

Ultrafast nonlinear optical studies of Cyclo[4]naphthobipyrroles

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Abstract

Expanded porphyrins belong to the class of porphyrinoids, where the core of the porphyrin macrocycle is increased either by incorporating additional pyrrolic units, or by increasing the number of bridging carbon atoms from more than four, or a combination of both. The significance of these classes of compounds lies in their novel photophysical and nonlinear optical properties. Superior nonlinear optical coefficients are usually observed for aromatic expanded porphyrins with large number of π -electrons owing to their distinct structural features. In this regard, cyclo[8]pyrrole is unique, owing to its large planar 30- π core macrocyclic ring in its diprotonated state. Here, all the eight pyrrole units are directly linked to each other through their α -positions. Recently, we have synthesized, cyclo[4]naphthobipyrroles, a unique class of cyclo[8]pyrroles, where alternate pyrrole units are fused with naphthalene moieties. This adds more rigidity to the resultant cyclo[8]pyrrole while further extending the resultant π -conjugation. Herein, we present some of our results from the picosecond nonlinear optical studies of a β -octa-isopropyl-cyclo[4]naphthobipyrrole. The nonlinear optical coefficients were extracted from the Z-scan measurements. The values of two-photon cross-sections obtained for these molecules were in the range of 10^4 GM.

Keywords: Ultrafast, Z-scan, naphthobipyrroles, picosecond, two-photon absorption.

1. Introduction

In the last two decades, expanded porphyrins have emerged as a new class of attractive compounds owing their variety of applications in near infrared (NIR) dyes, anion sensors, two-photon absorption (TPA) materials, photosensitizers, and in photodynamic therapy [1]. A large variety of expanded porphyrin can be prepared by adding more number of pyrrole or other hetero-aromatic compounds apart from tuning their number of bridging meso-carbons. Moreover, it is observed that aromatic expanded porphyrins display large third order nonlinear optical response while normal porphyrin monomers only exhibit small σ_2 values of <100 GM [2-4]. Similarly, porphycene, an isomer of porphyrin possess a slightly higher σ_2 values compared to the parent isomer i.e. porphyrin [5]. However, upon β -fusion of naphthalene at its periphery, through its constituent bipyrrrolic units, we observed a large enhancement of nonlinear optical response in dinaphthoporphycenes [6-8]. Therefore, in order to assess the effect of this naphthalene fusion (by both rigidification and π -extension), we chose to explore the nonlinear optical response of our recently reported cyclo[4]naphthobipyrrole, a unique class of cyclo[8]pyrrole, which has large aromatic expanded porphyrins that display the classic disk like structure of simple porphyrins with 30 π electrons [9,10]. The cyclo[8]pyrrole molecule can be derived, by replacing all four meso-carbon bridges of porphyrin with four additional pyrrolic rings. The significance of this class of compounds lies in their novel photophysical and nonlinear optical properties. Interestingly, unlike other porphyrinoids, these molecules have strong absorption at near infrared (1100 nm) and comparatively weaker absorption at UV band (430nm), which makes them a promising material for optical storage and signaling devices [11]. The fusion of alternate pyrrole units with naphthalene moieties adds rigidity to cyclo[8]pyrroles along with extended π -conjugation resulting in the formation of cyclo[4]naphthobipyrroles. Sarma et al [9] 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, which

is reflected on their photophysical properties. Due to their structural planarity, large number of π -electrons and aromaticity, they possess good optical nonlinearity. In this paper, we present picosecond (ps) Z-scan method to probe the nature and extent of nonlinear optical response and the calculation of two photon absorption cross sections provided a measure of a third-order nonlinear optical process produced in response to an intense external electric field, usually generated by pulsed lasers. The number of π electrons and/or the molecular geometry associated with the static and dynamic polarizability of these molecules can be considered as the determining parameters in controlling the nonlinear optical susceptibility. Herein, NLO data of β -octa-isopropyl-cyclo[4]naphthobipyrroles is presented

2. Experimental details

The synthesis of cyclo[4]naphthobipyrroles is discussed elsewhere [9, 10]. The data presented here is for the sample of β -octa-isopropyl-cyclo[4]naphthobipyrrole. The ps Z-scan measurements were performed at wavelengths of 800 nm, 600 nm, 640 nm and 680 nm. The laser source was Ti:sapphire laser system (LEGEND, Coherent) delivering nearly transform-limited pulses of ~ 2 ps and repetition rate of 1 kHz. The pulse duration was determined by Autocorrelation technique, by using 2 mm thick BBO crystal. Figure 1 shows the auto correlation trace and the pulse duration was obtained to be ~ 2.1 ps (FW1/e²M). The pulses other than 800nm were derived from an optical parametric amplifier (Light conversion, TOPAS) operating 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) [12-17]. 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 0.062 mM. The linear transmission was observed to be 75%-80%.

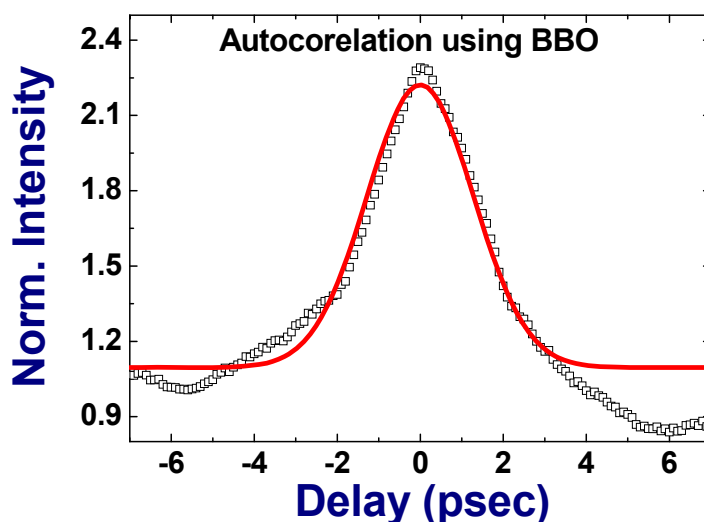


Figure 1 Autocorrelation data of picosecond pulses using a 2-mm thick BBO crystal.

3. Results and Discussions

Figure 2 shows the UV-Vis-NIR absorption spectra which consists of L bands at 244 nm, and B bands at 433 nm. Moreover, it has a strong Q bands at 1339 nm which is a characteristic of these molecules. Inset shows structure of the compound studied. The L-bands are very sensitive to the nature of the substituents in comparison to the B-bands. The nonlinear absorption coefficients were determined from open aperture Z-scan data. Figure 3 shows typical open aperture Z-scan data obtained at (a) 800 nm (b) 600 nm (c) 640 nm and (d) 680 nm. All the data show reverse saturable absorption kind of behavior with a valley near zero. The data was fitted by conventional Z-scan analysis in which the propagation equation (1) is solved [18].

$$\frac{dI}{dz} = -\alpha(I)I \dots \dots \dots (1)$$

where $\alpha(I)$ is intensity dependent absorption. The analysis shows that two-photon absorption (TPA) is the cause of decrease in the transmittance. The two photon absorption coefficients obtained from the fits are plotted versus the wavelength (figure 2). The variation of 2PA coefficient is in accordance with the availability of two photon states. The two photon resonance corresponding to 600 nm excitation is $33,333 \text{ cm}^{-1}$. Figure 1 also shows the 2PA coefficients plotted against the wavelength studied. Summary of the NLO coefficients obtained from the fits are provided in table 1.

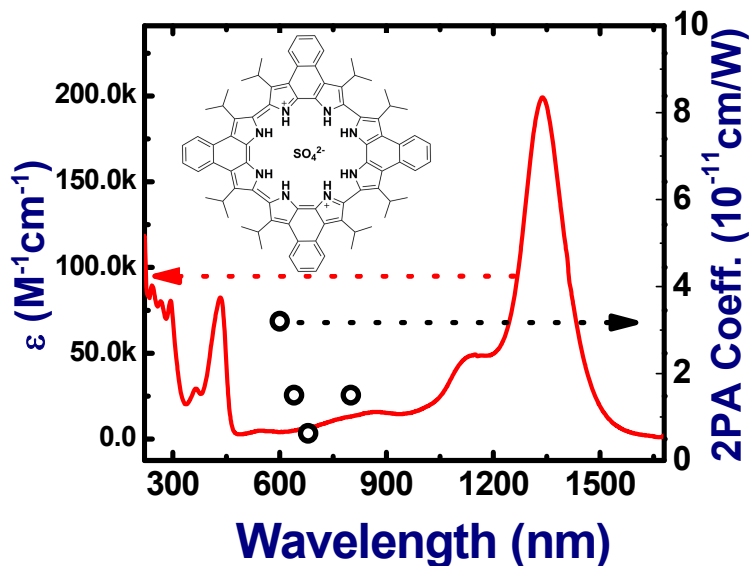


Figure 2 Solid (red) line depicts the linear absorption spectrum while open circles are the two-photon coefficient values.

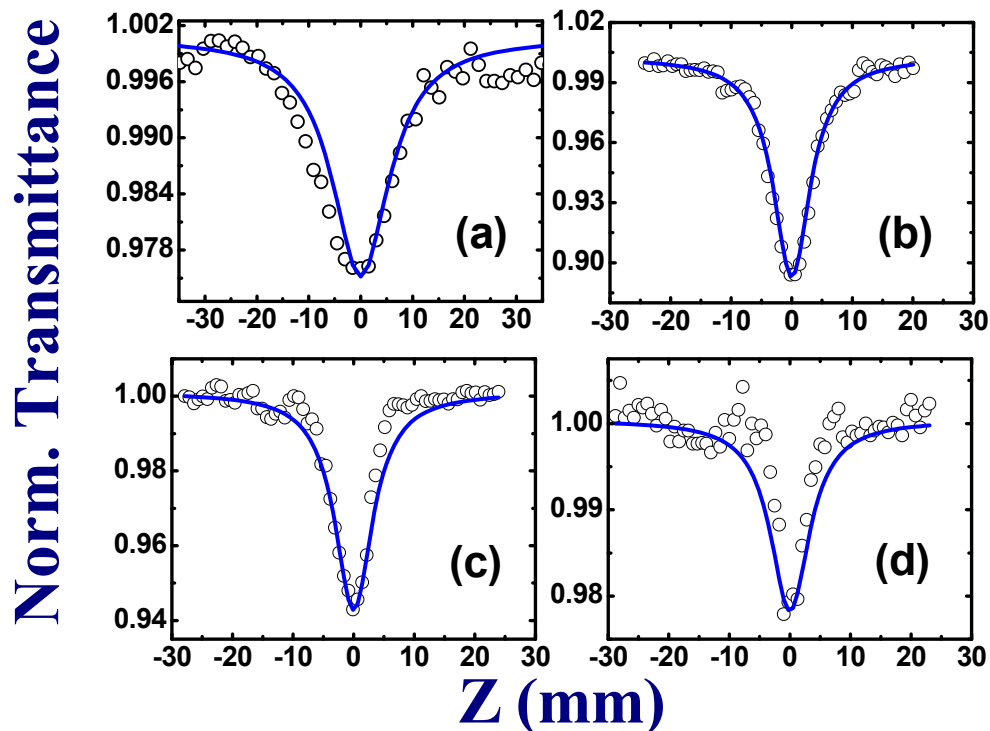


Figure 3 Open aperture Z-scan data of β -octa-isopropyl-cyclo[4]naphthobipyrrole at (a) 800 nm (b) 600 nm (c) 640 nm (d) 680 nm. Open circles are the experimental data while the solid lines are fits to the data.

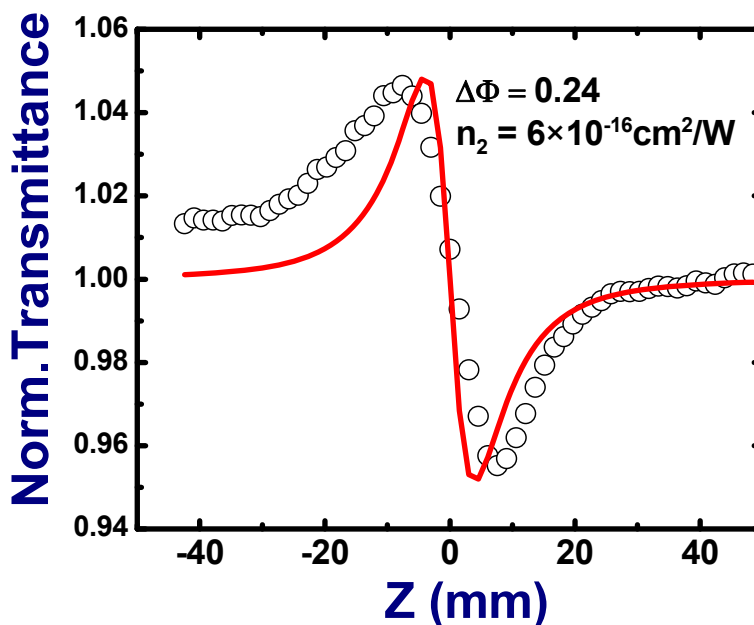


Figure 4 Closed aperture Z-scan data of β -octa-isopropyl-cyclo[4]naphthobipyrrole at 800 nm. Open circles are the experimental data while the solid line is theoretical fit.

The nonlinear coefficients are summarized in the table 1. After obtaining the nonlinear coefficient, β , the TPA cross section σ_{TPA} (in units of $1\text{GM} = 10^{-50} \text{ cm}^4\text{s}/\text{photon}/\text{molecule}$) of a single solute molecule sample can be determined by using the following relationship:

$$\sigma_{\text{TPA}} = \frac{\beta h\nu}{N_D} \dots \dots \dots (2)$$

Where N_D = Number density = $N_A C/1000$ (molecules/ cm^3) and N_A is Avogadro number, C is concentration of the sample. The value of σ_2 was in the range of $0.5\text{-}2.9 \times 10^4 \text{ GM}$. Roznyatovskiy [10] et al. studied the NLO properties of the same molecule and obtained 2PA cross sections in the range of 10^3 GM . However, their studies were performed in the $1.8\text{-}2.4 \mu\text{m}$ spectral range.

S. No.	Wavelength (nm)	I_{00} (GW/ cm^2)	β $\times 10^{-11}$ (cm/W)	σ_2 $\times 10^4$ (GM)
1	800	58	1.5	1
2	600	122	3.2	2.9
3	640	129	1.5	1.3
4	680	114	0.62	0.5

Table 1 The nonlinear coefficients extracted from the Z-scan fits for β -octa-isopropyl-cyclo[4]naphthobipyrrole

The closed aperture Z-scan data (depicted in figure 4) shows that these molecules exhibit negative nonlinearity. The nonlinear phase change $\Delta\Phi$ was $<\pi$ which indicates that the process is due to third order optical nonlinearity. The value of n_2 estimated from the fits was $\sim 6 \times 10^{-16} \text{ cm}^2/\text{W}$. The peak intensity used was very low in order to avoid higher order contributions. The solvent contribution was minimal at these peak intensities. Ultrafast excited state dynamics are being

probed with degenerate pump-probe methods [7] at 800 nm and 600 nm, with ps and fs pulses, respectively. The NLO coefficients are comparable to some of the recently investigated molecules by our group [19-23].

4. Conclusions

The nonlinear optical properties of β -octa-isopropyl-cyclo[4]naphthobipyrrole, a new cyclo[8]pyrrole derivative, which is also an expanded porphyrin, are explored. Two photon absorption observed in these molecules depends on the availability of two photon states and the intensity of laser pulses. The large TPA cross section of β -octa-isopropyl-cyclo[4]naphthobipyrrole compared to normal porphyrins, which exhibit σ_{TPA} values less than 100 GM, was higher making them a suitable candidates for NLO applications.

5. Acknowledgments

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6. References

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