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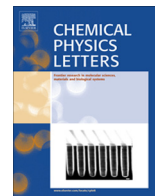


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# Dispersion studies of optical nonlinearity and excited state dynamics in cyclo[4]naphthobipyrroles



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## ABSTRACT

Herein we present results from the dispersion studies of nonlinear optical (NLO) properties of three novel cyclo[4]naphthobipyrroles at wavelengths of 600 nm, 640 nm, 680 nm, and 800 nm using picosecond (ps) pulses. NLO coefficients were extracted from Z-scan measurements using  $\sim 1.5$  ps pulses. Large two-photon absorption cross sections in the range of  $0.2\text{--}5.2 \times 10^4$  GM and  $n_2$  values of  $\sim 10^{-16}$  cm<sup>2</sup>/W were recorded for these moieties. The excited state decay dynamics were investigated using degenerate pump-probe experiments with  $\sim 70$  femtosecond pulses near 600 nm. Double exponential fits of the pump-probe data suggested two decay times for all the molecules investigated.

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## 1. Introduction

Several novel organic moieties with strong two-photon absorption (2PA) and three-photon absorption (3PA) coefficients/cross-sections have been investigated over the last decade due to their impending applications in the fields of photonics, biomedical applications, lithography etc. [1–14]. However, most of those investigations were confined to a single wavelength in the visible spectral region (800 nm or 532 nm) while using single pulse duration [femtosecond (fs) or nanosecond (ns)]. Multi-photon absorption in organic materials typically occurs at longer wavelengths ( $\geq 800$  nm) providing noteworthy advantages such as (a) minimal light losses due to scattering and (b) decrease in superfluous linear absorption. Our group has been working extensively over the last decade investigating several new molecules (e.g. Phthalocyanines, Porphycenes, Corroles etc.) for quantifying their nonlinear optical (NLO) coefficients/cross-sections over a range of wavelengths in the visible spectral region and using cw/ns/ps/fs pulses [15–26]. In the last two decades expanded porphyrins have emerged as a new class of attractive compounds because of their potential applications in near infrared (NIR) dyes, anion sensors, 2PA materials, photosensitizers, and in photodynamic therapy (PDT) [14,17,27]. A large array of expanded porphyrins can be prepared by increasing the number of pyrrole or other hetero-aromatic compounds apart from tuning their number of bridging meso-carbons. Furthermore, it was observed that aromatic expanded porphyrins display large third order nonlinear optical response while normal porphyrin monomers exhibit small  $\sigma_2$  values of  $<100$  GM [12–14].

Similarly, porphycenes (isomers of porphyrins) possess slightly higher  $\sigma_2$  values compared to the parent isomers i.e. porphyrins [14]. However, upon  $\beta$ -fusion of naphthalene at its periphery, through its constituent bipyrrolic units, we observed a large enhancement of NLO response in dinaphthoporphycenes [15–17]. Therefore, in order to assess the effect of this naphthalene fusion (by both rigidification and  $\pi$ -extension), we chose to explore the NLO response of our recently reported cyclo[4]naphthobipyrroles, a unique class of cyclo[8]pyrroles, which are expanded porphyrins displaying the classic disk like structure of simple porphyrins with  $30\pi$  electrons [28,29]. The cyclo[8]pyrrole molecule can be derived by replacing all four meso-carbon bridges of porphyrin with four additional pyrrolic rings. Consequently, these molecules contain direct linkage between the  $\alpha$ -pyrrolic positions, which imparts rigidity to the molecule thereby making a near planar arrangement despite having expanded core compared to porphyrins. The significance of these compounds is encompassed in their novel photophysical and NLO properties. The fusion of alternate pyrrole units with naphthalene moieties adds rigidity to cyclo[8]pyrroles along with extended  $\pi$ -conjugation resulting in the formation of cyclo[4]naphthobipyrroles. Sarma et al. [28] reported that the cyclo[4]-naphthobipyrrole moiety is very sensitive to the nature of the substituents at its periphery owing to the involvement of large number of non-bonding interactions. Due to their near planar structure, possessing a large aromatic core ( $30\pi$ -electrons) with extended  $\pi$ -conjugation, they are expected to possess strong third-order optical nonlinearity. The number of  $\pi$  electrons and/or the molecular geometry associated with the static and dynamic polarizability of these molecules can be considered as determining parameters in controlling the NLO susceptibility.

Herein we present results from (a) dispersion studies of nonlinear optical properties (studied using Z-scan technique) at

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wavelengths of 600 nm, 640 nm, 680 nm, and 800 nm and (b) excited state dynamics (studied near 600 nm using fs pump-probe technique) of three novel cyclo[4]naphthobipyrroles namely, octa-isopropylcyclo[4]naphthobipyrrole (herewith named as 5a), octa-*n*-propylcyclo[4]naphthobipyrrole (herewith named as 5b), and octa-*n*-pentylcyclo[4]naphthobipyrrole (herewith named as 5c). Initial NLO data of sample 5a have been presented in one of our earlier works [31]. The synthesis and NLO properties of 5a were studied by Sessler group [29]. They obtained significantly large and practically useful  $\sigma_2$  values in the range of 1000–2400 GM in the spectral regions of 1800–2400 nm when excited with fs pulses. They also observed fast lifetimes for singlet excited state in their pump-probe/transient absorption measurements. Our group has recently synthesized three molecules with different peripheral substituents and attempted studying their NLO properties. Interestingly, unlike other porphyrinoids, these molecules have strong absorption in the near infrared (1100 nm) wavelengths and comparatively weaker absorption in the UV spectral band (430 nm), which entitles them for niche applications such as optical storage, processing and signaling devices [30]. Furthermore, dispersion studies of NLO properties are essential to identify the potential of any new molecule designed. For example, depending on the non-linear absorption behavior at different wavelengths one can find apposite applications. Saturable absorption finds relevance in mode-locking; 2PA/3PA finds applications in biological imaging and lithography; excited state absorption (ESA) finds applications in optical limiting etc. The understanding of excited states lifetimes in such molecules is essential for various applications such as PDT, optical switching etc.

## 2. Experimental details

Complete synthetic details of cyclo[4]naphthobipyrroles are discussed elsewhere [28]. The ps Z-scan [32] measurements were performed at wavelengths of 600 nm, 640 nm, 680 nm, and 800 nm. The laser source was Ti:sapphire laser system (picosecond LEGEND, Coherent) delivering nearly transform-limited pulses of  $\sim 1.5$  ps duration and repetition rate of 1 kHz. The pulse duration (at 800 nm) was determined by external autocorrelation technique, by using 2 mm thick BBO crystal in a non-collinear geometry. From the auto correlation trace (See SI) pulse duration was estimated to be  $\sim 1.5$  ps (FW1/e<sup>2</sup>M). The pulses other than 800 nm were derived from an optical parametric amplifier (Light conversion, TOPAS) operating again at 1 kHz. A 200 mm focal length lens was used to focus the beam and the sample is scanned along the laser beam direction (Z-axis). The thickness of sample cell was 1 mm. The initial diameter of the beam was 3 mm. The sample was dissolved in chloroform and made to  $\sim 0.062$  mM corresponding to a linear transmittance of 60–70% in all the cases. The degenerate pump-probe experiments were carried out at 600 nm with pump-probe power ratios ranging from 20 to 50. The probe diameter was  $< 1$  mm and was always within the pump diameter of  $\sim 3$  mm. Data was acquired through the photo diode and lock-in amplifier. Complete details of both these experiments are detailed in our earlier works [15–17,33–36].

## 3. Results and discussions

The inset of Figure 1 illustrates the structure of the compounds investigated in the present study. UV–Vis–NIR absorption spectra of 5a–c are depicted in Figure 1. The complete description of the features observed is reported in our earlier work [28]. Open/closed aperture Z-scan data of 5a has been presented earlier by us [31]. While the report by Roznyatovskiy et al. [29] on 5a focused in the 1800–2400 nm spectral regions, we focused our efforts in the visible spectral range. Figure 2 shows typical open aperture Z-scan

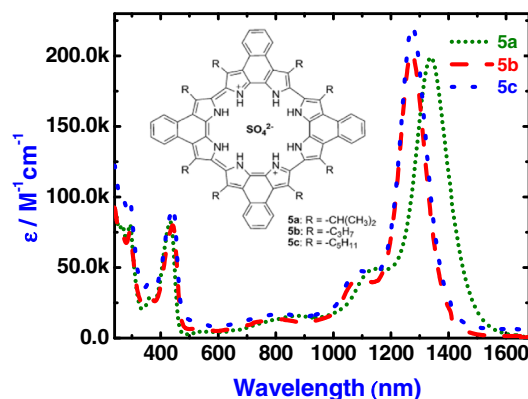


Figure 1. UV–visible absorption spectra of 5a–c. Structures are shown in the inset.

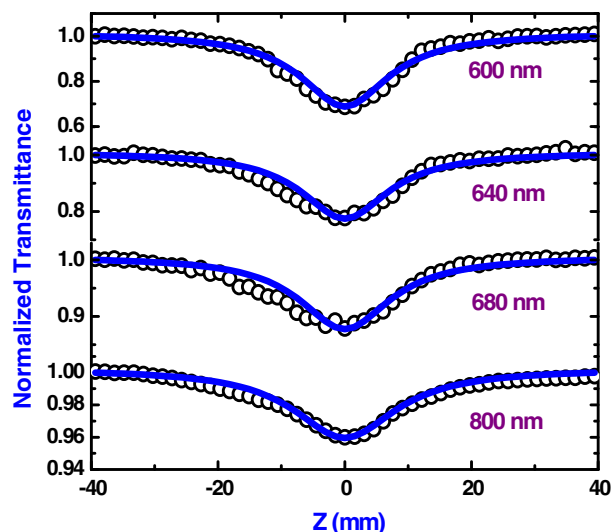


Figure 2. Open aperture Z-scan data of 5b at different wavelengths. Open circles are the experimental data while the solid lines are theoretical fits.

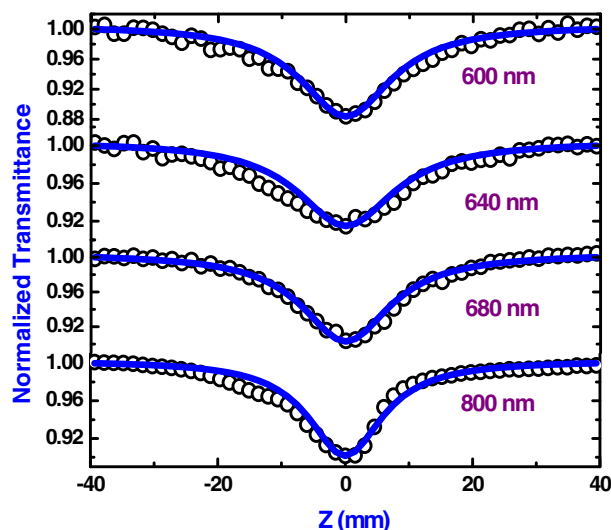
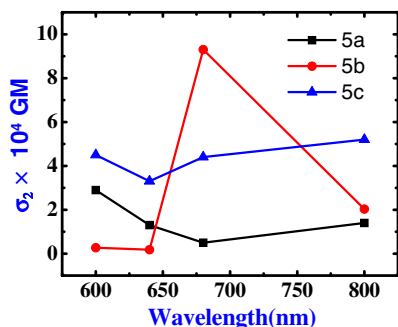


Figure 3. Open aperture Z-scan data of 5c at different wavelengths. Open circles are the experimental data while the solid lines are theoretical fits.

data of 5b obtained at wavelengths of (a) 600 nm (b) 640 nm (c) 680 nm and (d) 800 nm. All the data exhibited a valley near  $Z = 0$ . The data was fitted by conventional Z-scan analysis in which the propagation equation was solved.

**Table 1**Summary of nonlinear optical coefficients and cross sections of 5a–c. The values in parenthesis are peak intensities in GW/cm<sup>2</sup>.

| $\lambda$ (nm) | 5a                               |                                | 5b                               |                                | 5c                               |                                |
|----------------|----------------------------------|--------------------------------|----------------------------------|--------------------------------|----------------------------------|--------------------------------|
|                | $\beta$ (cm/W) $\times 10^{-11}$ | $\sigma_2$ ( $\times 10^4$ GM) | $\beta$ (cm/W) $\times 10^{-11}$ | $\sigma_2$ ( $\times 10^4$ GM) | $\beta$ (cm/W) $\times 10^{-11}$ | $\sigma_2$ ( $\times 10^4$ GM) |
| 600            | 3.20 (122)                       | 2.90                           | 0.15 (133)                       | 0.40                           | 3.35 (133)                       | 4.50                           |
| 640            | 1.50 (129)                       | 1.30                           | 0.11 (117)                       | 0.22                           | 2.65 (117)                       | 3.30                           |
| 680            | 0.62 (114)                       | 0.50                           | 5.80 (103)                       | 9.70                           | 3.65 (103)                       | 4.40                           |
| 800            | 1.50 (58)                        | 1.50                           | 2.15 (62)                        | 5.00                           | 5.60 (62)                        | 5.20                           |

**Figure 4.** Spectral dependence of  $\sigma_2$  in 5a–c. Squares represent 5a data, circles represent 5b data and triangles represent 5c data. The solid line is only a guide to the eye.

The open aperture Z-scan data have been fitted by using the following equations [15–18,20]:

$$I_{00} = \frac{2E}{\pi^{3/2} w_0^2 (HW \frac{1}{e} M) \tau_p (HW \frac{1}{e} M)}$$

$I_{00}$  is peak intensity at focus,  $E$  is the input pulse energy,  $\tau$  is the pulse duration,  $2w_0$  is the beam diameter at focus.

The propagation equation is:  $\frac{dI}{dz} = -\alpha(I)I$  where  $\alpha(I) = \alpha_0 + \beta I$

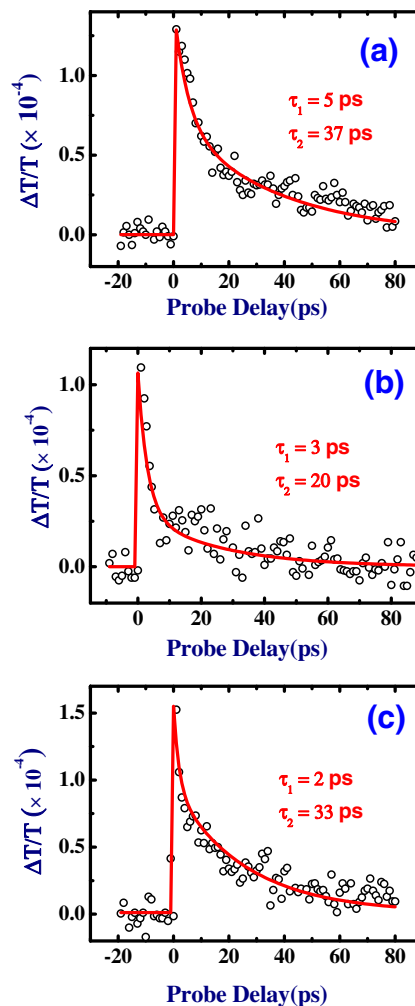
When the process is 2PA the following equation is obtained:

$$T_{OA}(z) = \frac{1}{\pi^{1/2} q_0} \int_{-\infty}^{\infty} \ln[1 + q_0 e^{-x^2}] dx$$

where  $T_{OA}(z)$  is the normalized transmittance as a function of  $z$ ,  $q_0 = \beta I_0 L_{eff}$ ,  $\beta = 2$ PA coefficient and  $I_0$  is the intensity,  $L_{eff} = \frac{1 - e^{-\alpha_0 L}}{\alpha_0}$ , are effective path lengths in a sample of length  $L$  and  $\alpha_0$  is the linear absorption coefficient.

One approach to identify the presence of ESA is to record the intensity dependent  $\beta$ . If  $\beta$  increases with input intensity it suggests the presence of higher order nonlinear absorption [22]. If  $\beta$  remains constant with input intensity it is fair to assume that the process is purely 2PA. If  $\beta$  decreases with intensity (which will be the most probable case with ns excitation) it suggests the presence of an ESA [24] and one requires rate equations [21,37,38] to solve for the NLO coefficients including both ESA and 2PA. Intensity dependent analysis of  $\beta$  (see SI) in our case demonstrated that 2PA, rather than ESA, was indeed the cause of decrease in transmittance. Furthermore, slopes calculated from the plots of  $\ln(I_{00})$  versus  $\ln(1 - T_{OA})$  yielded values close to 1 indicating the presence of 2PA [38].

The values of  $\beta$  evaluated for 5b were in the range of  $0.11$ – $5.80 \times 10^{-11}$  cm/W and the corresponding  $\sigma_2$  values were in the range of  $0.22$ – $9.70 \times 10^4$  GM. Figure 3 shows the open aperture data of 5c in the 600–800 nm spectral range and the values were in the range of  $2.65$ – $5.60$  cm/GW and the corresponding  $\sigma_2$  values were in the range of  $3.30$ – $5.20 \times 10^4$  GM. The values of  $\beta$  for 5a were in the range of  $0.62$ – $3.20$  cm/GW and the corresponding  $\sigma_2$  values were in the range of  $0.50$ – $2.9 \times 10^4$  GM. Summary of NLO coefficients obtained from the fits are provided in Table 1. These values are at least one order of magnitude higher than those

**Figure 5.** Femtosecond degenerate pump probe data of 5a–c recorded at 600 nm indicating two lifetimes. Open circles are the experimental data while the solid (red) lines are double exponential fits. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

reported earlier [29]. This could possibly be due to experiments being performed in the visible spectral region with residual absorption compared to the NIR region. The largest value of  $\sigma_2$  was observed for 5b at a wavelength of 680 nm. The closed aperture Z-scan data of all the molecules [see Supporting information (SI)] demonstrated that these molecules exhibited negative nonlinearity. The peak intensities used were lower than those used in open aperture case so as to avoid higher order contributions. The solvent contribution was minimal (<2%) in the open aperture case at the respective peak intensities. The magnitudes of  $n_2$  were in the range of  $1.9$ – $11 \times 10^{-16}$  cm<sup>2</sup>/W with 5c exhibiting the highest  $n_2$  of  $11 \times 10^{-16}$  cm<sup>2</sup>/W at a wavelength of 680 nm. Closed aperture data of the solvent (See SI) provided a value of  $2.8 \times 10^{-16}$  cm<sup>2</sup>/W but, most importantly, the sign was opposite to that of the solution

suggesting that the actual value of solutes could be higher than values estimated and presented here. SI provides the closed aperture data of 5a, 5b, and 5c obtained at different wavelengths and summarizes the  $n_2$  values retrieved from closed aperture data. From  $n_2$  and  $\beta$  we could estimate the real, imaginary, and total magnitude of  $\chi^{(3)}$  and the second hyperpolarizabilities ( $\gamma$ ) and corresponding figures of merit [detailed information and calculations are presented in SI]. The values of NLO coefficients presented in this work are within an error of  $\pm 15\%$ , which basically arises from (a) estimation of input beam diameter; beam waist; peak intensities (b) calibration of neutral density filters (c) fitting procedures etc. The 2PA coefficients are plotted against wavelength and the data is presented in Figure 4. The two photon resonance corresponding to 600 nm excitation is  $\sim 33333\text{ cm}^{-1}$  whereas for an 800 nm photon it is  $25000\text{ cm}^{-1}$ . Except for the molecule 5b, variation in  $\beta$  with wavelength was minimal. While 5b exhibited strongest  $\beta$  at 680 nm, 5c exhibited strongest  $n_2$  at 680 nm compared to others. However, 5c exhibited highest  $\beta$  at 600, 640 and 800 nm compared to 5a and 5b. The difference in the structures is the presence of isopropyl in 5a, n-propyl in 5b, and n-pentyl groups in 5c at the  $\beta$ -pyrrolic positions. The increase in strength of nonlinearity could be attributed to the increased conjugation from 5a to 5c, owing to increased planarity, as the neighbouring isopropyl substituents exert more non-bonding interaction compared to n-alkyl analogues [28]. The magnitudes of two-photon cross-sections obtained from these studies are comparable to some of the recently reported successful molecules. De Boni et al. [5] investigated perylene derivatives with two-photon cross-sections of typically 200–1200 GM obtained using 190 fs pulses. Andrade et al. [7] studied cytochrome solutions possessing two-photon cross-sections with a maximum value of 1000 GM using fs pulses. Sarma et al. [15] reported two-photon cross-sections in dinaphthoporphycenes in the range of  $10^4$ – $10^5$  GM obtained with ps pulses. Even though our present studies were also carried out with  $\sim 1.5$  ps

pulses the values obtained ( $\sim 10^3$ – $10^4$  GM) are superior to many of the recently reported ones. This is corroborated by the fact that values obtained with shorter pulses and at longer wavelengths were in the  $10^3$  GM range [29].

Figure 5 shows the degenerate pump-probe data of 5a–c obtained at 600 nm using  $\sim 70$  fs pulses with typical pump energies of  $\sim 10\text{ }\mu\text{J}$ . The data was fitted for a double exponential [17,20] and two lifetimes ( $\tau_1$  and  $\tau_2$ ) were retrieved from each of the fits. The values of  $\tau_1$  and  $\tau_2$  were 5 and 37 ps for 5a; 3 and 20 ps for 5b; and 2 and 33 ps for 5c, respectively. Figure 6 shows a simplified energy level diagram indicating the excitations and decay times for these molecules. Excitation with focused 600 nm photons enables 2PA resulting in populating the  $S_2$  states. The de-excitation mechanism, then, could be from (a) lowest vibrational state of  $S_2$  manifold to highest vibrational states of  $S_1$  manifold (Internal Conversion, IC) followed by intra-molecular vibrational relaxation (IVR) from highest states of  $S_1$  to lowest states of  $S_1$ ). However, we could not resolve these two lifetimes in our present data while we could in the case of porphycenes [17]. These are typically fast processes ( $<1$  ps for IC,  $\sim 1$ –3 ps for IVR) and, therefore, the shorter lifetimes observed in pump-probe data (3–5 ps) could be attributed to this relaxation and (b) from the lowest vibrational states of  $S_1$  manifold the molecules relax to ground state via non-radiative mechanism by releasing the energy to solvent (also called as vibrational cooling). This process typically occurs in few tens of ps in such molecules. The longer lifetime can be associated with such a process in 5a–c. Radiative lifetimes in similar molecules are typically few ns [20]. The pump-probe studies of 5a were carried out at 0.062 mM while that of 5b and 5c were carried out at  $10^{-4}$  M and at these concentrations we did not observe any aggregation effects (confirmed from absorption spectral studies) and, therefore, we can neglect the inter-molecular contributions to the lifetimes observed. Our initial ESR studies carried out recently suggest that the triplet ground state could be much closer to the

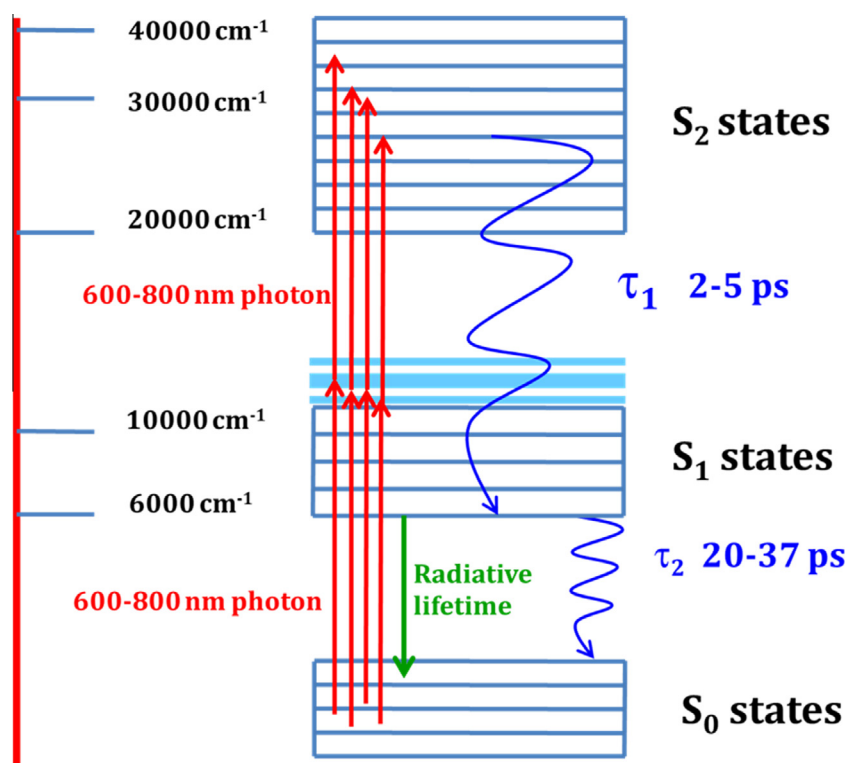


Figure 6. Schematic of energy level diagram of 5a–c explaining the double exponential behavior ( $\tau_1$  and  $\tau_2$ ) observed in pump-probe data.



singlet ground state and there could be a possible contribution of this to the longer decay times observed. However, further detailed studies (such as non-degenerate pump-probe and transient absorption) are essential to exactly identify the complicated decay dynamics in these molecules.

There are several studies which identify such processes in similar molecules [39–41]. Fita et al. [39,40] studied few zinc phthalocyanines and observed 10–50 ps time scale dynamics which were characteristic of the vibrational cooling (relaxation to ground state by transfer of heat to the solvent) from the  $S_1$  state. Kullmann et al. [41] working with a bisporphyrin recorded four different lifetimes. The fastest lifetime (100's of fs) was assigned to intramolecular vibrational relaxation within the  $S_2$  states, second fastest lifetime (few ps) to the decay of  $S_2$  states, slower lifetime (few tens of ps) to the cooling dynamics (non-radiative). These cyclo[4]naphthobipyrroles, particularly 5a (owing to its good solubility), are of great importance for realistic applications as NIR dyes, apart from their potential utility in light harvesting, dye-sensitized solar cells, bio-imaging, and optical limiting and switching applications. Our future studies will focus on incorporating these molecules in a suitable, transparent polymer and extend the studies of NLO coefficients evaluation and excited state dynamics over the entire visible spectral range.

#### 4. Conclusions

The NLO properties of cyclo[4]naphthobipyrroles, a novel class of materials belonging to  $30\pi$ -aromatic cyclo[8]pyrrole family, are explored. Two-photon absorption was the dominant mechanism observed in these molecules. Strong NLO coefficients (and corresponding two-photon cross-sections) were observed in the 600–800 nm spectral range from the data recorded with  $\sim 1.5$  ps pulses. Excited state dynamics studied using fs pump-probe technique revealed the presence of two lifetimes. The shorter lifetime was assigned to the non-radiative relaxation from lowest  $S_n$  vibrational states to lowest  $S_1$  vibrational states while the longer lifetime was assigned to the internal conversion from lowest  $S_1$  vibrational states to the ground state ( $S_0$ ). With strong near IR absorption and weak visible absorption these novel molecules possess potential for various photonic and photovoltaic applications.

#### 5. Supporting information

Closed aperture Z-scan data of 5a–c at 600 nm, 640 nm, 680 nm, and 800 nm are presented. Autocorrelation data of  $\sim 1.5$  ps pulses is also presented. Summary of  $n_2$ , real, imaginary, total  $\chi^{(3)}$  and figures of merit ( $T$ ) values of all molecules are presented.

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