

Optical, electrochemical and third-order nonlinear optical studies of triphenylamine substituted zinc phthalocyanine

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Dedicated to Professor Tomás Torres on the occasion of his 65th birthday

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ABSTRACT: Zinc phthalocyanine possessing triphenylamine at its peripheral position has been synthesized and its optical, emission, electrochemical and third-order nonlinear optical (NLO) properties were investigated. Soret band was broadened due to the presence of triphenylamine moiety. Electrochemical properties indicated that both oxidation and reduction processes were ring centered. Emission spectra were recorded in different solvents and the fluorescence yields obtained were in the range of 0.02–0.17 while the time-resolved fluorescence data revealed radiative lifetimes of typically few ns. Third-order NLO properties of this molecule have been examined using the Z-scan technique with picosecond (ps) and femtosecond (fs) pulses. Closed and open aperture Z-scan data were recorded with ~2 ps/~150 fs laser pulses at a wavelength of 800 nm and NLO coefficients were extracted from both the data. Our data clearly suggests the potential of this molecule for photonics applications.

KEYWORDS: phthalocyanine, Z-scan, picosecond, femtosecond, fluorescence.

INTRODUCTION

One of the main objectives of scientists working in the areas of materials science and chemistry is to incorporate new functionalities into existing materials without varying the fundamental response mechanisms that render the material originally interesting [1–3]. In this regard, phthalocyanines are versatile class of materials due to their diverse optical, redox properties, exceptionally high thermal and chemical stability and easy synthetic protocols for the preparation of these compounds [4–7]. Phthalocyanines are tetra pyrrolic cyclic organic molecules have two-dimensional 18 π -electron conjugated system and found in many fields

such as colorants, chemical sensors, electrochromism, catalysts, liquid crystals, nonlinear optics, hole transport materials and as sensitizers in photodynamic therapy as well as in dye-sensitized solar cells [8–17]. However, due to planarity of the phthalocyanine macrocycle, there exists a tendency to aggregate in solutions even at micromolar concentration and in solid-state and, therefore, results in poor solubility in common organic solvents. The aggregation phenomenon influences their spectroscopy and photophysical properties and, thereby, limiting the application potential of such molecules [18]. The introduction of substituents like alkyl, alkoxy, thioalkyl *etc.* either at axial position/s or at peripheral positions of phthalocyanine macrocycle not only reduces its aggregation but also alters its photophysical, electrochemical properties and thereby increases its potential for optoelectronic applications [19–21].

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Due to their extended π -conjugated system phthalocyanines are well suited for third-order nonlinear optical (NLO) applications and possess exceptional stability against photo-irradiation [22]. The NLO properties of metallophthalocyanines can be enhanced by changing its aggregation state. Various research groups, including our group, have studied in detail the NLO response of a number of phthalocyanines with different central metals and peripheral substitutions [23–31]. In order to minimize the aggregation of phthalocyanines, Swain *et al.* have introduced bulky aryloxy groups at peripheral positions and studied their electronic properties as well NLO response [25]. Swain and co-workers again have used thioaryl groups at non-peripheral positions of zinc phthalocyanine as a result absorption maxima of Q-band were red-shifted and studied their third-order NLO studies [26]. Here, in the present work, we have introduced a triphenylamine group at peripheral positions of zinc phthalocyanine to improve optical response of Soret band of macrocycle. The detailed absorption, emission (steady-state and time resolved), electrochemical, spectroelectrochemical properties along with the results from NLO studies performed with picosecond (ps) and femtosecond (fs) laser pulses are presented in this work.

EXPERIMENTAL

Materials

4-(Diphenylamino)phenylboronic acid, $[\text{Pd}(\text{pPh}_3)_4]$, 1-pentanol, 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) were purchased from Sigma Aldrich and were used as it is. All the solvents *viz.*, dichloromethane, tetrahydrofuran, dimethylsulfoxide, *N,N*-dimethylformamide, toluene, methanol, potassium carbonate, chloroform, *n*-hexane were purchased from SD Fine Chemicals Ltd., India and were dried before further use. Zinc Acetate was purchased from Qualigens Chemicals Ltd., India.

Instrumentation

Absorption spectra were recorded with a Shimadzu UV-3600, UV-visible-NIR. Steady-state fluorescence spectra were recorded using a Fluorolog-3 spectrofluorometer (Spex model, JobinYvon) for solutions with optical density at the wavelength of excitation (λ_{ex}) ≈ 0.05 . Fluorescence quantum yields (ϕ) were estimated by integrating the fluorescence bands of zinc *tert*-butyl phthalocyanine ($\phi = 0.37$ in benzene) [32]. Fluorescence lifetime measurements were carried out using a ps time-correlated single photon counting (TCSPC) setup (FluoroLog3-Triple Illuminator, IBH Horiba JobinYvon) employing a ps light emitting diode laser (NanoLED, $\lambda_{\text{ex}} = 670$ nm) as excitation source. The decay curves were recorded by monitoring the fluorescence emission maxima of the phthalocyanine macrocycle ($\lambda_{\text{em}} = 700$ nm).

Photomultiplier tube (R928P, Hamamatsu) was employed as the detector. The lamp profile was recorded by placing a scattered (dilute solution of Ludox in water) in place of the sample. The width of the instrument function was limited by full width at half maximum (FWHM) of the excitation source, ~ 635 ps at 670 nm. Decay curves were analyzed by nonlinear least-squares iteration procedure using IBH DAS6 (version 2.3) decay analysis software. The quality of the fits was judged by the χ^2 values and distribution of the residuals.

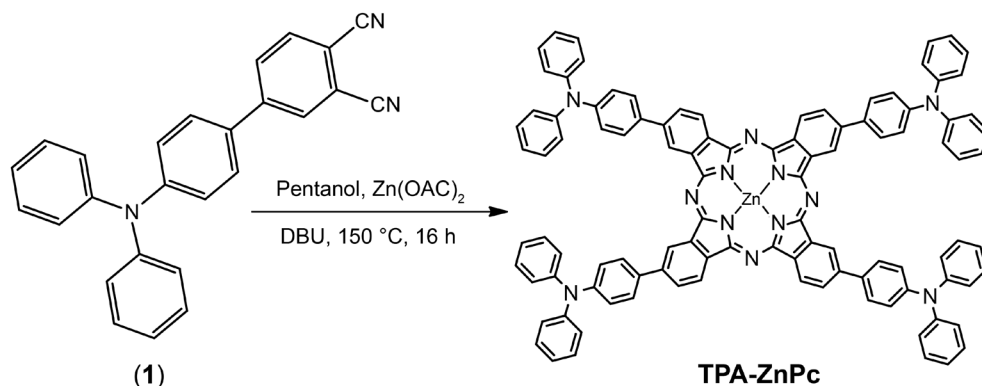
Electrochemical measurements were performed on a computer-controlled electrochemical analyzer (CH instruments, CHI 620C). The experiments were performed on 1 mM phthalocyanine solution in CH_2Cl_2 solvent at scan rate of 100 mV/s using 0.1 M tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte. The working electrode is glassy carbon, standard calomel electrode (SCE) is reference electrode and platinum wire is an auxiliary electrode. After a cyclic voltammogram (CV) had been recorded, ferrocene was added, and a second voltammogram was measured. The optical thin layer electrochemical studies were carried on Maya 2000 Ocean Optics software using DT-MINI-2-GS, UV-VIS-NIR LIGHTSOURCE. ^1H NMR spectra were recorded in CDCl_3 solutions on AVANCE 300 MHz spectrophotometer using TMS as standard. FT-IR spectra (KBr pellets) were recorded on a Perkin Elmer Spectrophotometer. Mass spectra were acquired using Electro Spray Ionization (ESI) method, operated in positive ion mode using m/z range 100–2000.

NLO experimental details

The ps and fs Z-scan experiments are described in detail in our earlier works [25–26]. Briefly, ~ 2 ps pulses at 800 nm with a repetition rate of 1 kHz were used for the experiments. The fs Z-scan experiments [25] were performed with ~ 150 fs pulses at 800 nm delivered from an oscillator (Chameleon, Coherent) with a repetition rate of 80 MHz. The concentration of **TPA-ZnPc** solution used was ~ 0.5 mM. The Z-scan studies were performed in 1-mm cuvettes and the contribution of solvent was neglected in the calculations. The NLO coefficients were obtained from the fits to the experimental data using standard equations described elsewhere [25, 26].

Synthesis

Synthesis of TPA-ZnPc. 4'-(diphenylamino)-[1,1'-biphenyl]-3,4-dicarboitrile (**1**) was synthesized according to the modified literature procedure [33, 34]. A mixture of anhydrous zinc acetate (1.90 g, 10 mmol), 4'-(diphenylamino)-[1,1'-biphenyl]-3,4-dicarbonitrile (1.70 g, 5 mmol), 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU, catalytic amount) and dry 1-pentanol (5 mL) was refluxed at 150°C for 16 h under a nitrogen atmosphere. After cooling, the solution was precipitated by addition of methanol, filtered and dried. The obtained solid material



Scheme 1. Synthetic scheme of TPA-ZnPc

was subjected to silica gel column chromatography and eluted with dichloromethane. The green colored band was collected and recrystallized from methanol, to get the desired compound in 70% yield. Elemental analysis of anal. calcd. for C₁₀₄H₆₈N₁₂Zn% (1551.11): C, 80.53; H, 4.42; N, 10.84. Found C, 80.50; H, 4.43; N, 10.80. ¹H NMR (500 MHz; CDCl₃): δ, ppm 7.68–7.63 (m, 4H), 7.55–7.54 (d, *J* = 8.3 Hz, 8H), 7.45 (s, 8H), 7.43 (d, *J* = 1.7 Hz, 8H), 7.35–7.29 (m, 40H). MALDI-TOF (C₁₀₄H₆₈N₁₂Zn): *m/z* 1550 (calcd. for [M]⁺) 1550. FT IR (KBr): ν, cm⁻¹ 3030, 2922, 1278 and 1099.

RESULTS AND DISCUSSION

Synthesis and characterization

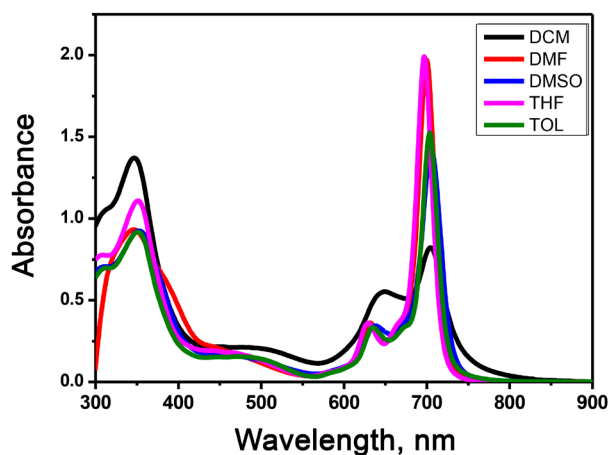
The phthalonitrile 4'-(diphenylamino)-[1,1'-biphenyl]-3,4-dicarbonitrile was synthesized according to the procedure reported in literature [33, 34]. Finally, **TPA-ZnPc** was accomplished by cyclotetramerization of **1** with anhydrous zinc acetate in 1-pentanol at reflux temperature under nitrogen atmosphere in the presence of DBU as non-nucleophilic base catalyst as shown in Scheme 1. The crude **TPA-ZnPc** was purified by column chromatography followed by recrystallization and characterized by elemental analysis, mass, FT-IR, ¹H NMR, UV-vis, and emission spectroscopy as well as electrochemical techniques. The elemental analysis data is presented in the experimental section and found to be satisfactory. MALDI-TOF spectrum consists of a molecular ion peak at 1550 that is assigned to the presence of corresponding phthalocyanine (see Supporting information Fig. S4).

UV-visible absorption studies

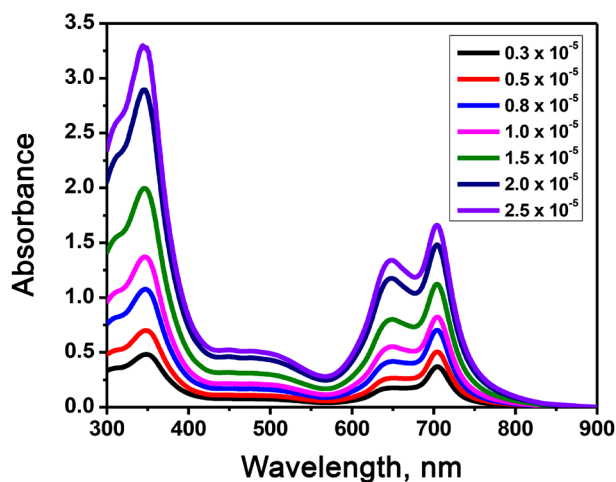
The electronic absorption spectra of **TPA-ZnPc** revealed characteristic features of the phthalocyanine. It shows a low intense Soret band (B-band) in 300–400 nm region arising from deeper π-levels to LUMO

transition and a relatively intense Q-band in 600–800 nm region attributed to HOMO to LUMO transition (π–π*) (Figs 1a and 1b). The intensity and absorption maxima of Q-band can be altered depending upon metallation, substitution either at peripheral or axial position/s as well as aggregation of phthalocyanine macrocycle [25, 26]. Substitution with strongly electron donating or strongly electron withdrawing groups potentially provide a method of tuning the Q-band absorption. The absorption spectra of **TPA-ZnPc** in various solvents including DCM, are shown in Fig. 1a and corresponding absorption maxim and molar extinction coefficient (ε) are presented in Table 1. The complex exhibited a Q-band at around 700 nm and a Soret band at 350 nm in the case of DCM. The absorption spectra also consists of a shoulder on the high energy side of the Q-band indicates the presence of aggregated species. It is apparent from Fig. 1a that in case of coordinated solvents such as DMF, DMSO and THF, the intensity shoulder peak reduces due to the solvent coordinated at axial positions of **TPA-ZnPc**. The Soret band of **TPA-ZnPc** is broaden due to the presences of triphenylamine group in the molecular structure.

The aggregation phenomena of phthalocyanines affect the photo-physical properties and these effects lead to reduced utility its practical device applications. The aggregation depends on concentration, solvent, substituents, complexed metal ions and temperature [35]. For many benzo or non-bulky substituted phthalocyanines, aggregation occurs readily, even at mM concentrations, making the spectral data more difficult to interpret. In dilute solutions phthalocyanines exist as single molecule and are surrounded by solvent molecules but with increasing the concentration the macrocycle aggregate. In the aggregated state the electronic properties of phthalocyanine alter from its ground state [36]. Taking into account of aggregation, we have carried out absorption studies of **TPA-ZnPc** at various concentrations in DCM solvent and the data is shown in Fig. 1b. It is apparent from Fig. 1b that the ratio of Q-band at 704 nm with shoulder at 640 nm reduces as the



(a)



(b)

Fig. 1. (a) Absorption spectrum of **TPA-ZnPc** in different solvents. (b) Absorption spectral changes of **TPA-ZnPc** in DCM at different concentrations: (a) 0.3×10^{-5} (b) 0.5×10^{-5} (c) 0.8×10^{-5} (d) 1.0×10^{-5} (e) 2.5×10^{-5} M

concentration increases (shoulder at 640 nm represents degree of aggregation phenomena in phthalocyanines). However, the shape and position of absorption maxima remains same at low and high concentration. It is apparent that the molar extinction coefficient remained almost constant and obeying the Beer–Lambert Law particularly at low concentrations. In contrast, we have carried out similar studies in coordinating solvents such as THF, it simply follows Beer–Lambert Law and as the concentration increases absorption increases without change of ratio between Q-band peak and shoulder at 640 nm (Fig. S7).

Electrochemical and spectroelectrochemical studies

Phthalocyanine is a 18π -electron aromatic system that, in its common oxidation state, carries two negative charges. Phthalocyanine is capable of oxidation, by

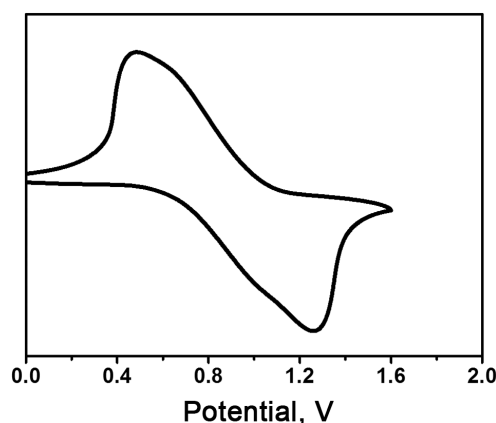


Fig. 2. Cyclic voltammogram of **TPA-ZnPc** in DCM using a glassy carbon electrode

losing one or two electrons, and reduction by gaining one to four electrons. The relative positions of the HOMO and LUMO levels can be shifted *via* changes in the electron density of the molecule brought about by electron donating or electron withdrawing substituents. The redox potentials of **TPA-ZnPc** were measured in dichloromethane by using differential pulse voltammetric technique as shown in Fig. 2. **TPA-ZnPc** presented either reversible or quasi-reversible oxidations at 0.80 & 1.00 V and reduction at -1.00 V vs. SCE.

Spectroelectrochemical studies were employed to confirm to monitor changes during redox reactions of **TPA-ZnPc**. Figures 3(a)–3(d) show the spectral changes of **TPA-ZnPc** during applied potential. Figure 3a shows the spectral changes during the controlled potential oxidation of **TPA-ZnPc** at an applied potential of 0.90 V. While the Q-band at 704 nm increases in intensity with appearance of a shoulder at 399 nm during the oxidation process. At the same time the Soret-band at 343 nm reduces its intensity was observed. The shoulder at 649 nm also decreases in intensity, which indicates disaggregation of the phthalocyanine macrocycle. During first oxidation process, clear isosbestic points were observed at 367, 459, 673 and 724 nm, which clearly indicate that the oxidation gives a single product. These changes are typical of a ring based oxidation and were assigned to the $[\text{Zn}^{\text{II}}\text{Pc}^{2-}]/[\text{Zn}^{\text{II}}\text{Pc}^{1-}]^{+}$ processes [37–39]. Spectroscopic changes during the controlled potential applied at 1.20 V support the further oxidation of the mono cationic species confirming the DPV assignment of the couple to $[\text{Zn}^{\text{II}}\text{Pc}^{1-}]^{+}/[\text{Zn}^{\text{II}}\text{Pc}^{0}]^{2+}$, as shown in Fig. 3b. During a second oxidation of the phthalocyanine macrocycle Soret-band at 343 nm reduces its intensity and the shoulder at 393 nm has completely vanished. While the Q-band intensity decreased the generation of a new band at 825 nm was observed. Clear isosbestic points were recorded at 421, 607 and 730 nm. These changes in the absorption spectrum were assigned to oxidation of species from $[\text{Zn}^{\text{II}}\text{Pc}]^{1+}$ to $[\text{Zn}^{\text{II}}\text{Pc}]^{2+}$.

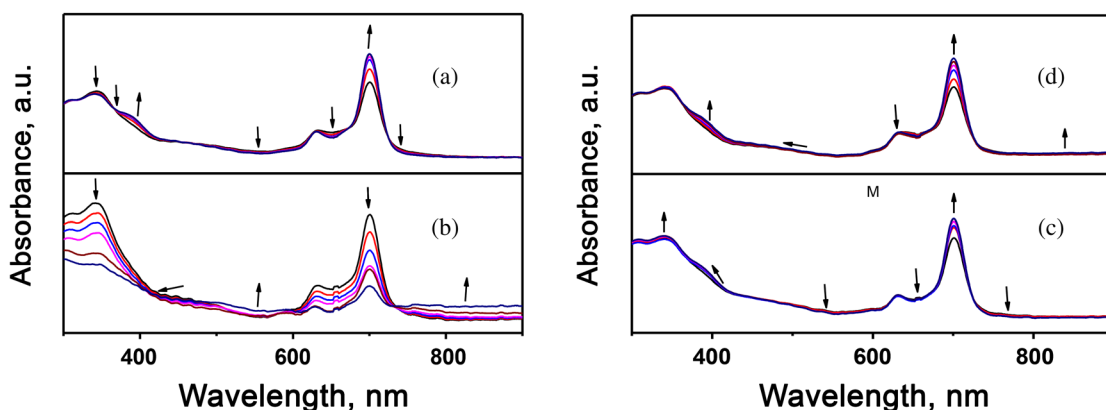


Fig. 3. *In situ* UV-vis spectral changes of TPA-ZnPc (a) $E_{app} = 0.90$ V (b) $E_{app} = 1.20$ V (c) $E_{app} = -1.00$ V (d) $E_{app} = -1.40$ V

Figure 3c shows the spectral changes during the reduction process at a controlled potential of -1.00 V. The intensity of Q-band absorption at 700 nm increased without shift, while new bands at 397 and 793 nm appeared with increasing intensity which are characteristics of ring based reduction process. Another band at 749 nm emerges and then decreased in intensity. The Soret band at 340 nm and the shoulder at 649 nm decreases in intensity without shift. Clear isosbestic points were recorded at 367 nm, 418 nm, 621 nm and 724 nm. These changes are typical of the ring based reduction and are assigned to the, $[Zn^{II}Pc^{4-}]^{2-}/[Zn^{II}Pc^{3-}]^{1-}$ process. Spectroscopic changes were observed during the controlled potential application at -1.40 V shows further increase in the intensity of Q-band and the B-band at 340 nm had moved onto 343 nm with decreased intensity while a new band at 397 nm raised its intensity. In contrast, a further decreasing in the intensity of the shoulder at 649 nm observed with appearance of a new band appears at 752 nm. The process gives isosbestic point at 365 nm, 630 nm and 728 nm. The spectroscopic changes are easily assigned to the reduction of the mono anionic species, $[Zn^{II}Pc^{3-}]^{1-}$ to dianionic species, $[Zn^{II}Pc^{4-}]^{2-}$, Fig. 3d.

Emission studies

Qualitative evaluation of emission, including quantitative analysis of the fluorescence spectra and determination of the quantum yields (ϕ_f) was performed for TPA-ZnPc in order to understand the effect of peripheral substitution on phthalocyanine macrocycle. Figure 4 demonstrates the emission spectra of TPA-ZnPc in various solvents (toluene, DCM, THF, DMF and DMSO) by exciting at ~ 700 nm. The corresponding emission maxima and quantum yields are presented in Table 1. As it is apparent from data presented in Fig. 4 and Table 1 the emission spectra of TPA-ZnPc is consistent with both the Stokes rule and the rule of mirror symmetry between the absorption and fluorescence bands. It is clear from the data presented in Table 1 the quantum yields are high in

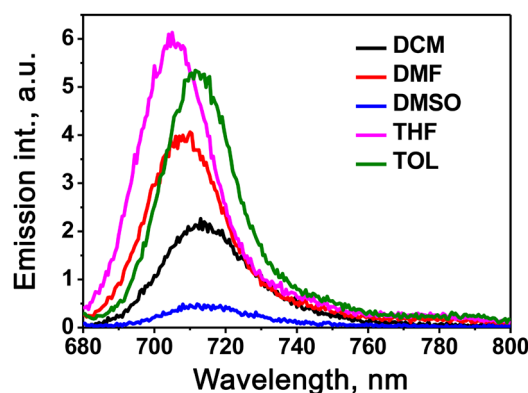


Fig. 4. Emission spectrum of TPA-ZnPc in different solvents

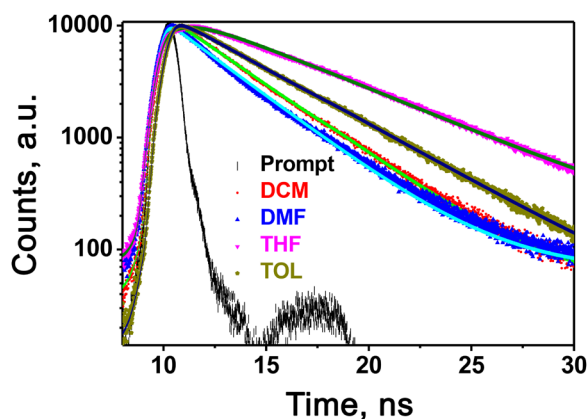


Fig. 5. Fluorescence decay signals of TPA-ZnPc in different solvents

non-coordinating solvents such as toluene and DCM. In contrast, the quantum yields are reduced in coordinating solvents such as THF, DMSO and DMF. A similar effect one can expect even in excited state life time. Figure 5 illustrates the fluorescence decay signals of TPA-ZnPc in

Table 1. Absorption, emission data of **TPA-ZnPc**

Sample	Solvent	λ_{max} , nm (log ϵ) M ⁻¹ .cm ⁻¹ ^a	$\lambda_{\text{em,max}}$, nm ^b	Φ_f ^c	τ_f , ns ^d
TPA-ZnPc	DCM	704 (4.91)	713	0.170	2.33
	DMF	700 (5.29)	710	0.110	2.20
	DMSO	705 (5.14)	714	0.020	<0.20 ^e
	THF	697 (5.30)	705	0.018	3.89
	Toluene	704 (5.18)	712	0.170	2.96

Error limits: λ_{max} , ± 1 nm, log ϵ , $\pm 10\%$. ^b λ_{ex} , ± 2 nm. ^c Φ_f , $\pm 10\%$. ^dError limit of $\tau \sim 10\%$.

^eShort lifetime components are limited by the instrument response function (IRF).

various solvents (toluene, DCM, THF, DMF and DMSO) and corresponding singlet state lifetime data presented in Table 1. We have observed biexponential decay using THF solvent.

Nonlinear optical studies

Figures 6(a) and 6(b) depict the closed and open aperture data, respectively, of **TPA-ZnPc** obtained with ~ 150 fs pulses and at a wavelength of 800 nm. It is evident from Fig. 6(a) that the signature of the nonlinear refractive index (n_2) is negative. Figure 6(b) data clearly suggests the presence of reverse saturable absorption (RSA) and the data was fitted for extracting two-photon absorption (TPA, β) coefficient. In such molecules there is a possibility of excited state absorption (ESA) playing a role in the nonlinear absorption, depending on the excited state vibrational lifetime [lifetime of population within S_1 states implying the time required for population to relax from highest of S_1 states (hot) to the lowest of S_1 states (cold)]. Since the excitation is with ~ 150 fs pulses the contribution of ESA can be ignored in this case and the obtained TPA coefficients represent instantaneous TPA. The magnitude of n_2 and β were estimated to be $\sim 3.0 \times 10^{-11}$ cm²/W and 9.5×10^{-7} cm/W, respectively. The magnitude of $\chi^{(3)}$ was found to be 2.3×10^{-9} e.s.u. Figures 7(a) and 7(b) illustrate the closed and open aperture data, respectively, of **TPA-ZnPc** obtained with ~ 2 ps pulses and at a wavelength of 800 nm. It is evident from Fig. 7(a) that the signature of the nonlinear refractive index (n_2) is positive. Our earlier detailed studies [40–43] on a variety of molecules suggest that such contribution is not very significant when excited with ~ 2 ps pulses. Therefore, we have fitted the data for TPA only. However, the TPA coefficient obtained here should be considered as an effective TPA with small contribution from the excited state absorption, the magnitude of which has to be determined through separate, detailed experiments. With ps excitation the magnitude of n_2 and β were estimated to be $\sim 1.2 \times 10^{-14}$ cm²/W and 15×10^{-11} cm/W, respectively. The magnitude of $\chi^{(3)}$ was found to be

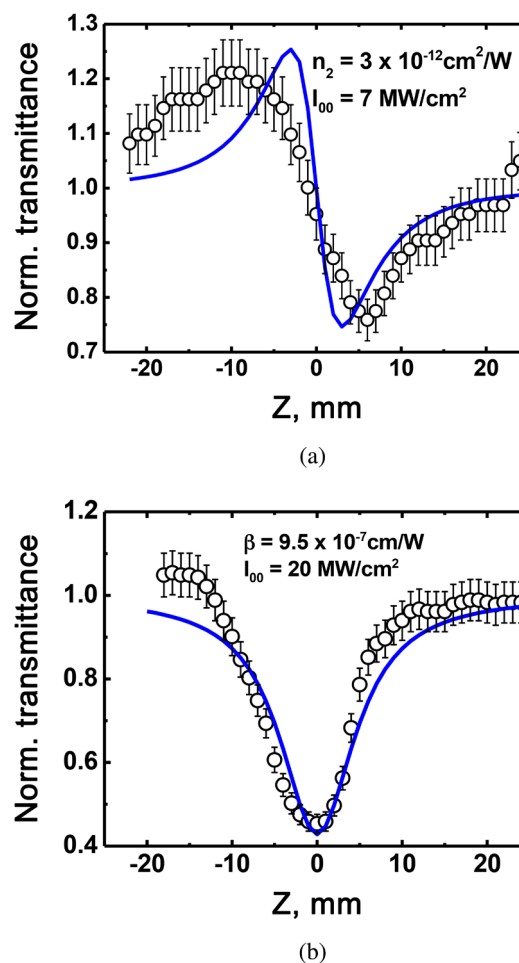


Fig. 6. (a) Closed aperture Z-scan data of **TPA-ZnPc** obtained with ~ 150 fs pulses (b) open aperture data of **TPA-ZnPc** depicting reverse saturable absorption at higher peak intensities of 20 MW/cm²

9.1×10^{-13} e.s.u. The NLO coefficients obtained with fs pulses are superior to those obtained with ps pulses since the repetition rate of fs pulses was 80 MHz while that of ps pulses was 1 kHz, due to which there is a possibility thermal effects dominating in the former case. Even

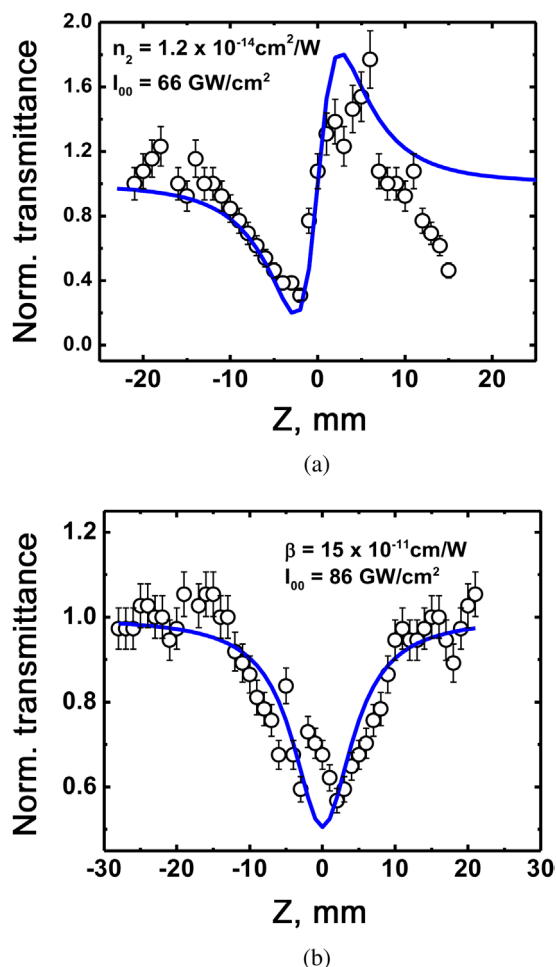


Fig. 7. (a) Closed aperture Z-scan data of TPA-ZnPc obtained with ~ 2 ps pulses clearly depicting negative nonlinearity (b) open aperture data obtained with ps pulses clearly suggesting the presence of reverse saturable absorption

though the 1 kHz measurements are performed with ~ 2 ps pulses, the NLO coefficients observed are one of the highest when compared with some of the recently reported organic molecules. This molecule has a strong absorption

in the visible spectral region of 600–800 nm whereas negligible linear absorption in the 400–600 nm spectral range. In the former case (of strong absorption) these molecules will find applications in saturable absorption based devices whereas in the latter case (negligible linear absorption) their potential could be used for optical limiting and optical switching applications. The NLO coefficients obtained for this molecule are summarized in Table 2 superior to some of the phthalocyanines and porphyrins [25, 26, 40–46] reported by our group previously. For example, we reported a $\chi^{(3)}$ values of $\sim 1.3 \times 10^{-14}$ e.s.u with ps, kHz, 800 nm pulses and $\sim 4.7 \times 10^{-11}$ e.s.u with fs, MHz, 800 nm pulses for a Thio-Zn-Pc [26]. In the case of alkyl phthalocyanines [40] we observed three-photon absorption (3PA) at 800 nm and fs excitation. However, the magnitude of n_2 was $10^{-15} \text{ cm}^2/\text{W}$ with fs, kHz excitation. Similarly, we observed 3PA in alkoxy phthalocyanines with 800 nm fs excitation. With ps, kHz excitation, though, the $\chi^{(3)}$ values were 2–3 times lower [44] than those reported for the molecule used in the present study. In the case of Zn(II)phthalocyanines [25] we observed the magnitude of $\chi^{(3)}$ in the 10^{-14} – 10^{-15} e.s.u. range for ps, kHz excitation and recorded in the spectral range of 640–800 nm. Further, with fs, MHz excitation the magnitudes of $\chi^{(3)}$ for these two phthalocyanines were in the 10^{-10} e.s.u. range (one order of magnitude lower than that of the values reported in this study). As well, we reported the magnitude of $\chi^{(3)}$ for novel porphyrins in the range of 10^{-14} e.s.u. obtained with ps, kHz pulses at 800 nm. The NLO coefficients of porphycenes [45], though, were superior to that of the molecules reported here while the novel corrole [46] molecules investigated by our group possessed coefficients with similar order of magnitude. In comparison with phenoxy phthalocyanines reported by Ma *et al.* [47] the n_2 value obtained in our case (ps case) was an order of magnitude higher than theirs (fs case). We cannot compare our fs n_2 value since this was obtained by using 80 MHz repetition rate pulses. Additionally, by tuning the input intensities and pumping wavelength [48] one could achieve switching

Table 2. Summary of NLO coefficients for TPA-ZnPc obtained with both ~ 2 ps, 1 kHz pulses and ~ 150 fs, 80 MHz pulses. The values in parentheses indicate the peak intensities used for those measurements

Sample	β (cm/W)	n_2 (cm ² /W)	$\chi^{(3)}$ (e.s.u.)
TPA-ZnPc			
Picosecond data (~ 2 ps, 800 nm, 1 kHz)			
	15×10^{-11} (86 GW/cm ²)	1.2×10^{-14} (66 GW/cm ²)	9.1×10^{-13}
Femtosecond data (~ 150 fs, 800 nm, 80 MHz)			
	9.5×10^{-7} (21 MW/cm ²)	3.0×10^{-12} (7 MW/cm ²)	2.3×10^{-9}

of nonlinear absorption (SA to RSA) in such molecules [44–46]. Furthermore, these molecules can be doped in suitable polymers (for *e.g.* we recently reported the NLO studies of a thermally evaporated copper tetra *tert*-butyl phthalocyanine thin film [49]) or glasses and can be utilized for practical device applications since these are very stable molecules. Detailed ps/fs studies (NLO and time-resolved) involving the polymers (solutions and films) of these molecules will be performed in near future.

CONCLUSION

In conclusion, we have explored photophysical, electrochemical, NLO properties of a triphenylamine substituted zinc phthalocyanine. The Soret band was broadened due to the presence of the triphenylamine group and obeyed Beer–Lambert's law. Spectroelectrochemical properties showed that the oxidation and reduction processes were ring centered. NLO properties of **TPA-ZnPc** have been investigated using Z-scan technique with ps and fs pulses. Both open and closed aperture Z-scan curves were recorded with ~2 ps, 1 kHz/~150 fs, 80 MHz laser pulses at a wavelength of 800 nm and large NLO coefficients were extracted from both the studies.

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Supporting information

Scheme S1 and Figs S1–S7 are given in the supplementary material. This material is available free of charge *via* the Internet at <http://www.worldscinet.com/jpp/jpp.shtml>.

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