dinaphthoporphycenes. The life times of excited state in these molecules,

studied using fs and ps pump-probe techniques, were estimated to be in the sub-ps regime [12, 17]. The dynamics was complicated and was dependent on input intensity of the pump beam. Two component carrier relaxation dynamics with the fast time constant in the range of 1.8-3.1 ps and the slower one in 7.0-10.0 ps range were observed with ps excitation. We could observe three decay time constants of 100-120 fs, 0.8-1.5 ps, and 7.3-10.0 ps in the fs pump-probe data. The lifetimes observed were comparable in both the cases. The fastest lifetime is attributed to intramolecular vibrational relaxation (IVR) in the  $S_2$  states while the intermediate lifetime to the  $S_2$  to  $S_1$  states de-excitation (internal conversion). The longest life time is characteristic of the  $S_1$  to  $S_0$  non-radiative decay. The present results demonstrating the strong nonlinear absorption properties of dinaphthoporphyrcenes combined with ultrafast response times may find possible applications in photonics. All the NLO coefficients along with the lifetimes measured are presented in table 2.

### Corroles

Four different Corrole molecules (TPC, TTC, GeTTC, PTTC) were examined using Z-scan technique with both ps and fs pulses. The NLO coefficients were evaluated along with the time response of these molecules using the pump-probe technique. With ps pulses TTC shows saturable absorption at low intensities, while switching from reverse saturable absorption with in saturable absorption at high intensities and other sample TPC showed switch from RSA with in SA at lower intensities and only RSA (TPA) at higher intensities. However, at a concentration of  $2.5 \times 10^{-4}$  M the ps open aperture data at higher peak intensities illustrated effective three-photon absorption (3PA or 2+1PA) for both the molecules. We have also investigated the spectral dependent Z-scan studies with ps pulses. At 700 nm TPC exhibited predominantly SA while RSA within SA was observed in TTC. The structural difference between these two samples is only  $R = -CH_3$  and  $R = -H$ . We have also carried out Z-scan studies with 800 nm, 40 fs pulses. From the fs open aperture data we derived that these molecules exhibit saturable absorption (SA) behavior. Both the samples exhibited negative nonlinear refractive index in both the time domains of investigation. In some of the cases we observed peak intensity being lesser than the saturation intensity and we calculated nonlinear absorption coefficients. The lifetimes of excited states estimated from pump-probe data was fast ( $<1$  ps). Complete details of the NLO coefficients extracted from all our studies are summarized in table 3.

Our future studies comprise (a) performing the NLO studies at different wavelengths in the entire visible spectral region (b) repeating the NLO and ultrafast studies in a polymer matrix, (c) model the nonlinear absorption behavior based on a five level model including all the possible absorption mechanisms such as excited state absorption, 2PA, 3PA, 2+1PA, 1+2PA etc. (d) fabricating structures for device applications (e.g. free-standing thin films for optical limiting applications, doped polymer waveguides for switching applications etc.).

## 4. CONCLUSIONS

Fs and ps pulses allowed us to evaluate the fast nonlinearities of several molecules including Phthalocyanines, Porphycenes, and Corroles. Strong 3PA along with fast response times of the nonlinearity was observed in some of these molecules and they find interesting applications in various areas of photonics. Further detailed studies are envisaged with varying wavelength in the visible and near IR spectral regions so as to enable us to categorize these molecules for different applications.

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| Pulses,<br>$\lambda$ (nm) | Sample   | $n_2$<br>( $\text{cm}^2/\text{W}$ ) | $\alpha_2$<br>( $\text{cm}/\text{GW}$ ) | $\alpha_3$<br>( $\text{cm}^3/\text{GW}^2$ ) | $\sigma^{(2)}$<br>$\text{cm}^4\text{s}/\text{photon}$ | $\sigma^{(3)}$<br>$\text{cm}^6\text{s}^2/\text{photon}^2$ | $\chi^{(3)}$<br>(e.s.u)                | P-P<br>(life time)      | Ref.     |
|---------------------------|--|-------------------------------------|---|---|---|---|--|-------------------------|----------|
| 100 fs,<br>800 nm         | (H <sub>2</sub> ) <sub>2</sub> SnPc (P1)                                   | $-2.0 \times 10^{-15}$              | -                                       | $4.0 \times 10^{-5}$                        | -   | -   | -                                      | -                       | [12]     |
|                           | Sn(OH) <sub>2</sub> Pc (P2)  | $-5.0 \times 10^{-15}$              | -                                       | $2.0 \times 10^{-5}$                        | -   | -   | -                                      | -                       | [12]     |
|                           | Sn(Cl) <sub>2</sub> Pc (P3)  | $-1.8 \times 10^{-15}$              | -                                       | $1.5 \times 10^{-5}$                        | -   | -   | -                                      | -                       | [12]     |
|                           | 2(3), 9(10), 16(17), 23(24) tetra tert butyl Pc (P4)                       | $-0.56 \times 10^{-15}$             | -                                       | $9.1 \times 10^{-4}$                        | -   | $\sim 1.85 \times 10^{-80}$                               | $(4.26 \pm 0.42) \times 10^{-14}$ DFWM | -                       | [20, 21] |
|                           | 2(3), 9(10), 16(17), 23(24) tetra tert butyl Zinc Pc (P5)                  | $-1.14 \times 10^{-15}$             | -                                       | $9.5 \times 10^{-4}$                        | -   | $\sim 1.93 \times 10^{-80}$                               | $(4.31 \pm 0.43) \times 10^{-14}$ DFWM | -                       | [20, 21] |
|                           | 2,3,9,10,16,17,23 ,24-Octakis-(heptyloxy) Pc (P6)                          | $-0.29 \times 10^{-15}$             | $1.5 \times 10^{-3}$                    | $0.8 \times 10^{-5}$                        | $1.24 \times 10^{-48}$                                | $1.64 \times 10^{-78}$                                    | -                                      | -                       | [24]     |
|                           | 2,3,9,10,16,17,23 ,24-Octakis-(heptyloxy) Pc Zinc(II) (P7)                 | $-0.39 \times 10^{-15}$             | $0.92 \times 10^{-3}$                   | $3.6 \times 10^{-5}$                        | $0.76 \times 10^{-48}$                                | $7.38 \times 10^{-78}$                                    | -                                      | -                       | [24]     |
|                           | 2,3,9,10,16,17,23 ,24-tetra-(tertbutyl) Zinc-Pc nanoparticles (Water) (P8) | $11.6 \times 10^{-16}$              | -                                       | $13.5 \times 10^{-5}$                       | -   | -   | -                                      | -                       | [25]     |
|                           | 2,3,9,10,16,17,23 ,24-tetra-(tertbutyl) Zinc Pc NPs (Chloroform)           | $-9.2 \times 10^{-16}$              | $3.5 \times 10^{-3}$                    | $8.5 \times 10^{-5}$                        | -   | -   | -                                      | -                       | [25]     |
| 40 fs,<br>600 nm          | P7, P5, P9-Thin films (PMMA+CHCl <sub>3</sub> )                            | -                                   | -                                       | -   | -   | -   | -                                      | 67 ps<br>30 ps<br>60 ps | [15, 16] |
| 6 ns,<br>532 nm           | 2(3), 9(10), 16(17), 23(24) tetra tert butyl Pc (P4)                       | $1.13 \times 10^{-11}$              | 310                                     | -   | -   | -   | $6.02 \times 10^{-10}$                 | -                       | [21]     |
|                           | 2(3), 9(10), 16(17), 23(24) tetra tert butyl Zinc Pc (P5)                  | $0.86 \times 10^{-11}$              | 420                                     | -   | -   | -   | $4.64 \times 10^{-10}$                 | -                       | [21]     |
|                           | 2,3,9,10,16,17,23 ,24-Octakis-(heptyloxy) Pc (P6)                          | $1.61 \times 10^{-11}$              | 1650                                    | -   | -   | -   | $10.0 \times 10^{-10}$                 | -                       | [23]     |

|                     |   |                        |       |    |           |             |                         |          |
|---------------------|---|------------------------|-------|----|-----------|-------------|-------------------------|----------|
|                     | 2,3,9,10,16,17,23,24-Octakis-(heptyloxy) Pc Zinc(II) (P7)                               | $1.56 \times 10^{-11}$ | 1680  | -  | -         | -           | $9.98 \times 10^{-10}$  | [23]     |
|                     | Cu(SO <sub>3</sub> Na)pc (P11)  | $1.2 \times 10^{-13}$  | 25    | -  | -         | -           | $0.04 \times 10^{-10}$  | [14]     |
|                     | Ni(SO <sub>3</sub> Na)pc (P12)  | $0.4 \times 10^{-13}$  | 1.1   | -  | -         | -           | $<0.04 \times 10^{-10}$ | [14]     |
|                     | 2(3),9(10),17(18),23(24)-((1,2-(dicarboxyethyl))-phthalocyanato zinc(II) (ZnOcPc) (P13) | $0.9 \times 10^{-13}$  | 43    | -  | -         | -           | $0.06 \times 10^{-10}$  | [19]     |
| <b>2 ps, 800 nm</b> | 2-(3-(Butane-1,4-dioic acid)-9(10),16,(17),23(24)-tri tert-butyl Pc Zinc(II) (P9)       | -2.95                  | 0.106 | -  | 2.7 (2.1) | 65.8 (88.2) | 2.13                    | [17]     |
|                     | 2-(3-(Butane-1,4-dioic acid)-8,11,15,18,22,25-hexakis-(butyloxy) Pc Zinc(II) (P10)      | -3.75                  | 0.275 | -  | 5.8 (4.6) | 73.2 (92.8) | 2.91                    | [17]     |
|                     | P11   | 1.50                   | -     | 15 | -         | -           | -                       | [13]     |
|                     | P12   | 1.40                   | -     | 14 | -         | -           | -                       | [13]     |
|                     | P13   | 0.013                  | -     | -  | -         | -           | -                       | [13]     |
|                     | Thin films  | -                      | -     | -  | -         | -           | -                       |          |
|                     | 2,3,9,10,16,17,23,24-octakis (heptyloxy) Pc   | 430                    | 60    | -  | 11.2      | 3.7         | 486                     | [15, 18] |
|                     | 2,3,9,10,16,17,23,24-octakis-(heptyloxy)phthalocyanine Zinc(II)                         | 694                    | 180   | -  | 20.7      | 7.3         | 1130                    | [15, 18] |
|                     | (2-(3-(Butane-1,4-dioic acid)-9(10),16(17),23(24)-tri tert-butyl Pc Zinc(II)            | 1440                   | 200   | -  | 11.1      | 2.6         | 1620                    | [15, 18] |
|                     | 2(3),9(10),16(17),23(24) tetra tert-butyl Pc  | 218                    | 60    | -  | 22.0      | 2.3         | 371                     | [15, 18] |
|                     | 2(3),9(10),16(17),23(24) tetra tert-butyl Zinc Pc                                       | 230                    | 15    | -  | 5.2       | 3.1         | 210                     | [15, 18] |

**Table 1** Summary of the NLO coefficients and excited state dynamics recorded for different Phthalocyanines [12-25] using ns, ps, and fs pulses at various wavelengths.

| Sample | Time Domain | $\lambda$ (nm) | $\alpha_2$ (cm/W)      | $n_2$ (cm <sup>2</sup> /W) | $\alpha_3$ (cm <sup>3</sup> /W <sup>2</sup> ) | $\sigma^{(2)}$ GM | $\sigma^{(3)}$ (cm <sup>2</sup> scc <sup>6</sup> / photon <sup>2</sup> ) $\times 10^{-75}$ | $\tau_3$ (fs) | $\tau_2$ (ps) | $\tau_1$ (ps) |
|--------|-------------|----------------|------------------------|----------------------------|---|-------------------|--|---------------|---------------|---------------|
| Po1    | 2 ps        | 800            | $5.00 \times 10^{-11}$ | $3.80 \times 10^{-15}$     | $3.5 \times 10^{-21}$                         | 8260              | 1.44   | -             | 2.0           | 7.2           |
|        |             | 600            | $0.30 \times 10^{-11}$ | $0.16 \times 10^{-15}$     | -   | -                 | -  | -             | -             | -             |
|        |             | 580            | $0.35 \times 10^{-11}$ | $0.07 \times 10^{-15}$     | -   | -                 | -  | -             | -             | -             |
|        |             | 560            | $0.23 \times 10^{-11}$ | $0.09 \times 10^{-15}$     | -   | -                 | -  | -             | -             | -             |
|        | 40 fs       | 800            | $6.00 \times 10^{-13}$ | $3.00 \times 10^{-17}$     | -   | -                 | -  | -             | -             | -             |
|        |             | 600            | -                      | -                          | -   | -                 | -  | 120           | 0.8           | 7.5           |
| Po2    | 2 ps        | 800            | $7.00 \times 10^{-11}$ | $2.60 \times 10^{-15}$     | $9.0 \times 10^{-21}$                         | 11600             | 3.69   | -             | 3.1           | 7.6           |
|        |             | 600            | $0.87 \times 10^{-11}$ | $0.78 \times 10^{-15}$     | -   | -                 | -  | -             | -             | -             |
|        |             | 580            | $0.10 \times 10^{-11}$ | $0.71 \times 10^{-15}$     | -   | -                 | -  | -             | -             | -             |
|        |             | 560            | $0.11 \times 10^{-11}$ | $0.35 \times 10^{-15}$     | -   | -                 | -  | -             | -             | -             |
|        | 40 fs       | 800            | $3.10 \times 10^{-13}$ | $3.00 \times 10^{-17}$     | -   | -                 | -  | -             | -             | -             |
|        |             | 600            | -                      | -                          | -   | -                 | -  | 105           | 1.4           | 7.3           |
| Po3    | 2 ps        | 800            | $8.00 \times 10^{-11}$ | $2.70 \times 10^{-15}$     | $25 \times 10^{-21}$                          | 14500             | 10.3   | -             | 2.0           | 7.2           |
|        |             | 600            | $0.37 \times 10^{-11}$ | $0.22 \times 10^{-15}$     | -   | -                 | -  | -             | -             | -             |
|        |             | 580            | $0.44 \times 10^{-11}$ | $0.07 \times 10^{-15}$     | -   | -                 | -  | -             | -             | -             |
|        |             | 560            | $0.30 \times 10^{-11}$ | $0.15 \times 10^{-15}$     | -   | -                 | -  | -             | -             | -             |
|        | 40 fs       | 800            | $0.95 \times 10^{-13}$ | $2.00 \times 10^{-17}$     | -   | -                 | -  | -             | -             | -             |
|        |             | 600            | -                      | -                          | -   | -                 | -  | 102           | 1.2           | 8.2           |
| Po4    | 2 ps        | 800            | $13.0 \times 10^{-11}$ | $3.70 \times 10^{-15}$     | $19.5 \times 10^{-21}$                        | 21500             | 8.01   | -             | 1.8           | 8.5           |
|        |             | 600            | $0.45 \times 10^{-11}$ | $0.22 \times 10^{-15}$     | -   | -                 | -  | -             | -             | -             |
|        |             | 580            | $0.50 \times 10^{-11}$ | $0.22 \times 10^{-15}$     | -   | -                 | -  | -             | -             | -             |
|        |             | 560            | $0.75 \times 10^{-11}$ | $0.07 \times 10^{-15}$     | -   | -                 | -  | -             | -             | -             |
|        | 40 fs       | 800            | $6.00 \times 10^{-13}$ | $5.00 \times 10^{-17}$     | -   | -                 | -  | -             | -             | -             |
|        |             | 600            | -                      | -                          | -   | -                 | -  | 100           | 1.5           | 10            |
| Po5    | 2 ps        | 800            | $4.80 \times 10^{-11}$ | $3.50 \times 10^{-15}$     | $11 \times 10^{-21}$                          | 7930              | 4.52   | -             | 1.8           | 7.0           |
|        |             | 600            | $0.32 \times 10^{-11}$ | $0.11 \times 10^{-15}$     | -   | -                 | -  | -             | -             | -             |
|        |             | 580            | $0.34 \times 10^{-11}$ | $0.10 \times 10^{-15}$     | -   | -                 | -  | -             | -             | -             |
|        |             | 560            | $0.35 \times 10^{-11}$ | $0.05 \times 10^{-15}$     | -   | -                 | -  | -             | -             | -             |
|        | 40 fs       | 800            | $1.15 \times 10^{-13}$ | $0.90 \times 10^{-17}$     | -   | -                 | -  | -             | -             | -             |
|        |             | 600            | -                      | -                          | -   | -                 | -  | 135           | 1.2           | 8.1           |

**Table 2** Summary of the NLO coefficients and excited state dynamics recorded for five different Porphycenes [26-29] using ps and fs pulses at various wavelengths.

| Sample | Time Domain | Wavelength (nm) | $\alpha_2$ (cm/W)   | $n_2$ (cm <sup>2</sup> /W) | $ \chi^{(3)}  \times 10^{-12}$ (e.s.u.) | Reference |
|--------|-------------|-----------------|---|----------------------------|---|-----------|
| TPC    | 2 ps        | 800             | $2.8 \times 10^{-11}$ (2PA)                               | $1.0 \times 10^{-14}$      | 5.3                                     | [40-42]   |
|        |             | 740             | $-2.9 \times 10^{-11}$ ( $I_s = 200$ GW/cm <sup>2</sup> ) | $1.0 \times 10^{-14}$      | 5.3                                     | [40-42]   |
|        |             | 700             | 0 ( $I_s = 28$ GW/cm <sup>2</sup> )                       | $0.8 \times 10^{-14}$      | -                                       | [40-42]   |
|        |             | 680             | 0 ( $I_s = 16$ GW/cm <sup>2</sup> )                       | $0.5 \times 10^{-14}$      | -                                       | [40-42]   |
|        |             | 660             | 0 ( $I_s = 35$ GW/cm <sup>2</sup> )                       | $0.6 \times 10^{-14}$      | -                                       | [40-42]   |
|        | 40 fs       | 800             | $-1.6 \times 10^{-13}$                                    | $3.4 \times 10^{-17}$      | 0.019                                   | [40-42]   |
| TTC    | 2 ps        | 800             | $5.4 \times 10^{-11}$ ( $I_s = 31$ GW/cm <sup>2</sup> )   | $0.6 \times 10^{-14}$      | 3.6                                     | [40-42]   |
|        |             | 740             | $-6.1 \times 10^{-11}$ ( $I_s = 150$ GW/cm <sup>2</sup> ) | $2.0 \times 10^{-14}$      | 10.6                                    | [40-42]   |
|        |             | 700             | $1.5 \times 10^{-11}$ ( $I_s = 8$ GW/cm <sup>2</sup> )    | $1.0 \times 10^{-14}$      | 5.3                                     | [40-42]   |
|        |             | 680             | 0 ( $I_s = 35$ GW/cm <sup>2</sup> )                       | $0.7 \times 10^{-14}$      | -                                       | [40-42]   |
|        |             | 660             | 0 ( $I_s = 52$ GW/cm <sup>2</sup> )                       | $0.8 \times 10^{-14}$      | -                                       | [40-42]   |
|        | 40 fs       | 800             | $-3.60 \times 10^{-13}$                                   | $2.5 \times 10^{-17}$      | 0.018                                   | [40-42]   |
| Ge-TTC | 2 ps        | 800             | $3.00 \times 10^{-12}$                                    | $-7.6 \times 10^{-16}$     | -                                       | 49        |
| P-TTC  |             | 800             | $5.73 \times 10^{-12}$                                    | $-5.1 \times 10^{-16}$     | -                                       | 49        |

**Table 3** Summary of the NLO coefficients and excited state dynamics recorded for four different Corroles [30-32] using ps and fs pulses at various wavelengths.

## REFERENCES

- [1] He, G.S., Tan, L.S., Zheng, Q., Prasad, P.N., "Multi-Photon Absorbing Materials: Molecular Designs, Syntheses, Characterizations, and Applications," *Chem. Rev.* **108**, 1245-1330 (2008).
- [2] Pawlicki, M., Collins, H.A., Denning, R.G., Anderson, H.L., "Two-photon absorption and the design of two-photon dyes," *Angew. Chem. Int. Ed. Engl.* **48(18)**, 3244-66 (2009).
- [3] Rumi, M., and Perry, J.W., "Two-photon absorption: an overview of measurements and principles," *Adv. Opt. Photon.* **2**, 451-518 (2010).
- [4] Senge, M.O., Fazekas, M., Notaras, E.G.A., Blau, W.J., Zawadzka, M., Locos, O.B, Mhuirheartaigh, Ni.E.M., "Nonlinear Optical Properties of Porphyrins", *Adv. Mater.* **19**, 2737-2774 (2007).
- [5] de la Torre, G., Vazquez, P., Agullo-Lopez, F., Torres, T., "Role of Structural Factors in the Nonlinear Optical Properties of Phthalocyanines and Related Compounds," *Chem. Rev.* **104**, 3723-3750 (2004).
- [6] Arnbjerg, J., Ana, J.B., Martin, J.P., Nonell, S., Borrell, J.I., Christiansen, O., Ogilby, P.R., "Two-Photon Absorption in Tetraphenylporphycenes: Are Porphycenes Better Candidates than Porphyrins for Providing Optimal Optical Properties for Two-Photon Photodynamic Therapy?" *J. Am. Chem. Soc.*, **129**, 5188-5199 (2007).
- [7] Dvornikov, A. S., Walker, E. P., and Rentzepis, P. M., "Two-Photon Three-Dimensional Optical Storage Memory," *J. Phys. Chem. A* **113**, 13633-13644 (2009).
- [8] Belfield, K.D., Schafer, K.J., Liu, Y., Liu, J., Ren, X., Van Stryland, E.W., "Multiphoton-absorbing organic materials for microfabrication, emerging optical applications and non-destructive three-dimensional imaging," *J. Phys. Org. Chem.* **13**, 837-849 (2000).
- [9] Narayana Rao, D., Venugopal Rao, S., Blanco, E., Aranda, F.J., Rao, D.V.G.L.N., and Akkara, J.A., "A comparative study of C<sub>60</sub> phthalocyanine and a porphyrin for optical limiting over the visible region," *J. Sci. Ind. Res.* **57(10,11)**, 664-667 (1998).
- [10] Mathews, S.J., Chaitanya Kumar, S., Giribabu, L., Venugopal Rao, S., "Large third order nonlinear optical and optical limiting properties of symmetric and unsymmetrical phthalocyanines studied using Z-scan," *Opt. Commun.*, **280(1)**, 206-212 (2007).
- [11] Mathews, S.J., Chaitanya Kumar, S., Giribabu, L., Venugopal Rao, S., "Nonlinear optical and optical limiting properties of phthalocyanines in solution and thin films of PMMA studied using a low power He-Ne laser," *Mater. Lett.*, **61(22)**, 4426-4431 (2007).
- [12] Venugopal Rao, S., "Femtosecond and continuous wave nonlinear optical properties of (H<sub>2</sub>)<sub>2</sub>SnPc, Sn(OH)<sub>2</sub>Pc, Sn(Cl)<sub>2</sub>Pc studied using Z-scan technique," *Proc. SPIE*, **7197**, 719715 (2009).
- [13] Venugopal Rao, S., "Phthalocyanines for photonic applications: a new perspective," *Proc. SPIE* **7728**, 77281N1 (2010)
- [14] Venugopal Rao, S., Prasad, A.K., Giribabu, L., Tewari, S.P., "Picosecond and nanosecond third order nonlinear optical characterization of Cu & Ni phthalocyanines using Z-scan technique," *Proc. SPIE*, **7599**, 75991O1 (2010).
- [15] Venugopal Rao, S., Swain, D., Tewari, S.P., "Pump-probe experiments with sub-100 femtosecond pulses for characterizing the excited state dynamics of phthalocyanine thin films," *Proc. SPIE*, **7599**, 75991P1 (2010).
- [16] Venugopal Rao, S., Anusha, P.T., Shuvan Prashant, T., Swain, D., Tewari, S.P., "Ultrafast nonlinear optical properties and excited state dynamics of phthalocyanine thin films," *Proc. SPIE*, **7935**, 793517-1 (2011).
- [17] Anusha, P.T., Giribabu, L., Tewari, S.P., Venugopal Rao, S., "Picosecond optical nonlinearities of unsymmetrical alkyl and alkoxy phthalocyanines studied using the Z-scan technique," *Mat. Lett.* **64**, 1915-1917 (2010).
- [18] Venugopal Rao, S., Anusha, P.T., Shuvan Prashant, T., Swain, D., Tewari, S.P., "Third order optical nonlinearities and optical limiting in phthalocyanine thin films," *Mater. Sci. Applns.*, **2**, 299-306 (2011).
- [19] Venugopal Rao, S., Anusha, P.T., Giribabu, L., Tewari, S.P., "Picosecond optical nonlinearities in symmetrical and unsymmetrical phthalocyanines studied using the Z-scan technique," *Pramana - J. Phys.*, **75(5)**, 1017-1023 (2010).
- [20] Kumar, R.S.S., Venugopal Rao, S., Giribabu, L., Narayana Rao, D., "Ultrafast nonlinear optical properties of alkyl phthalocyanines investigated using degenerate four-wave mixing technique," *Opt. Mat.*, **31**, 1042-1047 (2009).
- [21] Kumar, R.S.S., Venugopal Rao, S., Giribabu, L., Narayana Rao, D., "Femtosecond and nanosecond nonlinear optical properties of alkyl phthalocyanines studied using Z-scan", *Chem. Phys. Lett.* **447**, 274-278 (2007).
- [22] Kumar, R.S.S., Venugopal Rao, S., Giribabu, L., Narayana Rao, D., "Nonlinear absorption properties of alkyl phthalocyanines in the femtosecond, nanosecond, and cw regimes" *Proc. SPIE* **6875**, 68751D-1 (2008).



- [23] Venkatram, N., Giribabu, L., Narayana Rao, D., Venugopal Rao, S., "Nonlinear optical and optical limiting studies in alkoxy phthalocyanines studied at 532 nm with nanosecond pulse excitation", *Appl. Phys. B* **91**, 149-156 (2008).
- [24] Venkatram, N., Giribabu, L., Narayana Rao, D., Venugopal Rao, S., "Femtosecond nonlinear optical properties of alkoxy phthalocyanines at 800 nm studied with Z-scan technique," *Chem. Phys. Lett.* **464**, 211-215 (2008).
- [25] Venugopal Rao, S., Venkatram, N., Giribabu, L., Narayana Rao, D., "Ultrafast nonlinear optical properties of phthalocyanines nanoparticles at 800 nm studied using Z-scan," *J. Appl. Phys.* **105**, 053109 (2009).
- [26] Calvete, M., Yang, GY., Hanack, M., "Porphyrins and phthalocyanines as materials for optical limiting," *Synth. Met.* **141**, 231-243 (2004).
- [27] Ma, L., Zhang, Y., and Yuan, P., "Nonlinear optical properties of phenoxy-phthalocyanines at 800nm with femtosecond pulse excitation," *Opt. Express* **18**, 17666-17671 (2010).
- [28] Ma, G., Guo, L., Mi, J., Liu, Y., Qian, S., Pan, D., Huang, Y., "Ultrafast optical nonlinearity of titanylphthalocyanine films," *Thin Solid Films* **410**, 205-211 (2002).
- [29] Fang, S., Hoshi, H., Kohama, K., and Maruyama, Y., "Nonlinear Optical Characteristics of Vanadyl Phthalocyanine Thin Film Grown by the Molecular Beam Epitaxial Method," *J. Phys. Chem.* **100**, 4104-4110 (1996).
- [30] Morisue, M., Ogawa, K., Kamada, K., Ohta, K., Kobuke Y., "Strong two-photon and three-photon absorptions in the antiparallel dimer of a porphyrin-phthalocyanine tandem," *Chem. Commun.* **46(12)**, 2121-2123 (2010).
- [31] Fu, G., Yoda, T., Kasatani, K., Okamoto, H. and Takenaka, S., "Third-Order Optical Nonlinearities of Naphthalocyanine-Derivative-Doped Polymer Films Measured by Resonant Femtosecond Degenerate Four-Wave Mixing," *Jpn. J. Appl. Phys.* **44**, 3945-3950 (2005).
- [32] Vagin, S., Barthel, M., Dini, D., Hanack, M., "Synthesis and Characterization of (Octaaryl-tetraazaporphyrinato)indium(III) Complexes for Optical Limiting" *Inorg. Chem.* **42**, 2683-2694 (2003).
- [33] Sarma, T., Panda, P.K., Anusha, P.T., Venugopal Rao, S., "Dinaphthoporphyrcenes: Synthesis and Nonlinear Optical Studies" *Org. Lett.* **13**, 188-191 (2010).
- [34] Venugopal Rao, S., Shuvan Prashant, T., Sarma, T., Panda, P.K., Swain, D., Tewari, S.P., "Two-photon and three-photon absorption in dinaphthoporphyrcenes," *Chem. Phys. Lett.*, **514**, 98-103 (2011).
- [35] Swain, D., Anusha, P.T., Shuvan Prashant, T., Tewari, S.P., Sarma, T., Panda, P.K., Venugopal Rao, S., "Ultrafast excited state dynamics and dispersion studies of nonlinear optical properties in dinaphthoporphyrcenes," *Appl. Phys. Lett.* **100**, 141109 (2012).
- [36] Swain, D., Anusha, P.T., Shuvan Prashant, T., Tewari, S.P., Sarma, T., Panda, P.K., Venugopal Rao, S., "Multiphoton absorption studies in porphyrcenes using picosecond and femtosecond pulses," *AIP conf. Proc.* **1391**, 674-676 (2011).
- [37] Dobkowski, J., Galievsky, V., Starukhin, A., Vogel, E., and Waluk J., "Spectroscopy and Photophysics of Tetraalkyldibenzoporphyrcenes," *J. Phys. Chem. A* **102**, 4966-4971 (1998).
- [38] Dobkowski, J., Lobko, Y., Gawinkowski, S., and Waluk, J., "Energy relaxation paths in matrix-isolated excited molecules: Comparison of porphyrcene with dibenzoporphyrcenes," *Chem. Phys. Lett.* **416**, 128-132 (2005).
- [39] Fita, P., Radzewicz, C., and Waluk, J., "Electronic and Vibrational Relaxation of Porphyrcene in Solution," *The J. Phys. Chem. A* **112**, 10753-10757 (2008).
- [40] Hamad, S., Tewari, S.P., Giribabu, L., Venugopal Rao, S., "Picosecond and Femtosecond Optical Nonlinearities of Novel Corroles," In Press, *J. Porphyrins Phthalocyanines* (2012). (DOI No: [10.1142/S108842461200446X](https://doi.org/10.1142/S108842461200446X))
- [41] Hamad, S., Krishna, G.P., Giribabu, L., Tewari, S.P., and Venugopal Rao, S., "Femtosecond and picosecond optical nonlinearities of Corroles studied using Z- scan technique" *AIP Conf. Proc.* **1391**, 683-685 (2011).
- [42] Hamad, S., Krishna, G.P., Giribabu, L., Tewari, S.P., and Venugopal Rao, S., "Femtosecond and picosecond nonlinear optical studies of Corroles," *Proc. SPIE* 8258, 82581C (2012).
- [43] Rebane, A., Drobizhev, M., Makarov, N.S., Koszarna, B., Tasior, M., Gryko, D.T., "Two-photon absorption properties of meso-substituted A3-Corroles," *Chem. Phys. Lett.* **462**, 246-250 (2008).
- [44] Rebane, A., Makarov, N., Drobizhev, M., Koszarna, B., Galezowski, M., Gryko, D.T., "Two-photon absorption spectroscopy of Corroles," *Proc. SPIE.* **7213**, 72130Q-1 (2009).
- [45] Karotki, A., Drobizhev, M., Kruk, M., Spangler, C.W., Nickel, E., Mamardashvili, N., Rebane, A., "Enhancement of two-photon absorption in tetrapyrrolic compounds," *J. Opt. Soc. Am. B* **20**, 321 (2003).
- [46] Sheik-Bahae, M., Said, A.A., Wei, T.-H., Hagan, D.J., Van Stryland, E.W., "Sensitive measurement of optical nonlinearities using a single beam," *IEEE J. Quant. Electron.* **26(4)**, 760-769 (1990).

- [47] Venkata Saravanan, K., James Raju, K.C., Ghanashyam Krishna, M., Tewari, S.P., Venugopal Rao, S., "Large three-photon absorption in  $Ba_{0.5}Sr_{0.5}TiO_3$  films studied using Z-scan technique," *Appl. Phys. Lett.* **96**, 232905 (2010).
- [48] Sutherland, R.L., Brant, M.C., Heinrichs, J., Slagle, J.E., McLean, D.G., and Fleitz, P.A., "Excited state characterization and effective three-photon absorption model of two-photon-induced excited-state absorption in organic push-pull charge-transfer chromophores," *J. Opt. Soc. Am. B* **22**, 1939-1948 (2005).
- [49] Anusha, P.T., Swain, D., Giribabu, L., Tewari, S.P., Venugopal Rao, S., "Ultrafast excited state dynamics and third order optical nonlinearities of novel Corroles," Submitted to *J. Phys. Chem. B* (2012).