



Nonlinear absorption and excited state dynamics of porphyrin and phthalocyanine in the presence of explosive molecules



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ARTICLE INFO

Article history:

Received 18 September 2015

In final form 20 October 2015

Available online 25 October 2015

ABSTRACT

Nonlinear absorption (NLA) properties and excited state dynamics of a porphyrin and phthalocyanine in the presence of explosive molecules were investigated using the nanosecond Z-scan and femtosecond pump-probe techniques, respectively. The NLA coefficients I_s and β increased in the presence of explosive molecules. The change in first excited state decay time was evaluated through degenerate pump-probe measurements near 700 nm and it was observed that decay time decreased in the presence of explosive molecules. The reduction in decay time and increase in NLA coefficients varied with different molecules according to their absorption, emission properties and affinity towards the explosive molecule.

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1. Introduction

The scientific community over the last decade has been investigating various analytical methods rigorously to understand the interaction of conjugated organics with nitrated energetic moieties (or explosive molecules) with an aim to discover suitable molecules and methodologies for practical applications in sensing devices [1–4]. A very recent review article articulates the various molecules used (polymers, small and large organic molecules, metal organic frameworks, etc.) and the methodologies developed for detection of explosive molecules [5]. Amongst the investigated lot, organics have been proved to be one of the versatile molecules for sensing a variety of explosive molecules. Most of the conjugated organic moieties such as porphyrins, phthalocyanines, specific polymers, etc. have been reported to demonstrate strong fluorescence quenching when they bind with the energetic moieties [14–23,9,24,25,12,26,27]. There are multitudes of mechanisms which occur during these interactions such as electron transfer, ground state complex formation, charge transfer, etc. [5] which cause changes in the excited state lifetime, excited state cross-section and the formation of aggregates, etc. Many of the organic compounds which are used in explosive sensing are active nonlinear optical (NLO) materials [6–8] and, therefore, any change in the aforementioned properties will directly affect the nonlinear absorption (NLA) properties [e.g. excited state absorption (ESA), saturable absorption (SA), etc.]. Consequently, it is important to

understand the changes in NLA properties of the fluorophore in the presence of nitrated compounds which helps categorize the fluorophore according to their efficacy towards effective explosive sensing. Geng et al. recently reported detection of vapors of explosives and taggants selectively using thin films of light-emitting dendrimers [28]. They observed that the fluorescence quenching was not observed for a range of common interferents. Using a combination of photophysical and other measurements they demonstrated that the origin of selectivity is primarily electronic in nature and not the diffusion kinetics of the analyte or its distribution in the film. It is, therefore, imperative to understand the dynamics of these sensing molecules in presence of the nitrated compounds for designing improved sensing molecules. The major mechanism in explosive sensing is the utilization of the electron withdrawing property of $-\text{NO}_2$ group present in the energetic molecule [9–12]. The presence of $-\text{NO}_2$ not only enables an energetic molecule to release large amount of energy but also alter the photophysical parameters of the organic conjugates with which it interacts.

Several earlier studies were focused on monitoring the luminescence properties of different fluorophores in the presence of a variety of energetic molecules. In energetic molecules (or explosive molecules) the charges are strongly localized on the electron withdrawing nitro groups which favors the formation of several complexes in the presence of π electron rich compounds [13]. These effects vary according to the molecular structure and properties of central metal atom and peripheral moieties. Venkatramaiah et al., e.g., reported on peripherally modified dimethylamine substituted Zn(II)phthalocyanines [4] possessing both electron donating and electron withdrawing substituents

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at their periphery and investigated those molecules towards the detection of nitro-aromatic compounds (including trinitrophenol) in solution and vapor phase. Their detailed experimental studies and density functional theory calculations revealed that the fluorescence quenching behavior occurred through photo-induced electron transfer from the excited state of phthalocyanines to trinitrophenol with static quenching as the predominant mechanism [4]. Gupta et al. recently reported the fluorescence quenching of Zn-Phthalocyanine triad $\{Zn[Pc(O-Bn-CH_3)_4]\}$ in the presence of explosive molecules of picric acid (PA) [26]. They observed that a charge-transfer complex from phthalocyanine derivative (donor) to picric acid (acceptor) was formed through nitrogen atoms. Their derivative demonstrated an efficient and selective fluorescence quenching toward picric acid, during which the compound exhibited a significant morphological change from round spheres to irregularly square-like aggregates [26]. Gupta et al. [27] again reported the fluorescence quenching of an electron-rich phthalocyanine–thiophene–phthalocyanine triad in the presence of PA molecules. They demonstrated that PA molecules interacted with the phthalocyanine molecules through intermolecular π – π interaction and that the photo-induced electron transfer complex arose from the electron-rich pendant phthalocyanine rings to the PA reagents, leading to an efficient fluorescence quenching mechanism. In general, the detection sensitivity can be enhanced by reducing the band gap, size of the molecule, increasing the rigidity of the structure, and possibility of strong intermolecular and π – π interactions with nitrated compounds [29,30]. In this paper, we present the effect of nitrated energetic compounds on the NLA properties of advanced organic molecules of porphyrin and phthalocyanine. We present the results from our detailed studies of NLA and excited state dynamics of an octamethyl porphyrin (OMP) and tetratertbutyl phthalocyanine (Pc) in the presence of explosive molecules [e.g. 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20)] containing electron withdrawing groups using nanosecond (ns) Z-scan and femtosecond (fs) pump probe techniques, respectively. The ns Z-scan measurements revealed the presence, and changes, of saturable absorption and excited state absorption mechanisms, whereas the fs pump probe data provided information on the first excited state decay rates (S_1). Such studies could possibly be extended towards the realization of a simple technique such as open aperture ns Z-scan through quantification of the nonlinear absorption properties and excited state dynamics of a variety of fluorophores which ultimately could lead to the identification of an efficient fluorophore for screening explosive molecules. We also highlight some of the issues related to these and provide suggestions to improve upon the present studies.

2. Experimental details

The ns Z-scan experiments were performed to investigate the interaction of Pc and OMP with nitro-rich compounds such as CL-20, RDX and TNT molecules (henceforth referred to as C, R and T, respectively, through the MS), which are generally referred to as high energy materials/molecules (HEMs). The input laser source was a second harmonic of Nd:YAG laser with ~ 5 ns pulse duration at 10 Hz repetition rate. The input laser beam was focused to a spot size of ~ 14 μ m with a ~ 10.5 cm focal length convex lens. A quartz cuvette of 1 mm thickness was used to hold the sample. The sample was translated using a linear translation stage interfaced to a computer. The fs degenerate pump-probe experiments were performed near 700/690 nm for Pc/OMP solutions. The source was an optical parametric amplifier pumped by a Ti:sapphire amplifier and tunable in the spectral range of 260 nm to 20 μ m delivering ~ 60 fs

pulses at a repetition rate of 1 kHz. The polarization of the pump and probe beams were ensured to be perpendicular using a half wave plate (HWP). The pulse width at the sample was estimated to be 80–90 fs accounting for the pulse broadening due to the optics and focusing lenses involved. The pump and probe beams were focused to the sample in the 5 mm glass cuvette using lenses of ~ 30 and ~ 20 cm focal length, respectively. The zero delay was confirmed by performing autocorrelation in a BBO crystal at 700 nm. The probe transmittance was collected using a Si photodiode. The pump to probe energy ratio was typically maintained at 10:1. The pump pulse energy was ~ 960 nJ while the probe pulse energy was ~ 90 nJ. The experiment was repeated after titrating with C, R, T solutions with a molar ratio of 1:10.

3. Results and discussions

The structures the molecules used in the present study have been reported elsewhere [18,31,32]. The absorption and emission spectra of these molecules are illustrated in Fig. 1. The ns Z-scan experiments were conducted with 0.6 mM Pc solution titrated with C, R, T solutions in molar ratio of $\sim 1:30$ at two peak input intensities of ~ 0.3 and ~ 2.5 GW/cm². Table 1 in supporting information (SI) provides the detailed calculations for different molar ratios of C, R, and T solutions. The ns open aperture Z-scan data obtained from these molecular solutions at 532 nm is presented in Fig. 2. Pc1 represents the ns Z-scan measurements performed with 0.6 mM Pc solution without any addition of the quenching molecules. PcC1, PcR1, PcT1 and PcA1 indicated the ns Z-scan measurements of Pc after adding C, R, T solutions and acetonitrile solvent such that the molar ratio between Pc and the C, R, T solutions were 1:30. Due to dilution effects we could not perform further titrations (which also complicated the analysis). The concentrations of Pc and OMP were optimized so as to maintain a linear transmittance in the 55–65% range. It is evident from the experimental data in Fig. 2 that the signature represents the presence of reverse saturable absorption (RSA) at both the peak intensities, typically observed with ns excitation in such molecules. However, the subtle changes observed in the data were retrieved from the theoretical fits (represented by solid lines) and the magnitude of an effective two-photon absorption coefficient (β_{eff}) was obtained from all the fits. The nonlinear absorption coefficient β_{eff} in this case will be an 'effective two photon absorption' taking into account the transitions occurring through (a) 1 + 1 photon absorption process (via excited state absorption either from singlet states or triplet states) and/or (b) instantaneous/pure two photon absorption [33]. The NLA of Pc was found to be RSA and the nonlinear absorption coefficient

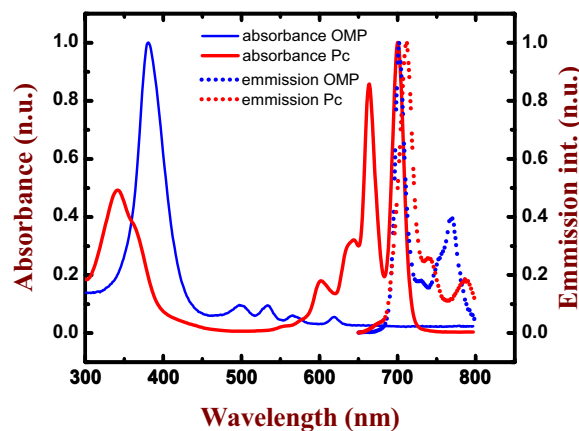


Fig. 1. Absorption and emission spectra of OMP and Pc. The solid lines indicate the absorbance in normalized units and the dashed lines indicate the emission spectra of OMP and Pc. The solvent used for OMP and Pc was chloroform.

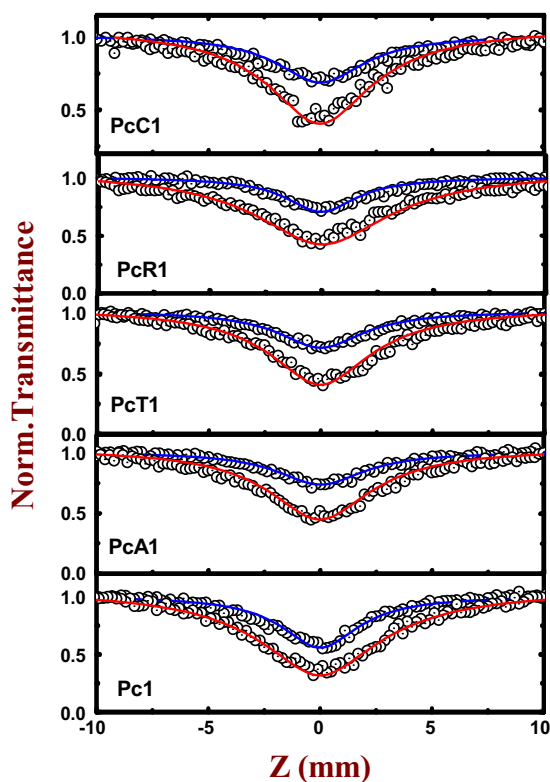


Fig. 2. ns Z-scan measurements of Pc before and after the addition of C, R, T solutions and acetonitrile solvent which was the solvent for the NCs (denoted as Pc1, PcC1, PcR1, PcT1, PcA1, respectively). The blue lines indicate the fit for the data taken at ~ 0.3 GW/cm² and the red lines indicate fit for data taken at ~ 2.5 GW/cm². The concentration Pc solution before the addition was ~ 0.6 mM. After addition of NCs, the concentration of Pc solution was ~ 0.43 mM and that of additives were ~ 14 mM in the mixture.

was extracted by solving the propagation equation $dI/dz' = \alpha_0 I + \beta I^2$, where α_0 is linear absorption coefficient and β is NLA coefficient (complete details of fitting procedure is provided at the end of SI). To understand the concentration dependence, experiments were performed by diluting the 0.6 mM Pc solution (in chloroform) with the same volume of acetonitrile which used as solvent in preparation of C, R, T solutions. The β value was observed to be decreased as we diluted the Pc solution which confirmed the results reported in literature [33]. However, post titration (PcC1, PcR1 and PcT1 with C, R, T solutions in 1:30 molar ratio) we observed a higher value for β which clearly suggests the effect of interaction of these molecules with Pc molecule. The titration, PcA1, with solvent gave β value as ~ 4.4 and ~ 2.4 cm/W at 0.3 and 2.5 GW/cm², respectively. The addition of nitro compounds (NCs) enhanced the β values of (a) PcC1 to ~ 5.7 cm/GW and ~ 3.3 cm/W at 0.3 and 2.5 GW/cm², respectively, (b) PcT1 to ~ 5.0 cm/GW and ~ 2.9 cm/W at 0.3 and 2.5 GW/cm², respectively, (c) PcR1 to ~ 5.0 cm/GW and ~ 2.8 cm/W at 0.3 and 2.5 GW/cm², respectively. The values estimated from these measurements have an error of $\pm 5\%$ owing to the uncertainties in fitting procedures, pulse-to-pulse fluctuations, etc. The changes in coefficients obtained were higher the error bars in these experiments.

In the case of OMP, the ns Z-scan measurements were performed with 0.23 mM (data presented in Fig. 3). The solutions of C, R, T (4.2 mM in acetonitrile) were added and the molar ratio between OMP and the C, R, T solutions were maintained at 1:20. The data clearly suggests the presence of saturable absorption (SA) at lower peak intensities, whereas the behavior switched from SA to RSA at higher peak intensities. The experiment was repeated for 1:40 molar ratio also to understand the concentration effect and results

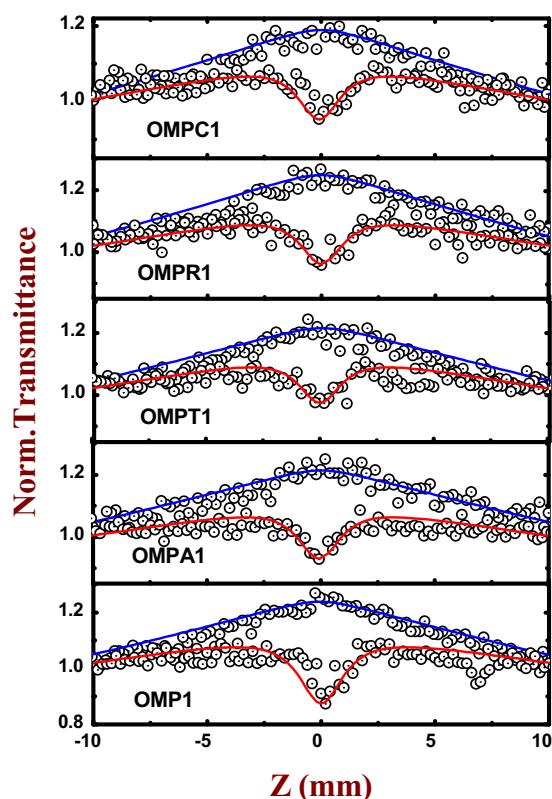


Fig. 3. ns Z-scan measurements of OMP before and after the addition of C, R, T solutions and acetonitrile solvent which was the solvent for the NCs (denoted as OMP1, OMP1C1, OMP1R1, OMP1T1, OMP1A1, respectively). The blue lines indicate the fit for the data taken at ~ 0.3 GW/cm² and the red lines indicate fit for data taken at ~ 2.5 GW/cm². The concentration OMP solution before the addition was ~ 0.2 mM. After addition of NCs, the concentration of OMP solution was ~ 0.2 mM and that of additives were ~ 4.2 mM in the mixture.

from the measurements are shown in SI (Fig. 1 of SI) wherein similar behavior was observed. To understand the concentration dependence, the experiment was performed by diluting the OMP solution at lower (0.3 GW/cm²) and higher (2.5 GW/cm²) peak intensities which are indicated as OMPA1 in Fig. 3. The same volume of solvent (acetonitrile) was added and we observed that the NLO coefficients for OMPA1 decreased when compared to the coefficient of original solution OMP1. When the NCs were added there was a reverse trend observed in the data. The I_s [33] value of OMP decreased from 3×10^6 W/cm² (OMP1) to 2.0×10^6 W/cm² (OMPA1) upon addition of acetonitrile. The I_s value of OMP after the addition of acetonitrile was compared with that of OMP with the addition of C, R, T solutions and found that it increased from 2.0×10^6 W/cm² (OMPA1) to 2.8×10^6 W/cm² (OMPR1). At higher peak intensities the I_s value increased whereas the β value decreased. A similar trend was observed in the studies performed with 1:40 molar solutions.

3.1. fs degenerate pump probe measurements

The degenerate pump probe measurements were performed in the emission band of the corresponding molecules. Fig. 4 depicts the fs pump probe measurements of Pc at 700 nm with and without the presence of the binder molecules. Pc2 represents the fs data of Pc solution of 0.6 mM concentration without adding the quencher solutions and PcR2, PcT2, PcC2 represent the measurements of Pc after adding C, R, T solutions, respectively. The differential transmittance demonstrated a positive rise followed by the decay of signal. Though the probe wavelength was within emission band, Pc still had resonance absorption at 700 nm which suggests that

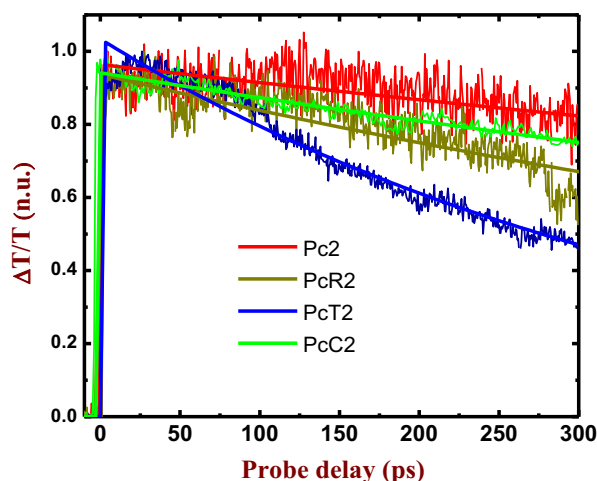


Fig. 4. Degenerate fs pump probe measurements (near 700 nm) of Pc solution before and after adding C, R, T solutions (denoted as Pc2, PcC2, PcR2, PcT2, respectively). The concentration of Pc solution was ~ 0.6 mM (in Pc2) and after the addition of NCs the concentration of Pc was ~ 0.3 mM and that of NCs were ~ 5 mM. Wiggly lines are the experimental data while the solid lines are the theoretical fits.

Table 1
The non-radiative decay constants from fs pump probe measurements.

Sample	τ_1 (ps)	τ_2 (ps)		τ_1 (ps)
OMP2	11	270	Pc2	1900
OMPR2	1.8	129	PcR2	896
OMPT2	2.0	170	PcT2	381
OMPC2	9.0	153	PcC2	1300

the pump probe signal had contribution from photo bleach (PB) as well as stimulated emission (SE). Bellier et al. recorded similar observations in which the one photon absorption was strongly dominated by stimulated emission [34]. The decay profile was fitted with a single exponential function. The decay constant provided the rate of change of excited state population and it decreased as we added the quencher molecules. The decay constants obtained from the fits to experimental data are summarized in Table 1. The Pc demonstrated a decay constant of ~ 1.9 ns (Pc2) which quenched to ~ 381 ps (PcT2) in the presence of TNT solution. Kumar et al. have reported that these phthalocyanine molecules possessed radiative lifetime of ~ 6.3 ns [31]. The lifetime measured with our pump-probe experiments probably has predominant contribution from the radiative decay part (S_1 to S_0) with contribution from non-radiative part also [35]. Fig. 5 illustrates the pump-probe data OMP solution before and after adding C, R, T solutions (denoted as OMP2, OMPC2, OMPR2, OMPT2, respectively). The data was fitted to a double exponential decay. The fast decay could be attributed to the inter-molecular vibrational relaxation from high lying excited states to the lowest lying excited state and the slow decay could be assigned to the relaxation from S_1 (first excited) states to the S_0/T_0 (ground) states. Both the decays were affected by the addition of nitro-compounds. The fast decay time was observed to be quenched from ~ 11 ps (OMP2) to ~ 1.8 ps (OMPR2) and the slow component was modified from ~ 270 ps (OMP2) to ~ 129 ps (OMPR2). Earlier we had reported the radiative lifetime of OMP to be ~ 3.77 ns [6,19]. Again, there could be contributions from radiative (S_1 to S_0) and non-radiative decays (S_1 to T_0 intersystem crossing and S_1 to S_0 non-radiative decay by supplying energy to solvent) involved in these data, which we were unable to decouple from the present pump probe measurements.

Typically, ns pulse excitation involves transitions from S_0 levels to S_1 levels with cross-section σ_{S_0} and S_1 states to S_n states with cross-section σ_{S_1} [36]. The subsequent relaxation may include

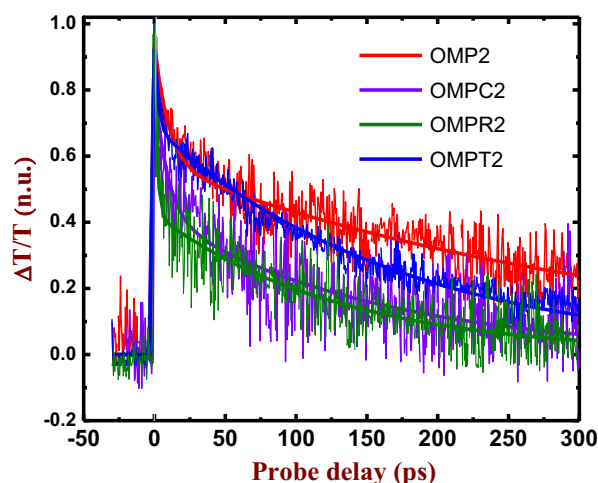


Fig. 5. Degenerate fs pump probe measurements (near 690 nm) of OMP solution before and after adding C, R, T solutions (denoted as OMP2, OMPC2, OMPR2, OMPT2, respectively). The concentration of OMP solution was ~ 1 mM (in OMP2) and after the addition of NCs the concentration of OMP was ~ 0.5 mM and that of NCs were ~ 5 mM. Wiggly lines are the experimental data while the solid lines are the theoretical fits.

transition from S_n states to S_1 states which is very fast compared to the duration of input pulse (ns) and from S_1 states the molecule may undergo internal conversion to S_0 through radiative and/or non-radiative transitions. There is also a possibility of intersystem crossing from S_1 states to a triplet state, T_0 , depending on the spin orbit coupling. The triplet states (T_1) are generally populated through intersystem crossing from S_1 states to T_0 states. During fluorescence quenching the lifetime of S_1 is reduced and, therefore, the population in S_1 state gets transferred to either S_0 or T_0 (through non-radiative means). We summarize the following from our experimental data and a qualitative analysis.

- We observed that the ' β ' value increased in the case of PcR1, PcT1 and PcC1 (i.e. in the presence of the quencher molecules) when compared with PcA1. We believe that the change in life time of S_1 state and the excited state cross-sections play an equally important role in such interactions. In the presence of quencher molecules the lifetime of S_1 state was reduced (supported by the pump-probe data) which suggests the increase in possibility of population being transferred to triplet states [see an effective energy level diagram (Fig. 2 of SI) of such molecules in the presence and absence of an explosive molecule]. In such molecules it is well established that triplet state cross-sections are stronger than the singlet state cross-sections and moreover the excitation is with ns pulses in the present case. Therefore, the triplet cross-section influences the population in excited state and we observe an increase in the β (an effective NLA coefficient) value. In the possible scenario of population coming back to ground state via non-radiative decay only (i.e. no triplet contribution) the NLA coefficient should have decreased, which was not observed in our case.
- The decrement of S_1 state lifetime (due to quenching of fluorescence) in the presence of explosive molecules causes an increase in I_s (higher intensity is required to saturate the excited state) and it was observed experimentally from the open aperture Z-scan data for OMP molecule (lower peak intensities).
- In the case of higher peak intensity studies for OMP, SA and RSA were simultaneously observed and I_s , β were obtained from the fits to experimental data. The I_s value increased and the β value decreased. Here, the formation of RSA could be due to the transition of population from S_1 to S_2 states (and T_0 to T_n states) since higher peak intensities are involved. However, in the presence

Table 2
NLO coefficients obtained from ns Z-scan measurements.

Sample	1:30 (molar ratio)		Sample	1:20 (molar ratio)		
	$I_{00} = 0.3 \text{ GW/cm}^2$			$I_{00} = 0.3 \text{ GW/cm}^2$		$\beta \text{ (cm/W)} \times 10^{-10}$
	$\beta \text{ (cm/W)} \times 10^{-8}$	$\beta \text{ (cm/W)} \times 10^{-8}$		$I_s \text{ (W/cm}^2) \times 10^6$	$I_s \text{ (W/cm}^2) \times 10^5$	
PcR1	5.0	2.8	OMPR1	2.8	9.0	7.3
PcT1	5.0	2.9	OMPT1	2.1	9.0	6.7
PcC1	5.7	3.3	OMPC1	2.4	9.0	7.2
PcA1 (acetonitrile)	4.4	2.4	OMPA1 (acetonitrile)	2.0	8.0	9.4
Pc1 (chloroform)	10	5.5	OMP1 (chloroform)	3	9.0	12

of quencher molecule, this transition gets weakened and the β value decreases with I_s value increasing simultaneously.

- (d) From the data presented in Table 1 (life time data) and the Table 2 (NLO coefficients) it is evident that the largest change in nonlinear absorption was observed for Pc molecules with the presence of TNT and CL-20 (for both the input peak intensities) and, correspondingly, the largest change in life times was also observed for PcT2 and PcC2 (though PcR2 also demonstrated large change in lifetime). Similarly, the largest change in NLO coefficients (for both lower and higher peak intensities) was observed for OMP with R and C and, consistently, the largest change in lifetime was observed for OMPR2 and OMP2. This clearly suggests a strong correlation between the quenching dynamics and the nonlinear absorption in Pc and OMP in the presence of explosive molecules. We cannot rule out the possibility of fluorescence quenching and reduction in lifetimes of S_1 state due to aggregation related effects. With limited data at our disposal we cannot completely rule out the possibility of aggregation. Further detailed studies are essential for supporting these arguments.
- (e) We had performed simulation experiments (data presented in Fig. 3 of SI) and the results could qualitatively explain the increase in NLA coefficients in the presence of explosive molecules.
- (f) We had also performed steady-state fluorescence measurements of OMP and Pc (data presented in Figs. 4–7 of SI). The fluorescence of OMP was quenched when titrated with T, R, C and results were in accordance with previous report [19] while the magnitude of quenching in Pc was not as significant as that of OMP. These experiments had been conducted only at lower concentrations of typically $6 \mu\text{M}$. At higher concentrations ($100 \mu\text{M}$ and above) the emission will also be quenched for different reasons (e.g. aggregation). Further, at similar concentrations (to those used in Z-scan and pump-probe experiments) we could observe formation of complexes [26] in these molecules rendering the data unfit for comparison and analysis.

It has been recently reported that the quantum of quenching depends on the type of explosive molecule [4,26,27]. Further studies with a range of explosive molecules (e.g. picric acid where the quenching has been observed to be significant with different porphyrin and phthalocyanine molecules [26,27]) are required to completely understand the quenching mechanism. Detailed measurements with white light probe are required to thoroughly understand the complex excited state dynamics. Fluorescence quenching, Z-scan, pump-probe measurements should be performed at similar concentrations (avoiding aggregation and other unwanted effects such as complex formation) and support from simulations will unquestionably provide an insight into the correlation between quantity, type of explosive molecule's role in the nonlinear absorption changes expected. Furthermore, if these fluorophores (porphyrins, phthalocyanines) are appropriately designed and thoroughly optimized the Z-scan could be a potential technique for screening explosive molecules.

4. Conclusions

In summary, we have attempted studying the dynamics of fluorophore and nitro rich energetic molecules using ns Z-scan and fs pump probe techniques. Being an NLO active material, OMP found to exhibit SA at lower energies and RSA in SA at higher energies whereas tetratertbutyl phthalocyanine was showing RSA. The NLO coefficients, I_s and β were observed to be changing in the presence of quencher molecules and the non-radiative decay was found to be reduced in all cases. The mechanisms of SA and RSA in the presence of quencher molecules were explained in detail. A deeper understanding of excited state dynamics is required for transforming these studies into sensing applications.

Acknowledgements

Authors thank DRDO, Government of India for continued financial support. APT acknowledges CSIR for financial support. We thank Dr. A. Rana and Dr. P.K. Panda, School of Chemistry, University of Hyderabad for the porphyrin sample and Dr. L. Giribabu, ICT, Hyderabad for the phthalocyanine sample.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:10.1016/j.cplett.2015.10.049.

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