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

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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} cm^4 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).

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″-

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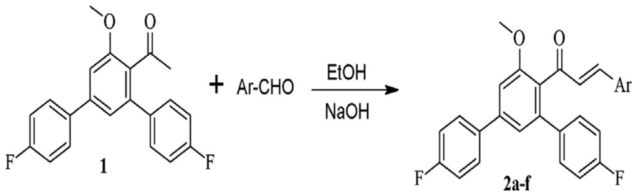


Fig. 1. Synthesis scheme of the molecules.

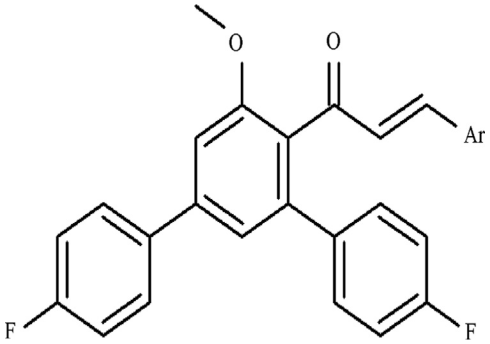


Fig. 2. Molecular structure the compounds.

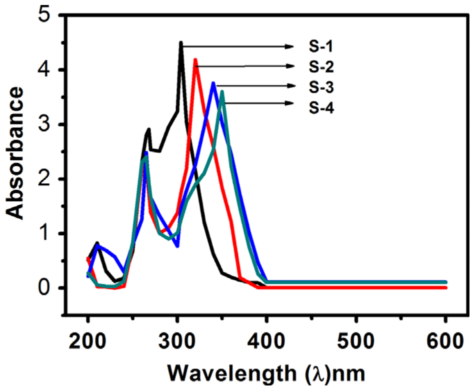


Fig. 3. UV–vis spectra of the molecules.

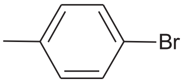
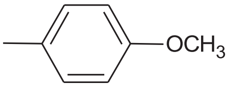
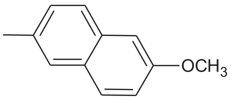
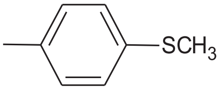
difluoro-5′-methoxy-1,1′:3′,1″-terphenyl-4′-yl)-3-(4-methoxyphenyl) prop-2-en-1-one [17], **S3:** (*E*)-1-(4,4″-difluoro-5′-methoxy-1,1′:3′,1″-terphenyl-4′-yl)-3-(6-methoxynaphthalen-2-yl)prop-2-en-1-one [18] and **S4:** (2*E*)-1-(4,4″-difluoro-5′-methoxy-1,1′:3′,1″-terphenyl-4′-yl) -3-[4-(methylsulfanyl)phenyl] 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 μm and the corresponding Rayleigh length is 2.11 mm. The Z-scan measurements were carried out using a cuvette of 1 mm thick ness, 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)