Optical Materials 35 (2013) 962-967

Contents lists available at SciVerse ScienceDirect

Optical Materials



journal homepage: www.elsevier.com/locate/optmat

Thiazole based novel functional colorants: Synthesis, characterization and nonlinear optical studies using picosecond Z-scan technique

Balvant Shyam Singh^a, Hyacintha Rennet Lobo^a, G. Krishna Podagatlapalli^b, S. Venugopal Rao^b, Ganapati Subray Shankarling^{a,*}

^a Department of Dyestuff Technology, Institute of Chemical Technology, N.P. Marg, Matunga, Mumbai 400 019, India ^b Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad, Hyderabad 500 046, India

ARTICLE INFO

Article history: Received 2 July 2012 Received in revised form 20 November 2012 Accepted 21 November 2012 Available online 3 January 2013

Keywords: Colorants Thiazole Nonlinear optical Z-scan Three-photon absorption

1. Introduction

The basic phenomena of multi-photon absorption proposed theoretically by Goppert-Mayer [1] in the early 1930s and the recent observation/demonstration of such phenomena using intense laser pulses has opened up several important and advanced applications like high-density optical data storage [2,3], photo-dynamic therapy [4], and optical limiting [5]. The success of such applications and several others demand efficient materials exhibiting multi-absorption phenomena. The design of novel chromophores based on structure-property relationship and their synthesis is especially challenging. In this context, organic materials have contributed significantly towards understanding and creating materials with large multi-photon absorption coefficients and several reports are available in the literature [6–8]. The field of two-photon absorption (2PA) has been successfully explored in the last two decades including many systems containing strong-electron donor (D), a polarisable π -bridge (π), and a strong π -electron acceptor (A). In an experimental report He et al. [8] have demonstrated that certain two-photon active organic molecules provided excellent results in three-photon absorption (3PA) applications. Nevertheless, only a few reports are documented for materials, especially organic molecules, with strong 3PA. Some of the active molecules reported

* Corresponding author.

ABSTRACT

Organic push–pull chromophoric system containing thiazole Schiff bases were synthesized from aminothiazole intermediate. These novel chromophores possessed excellent thermal and optical properties with complete transparency in the visible spectral region. Thermogravimetric analysis revealed that all dyes were thermally stable at temperatures above 300 °C. The third-order nonlinear optical studies, performed using the Z-scan technique with ~2 ps pulses, revealed excellent three photon absorption coefficients/cross-sections combined with reasonably high values of nonlinear refractive index (n_2). The solute n_2 was of opposite sign compared to that of solvents. To the best of our knowledge, this is the first report of three-photon absorption studies in Schiff base compounds.

© 2012 Elsevier B.V. All rights reserved.

in literature include metal complexes such as dinaphthoporphycenes [9-11], phthalocyanines [12,13], organometallic ruthenium dendrimer [14], and platinum acetylide [15]. Metal free molecules have reports of some moieties like fluorene derivatives [16,17], triphenylamine derivative with three conjugated branches [18], stilbazolium-like dyes [19] involving C=C bond or C=C bond as the conjugation bridge and Y-shaped chromophores with heterocyclic bridges [20]. These molecules investigated as three photon active materials have variable systems wherein $D-\pi-D$ and $D-\pi-A$ are usually used. Wu et al. [21] have designed D- π -A chromophore using diphenyl amino group as donor, oligofluorene as linker and triazole ring as an electron acceptor and studied their NLO properties using femtosecond (fs) pulses. Lin et al. [22] have synthesized D- π -D system in the central part with electron acceptor system like 2,5-diphenyloxadiazole extended identically from both sides of the donor. Zhou et al. [23] reported high cross section values with an organic dve containing two pyrrolidinyl units connected by Stilbene Bridge. Cronstrand et al. [24] have theoretically predicted that a donor-acceptor system connected to dithienothiophene linker increased 3PA probability by a factor of six as compared to donor-donor system. However, till date and to the best of our knowledge, no molecules based on strong acceptor system like phenyl nitro groups have been experimentally studied for 3PA. Furthermore, conjugation systems like C=N bond or Schiff bases have been explored only for 2PA [25] and no report on C=N bond containing Schiff bases with 3PA has occurred yet, to the best of our knowledge. Looking at these aspects, it is clear that organic



E-mail addresses: soma_vanu@yahoo.com (S. Venugopal Rao), gsshankarling@ gmail.com, gs.shankarling@ictmumbai.edu.in (G.S. Shankarling).

^{0925-3467/\$ -} see front matter @ 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.optmat.2012.11.018

chromophores with push-pull chromophoric system possess wide scope for further exploration for applications in the fields utilizing 3PA. Herein, for the first time, we investigate 3PA studies in pushpull chromophoric system containing phenyl substituted or heterocyclic donors connected to thiazole based linker via imine bond and nitrophenyl groups as acceptor. Ultrafast all-optical switching devices are key components for next generation broadband optical networks. The implementation of such devices requires materials with low linear and nonlinear losses, high refractive nonlinearities and response times of a few picoseconds or less. It has been developed that inclusion of a sulfur heteroatom in the π -conjugated system might favor the enhancement of nonlinearity. Furthermore, thiazole or benzthiazole units have been shown to be attractive building blocks for synthesis of dyes with 2PA. In addition, incorporating a good donor group improves desirable nonlinear optical (NLO) properties such as high values of 3PA cross sections [26]. In this context we studied the NLO properties of thiazole based Yshaped chromophores containing C=N bond as the conjugation bridge. The donor groups were varied by including moieties like indole, diethylaminohydroxybenzene, and carbazole in the chromophoric system. A systematic investigation of nonlinear absorption and nonlinear refraction of these chromophores using ps pulses is discussed.

2. Synthesis and experimental details

All the solvents and chemicals were procured from S D fine chemicals (India) and were used without further purification. The reactions were monitored by TLC using 0.25 mm E-Merck silica gel 60 F254 pre-coated plates, which were visualized with ultraviolet light. UV-visible absorption spectra were recorded on Spectronic genesis 2 spectrophotometer instruments from dye solutions (~mM) in chloroform. The ¹H NMR spectra were recorded on 400 MHz on Varian mercury plus spectrometer. Chemical shifts are expressed in δ ppm using TMS as an internal standard. Mass spectral data were obtained with micromass-Q-Tof (YA105) spectrometer. Elemental analysis was done on Harieus rapid analyzer. Melting points measured and thermogravimetric analysis was carried out on SDT Q600 v8.2 Build 100 model of TA instruments.

2.1. Synthesis of Schiff base 8a-8c

We synthesized three novel and rigid chromophoric Y-shaped systems containing thiazole based Schiff bases. The novel Schiff base derivatives **8a-8c** were prepared by refluxing the intermediate 4,5-bis(4-nitrophenyl)-1,3-thiazole-2-amine 6 with carbaldehyde compound 7a-7c in glacial acetic acid as illustrated in Fig. 1. The aldehydes 7a-7c were obtained by the classical Vilsmeier Haack reaction [27]. The aminothiazole intermediate was synthesized in a sequence of five steps in accordance with literature report [28] wherein in the initial stage, 2-hydroxy-1,2-diphenylethanone 1 was refluxed in pyridine followed by addition of thionyl chloride to obtain 2-chloro-1,2-diphenylethanone 2. This was subsequently condensed with thiourea in ethanol and then soaked in sodium hydroxide to afford 4,5-diphenyl-1,3-thiazol-2-amine 3 in excellent yield. Acetylation of 3 with acetic anhydride in glacial acetic acid and few drops of concentrated sulphuric acid vielded N-(4,5-diphenyl-1,3-thiazol-2-yl) acetamide 4. Nitration of 4 with fuming nitric acid to yield N-[4,5-bis(4-nitrophenyl)-1,3-thiazol-2-yl]acetamide 5. Deacylation of 5 with aqueous hydrochloride affords 4,5-bis(4-nitrophenyl)-1,3-thiazol-2-amine 6 in excellent yield. The structures of the compounds (8a-8c) were characterized by FT-IR, ¹H NMR spectroscopy, mass spectrometry and elemental analysis.

2.1.1. N,N'-((9-butyl-9H-carbazole-3,6-diyl)bis

(methanylylidene))bis(4,5-bis(4-nitrophenyl) thiazol-2-amine) (8a)

A mixture of N-butyl-3,6-carbazoledialdehyde **7a** (0.81 g, 2.91 mM) and 4,5-bis(4-nitrophenyl)-1,3-thiazol-2-amine compound **6** (2 g, 5.84 mM) was added to the glacial acetic acid (60 ml) with stirring for 24 h at 110 °C. The reaction was monitored by TLC. For work-up, the mixture was added to cold water. The product was filtered and residual product was dried in an oven under vacuum. The crude product on purification by column chromatography (mobile phase: hexane and silica gel 60–120 mesh).

2.2 g, 65 % yield; M.P.: 302 °C; ¹H NMR (CDCl₃, 300 MHz): δ 8.18–8.10 (m, 10H, CH); δ 7.62–7.56 (m, 6H, CH); δ 7.48–7.42 (m, 6H, CH); δ 7.20 (m, 2H, CH); δ 7.20 (m, 2H, CH); δ 2.40–2.20 (m, 2H, CH₂); δ 2.18–2.10 (m, 2H, CH₂); δ 1.22–1.18 (m, 2H, CH₂); δ 0.80 (m, 3H, CH₃); LCMS: *m*/*z* calculated for C₄₈H₃₃N₉O₈S₂ (M+H) 928.8 calculated 927.1; Elemental analysis calculated (found); C 62.13 (62.09), H 3.58 (3.42), N 13.58 (13.75), S 6.91(6.90); IR (neat): ν (cm⁻¹) 2921 (Ar C–H), 1695 (C=N), 1591 (C=C), 1506 (NO₂), 1336 (NO₂), 1280 (C=C), 1105 (C–N).

2.1.2. 2-(((4,5-bis(4-nitrophenyl)thiazol-2-yl)imino)methyl)-5-(diethylamino)phenol (**8b**)

The product **8b** was prepared by a similar procedure as stated for **8a** except that a mixture of N,N-diethylaminophenolaldehyde **7b** (0.96 g, 5.84 mmol) and 4,5-bis(4-nitrophenyl)-1,3-thiazol-2amine compound **6** (2 g, 5.84 mmol) were taken as substrates.

1.97 g, 69% yield; M.P.: 258 °C ¹H NMR (CDCl₃, 300 MHz): δ 8.22–8.14 (m, 5H, CH); δ 7.68–7.46 (m, 6H, CH); δ 7.34–7.32 (m, 1H, CH); δ 2.30 (m, 10H, CH); LCMS: *m/z* calculated for C₂₆H₂₃N₅O₅₋S (M+H) 518.4 calculated 517.4; Elemental analysis calculated (found); C 60.34 (60.38), H 4.48 (4.18), N 13.53 (13.93), S 6.20(6.37); IR (neat): *v* (cm⁻¹) 3380 (O–H), 3186 (Ar C–H), 1670 (C=N), 1595 (C=C), 1508 (NO₂), 1338 (NO₂), 1278 (C=C), 1105 (C–N).

2.1.3. N-((1-butyl-1H-indol-3-yl)methylene)-4,5-bis(4nitrophenyl)thiazol-2-amine (8c)

The product **8c** was prepared by a similar procedure as stated for **8a** except that a mixture of indole-3-aldehyde **7c** (1.2 g, 5.84 mmol) and 4,5-bis(4-nitrophenyl)-1,3-thiazol-2-amine compound **6** (2 g, 5.84 mmol) were taken as substrates. 2.2 g, 71% yield; M.P.: 266 °C ¹H NMR (CDCl₃, 300 MHz): δ 8.24–8.16 (m, 6H, CH); δ 7.60–7.66 (m, 3H, CH); δ 7.52–7.48 (m, 3H, CH); δ 7.20 (m, 2H, CH); δ 2.30–2.15 (m, 4H, CH₂); δ 1.80 (m, 2H, CH₂); δ 1.30 (m, 3H, CH₃); LCMS: *m*/*z* calculated for C₂₈H₂₃N₅O₄S (M+H) 527.2 calculated 526.0; Elemental analysis calculated (found); C 63.99 (64.02), H 4.41 (4.43), N 13.33 (13.48), S 6.10 (6.45); IR (neat): ν (cm⁻¹) 3060 (Ar C–H), 1670 (C=N), 1593 (C=C), 1510 (NO₂), 1340 (NO₂), 1278 (C=C), 1105 (C–N).

The linear absorption spectra of novel synthesized push pull chromophores were measured for concentrations of 1×10^{-3} M (in chloroform) in a cell of 1 cm path length whereby influences of the quartz cuvette and solvent have been subtracted. We had also tested the thermal stability of dyes by thermal gravimetric analysis (DSC-TGA) carried out in the temperature range 25-600 °C under nitrogen gas at a heating rate of 10 °C min⁻¹. Nonlinear absorption (NLA) of **8a-c** were measured by the open aperture Z-scan technique at room temperature with laser pulses from a chirped pulse amplified Ti:sapphire laser system operating at a wavelength 800 nm delivering nearly transform-limited (~ 2 ps, 1 kHz repetition rate) pulses [9,11,12,29–33]. The measurements were performed with solutions (chloroform) at a concentration of 2-5 mM. A guartz cuvette (1-mm thick) containing the sample solution was traversed in the focusing geometry enabled by an achromat lens of 200 mm focal length. The beam waist $(2\omega_0)$ at focal plane was estimated to be $\sim 68 \,\mu m$ (FW1/e²M) with a



Fig. 1. Schematic route for synthesis of Schiff base colorants 8a-8c.

corresponding Rayleigh range (Z_r) of ~4.5 mm ensuring the validity of thin sample approximation. Typically <3 µJ energy pulses were used for the experiments. The nonlinear absorption coefficients [3PA coefficients (α_3) in this case] were obtained from the open aperture data analysis whereas the intensity dependent non-linear refractive indices (n_2) of the samples were obtained from the closed aperture data.

3. Results and discussion

The heterocyclic donor group containing thiazole Schiff bases **8a** and **8c** exhibited similar spectral features in the absorption spectra recorded, clearly illustrated in Fig. 2. Both these dyes contained a broad band starting from 225 nm and dropping at 350–370 nm, in addition to a hump ending at 450 nm. In case of compound **8b**, two major bands existed in the spectral range of 225–300 nm and 350–370 nm followed by a slight hump ending at 440 nm. It should be noted that there is no linear absorption attributed beyond 450 nm and, therefore, represents excellent transparency in the visible region. Inset of Fig. 2 illustrates the structures of compounds **8a–8c**.

The TGA curves revealed that all dyes were thermally stable even above $300 \,^{\circ}$ C as revealed in Table 1. The thermogravimetric



Fig. 2. UV-visible absorption spectra of 8a-8c in chloroform (CHCl₃).

curves indicates that compound **8a** showed best thermal stability up to 333 °C which might be owing to the rigid nature of the di-substituted Schiff base chromophore. Differential scanning calorimetric (DSC) analysis of chromophores **8a**, **8b**, and **8c**, illustrated exothermal peaks at 257 °C, 256 °C, and 266 °C, respectively. Fig. 3a–c shows typical open aperture and closed aperture (inset) Z-scan data for the compounds **8b**, **8a**, and **8c** with concentrations of 2 mM, 2 mM, and 5 mM, respectively. Solvent contribution, obtained by recording the open aperture data with pure solvents, was negligible (at least 25 times lower) in the present studies. Open aperture data was recorded with a peak intensity of 83 GW/cm² while the closed aperture data was recorded at 28 GW/cm² in order to avoid any contribution from higher order nonlinearities. Closed aperture of the solvent provided a value of 2.8×10^{-16} cm²/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.

Three-photon absorption (3PA) equation used for fitting the data was

$$T_{\rm OA}(3\rm{PA}) = \frac{1}{\pi^{1/2}p_0} \int_{-\infty}^{\infty} \ln\left\{ \left[1 + p_0^2 \exp(-2\tau^2)\right]^{1/2} + p_0 \exp(-\tau^2) \right\} d\tau$$

where $p_0 = (2\alpha 3 L'_{\text{eff}} l_0^{2})^{1/2}$, α_3 is the 3PA coefficient, I_0 is the intensity as a function of *z*, *z* is the sample position, $Z_0 = \pi \omega_0^2 / \lambda$ is the Rayleigh range: ω_0 is the beam waist at the focal point (*z* = 0), λ is the laser wavelength; effective path length in the sample of length *L* for 3PA is given as:

$$L_{\rm eff}' = \frac{1 - e^{-2\alpha_0 L}}{2\alpha_0}$$

We have evaluated the three photon cross-section (σ_3) using the relation:

$$\sigma_3 = \frac{(\hbar\omega)^2}{N} \alpha_3$$

where ω is the frequency of the laser radiation, and *N* is the number density given by $C \times N_A/1000$, where *C* is the molar concentration, N_A is the Avogadro number.

The closed aperture data were fitted using the equation [9]:

$$T_{CA} = 1 + \frac{4\Delta\phi(\frac{z}{z_0})}{((\frac{z}{z_0})^2 + 9)((\frac{z}{z_0})^2 + 1)}$$

T is the normalized transmittance, $\Delta \phi$ is the nonlinear phase shift, $x = Z/Z_r$ is the normalized position with respect to the Rayleigh range.

$$I_0 = \frac{I_{00}}{\left(1 + \frac{Z^2}{Z_0^2}\right)}$$

where I_{00} is the peak intensity at focus calculated using the relation:

$$I_{00} = \frac{2E}{\pi^{3/2} w_0^2 (HW1/e^2 M) \tau_{\rm p} (HW1/eM)}$$

E is the input pulse energy, τ is the pulse duration, $2\omega_0$ is the beam diameter at focus.

The fits to the data in Fig. 3a–c were performed with 3PA equation and when we tried fitting with 2PA equation the fits were not

Table 1Physical data and thermal behavior of dyes 8a-c.

Dye no.	Yield (%)	Melting point	Temperature of stability (°C)	Weight of compound (in %)
8a	82	302	333	90.6
8b	78	258	300	95.1
8c	80	266	310	97.8



Fig. 3. Open aperture Z-scan data of compounds (a) **8a** (b) **8b** (c) **8c** (in $CHCI_3$). Inset shows the closed aperture data. Solid lines are fits while scattered points are experimental data.

matching the experimental data, especially near focal region. The error bars presented in Fig. 3a–c represents errors in (a) intensity fluctuation of laser pulses (b) errors in data collection. Insets of Fig. 3a–c depicts the closed aperture data (open circles) and the fits (solid lines). The closed aperture data was divided by open aperture data to account for the presence of any nonlinear absorption. 3PA fits obtained at lower peak intensities (Fig. 4a–c) indicated much higher values suggesting that there could be contribution from excited state absorption and the 3PA coefficient presented

here is an effective coefficient with 2 + 1 photon kind of absorption (2PA + excited state absorption) [11]. To confirm whether the process was indeed due to 3 photons we plotted the graph of $\ln(I_{00})$ versus $1 - T_{OA}$ for sample **8c**. The data, shown in Fig. 5 for such a plot with value of slope close to 2, clearly indicates the process is indeed 3PA process. Interestingly, **8b** demonstrated strong 3PA coefficient and cross-section magnitude compared to dyes **8a** and **8c** which could, probably, be due to greater intramolecular charge transfer from the hydroxy groups to the conjugated core in the D- π -A system. In addition, disubstituted molecule (**8c**) owing to greater charge separation.

The values of n_2 obtained from closed aperture data were $5.9 \times 10^{-16} \text{ cm}^2/\text{W}$, $5.7 \times 10^{-16} \text{ cm}^2/\text{W}$, and $7.4 \times 10^{-16} \text{ cm}^2/\text{W}$, for 8a, 8b, and 8c, respectively, indicating that 8c had better coefficient. The real part of second hyperpolarizability (γ_R) has also been evaluated using n_2 values [37]. The magnitude of γ_R was estimated to be $\sim 10^{-31}$ e.s.u. for all the molecules investigated. However, when the figure of merit ($V = \lambda \alpha_3 I_0 / 3n_2$) was calculated [34], taking into account the linear absorption and the value of n_2 , all the compounds had similar values in the range of 0.5-0.6, indicating excellent potential. The complete NLO coefficients and crosssections of 8a-8c are summarized in Table 2. These coefficients are comparable to some of the successful compounds reported recently in literature. For example, porphycenes [9,10] had cross-sections in the range of $14-103 \times 10^{-77}$ cm⁶ s²/photon² where as phthalocyanines [11] possessed cross-sections in the range of 10⁻⁸⁰ cm⁶ s²/photon² wherein the measurements were performed under similar conditions with \sim 2 ps pulses. Hernandez et al. [17] observed 3PA in fluorene derivatives with cross sections of $\sim 10^{-77}$ cm⁶ s²/photon² using 35 ps pulses. The 3PA cross-section of D- π -D analog was 2.2 times greater than that of its D- π -A counterpart demonstrating that symmetric charge transfer enhanced 3PA. Cohanoschi et al. [16] demonstrated that symmetrical charge transfer from the center to the periphery in A– π –A fluorene derivatives enhanced their 3PA cross-section. Wu et al. [21] obtained cross sections in the range of 10^{-80} cm⁶ s²/photon² in D- π -A systems with fs pulses. Zhan et al. [35] working with 35 ps pulses observed that the σ_3 values (~10⁻⁷⁷ cm⁶ s²/photon²) of six stilbazolium derivatives increased linearly with the electrondonating ability of the donor units, from N-methylpyrrole, to pyrrole, to furan, and to thiophene. Liu et al. [36] studied symmetrical fluorene-based molecule suing 38 ps pulses and observed 3PA induced optical limiting with 3PA cross-section of $\sim 10^{-76}$ cm⁶ s²/ photon². Ma et al. [38] explored 3PA of two novel symmetrical charge transfer fluorene-based molecules again using 38 ps pulses and obtained magnitudes similar to those of Liu et al. [36]. Audebert et al. [39] investigated range of two families of D- π -A molecules possessing the same withdrawing group and π connecting system, donor groups with various strengths and observed 2PA with 130 fs pulses instead of 3PA. Therefore, it is imperative to thoroughly investigate all the novel molecules synthesized to understand the structure property relationship and thereby tailoring these molecules to suit specific requirements for practical applications.

The stability of the colorant molecules was tested both in terms of thermal stability and chemical stability. The high thermal stability of these molecules (decomposition temperature >300 °C) was clearly observed from thermogravimetric analysis data. In addition, the samples were also very stable in terms of chemical and time stability. This was clear from the fact that there was no change in sample even after storing it for 6 months as per the analysis done by FTIR and NMR methods. Z-scan experiments were performed using peak intensities up to 100 GW/cm² and we did not observe any physical damage to the samples. However, independent experiments were performed to test the molecules in



Fig. 4. Open aperture Z-scan data of (a) Compound **8a** (b) Compound **8b** (c) Compound **8c** recorded at low peak intensity of 55 GW/cm². Solid lines are fits while scattered points are experimental data.

solution form for any laser damage using peak intensities up to 200 GW/cm². We did not observe any damage which was confirmed from the absorption spectra recorded before and after the exposure to these peak intensities.

Our initial studies, obtained using much shorter pulses, strongly suggest that these are potential molecules with strong 3PA



Fig. 5. Plot of $\ln(I_{00})$ versus $1 - T_{OA}$ for sample **8(c)** at peak intensity of (83 GW/ cm²).

Table 2

Summary of NLO coefficients extracted from data for dyes 8a-c.

Dye no.	I ₀ (GW/ cm ²)	$\begin{array}{l} \alpha_3 \\ (cm^3/W^2) \\ \times \ 10^{-22} \end{array}$	$\begin{array}{l} \sigma^{3} \\ (cm^{6}s^{2}/\\ photon^{2}) \\ \times 10^{-77} \end{array}$	$n_2 \ (cm^2/W) \times 10^{-16}$	Re [χ ³] (e.s.u.)	$\gamma_{\rm R}$ (e.s.u.)
8a	83 (55)	3.60 (9.30)	1.85	5.90	$\textbf{6.7}\times \textbf{10}^{-13}$	$\textbf{3.29}\times \textbf{10}^{-\textbf{31}}$
8b	83 (55)	6.50 (13.2)	3.34	5.70	$\textbf{6.5}\times 10^{-13}$	3.19×10^{-31}
8c	83 (55)	3.95 (10.4)	0.81	7.40	8.6×10^{-13}	1.69×10^{-31}

coefficients with relevant possible applications in bio-imaging. Our future studies comprise (a) studying their NLO properties at visible and near-IR wavelengths (and with femtosecond pulses) to examine their true potential for device applications (b) dope these dyes in a suitable matrix and extend the NLO studies (c) examine the excited state dynamics using fs/ps pump-probe techniques [12].

4. Conclusions

In conclusion, we have synthesized three novel Schiff bases with excellent thermal properties and no absorption in the visible region. The synthesized compounds were subjected to NLO studies at 800 nm where they were exhibited three-photon absorption. All these dyes possessed good values of nonlinear refractive index (n_2) that is useful for optical switching applications. Importantly, these values were obtained at a non-resonant wavelength of 800 nm. The magnitudes of three photon absorption cross sections obtained were 1.85×10^{-77} cm⁶ s²/photon², 3.34×10^{-77} cm⁶ s²/photon², 0.81×10^{-77} cm⁶ s²/photon² for dyes **8a**, **8b**, and **8c**, respectively. These values are comparable/higher than some of the recently reported molecules. Moreover, this is the first study of three photon absorption in case of Schiff base compounds. There is further scope for tailoring these molecules to achieve superior cross-sections.

Acknowledgments

Authors (BSS and HRL) are thankful to TEQUIP, UGC-CAS, New Delhi for providing fellowship and SAIF IIT – Bombay for recording Mass, ¹H NMR spectra and elemental analysis. SVR and GKP thank DRDO for financial support.

References

- [1] A.A. Said, T. Xia, D.J. Hagan, J. Opt. Soc. Am. B: Opt. Phys. 14 (1997) 824.
- [2] D.A. Parthenopoulos, P.M. Rentzepis, J. Appl. Phys. 68 (1990) 5814.
- [3] A.S. Dvornikov, P.M. Rentzepis, Opt. Commun. 119 (1995) 341.
- [4] J.D. Bhawalkar, G.S. He, P.N. Prasad, Rep. Prog. Phys. 60 (1997) 689.
- [5] G.S. He, J.D. Bhawalkar, P.N. Prasad, B.A. Reinhardt, Opt. Lett. 20 (1995) 1524.
- [6] X.J. Tang, L.Z. Wu, L.P. Zhang, C.H. Tung, Chem. Phys. Lett. 356 (2002) 573.
- [7] Y.C. Kim, T.W. Lee, O.O. Park, C.Y. Kim, H.N. Cho, Adv. Mater. 13 (2001) 646.
 [8] G.S. He, P.P. Markowlez, T.C. Lin, P.N. Prasad, Nature 415 (2002) 767.
- [9] T. Sarma, P.K. Panda, P.T. Anusha, S. Venugopal Rao, Org. Lett. 13 (2011) 188.
- [9] I. Sarma, F.K. Fahua, F.T. Anusha, S. Venugopar Rao, Org. Lett. 19 (2011) 166.
 [10] R.S.S. Kumar, S. Venugopal Rao, L. Giribabu, D.N. Rao, Chem. Phys. Lett. 447 (2007) 274.
- [11] S. Venugopal Rao, S.T. Prashant, D. Swain, T. Sarma, P.K. Panda, S.P. Tewari, Chem. Phys. Lett. 514 (2011) 98.
- [12] D. Swain, P.T. Anusha, T. Shuvan Prashant, Surya P. Tewari, Tridib Sarma, Pradeepta K. Panda, S. Venugopal Rao, Appl. Phys. Lett. 100 (2012) 141109.
- [13] M. Morisue, K. Ogawa, K. Kamada, K. Ohta, Y. Kobuke, Chem. Commun. 46 (2010) 2121.
- [14] M. Samoc, J.P. Morrall, G.T. Dalton, M.P. Cifuentes, M.G. Humphrey, Angew. Chem. Int. Ed. 46 (2007) 731.
- [15] M.G. Vivas, E. Piovesan, D.L. Silva, T.M. Cooper, L.D. Boni, C.R. Mendonca, Opt. Mater. Express 1 (2011) 700.
- [16] I. Cohanoschi, M. Garcia, C. Toro, K.D. Belfield, F.E. Hernandez, Chem. Phys. Lett. 430 (2006) 133.
- [17] F.E. Hernandez, K.D. Belfield, I. Cohanoschi, Chem. Phys. Lett. 391 (2004) 22.
 [18] C. Lu, W. Huang, J. Luan, Z. Lu, Y. Qian, B. Yun, G. Hu, Z. Wang, Y. Cui, Opt.
- Commun. 281 (2008) 4038. [19] D.Y. Wang, C.L. Zhan, Y. Chen, Y. Li, J. Lu, Chem. Phys. Lett. 369 (2003) 621.
- [20] L.D. Boni, D.L. Silva, U.M. Neves, K. Feng, M. Meador, X.R. Bu, L. Misoguti, C.R.
- Mendonca, Chem. Phys. Lett. 402 (2005) 474. [21] P.L. Wu, X.J. Feng, H.L. Tam, M.S. Wong, K.W. Cheah, J. Am. Chem. Soc. 131
- (2009) 886.
- [22] T.C. Lin, G.S. He, Q. Zheng, P.N. Prasad, J. Mater. Chem. 16 (2006) 2490.
- [23] G. Zhou, X. Wang, D. Wang, Z. Shao, M. Jiang, Appl. Opt. 41 (2002) 1120.
- [24] P. Cronstrand, Y. Luo, P. Norman, H. Agren, Chem. Phys. Lett. 375 (2003) 233.
- [25] L. Tian, Z. Hu, P. Shia, H. Zhou, J. Wu, Y. Tian, Y. Zhou, X. Tao, M. Jiang, J. Lumin. 127 (2007) 423.
- [26] W. Ma, Y. Wu, J. Han, D. Gu, F. Gan, Chem. Phys. Lett. 403 (2005) 405.
- [27] G. Bai, J. Li, D. Li, C. Dong, X. Han, P. Lin, Dyes Pigm. 75 (2007) 93.
- [28] J. Ren, S.M. Wang, L.F. Wu, Z.X. Xu, B.H. Dong, Dyes Pigm. 76 (2008) 310.
- [29] G. Krishna Podagatlapalli, S. Hamad, S. Sreedhar, Surya P. Tewari, S. Venugopal Rao, Chem. Phys. Lett. 530 (2012) 93.
- [30] S. Hamad, Surya P. Tewari, L. Giribabu, S. Venugopal Rao, J. Porphy. Phth. 16 (2012) 140.
- [31] K.V. Saravanan, K.C.J. Raju, M.G. Krishna, S.P. Tewari, S. Venugopal Rao, Appl. Phys. Lett, 9 (2010) 232905.
- [32] P.T. Anusha, Debasis Swain, S. Hamad, T. Shuvan Prashant, L. Giribabu, Surya P. Tewari, S. Venugopal Rao, J. Phys. Chem. C 116 (2012) 17828-17837.
- [33] P.T. Anusha, L. Giribabu, Surya P. Tewari, S. Venugopal Rao, Mater. Lett. 64 (2010) 1915.
- [34] R.S.S. Kumar, S. Venugopal Rao, L. Giribabu, D. Narayana Rao, Opt. Mater. 31 (2009) 1042.
- [35] C. Zhan, Y. Li, D. Li, D. Wang, Y. Nie, Opt. Mater. 28 (2006) 289.
- [36] J. Liu, Y. Mao, Y. Gu, M. Huang, W. Zhang, L. Guo, W. Ma, Opt. Express 16 (2008) 4739.
- [37] J.G. Breitzer, D.D. Dlott, L.K. Iwaki, S.M. Kirkpatrick, T.B. Rauchfuss, J. Phys. Chem. A 103 (1999) 6930–6937.
- [38] W. Ma, Y. Wu, J. Han, D. Gu, F. Gan, Chem. Phys. Lett. 410 (2005) 282.
- [39] P. Audebert, K. Kamada, K. Matsunaga, K. Phta, Chem. Phys. Lett. 367 (2003) 62-71.