

Synthesis and nonlinear optical characterization of new poly{2,2'-(3,4-didodecyloxythiophene-2,5-diyl)bis[5-(2-thienyl)-1,3,4-oxadiazole]}

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ABSTRACT

A new donor–acceptor type poly{2,2'-(3,4-didodecyloxythiophene-2,5-diyl)bis[5-(2-thienyl)-1,3,4-oxadiazole]} (**P**) was synthesized starting from thiodiglycolic acid and diethyl oxalate through multistep reactions. The polymerization was carried out using chemical polymerization technique. The optical and charge-transporting property of the copolymer was investigated by UV–vis, fluorescence emission spectroscopic and cyclic voltammetric studies. The copolymer shows UV absorption maxima at 375 nm and displays bluish–green fluorescence in DMF solution. Its electrochemical band gap was determined to be 2.07 eV. The nonlinear optical (NLO) properties of the copolymer was investigated at 532 nm using single beam Z-scan and degenerate four-wave mixing (DFWM) techniques with nanosecond laser pulses. The copolymer exhibits strong optical limiting behavior due to effective three-photon absorption (3PA). Values of the effective 3PA coefficient (γ), third-order nonlinear susceptibility ($\chi^{(3)}$) and figure of merit (F) have been calculated.

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1. Introduction

Materials exhibiting high nonlinear optical (NLO) properties have received considerable attention due to their potential applications in optical switching, optical communications, optical data storage, and eye and sensor protection [1–3]. In the past several materials have been investigated for their NLO properties, and organic materials are attractive in this regard due to their large variety, high nonlinearity and ease of synthesis. Over the years, conjugated polymeric systems have emerged as a promising class of NLO materials, due to the large third-order susceptibility observed along the directions of polymer chain. These macromolecules are highly flexible at both the molecular and bulk levels, so that structural modifications are possible to optimize them for specific device applications. Since the nonlinear response of these systems is primarily determined by their chemical structure, one can design unique molecular structures and synthesize compounds with enhanced nonlinear response by introducing suitable substituent groups. In general, the presence of strong π -electron delocalization in the molecular structure is found to enhance the NLO properties. According to Cassano et al. [4], incorporation of alternate

electron–acceptor and electron–donor units in the polymer backbone in conjugated polymers would enhance the NLO properties arising from higher order hyperpolarizabilities. Conjugated polymers find applications in devices such as Light Emitting Diodes (LEDs), Field Effect Transistors, Electrochemical Cells and Organic Photovoltaic Cells as well. Among the newly developed polymers, poly(1,4-phenylenevinylene) (PPV) [5], poly(*p*-phenylene) (PPs) [6], polyfluorenes (PFs) [7] and polythiophenes (PTs) [8] were in the focus of recent investigations.

Because of easy processability, chemical stability and readiness of functionalities, thiophene based polymers are currently under active investigation for third-order NLO properties [9–11]. The good film forming characteristics, solubility, and adequate mechanical strength have made them more attractive for device fabrication in comparison to their inorganic counterparts. In polythiophenes, nonlinear optical properties can be synthetically tuned by introducing electron releasing and electron accepting segments in the polymer chain, which would result in increased delocalization in the molecule. In similar lines, Adhikari and coworkers have recently synthesized a few donor–acceptor type polythiophenes and studied the relationship between their structure and NLO properties [12–14]. These studies showed that the incorporation of electron releasing and electron accepting groups along the polymer backbone would be a promising molecular design for enhancing the third-order NLO properties. Therefore now we have incorporated two additional unsubstituted thiophene moieties in between the 3,4-dialkoxy substituted thiophenyl oxadiazole systems in our new synthetic design, in order to enhance the electron

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acceptance nature within the polymer chain, with the intention of obtaining a copolymer with better NLO properties. Moreover, it has been predicted that the presence of unsubstituted thiophene rings reduces the steric repulsion between the bulky alkyl groups and increases the planarity of the polymer chain that could help to reduce the band gap. In this communication, we hereby report the synthesis of hitherto unknown copolymer carrying 2,2'-(3,4-didodecyloxythiophene-2,5-diyl)bis[5-(2-thienyl)-1,3,4-oxadiazole units and the investigation of their NLO properties in detail.

2. Experimental

2.1. Materials

3,4-didodecyloxythiophene-2,5-dicarbohydrazide was synthesized according to the reported literature procedure [15,16]. Dimethylformamide acetonitrile were dried over CaH_2 . Thiodiglycolic acid, diethyl oxalate, tetrabutylammoniumperchlorate (TBAPC) and *n*-bromoalkanes were purchased from Lanchester (UK) and were used as received. Thiophene-2-carbonyl chloride was purchased from Aldrich and directly used. All the solvents and reagents were of analytical grade. They were purchased commercially and used without further purification. Diethyl 3,4-didodecyloxythiophene-2,5-dicarboxylate was synthesized according to the reported literature procedure [17–19].

2.2. Instrumentation

Infrared spectrum of all intermediate compounds and the copolymer was recorded on a Nicolet Avatar 5700 FTIR (Thermo Electron Corporation). The UV–vis and fluorescence emission spectra of the copolymer were measured in GBC Cintra 101 UV-visible and PerkinElmer LS55 spectrophotometers respectively. ^1H and ^{13}C NMR spectra were obtained with AMX 400 MHz FT-NMR spectrophotometer using TMS/solvent signal as internal reference. Mass spectra were recorded on a Jeol SX-102 (FAB) Mass Spectrometer. Elemental analysis was performed on a Flash EA1112 CHNS analyzer (Thermo Electron Corporation). The electrochemical study of the copolymer was carried out using a AUTOLAB PGSTAT30 electrochemical analyzer. Cyclic voltammogram was recorded using a three-electrode cell system, with glassy carbon button as working electrode, a platinum wire as counter electrode and an Ag/AgCl electrode as the reference electrode. Molecular weight of the polymer was determined on Waters make Gel Permeation Chromatography (GPC) using polystyrene standards in THF solvent.

2.2.1. Z-scan measurement

The Z-scan is a popular technique developed by Sheik-Bahae et al. [20] for measuring the nonlinear optical refraction and absorption coefficients of materials. The “open aperture” Z-scan is used for nonlinear absorption coefficient measurements. In this technique a Gaussian laser beam is used for molecular excitation, and its propagation direction is taken as the *z*-axis. The beam is focused using a convex lens, and the focal point is taken as $z=0$. The experiment is done by placing the sample in the beam at different positions with respect to the focus (different values of *z*), and measuring the corresponding transmission. The beam will have maximum energy density at the focus, which will symmetrically reduce towards either side of it, for the positive and negative values of *z*. Thus the sample sees different laser intensity at each *z* position. From the corresponding transmission values, the nonlinear absorption coefficient of the sample can be calculated.

The second harmonic output from a Q-switched Nd:YAG nanosecond laser (Quanta Ray, Spectra Physics) was used for the measurements. The laser had a nominal pulse width of 7 ns and

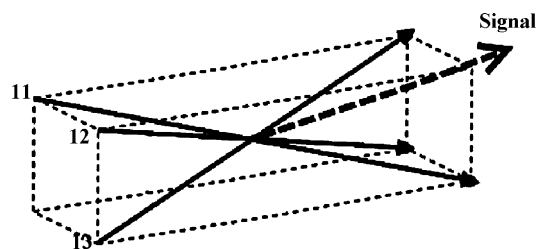


Fig. 1. Four-wave mixing in the BOXCARS geometry.

laser pulse energy of $15\ \mu\text{J}$ was used for the experiments. The output of the laser had a nearly Gaussian Intensity profile. The sample was taken in a 1 mm cuvette. The transmission of the sample at each point was measured by means of two pyroelectric energy probes (Rj7620, Laser Probe Inc.). One energy probe monitors the input energy, while the other monitors the transmitted energy through the sample. The pulses were fired in the “single shot” mode, allowing sufficient time between successive pulses to avoid accumulative thermal effects in the sample.

2.2.2. DFWM studies

The interaction of four electromagnetic waves in a nonlinear optical medium via the third-order polarization is termed as four-wave mixing. When all the waves have the same frequency, it is called degenerate four-wave mixing (DFWM). There are different geometries like phase conjugate geometry, BOXCARS geometry etc., in which a four-wave mixing experiment can be set up. In the present experiment, we used the forward folded BOXCARS geometry, where a laser beam is split into three and the beams are aligned such that they form three corners of a square, as given in Fig. 1. The diametrically opposite beams are the pump beams, and they have the same intensity. The third beam is the probe, which has an intensity of about 20% of the pump beam. These three beams will interact nonlinearly when focused on to a sample to generate a fourth beam (signal beam), which will appear at the fourth corner of the square.

In our DFWM experiment we used 7 ns pulses at 532 nm obtained from the second harmonic output of a Q-switched Nd:YAG laser. The intensity of the input laser beam was changed using a rotating polarizer. The sample was taken in a 2 mm glass cuvette and the input energy was monitored using a pyroelectric energy probe. The generated signal beam was isolated and measured in the far field using a calibrated photodiode.

2.3. Synthesis of intermediates and monomers

2.3.1. 3,4-Didodecyloxythiophene-2,5-carboxyhydrazide (**a**)

Diethyl 3,4-didodecyloxythiophene-2,5-dicarboxylate (0.5 g) was added into a solution of 10 mL hydrazine monohydrate in 40 mL of methanol. The reaction mixture was refluxed for 2 h. Upon cooling the solution to room temperature a white precipitate was obtained. The precipitate was filtered, washed with petroleum ether, dried under vacuum and finally recrystallized from ethanol to get white solid. Yield: 85%, IR (KBr, cm^{-1}): 3334, 3284 (>N–H–), 3195, 2966, 2931, 2874, 1610 (>C=O). ^1H NMR (400 MHz, CDCl_3). δ (ppm): 8.33 (s, 2H, >N–H), 4.90 (s, 4H, –NH₂), 4.15 (t, 4H, –OCH₂–), 1.27–1.81 (m, 40H, –(CH₂)₁₀–), 0.88 (t, 6H, –CH₃). Anal. Calcd. for $\text{C}_{30}\text{H}_{56}\text{N}_4\text{O}_4\text{S}$: C, 63.34; H, 9.92; N, 9.85; S, 5.64. Found: C, 62.60; H, 10.40; N, 9.06; S, 5.12.

2.3.2. *N*²,*N*⁵-Bis-(thiophene-2-ylcarbonyl)-3,4-didodecyloxythiophene-2,5-dicarbohydrazide (**c**)

A mixture 0.1 mol of 3,4-didodecyloxythiophene-2,5-carboxyhydrazide, 0.2 mol of thiophene-2-carbonyl chloride

in 20 mL of *N*-methyl pyrrolidone was taken in a round bottom flask. After adding 2 to 3 drops of pyridine as catalyst, the mixture was refluxed for 10 h. The completion of the reaction was monitored by TLC. When the reaction was complete, the contents were poured into excess of water. The separated solid was filtered, washed with pet. ether (boiling range 40–60 °C), dried and recrystallized from ethanol/chloroform mixture. Yield: 80%. IR (KBr, cm^{-1}): 3235 ($-\text{N}-\text{H}-$), 1681 and 1644 ($>\text{C}=\text{O}$). FABHRMS: m/z , 788. ^1H NMR spectrum (400 MHz, CDCl_3 , ppm): 10.12 (s, 2H, $-\text{N}-\text{H}$), 9.91 (s, 2H, $-\text{N}-\text{H}-$), 7.72 (d, 2H, thiophene proton at position 3), 7.50 (d, 2H, thiophene proton at position 5), 7.06 (t, 2H, thiophene proton at position 4), 4.26 (t, 4H, $-\text{OCH}_2-$), 1.24–1.96 (m, 40H, $-(\text{CH}_2)_{10}-$), 0.89 (t, 6H, $-\text{CH}_3$). Anal. Calcd. for $\text{C}_{36}\text{H}_{52}\text{N}_4\text{O}_6\text{S}_3$: C, 60.88; H, 7.66; N, 7.10; S, 12.19. Found: C, 59.25; H, 7.34; N, 7.67; S, 13.00.

2.3.3. 2,2'-(3,4-Didodecyloxythiophene-2,5-diyl)bis[5-(2-thienyl)-1,3,4-oxadiazole (d)]

A mixture of 20 mmol of biscarbohydrazide (c) and 25 mL of phosphorous oxychloride were heated at 100 °C for 6 h. The reaction mixture was then cooled to room temperature and poured into excess of crushed ice. The resulting precipitate was collected by filtration and washed with water followed by acetone. The crude product was dried in vacuum oven and recrystallized with ethanol/chloroform mixture. Yield: 78 %, IR (KBr, cm^{-1}): 2922, 2855, 2763, 1573 ($-\text{C}=\text{N}-$), 1462, 1060. FABHRMS: m/z , 753. ^1H NMR spectrum (400 MHz, CDCl_3 , ppm): 7.85 (d, 2H, thiophene proton at position 3), 7.60 (d, 2H, thiophene proton at position 5), 7.21 (t, 2H, thiophene proton at position 4), 4.30 (t, 4H, $-\text{OCH}_2-$), 1.26–1.92 (m, 40H, $-(\text{CH}_2)_{10}-$), 1.06 (t, 6H, $-\text{CH}_3$). Anal. Calcd. for $\text{C}_{40}\text{H}_{56}\text{N}_4\text{O}_4\text{S}_3$: C, 63.79; H, 7.50; N, 7.44; S, 12.77. Found: C, 62.88; H, 7.06; N, 7.90; S, 12.11.

2.4. Synthesis of copolymer (P)

To a stirred solution of 4 equivalents of anhydrous ferric chloride in 20 mL of chloroform, the 1 equivalent of monomer (d) in 10 mL of chloroform was added slowly for 30 min. The reaction mixture was heated to 65–70 °C for 24 h. The completion of the reaction was monitored by TLC. After the completion of the reaction, the chloroform was removed by rotary evaporator under vacuum. The solid product obtained was washed with excess of methanol to remove the ferric chloride. The last trace of ferric chloride was removed by Soxhlet extraction technique using methanol as solvent. The copolymer (P) was obtained as black powder. Yield: 65%, IR (KBr, cm^{-1}), 2927, 2860, 2634, 1593 ($>\text{C}=\text{N}-$), 1495, 1234. ^1H NMR spectrum (400 MHz, $\text{DMSO}-d_6$, ppm): 7.80 (d, 2H, thiophene proton at position 3), 7.34 (d, 2H, thiophene proton at position 4), 4.32 (t, 4H,

$-\text{OCH}_2-$), 1.32–1.95 (m, 40H, $-(\text{CH}_2)_{10}-$), 1.02 (t, 6H, $-\text{CH}_3$). Anal. Calcd. for $(\text{C}_{40}\text{H}_{54}\text{N}_4\text{O}_4\text{S}_3)_n$, C, 63.97; H, 7.25; N, 7.46; S, 12.81. Found: C, 63.20; H, 7.79; N, 7.00; S, 12.11. Molecular weight, $M_w = 3490$, $M_n = 2458$. Polydispersity (PD): 1.42.

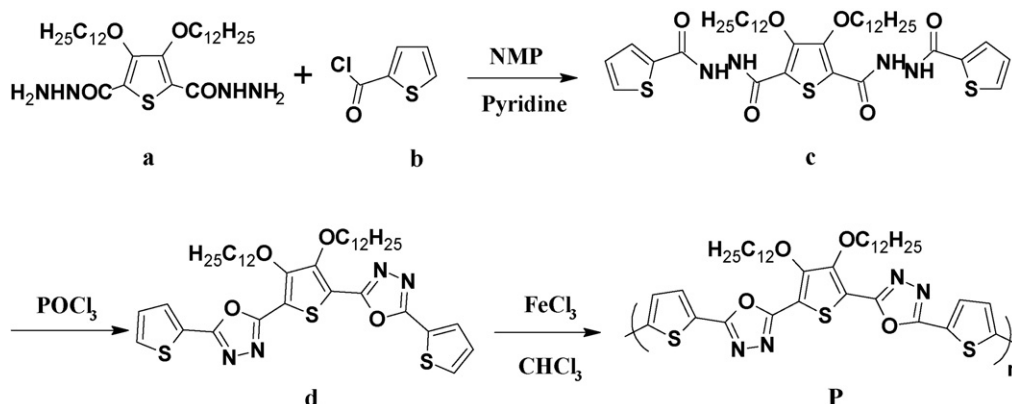
3. Results and discussion

3.1. Synthesis and characterization of copolymer

Scheme 1 shows the synthetic route for the preparation of monomers and the copolymer. The required 3,4-didodecyloxythiophene-2,5-carboxyhydrazides (a) was synthesized by refluxing diethyl 3,4-didodecyloxythiophene-2,5-dicarboxylate with hydrazine monohydrate in methanol. These carboxyhydrazide was condensed with thiophene-2-carbonyl chloride (b) to get the corresponding dicarbohydrazide (c), which on treatment with phosphorous oxychloride afforded bis-oxadiazole (d). The monomer, bis-oxadiazole (d) was polymerized via chemical polymerization route using anhydrous ferric chloride as polymerization catalyst. The structure of newly synthesized monomers and the copolymer (P) were confirmed by its FTIR, ^1H , ^{13}C NMR, mass spectral and elemental analyses.

Formation of 3,4-didodecyloxythiophene-2,5-carboxyhydrazide (a) from the corresponding diester was evidenced by its IR and ^1H NMR spectral data. Its IR spectrum showed sharp peaks at 3284 and 1610 cm^{-1} indicating the presence of $-\text{NH}_2$ and $>\text{C}=\text{O}$ groups respectively. ^1H NMR spectrum of it displayed peaks at δ 8.33 (s, 2H) and δ 4.90 (s, 4H) for $>\text{NH}$ and $-\text{NH}_2$ protons respectively. Conversion of bishydrazide (a) to biscarbohydrazide (c) was confirmed by its IR, ^1H NMR and mass spectral studies. Its IR spectrum exhibited sharp peaks at 3235 and 1681 cm^{-1} for $>\text{NH}$ and $>\text{C}=\text{O}$ groups respectively (Fig. 2). ^1H NMR spectrum of it showed two $>\text{NH}$ protons as singlet at δ values 10.12 and 9.91, thiophene protons as two doublets at δ 7.72 and 7.50 and a triplet at δ 7.06. Its mass spectrum displayed the molecular ion peak at m/z 788. Cyclization of biscarbohydrazide c to form bisoxadiazole d was established by its IR, ^1H NMR and mass spectral data. Its IR spectrum showed no absorption peaks due to $>\text{NH}$ and $>\text{C}=\text{O}$ groups and appearance of sharp peak at 1573 cm^{-1} (Fig. 2) indicating the formation of oxadiazole ring. Further, in its ^1H NMR spectrum disappearance of two singlets corresponding to $>\text{NH}$ protons confirmed the cyclization.

Finally, polymerization of monomer (d) to copolymer (P) was established by its IR, ^1H NMR, GPC and elemental analyses. IR spectrum of P showed characteristic absorption peaks at 2927, 2860 cm^{-1} (C–H stretching aliphatic segments), 1593 cm^{-1} (1,3,4-oxadiazole), 1234 cm^{-1} (C–O–C stretching of ether bond), 1495 cm^{-1} (aromatic). The ^1H NMR spectrum of the copolymer (Fig. 3) in CDCl_3 displayed two doublets δ 7.80 and 7.34 which



Scheme 1. Designed synthetic route for the preparation of copolymer.

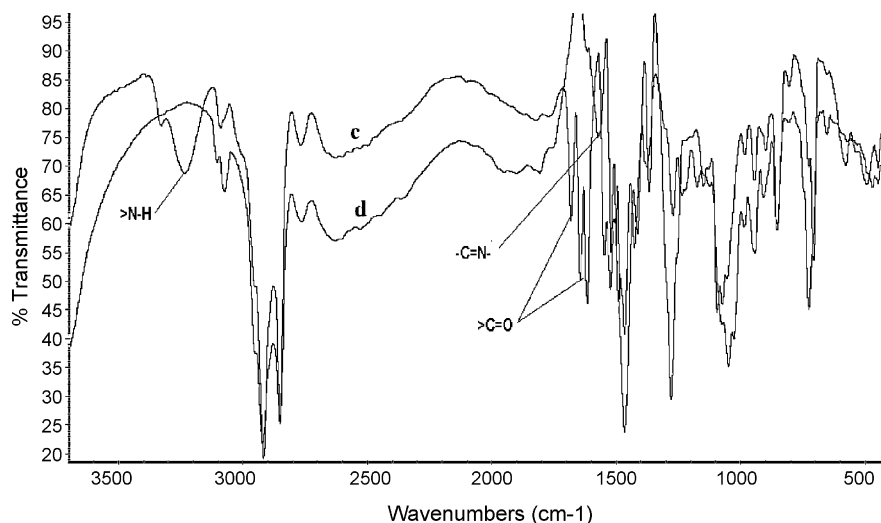


Fig. 2. IR spectra of bis-carbohydrazone (c) and bis-oxadiazole (d).

are due to two thiophene protons. Disappearance of one doublet and conversion of a triplet peak into doublet in the aromatic region clearly confirmed the polymerization of the monomer (d). Further, four protons of $-\text{OCH}_2-$ groups attached to thiophene ring resonated at δ 4.32 as triplet. In addition multiplet peaks were observed in the range δ 1.95–1.32 due to $-(\text{CH}_2)_n-$ protons of dodecyloxy group. The number and weight average molecular weights of THF soluble part of the copolymer **P** were found to be 2458 and 3490 respectively. Its polydispersity is 1.42.

3.2. Electrochemical properties

Cyclic voltammetry (CV) was employed to determine redox potentials of new copolymer and then to estimate the HOMO and LUMO energy of the copolymer, which is of importance to determine the band gap. The cyclic voltammogram of the copolymer coated on a glassy carbon electrode was measured on AUTOLAB PGSTAT 30 electrochemical analyzer, using a Pt counter electrode and a Ag/AgCl reference electrode, immersed in the electrolyte [0.1 M (*n*-Bu)₄NClO₄ in acetonitrile] at a scan rate of

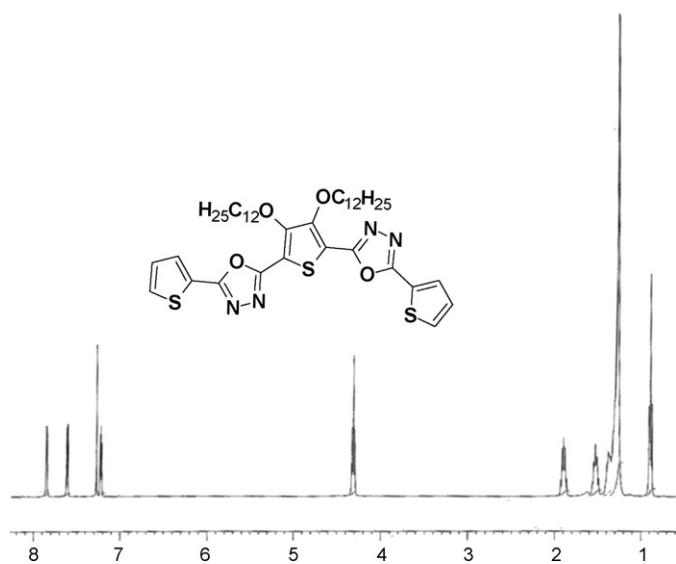


Fig. 3. ¹H NMR spectrum of bis-oxadiazole (d).

25 mV/S. Electrochemical data of the copolymer is summarized in Table 1.

While sweeping cathodically (Fig. 4), the copolymer showed reduction peak at -1.40 V. This reduction potential is lower than those of 2-(4-tert-butyl phenyl)-1,3,4-oxadiazole (PBD) [21,22], one of the most widely used electron transporting materials. In the anodic sweep (Fig. 4), copolymer showed oxidation peak at about 1.53 V, comparable with some donor acceptor type of copolymers containing oxadiazole moieties [15,16]. The onset potentials of n- and p-doping processes can be used to estimate the HOMO and LUMO of the copolymer. The equations reported by de Leeuw et al. [23], $E_{\text{HOMO}} = -[E_{\text{onset}}^{\text{oxd}} + 4.4 \text{ eV}]$ and $E_{\text{LUMO}} = -[E_{\text{onset}}^{\text{red}} - 4.4 \text{ eV}]$ where $E_{\text{onset}}^{\text{oxd}}$ and $E_{\text{onset}}^{\text{red}}$ are the onset potentials versus SCE for the oxidation and reduction of the copolymer.

Table 1
Electrochemical potential and energy levels of the copolymer.

Copolymer	P
E_{oxd}	1.53
E_{red}	-1.40
$E_{\text{oxd}}(\text{onset})$	1.22
$E_{\text{red}}(\text{onset})$	-0.85
$E_{\text{HOMO}}(\text{eV})$	-5.56
$E_{\text{LUMO}}(\text{eV})$	-3.49
$E_{\text{g}}(\text{eV})$	2.07

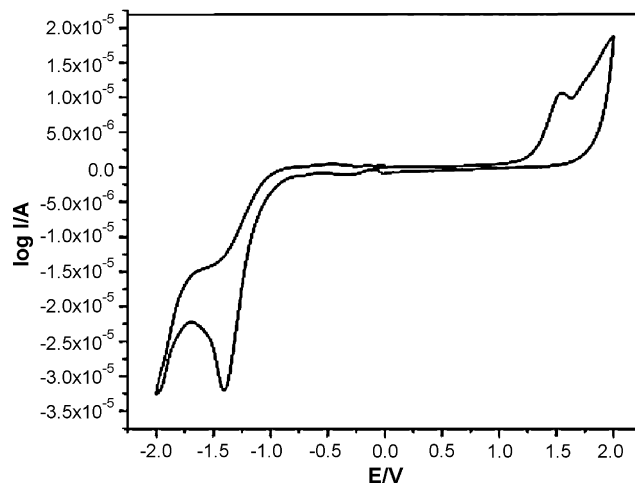


Fig. 4. Oxidation and reduction cyclic voltammetric waves of the copolymer.

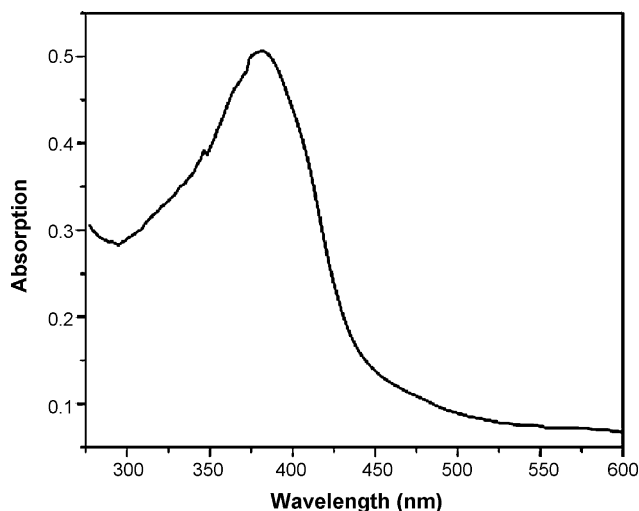


Fig. 5. UV-vis absorption spectra of the copolymer in DMF solution.

The HOMO energy level of the copolymer was estimated to be -5.56 eV. The HOMO energy level is comparable with CN-PPV and some reported polyoxadiazoles [15,16]. The LUMO energy level (-3.49 eV) is lower than those of PPV and some other conjugated p-type conjugated polymers indicating the copolymer is having better electron transporting property. Further, it has been noticed that the LUMO level is lower than some reported polyoxadiazoles [15,16], showing that the copolymer possess much better electron injection ability. This may be attributable to the introduction of additional electron withdrawing thiophene rings within the polymer backbone. The very high electron affinity of this copolymer may be attributed to the incorporation of electron deficient oxadiazole ring in the copolymer backbone. From the onset potentials of oxidation and reduction process, the band gap of the copolymer is estimated to be 2.07 eV. It is clear from the results that improved charge carrying property is expected for the new copolymer.

3.3. Linear optical properties

The UV-visible absorption and fluorescence emission spectrum of the copolymer were recorded in dilute DMF solution. As shown in Fig. 5 the copolymer exhibits absorption maxima at 375 nm. The fluorescence emission spectrum of the copolymer (Fig. 6) shows emissive maxima (excitation wavelength 360 nm) at 435 nm. These results indicate that the copolymer emits intense bluish-green light under the irradiation of UV light.

3.4. Nonlinear optical properties

3.4.1. Z-scan

The linear absorption spectrum of the copolymer shows that the excitation wavelength of 532 nm is close to one of the absorption edges. Small absorption tails at 532 nm give the linear absorption coefficient (α) for the copolymer, which is given in Table 2. As shown in Fig. 7 the copolymer shows strong optical limiting behavior, where the transmittance decreases when the pump fluence is increased. It is seen that a three-photon absorption (3PA) type process gives the best fit to the obtained experimental data. The Z-scan curves obtained are therefore numerically fitted to the nonlinear transmission equation for a 3PA process, given by Eq. (1):

$$T = \frac{(1-R)^2 \exp(-\alpha L)}{\sqrt{\pi p_0}} \int_{-\infty}^{+\infty} \ln \left[\sqrt{1 + p_0^2 \exp(-2t^2)} + p_0 \exp(-t^2) \right] dt \quad (1)$$

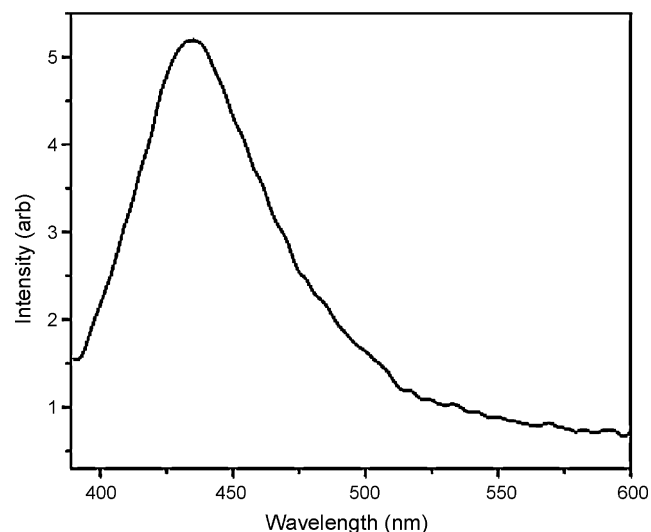


Fig. 6. Fluorescence emission spectra of copolymer in DMF solution.

where T is the transmission of the sample. R is the Fresnel reflection coefficient at the sample-air interface, α is the absorption coefficient, and L is the sample length. p_0 is given by $[2\gamma(1-R)^2 I_0^2 L_{\text{eff}}]^{1/2}$ where γ is the 3PA coefficient, and I_0 is the incident intensity. L_{eff} is given by $[1 - \exp(-2\alpha L)]/2\alpha$. The 3PA coefficients obtained from the curve fitting are tabulated in Table 2. While doing the calculation

Table 2
Linear and nonlinear optical parameters for the copolymer.

Linear optical properties	
Sample	P
n_0^a	1.431
α^b (m^{-1})	68.3
Z-scan	
γ ($10^{-22} \text{ m}^3/\text{W}^2$)	4.8
DFWM	
$\chi^{(3)}$	
($10^{-20} \text{ m}^2/\text{V}^2$)	1.794
(10^{-12} esu)	1.28
F	
(10^{-22} m/V^2)	2.627
(10^{-12} esu)	1.874

^a Refractive index.

^b Absorption coefficient.

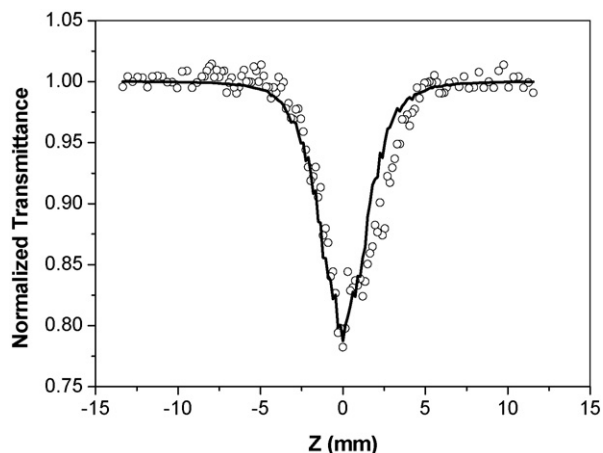


Fig. 7. Open aperture Z-scan curve for copolymer with 3PA fitting.

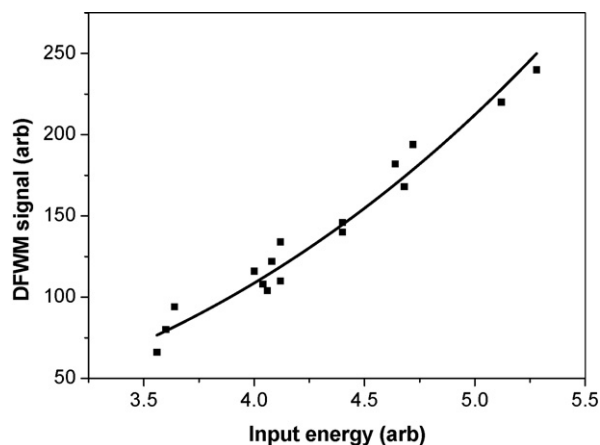


Fig. 8. DFWM signal versus input for CS₂.

the pulse-to-pulse energy fluctuations of the laser also are taken into account, and hence the simulated curve is not fully smooth.

Considering the absorption spectra of the copolymer and recalling that pure 3PA cross-sections are generally very low, it seems that the observed nonlinearity arises from sequential 3PA involving excited states. Two-photon absorption followed by excited state absorption is another possibility. Therefore the nonlinearity can be considered as an “effective” 3PA process. During the 3PA process, excitation is proportional to the cube of the incident intensity. This feature may help to obtain higher contrast and resolution in imaging, since 3PA provides a stronger spatial confinement. With the availability of ultrafast-pulsed lasers in recent years, significant progress in 3PA-based applications has been witnessed including three-photon pumped lasing and 3PA-based optical limiting and stabilization [24].

In π -conjugated polymeric systems, electrons can move in large molecular orbitals which results from the linear superposition of the carbon p_z atomic orbitals, leading to a very high optical nonlinearity, which increases with the conjugation length [25]. The copolymer studied in the present work consists of thiophene ring substituted with dodecyloxy pendant at 3,4-position as electron donating group and 1,3,4-oxadiazole along with unsubstituted thiophene moieties as electron withdrawing groups. This leads to formation of a donor–acceptor type of arrangement in the polymer backbone. The enhanced third order nonlinearity in the copolymer arises due to the high π -electron density along the polymeric chain, which are easily polarizable as a result of the alternating donor–acceptor type of arrangements. The substitution of the electron donating alkoxy group not only enhances the delocalization electrons in the copolymer, but also acts as a solubilizing group. Such absorptive nonlinearities involving real excited states have been reported earlier in C₆₀ (fullerenes), semiconductors, metal-nanoclusters, phthalocyanines and some fluorine derivatives [26–31].

3.4.2. DFWM

Fig. 8 shows the variation of the DFWM signal as a function of the pump intensity obtained from the reference sample, CS₂. The DFWM signal obtained for the copolymer is shown in Fig. 9. The signal is proportional to cubic power of the input intensity as given by the equation:

$$I(\omega) \propto \left(\frac{\omega}{2\epsilon_0 c n^2} \right) |\chi^{(3)}|^2 I_0^3(\omega) \quad (2)$$

where $I(\omega)$ is the DFWM signal intensity, $I_0(\omega)$ is the pump intensity, l is the length of the sample and n is the refractive index of the medium. The solid curve in the figure is the cubic fit to the exper-

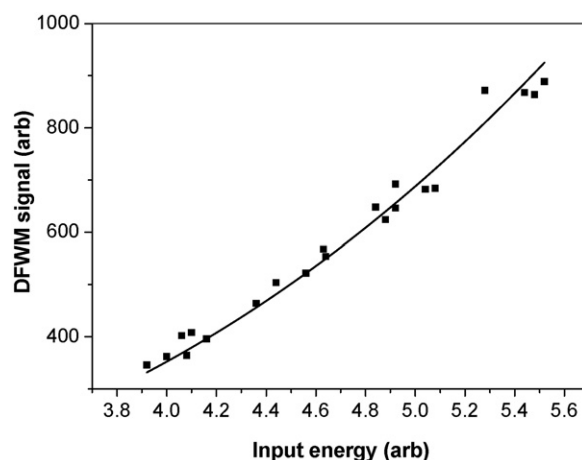


Fig. 9. DFWM signal versus input for the copolymer.

imental data. The third-order susceptibility, $\chi^{(3)}$ of the sample can be calculated from the fit using the equation:

$$\chi^{(3)} = \chi_R^{(3)} \left[\frac{I/I_0^3}{(I/I_0^3)_R} \right]^{1/2} \left[\frac{n}{n_R} \right]^2 \frac{I_R}{l} \left(\frac{\alpha l}{(1 - e^{-\alpha l}) e^{-\alpha l/2}} \right) \quad (3)$$

where the subscript R refers to the standard reference, CS₂. $\chi_R^{(3)}$ is taken to be $9.5 \times 10^{-21} \text{ m}^2/\text{V}^2$ [32]. The figure of merit F , given by $\chi^{(3)}/\alpha$, is then calculated. F is a measure of nonlinear response that can be achieved for a given absorption loss in the medium. The F value is useful for comparing the nonlinearity of different materials when excited in spectral regions of non-zero absorption. Table 2 shows that the copolymers have good F values. The $\chi^{(3)}$ and F values are given in both cgs and SI units.

4. Conclusions

A novel conjugated copolymer (**P**) carrying 2,2'-(3,4-didodecyloxythiophene-2,5-diyl)bis[5-(2-thienyl)-1,3,4-oxadiazole] unit with donor and acceptor moieties in the molecular architecture has been successfully synthesized through multistep reactions. The newly synthesized monomers and the copolymer were characterized by spectroscopic techniques. The optical properties revealed that the copolymer emits bluish-green fluorescence under the irradiation of light. The electrochemical properties showed that the copolymer possess high-lying HOMO energy level (−5.56 eV) and low lying LUMO energy level (−3.49 eV). This is attributed to the presence of alternate donor–acceptor conjugated units along the copolymer backbone. The nonlinear optical properties of the copolymer have been studied using the Z-scan and DFWM techniques. The copolymer exhibited effective 3PA. Values of the 3PA coefficients (γ), third-order nonlinear susceptibilities ($\chi^{(3)}$) and figures of merit (F) have been calculated. The absorptive nonlinearity observed in this copolymer is of optical limiting type, which can have potential applications.

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