



Investigation of third-order nonlinear and optical power limiting properties of terphenyl derivatives

Laxminarayana Kamath^{a,b}, Manjunatha K.B.^{a,*}, Seetharam Shettigar^a,
G. Umesh^c, B. Narayana^d, S. Samshuddin^d, B.K. Sarojini^e

^a Department of Physics, NMAM Institute of Technology, Nitte 574110, Karnataka, India

^b Department of Physics, Bhuvanendra College, Karkala, Karnataka, India

^c Optoelectronics Laboratory, Department of Physics, National Institute of Technology Karnataka, Mangalore - 575025, India

^d Department of Chemistry, Mangalore University, Mangalagangothri 574199, India

^e Department of Chemistry, P.A. College of Engineering, Nadupadavu, Mangalore 574153, India

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ABSTRACT

A series of new chalcones containing terphenyl as a core and with different functional groups has been successfully synthesized by Claisen–Schmidt condensation method in search of new nonlinear optical (NLO) materials. Molecular structural characterization for the compounds was achieved by FTIR and single crystal X-ray diffraction. The third-order NLO absorption and refraction coefficients were simultaneously determined by Z-scan technique. The measurements were performed at 532 nm with 7 ns laser pulses using a Nd:YAG laser in solution form. The Z-scan experiments reveal that the compounds exhibit strong nonlinear refraction coefficient of the order 10^{-11} esu and the molecular two photon absorption cross section is 10^{-46} cm⁴ s/photon. The results also show that the structures of the compounds have great impact on NLO properties. The compounds show optical power limiting behavior due to two-photon absorption (TPA).

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1. Introduction

Organic molecules with nonlinear optical process have gained great interest for applications in a wide variety of optoelectronic and photonic devices [1,2]. The π -conjugated organic compounds have emerged as a promising class of third-order NLO materials because of their potentially large third-order susceptibilities associated with fast response time in addition to their process ability [3,4]. The NLO behavior of organic molecules originates mainly from a strong donor–acceptor intermolecular interaction and delocalized π -electron system. The NLO properties can also be tuned by adopting suitable design strategies, such as donor–acceptor–donor (D–A–D), donor– π -donor (D– π -D), donor– π -acceptor (D– π -A) and acceptor–donor–acceptor (A–D–A) [5,6].

Chalcones belong to a class of organic molecules gaining importance as NLO materials because of noticeable third-order nonlinearity and good optical power limiting properties [7–12]. The chalcone derivatives are known to offer large nonlinear coefficients on account of the fact that they consist of two planar rings connected through a conjugated double bond [13].

In this paper, we present synthesis, characterization and investigation of third-order nonlinear and optical power limiting properties of

four newly synthesized chalcones with terphenyl as a core with different functional group at the termini using the single beam Z-scan technique under nanosecond excitation.

2. Experiment

2.1. General procedure for the synthesis of terphenyl chalcones S1–S5 [1]

A mixture of 1-(4,4'-difluoro-5'-methoxy-1,1':3',1''-terphenyl-4'-yl)ethanone **1** (0.005 mol) and substituted benzaldehyde (0.005 mol) in 30 mL ethanolic sodium hydroxide was stirred at 5–10 °C for 3 h, then maintained at room temperature for 24 h. The precipitate formed after neutralization with dilute hydrochloric acid was collected by filtration and purified by recrystallization from 1:1 mixture of DMF and ethanol.

New terphenyl chalcones were prepared by the base-catalyzed Claisen–Schmidt condensation of acetyl terphenyl derivative (**1**) with substituted benzaldehydes (**2**) as described in our earlier work [14]. The scheme is shown in Fig. 1. The starting material **1**, is in turn prepared by the condensation of acetylacetone with the 4,4'-difluoro chalcone followed by the aromatization using iodine in methanol [15]. The structures and UV–vis spectra of the molecules are shown in Fig. 2 and Fig. 3 respectively. We have also reported the crystal structure of compounds **S1**: (2*E*)-3-(4-bromophenyl)-1-(4,4'-difluoro-5'-methoxy-1,1':3',1''-terphenyl-4'-yl)prop-2-en-1-one [16], **S2**: (E)-1-(4,4'-

* Corresponding author. Tel.: +91 8258 281264; fax: +91 8258 281265.

E-mail address: manjukb15@yahoo.com (Manjunatha).

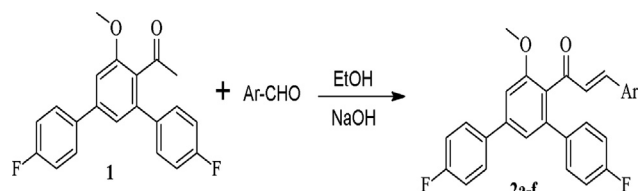


Fig. 1. Synthesis scheme of the molecules.

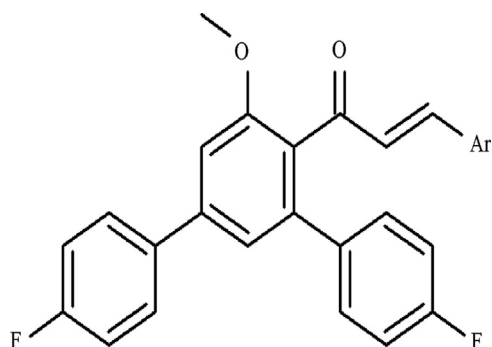


Fig. 2. Molecular structure of the compounds.

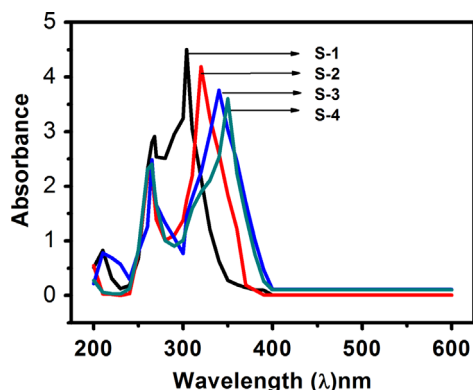


Fig. 3. UV-vis spectra of the molecules.

difluoro-5'-methoxy-1,1':3',1''-terphenyl-4'-yl)-3-(4-methoxyphenyl) prop-2-en-1-one [17], **S3**: (E)-1-(4,4''-difluoro-5'-methoxy-1,1':3',1''-terphenyl-4'-yl)-3-(6-methoxynaphthalen-2-yl)prop-2-en-1-one [18] and **S4**: (2E)-1-(4,4''-difluoro-5'-methoxy-1,1':3',1''-terphenyl-4'-yl)-3-[4-(methylsulfonyl)phenyl] prop-2-en-1-one [19]. The characterizations data are given in Table 1.

2.2. Nonlinear optical measurements

Solutions of the synthesized compounds were prepared using spectroscopic grade N,N-Dimethylmethanamide (DMF), concentration was 1×10^{-3} mol/L. Single beam Z-scan technique [20] was employed to measure the third-order optical nonlinearities of series of chalcone samples. The schematic experimental set up for Z-scan used in our laboratory is shown in Fig. 4. This technique enables simultaneous measurement of nonlinear refraction (NLR) and nonlinear absorption (NLA). Basically, in this technique a Gaussian laser beam is focused, using a lens, on the vial containing the liquid sample. The vial is translated across the focal region and changes in the far-field intensity pattern were monitored. The experiments were performed using a Q-switched, frequency doubled Nd:YAG laser (Spectra-Physics GCR 170) which produces 7 ns pulses at 532 nm and at a pulse repetition rate of 10 Hz. The laser beam was focused by using a lens of 25 cm focal length. The laser beam waist at the focused spot was estimated to be $18.9 \mu\text{m}$ and the corresponding Rayleigh length is 2.11 mm. The Z-scan measurements were carried out using a cuvette of 1 mm thickness, which is less than the Rayleigh length. Hence, the thin sample approximation is valid. The Z-scan experiment was performed at an input peak-intensity of 2.39 GW/cm^2 . The nonlinear transmission of the sample, with and without the aperture in front of the detector was measured in the far-field using Laser Probe Rj-7620 Energy Meter with Pyroelectric detectors (FOV 10 mm^2). The linear absorption spectrum of the samples was recorded using fiber optic spectrometer (model SD 2000, Ocean Optics Inc) in the wavelength region 200–600 nm at room temperature using DMF solvent as the reference. The UV-visible absorption spectra of the conjugated molecules are shown in Fig. 2. The spectra show negligible single photon absorption at 532 nm wavelength. Therefore, the nonlinear optical measurements carried out in our experiments are under nonresonant excitation.

Linear refractive index values of the samples used for the experiment have been obtained using Mettler Toledo Refractometer at the

Table 1
Characterization data of terphenyl chalcones.

Compound	-Ar	Yield (%)	Melting point (°C)	Analytical data, % found (calculated)		IR (KBr, ν_{max} in cm^{-1})
				C	H	
S1		89	190–192	66.54 (66.55)	3.81 (3.79)	3066 (Ar-H), 2920 (C-H), 1647 (C=O), 1232 (C-F).
S2		79	178–180	76.28 (76.30)	4.88 (4.86)	3022 (Ar-H), 2972, 2845 (C-H), 1631 (C=O), 1217 (C-F)
S3		84	204–206	78.20 (78.25)	4.79 (4.78)	3066 (Ar-H), 2945, 2848 (C-H), 1670 (C=O), 1222 (C-F)
S4		67	132–134	73.69 (73.71)	4.73 (4.69)	3026 (Ar-H), 2931, 2848 (C-H), 1649 (C=O), 1228 (C-F)

experimental wavelength. Linear refractive index values of S1, S2, S3 and S4 are 1.417, 1.421, 1.418 and 1.420 respectively.

3. Results and discussions

The nonlinear transmission of compounds without aperture (open aperture) was measured in the far field as the sample was moved through the focal point. This allows us to determine the nonlinear absorption β . The open aperture curve of sample S1 is shown in Fig. 5. Here, the transmission is symmetric with respect to focus ($z=0$), where it reaches a minimum value, showing an intensity dependent absorption effect. To study the variation in nonlinear optical parameters with substituent group, Z-scan experiments have also been conducted on other samples of this series and similar curves have been obtained. The shape of the open aperture curve suggests that the compound exhibits two-photon absorption [21–23]. The corresponding normalized transmission as a function of sample position in open aperture condition is given by [20,24],

$$T(z) = 1 - (q_0/2\sqrt{2}) \quad \text{for } |q_0| < 1 \quad (1)$$

where $q_0 = \beta I_0(1 - \exp^{-\alpha L})/(1 + z^2/z_0^2)\alpha$, α is the linear absorption coefficient, L is the sample thickness, I_0 is the intensity of the laser beam at the focus, z is the distance of the sample from the focus, z_0 is the Rayleigh length given by the formula $z_0 = 2\pi w_0^2/\lambda$ (λ is the

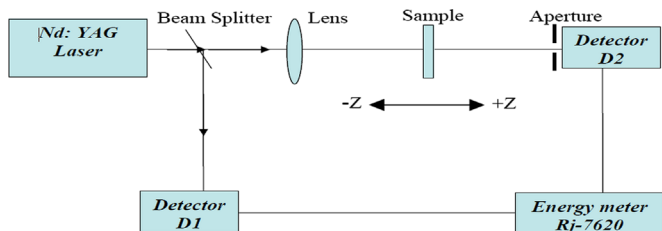


Fig. 4. Schematic experimental setup of Z-scan used in our laboratory.

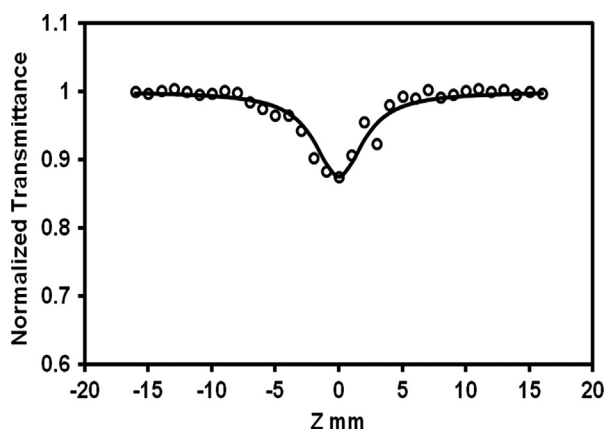


Fig. 5. Open aperture Z-scan curves of compound S1 in DMF solution. Solid line is a theoretical fit to the experimental data.

wavelength and w_0 is the beam waist at the focus) and β is the nonlinear absorption coefficient of the sample obtained by fitting the experimental data using Eq. (1).

It is known that nonlinear absorption coefficient β , depends on the number of absorptive centers in a unit volume. Assuming that this number is N_0 , in units of cm^{-3} , we have [25,26],

$$\beta = \sigma_2 N_0 = \sigma_2 N_A d \times 10^{-3} \quad (2)$$

here, N_0 is the molecular density of the sample (in units of $1/\text{cm}^3$), σ_2 is the molecular TPA coefficient (or cross-section) (in units of cm^4/GW), d is the concentration of the sample and N_A is the Avogadro number. For known β and d , the value of σ_2 can be obtained. Molecular TPA cross-section (in units of $\text{cm}^4 \text{ s/photon}$) is also defined as [27],

$$\sigma'_2 = \sigma_2 h\nu, \quad (3)$$

The imaginary part of $\chi^{(3)}$ ($\text{Im}\chi^{(3)}$) of the compounds are determined using relation given in the literature [10]. The calculated β , molecular TPA cross sections σ_2 and σ'_2 , and $\text{Im}\chi^{(3)}$ values of the compounds are tabulated in Table 2. The value σ'_2 of the investigated compounds are nearly two orders of magnitude larger than that of commercially used compound, Rhodamine 6G which is 10^{-48} to $10^{-50} \text{ cm}^4 \text{ s/photon}$ [28]. It is also comparable with values obtained in stilbazolium like dyes such as trans-4-[2-(pyrrol) vinyl]-1-methylpyridium iodide [29].

To determine the sign and magnitude of nonlinear refraction, closed-aperture Z-scan was performed by placing an aperture in front of the detector (closed aperture). The closed aperture Z-scan curve of S1 is shown in Fig. 6. To obtain a pure nonlinear refraction curve we adopted the division method described in [20]. The investigated samples were found to exhibit peak–valley characteristic, indicating negative nonlinear refraction or self defocusing effect of S1 shown in Fig. 7. The normalized transmittance for pure nonlinear refraction is given by [20],

$$T(Z) = 1 - \frac{4x\Delta\phi_0}{[(x^2 + 9)(x^2 + 1)]}, \quad (4)$$

where $T(z)$ is the normalized transmittance for the pure refractive nonlinearity at different z , $x = z/z_0$ and $\Delta\Phi_0 = 2\pi n_2 I_0 L_{\text{eff}}/\lambda$ is the on-axis nonlinear phase shift. The nonlinear refractive index (n_2) is obtained by fitting the experimental data using Eq. (2). The real part of third-order nonlinear optical susceptibility ($\text{Re}\chi^{(3)}$) can be determined using the relation given in the literature [10]. The determined values of n_2 and $\text{Re}\chi^{(3)}$ are given in Table 2.

Nonlinear optical parameters are given in Table 2. Nonlinearity originated in these compounds is due to strong delocalization of π -electrons. The compounds investigated here are designed based on the scheme donor–acceptor–donor scheme. In the compound S1, bromine is attached with the mentioned molecular structure, bromine acts as an acceptor and the molecular structure acts as donor because bromine shows highly negative inductive effect. Charge transfer takes place from molecular structure to the bromine. In S2 where OCH_3 is attached with mentioned molecular structure, OCH_3 acts as a donor and the molecular structure acts as acceptor because OCH_3 shows highly positive inductive effect. Charges transfer from OCH_3 to molecular compound. In S3 double benzene ring where OCH_3 is attached with the mentioned structure, OCH_3 acts as a donor and the molecular compound acts as

Table 2

Third-order nonlinear optical parameters of samples in DMF solution at the concentration of $1 \times 10^{-3} \text{ mol/L}$.

Sample	$n_2 (\times 10^{-11} \text{ esu})$	$\beta (\text{cm/GW})$	$\text{Re}\chi^{(3)} (\times 10^{-13} \text{ esu})$	$\text{Im}\chi^{(3)} (\times 10^{-13} \text{ esu})$	$\sigma_2 (\times 10^{-18} \text{ cm}^4/\text{GW})$	$\sigma'_2 (\times 10^{-46} \text{ cm}^4 \text{ s/photon})$
S1	−1.148	1.489	−1.230	0.228	2.467	9.183
S2	−1.185	2.025	−1.270	0.312	3.362	12.54
S3	−1.787	2.352	−1.914	0.362	3.906	14.57
S4	−2.006	5.206	2.149	0.801	8.643	32.24

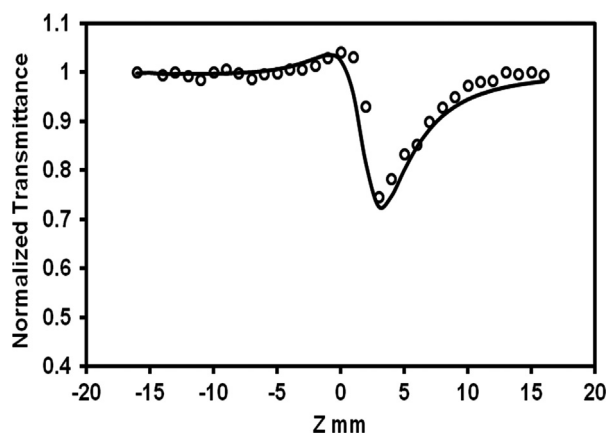


Fig. 6. Closed aperture pure nonlinear refraction Z-scan curves of compound S1 in DMF solution. Solid line is a theoretical fit to the experimental data.

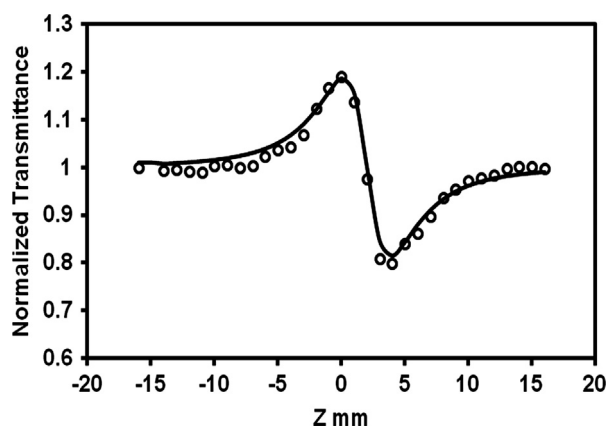


Fig. 7. Pure nonlinear refraction Z-scan curves of compound S1 in DMF solution. Solid line is a theoretical fit to the experimental data.

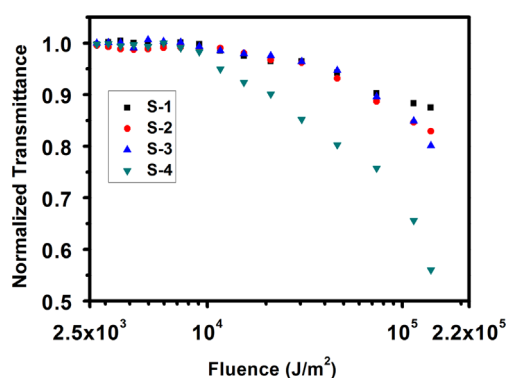


Fig. 8. Optical limiting behavior of the samples.

acceptor because OCH_3 shows highly positive inductive effect. Charges transfer from OCH_3 to molecular compound. In S4 where SCH_3 is attached with mentioned molecular compounds, in this structure SCH_3 act as a donor and the molecular compound act as acceptor because SCH_3 shows highly positive inductive effect. Strong electrons delocalization from SCH_3 group to molecular compound takes place. Among the investigated compounds, S4 reveals higher nonlinearity than the others because of the strong electron donating ability of SCH_3 group. The increase in nonlinear optical properties are clearly observed in Table 2.

An optical power limiter is a device which has very high transmission for weak optical signals, but becomes opaque for

intense optical signals [26]. The optical power limiting is mainly due to nonlinear absorption in the molecule. The optical power limiting behaviors of the molecules are obtained from the open aperture Z-scan curve, schematic representation shown in Fig. 4. The optical power limiting behaviors of the molecules are shown in Fig. 8. The optical limiting threshold will determine the ability of the limiter. The lower the threshold value is better the optical limiter. Optical limiting threshold of the molecules S1, S2 and S3 are $4 \times 10^4 \text{ J/m}^2$ whereas, S4 is $1 \times 10^4 \text{ J/m}^2$. The molecule S4 exhibits the better optical limiting behavior than all other molecules.

4. Conclusions

In summary, third-order nonlinear optical parameters of four terphenyl containing chalcones in DMF solution were studied using Z-scan technique. The Z-scan results indicate the molecules exhibits negative nonlinear refractive index and nonlinear absorption. The nonlinear index found to be negative and magnitude is of the order of 10^{-11} esu. We also measured the molecular two-photon absorption cross-section of this molecule and it is of the order of $10^{-46} \text{ cm}^4/\text{s/photon}$ which is nearly two orders of magnitude larger than that of Rhodamine dyes [28]. The molecules studied here exhibits optical power limiting behavior of nanosecond laser pulses at 532 nm wavelength. Hence, the samples investigated seem to be promising candidates for future photonic and optoelectronic applications.

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