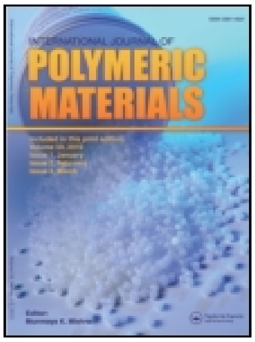

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Large Third-Order Nonlinearity of New π-conjugated Donor-Acceptor Polymers with Substituted Thiophene and 1,3,4-Oxadiazole Moieties

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We present the synthesis of two newly designed, thiophene-based conjugated polymers (**P1** and **P2**) carrying 1,3,4-oxadiazole, 3,4-dinaphthyloxy thiophene, and 3,4-dialkoxy thiophene moieties as potential NLO active materials. Their NLO properties have been investigated both by the Z-scan and degenerate four-wave mixing (DFWM) techniques using 532 nm, 7 nanosecond laser pulses. The measured β and $\chi^{(3)}$ values for the polymers are found to be in the range of 10^{-11} m/W and 10^{-11} esu, respectively. The results indicate that they exhibit good optical-limiting behavior and are promising materials for nonlinear optical applications due to effective two-photon absorption (TPA).

Keywords conjugated polymer, electrochemical properties, optical materials, oxadiazole, thiophene-based polymer

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INTRODUCTION

The field of nonlinear optics has attracted a lot of interest in the past two decades mainly because of its possible applications in optical recording, optical data storage, optical information processing, optical signal processing, optical limiting, electro-optic and optical switching [1–6]. It also provides the fundamental research connected to charge transfer, conjugation, hyperpolarizability, dipole moment, and other structure related properties [7–10]. During the past decade, a large number of systems, including inorganic materials, organometallics, organic molecules, polymers and their composites, have been extensively studied as optical materials [11–16]. Recently, organic molecules have received much attention in this field owing to several advantages like chemical tenability, flexibility, and choice of synthetic strategies [17–22].

Amongst the organics, conjugated polymeric systems have emerged as a promising class of NLO materials as they are characterized by large third-order NLO susceptibilities along the direction of the polymer chain. Interestingly, their chemical stability, easy processibility, and good mechanical properties associated within their thin film state have made them better choices for device fabrication. Presently, donor-acceptor (D-A)-type conjugated polymers are of great interest due to their high molecular hyperpolarizability (β) and dipole moment (μ), which are essential requisites for large third-order nonlinear susceptibility [23,24].

In the literature [25–37], several reports have appeared on synthesis, NLO, and other optoelectronic studies of different class of D-A type polymers, out of which thiophene-based polymers and oligomers [38–40] have been of central focus because of their high thermal stability, readiness to accommodate functional groups/functionalization, and solubility in common organic solvents. It has been noticed that the low band gap in such polymers leads to high intrinsic conductivity, which adds to better nonlinear optical behavior and good electronic properties. Also, it has been shown that their optical nonlinearity can be enhanced by introducing proper electron donating and withdrawing entities as well as by optimizing steric repulsion between donor and acceptor groups. This generates a highly polarizable charge transfer system with an asymmetric electron distribution. Further, the strength of D-A interactions is determined by the nature of donor and acceptor groups with π-conjugated spacers. Strong electron accepting groups and short spacers generally enhance D-A interactions, whereas weak electron-accepting groups and long spacers lower the D-A strength [41–46].

Presently, the design and synthesis of organic D-A type polymers possessing high molecular hyperpolarizability and dipole moment are a major challenge [47]. According to recent literature reports, it is possible to fine-tune their optoelectronic properties depending on the choice of the functional substituents [48–50]. Literature studies also reveal that the incorporation of various aromatic segments along the polymer backbone/side chain would be a promising molecular design for enhancing the third-order NLO properties [51]. In this direction, with the aim of developing new D-A type polymers for optical applications, we have designed two new polymers with 3,4-aryloxy/alkoxy groups as electron donor segments with 1,3,4-oxadiazole as electron withdrawing segments along the polymer backbone. Here, we have incorporated naphthyloxy segments into 3,4-positions of thiophene units as aryloxy pendants and investigated the effect of this substitution on NLO properties. It has been expected that the new design would lead to high molecular polarizability due to effective delocalization of π-electron cloud along the polymer main chain. In addition, charge transfer (CT) can take place over nonconjugated bonds between naphthyl and thiophene units owing to the presence of $-OCH_2$ linkage, which may also decrease the torsional angle between the naphthyl groups. The CT in these molecules arise owing to the interaction of π-orbitals of the D and A moiety through the σ-bond ($\pi-\sigma-\pi$ bond coupling). It is observed that $\pi-\sigma$ orbital mixing through bond interaction between the π-aromatic rings and the σ-spacers is enhancing the NLO response. There are several reports on the intramolecular CT absorption observed for the systems of type D-CH_2-CH_2-A [52].

In the present work, we report the synthesis and characterization of hitherto unknown D-A-type conjugated polymers, poly{2-(3,4-naphthalen-1-ylmethoxy-2-yl)-5-[3,4-didodecyloxy-5-(1,3,4-oxadiazol-2-yl)thiophen-2-yl]-1,3,4-oxadiazole} (**P1**) and {2-(3,4-naphthalen-1-ylmethoxy-2-yl)-5-[3,4-dihexyloxy-5-(1,3,4-oxadiazol-2-yl)thiophen-2-yl]-1,3,4-oxadiazole} (**P2**). We also report the detailed studies of their third-order NLO properties by the Z-scan and degenerate four-wave mixing techniques. The results are discussed in detail.

EXPERIMENTAL

Materials

The required starting materials, diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate (**1**), 3,4-didodecyloxythiophene-2,5-dicarbohydrazide (**5a**) and 3,4-dihexloxythiophene-2,5-dicarbohydrazides (**5b**), were synthesized according to the reported procedures [53,54]. Dimethylformamide (DMF) and acetonitrile (ACN), dried over CaH_2, were used. Thiodiglycolic acid, diethyloxalate, and tetrabutylammoniumperchlorate (TBAPC) were purchased from Lanchaster (UK). 2-(Chloromethyl)naphthalene and lithium chloride were purchased from Aldrich and were used as received. All the solvents and reagents were of analytical grade, purchased commercially, and used without further purification.

Instrumentation

Infrared spectra of all intermediate compounds and polymers were recorded on a Nicolet Avatar 5700 FTIR (Thermo Electron Corporation). The UV–visible and fluorescence spectra were taken in GBC Cintra 101 UV–visible and Perkin Elmer LS55 fluorescence spectrophotometers, respectively. ^{1}H NMR spectra were obtained with 300 MHz on a Bruker NMR spectrometer using TMS/solvent signal as an internal reference. Elemental analyses were performed on a Flash EA1112 CHNS analyzer (Thermo Electron Corporation). Electrochemical studies of the polymers were carried out using an AUTOLAB PGSTAT30 electrochemical analyzer. Cyclic voltammograms were recorded using a three-electrode cell system, with a glassy carbon button as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl electrode as the reference electrode. The ferrocene/ferrocenium (Fe/Fe^+) oxidation couple was used as an internal calibration with all potentials adjusted to the Ag/AgCl scale. Molecular weights of the polymers were determined with a Waters-make Gel Permeation Chromatograph (GPC) against poly(styrene) standards with teterhydrofuran (THF) as an eluent. The thermal stability of polymers was studied by SII-EXSTAR6000-TG/DTA6300 thermogravimetric analyzer. Q-Switched Nd:YAG laser was used for NLO studies.

Z-Scan Measurements

The Z-scan is a widely used technique developed by Sheik Bahae et al. [46,55] to measure the nonlinear absorption coefficient and nonlinear refractive index of materials. The "open aperture" Z-scan gives information about the nonlinear absorption coefficient. Here 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 $z = 0$. Obviously, 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. 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. For a focused Gaussian beam, each z position corresponds to an input laser energy density of $F(z) = 4\sqrt{\ln 2}E_{in}/\pi^{3/2}\omega(z)^2$, and intensity of $I(z) = F(z)/\tau$, where E_{in} is the input laser pulse energy, $\omega(z)$ is the beam radius, and τ is the laser pulse width. Thus the sample sees different laser intensity at each position, and hence the measured position-dependent transmission gives information about its intensity-dependent transmission. From the open aperture z-scan data, the nonlinear absorption coefficient of the material can be calculated.

In our Z-scan set-up we used a stepper-motor controlled linear translation stage to move the sample through the beam in precise steps (Figure 1). The samples were taken in 1 mm cuvettes. The transmission of the sample at each

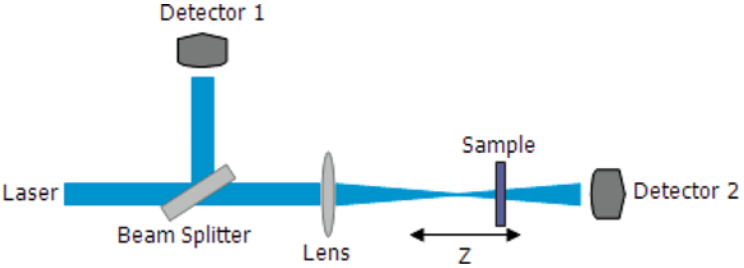


Figure 1: The open aperture Z-scan experimental set-up. (*Figure is provided in color online.*)

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 second harmonic output (532 nm) of a Q-switched Nd:YAG laser (Quanta Ray, Spectra Physics) was used for exciting the molecules. The laser pulse width is 7 nanoseconds. Laser pulse energy of approximately 200 microjoules was used for the experiments. The pulses were fired in the “single shot” mode, allowing sufficient time between successive pulses to avoid accumulative thermal effects in the sample.

DFWM Studies

Four-wave mixing refers to the interaction of four electromagnetic waves in a nonlinear optical medium via the third-order nonlinear polarization. When all the waves have the same frequency, it is called degenerate four-wave mixing (DFWM). We used the forward folded BOXCARS geometry for the experiment, where a laser beam is split into three and the beams are aligned such that they form three corners of a square (Figure 2). 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. When the beams are focused onto the sample, the fourth beam (signal beam) is generated due to nonlinear interaction, which will appear on the fourth corner of the square. It is measured using a photodetector.

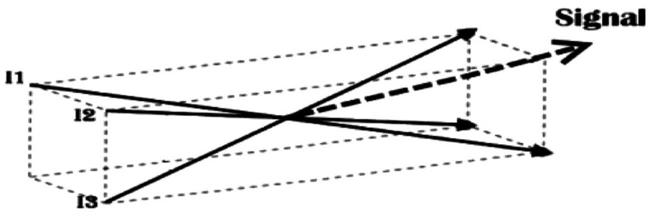


Figure 2: Four wave mixing in the BOXCARS geometry.

In the DFWM experiment we used plane-polarized 7 ns pulses at 532 nm obtained from the second harmonic output of a Q-switched Nd:YAG laser. A polarizer kept in the beam path on a rotatable mount was used to change the intensity of the beam falling on the sample. The sample was taken in a 2 mm glass cuvette. The input energy was monitored using a pyroelectric energy probe. The generated signal beam was measured in the far field using a calibrated photodiode.

Synthesis of Monomers and Polymers

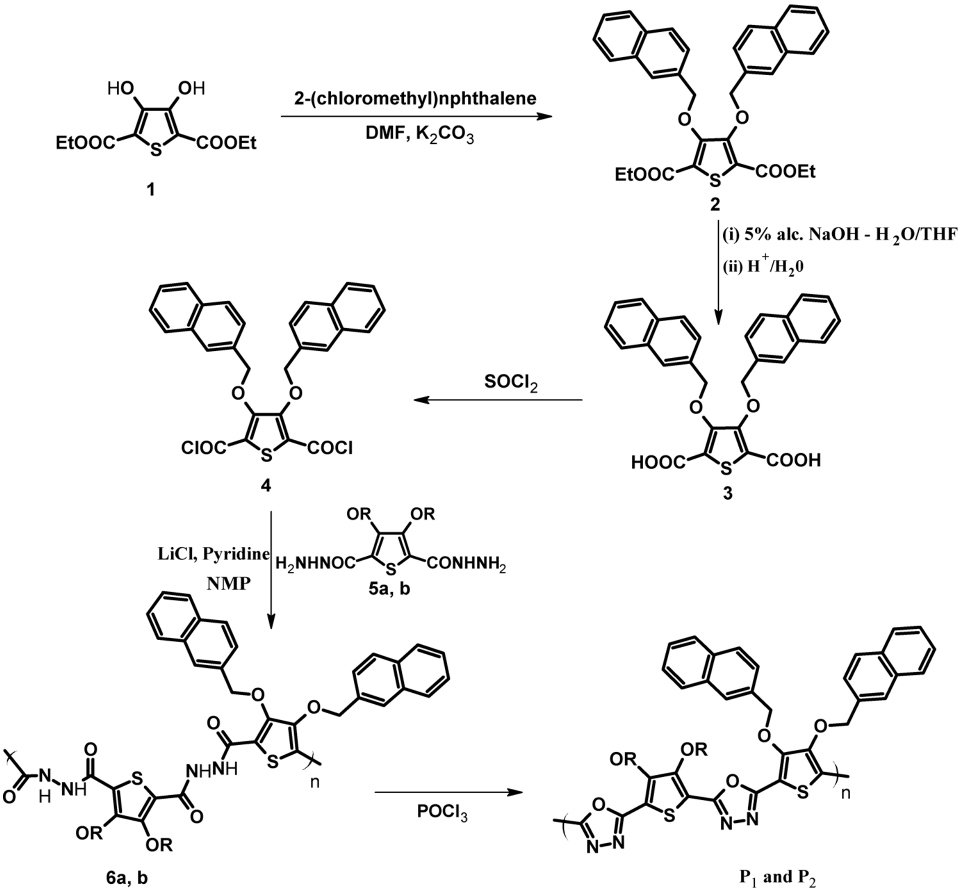
The synthetic route towards the preparation of new intermediates, monomers, and polymers is outlined in Scheme 1. Required intermediate 3,4-bis(naphthalen-2-ylmethoxy)thiophene-2,5-dicarboxylic acid (**3**) was synthesized by alkali hydrolysis of the diethyl 3,4-bis(naphthalen-2-ylmethoxy)thiophene-2,5-dicarboxylate (**2**), which was obtained by condensation of 3,4-dihydroxy-thiophene-2,5-diester (**1**) with 2-(chloromethyl)-naphthalene in presence of potassium carbonate and DMF. The diacid (**3**) was refluxed with excess thionyl chloride to obtain 3,4-bis(naphthalen-2-ylmethoxy)thiophene-2,5-dicarbonyl dichloride (**4**), which on treatment with the dihydrazides **5a-b**, in presence of lithium chloride and pyridine, underwent polycondensation to give required polyhydrazides **6a-b**. The compounds **6a-b** obtained were converted into corresponding target polymers (**P1** and **P2**) through cyclo-dehydration reaction using phosphorus oxychloride as a dehydrating agent. The experimental procedures for the synthesis of new compounds are as follows.

Synthesis of Diethyl 3,4-Bis(naphthalen-2-ylmethoxy)thiophene-2,5-dicarboxylate (2)

To a mixture of 3,4-dihydroxythiophene-2,5-dicarboxylate (**1**) (3.0 g, 12 mmol) and K_2CO_3 (4.77 g, 36 mmol) in 30 ml of DMF was added drop-wise 2-(chloromethyl)naphthalene (4.0 g, 23 mmol). The reaction mixture was refluxed for 20 h. When the reaction was completed, it was cooled to room temperature and poured into water. The yellow precipitate formed was filtered, dried, and recrystallized using ethanol. FTIR (KBr, υ, cm^{-1}), 2973 (-CH), 1696 (>C=O). Element. Anal. Calcd. For $C_{32}H_{28}O_6S$: C, 71.09%, H, 5.22%, S, 5.93%. Found: C, 70.45%, H, 4.95%, S, 5.81%.

Synthesis of 3,4-Bis(naphthalen-2-ylmethoxy)thiophene-2,5-dicarboxylic Acid (3)

A mixture of diethyl 3,4-bis(naphthalen-2-ylmethoxy)thiophene-2,5-dicarboxylate (**2,** 2.0 g, 4.5 mmol), 50 mL of 5% alcoholic sodium hydroxide,



where 5a, 6a, P1: R = n-$C_{12}H_{25}$

5b, 6b, P2: R = n-C_6H_{13}

Scheme 1: Synthetic route for the preparation of polymers **P1** and **P2**.

and 5 mL THF was refluxed for 8 h to get a clear solution. The resulting solution was concentrated and cooled. Further, it was washed with ethyl acetate to remove traces of organic impurities and then was acidified with concentrated HCl to get white precipitate. The precipitate was filtered, washed with water, and recrystallized from ethyl acetate. MP: 216–218°C, yield: 85%, FTIR (KBr, υ, cm^{-1}): 3468 (-OH), 2767 (-CH), 1650 (>C=O). ^1H NMR (DMSO-d^6, δ ppm): 13.6 (s, broad), 7.27–8.16 (m, 14H, naphthyl), 5.59 (s, 4H, -OCH_2-). Element. Anal. Calcd. for $C_{28}H_{20}O_6S$: C, 69.41%; H, 4.16%; S, 6.62%. Found: C, 68.85%, H, 3.96%, S, 6.43%.

Synthesis of 3,4-Bis(naphthalen-2-ylmethoxy)thiophene-2,5-dicarbonyl dichloride (4)

Excess of thionyl chloride (20 mL) was added to 0.5 g of 3,4-bis(naphthalen-2-ylmethoxy)thiophene-2,5-dicarboxylic acid (**3**) and the reaction mixture was refluxed for 6 h. After the completion of the reaction, the excess thionyl chloride was distilled off to get a cream-colored solid. Yield: 70%, IR (KBr, υ, cm^{-1}): 1670 (>C=O).

Synthesis of Precursor Polyhydrazides (6a, b)

To a mixture of 1 equivalent of appropriate dihydrazide (**5**), 2 equivalents of lithium chloride and 0.1 mL of pyridine, 1 equivalent of diacid chloride (**4**) was added slowly at room temperature with stirring, and stirring was continued for 3 h. Further, it was heated at 80°C for 12 h. After cooling to room temperature, the reaction mixture was poured into ice-cold water and the separated precipitate was collected by filtration. The polymer was purified by soxhlet extraction technique using ethyl acetate as solvent, and finally it was dried in a vacuum oven at 40°C.

6a: Yield: 79%, FTIR (KBr, υ, cm^{-1}): 3330 (>NH), 1638 (>C=O), ^{1}HNMR (DMSO-d^6, δ ppm): 10.84 (s, 1H, -NH), 9.91 (s, 1H, -NH), 7.45–8.19 (m, 14H, naphthyl), 5.27 (s, 4H, -OCH$_2$- naphthyl), 4.30 (s, 4H, -OCH$_2$- dodecyl), 1.31-2.51 (m, 40H, -$C_{20}H_{40}$). Element. Anal. Calcd. for $C_{58}H_{72}N_4O_8S_2$: C, 68.47%; H, 7.13%; N, 5.51; S, 6.30%. Found: C, 67.23%; H, 6.97%; N, 5.39%; S, 6.17%.

6b: Yield: 84%, FTIR (KBr, υ, cm^{-1}): 3330 (>NH), 1642 (>C=O), ^{1}HNMR (DMSO-d^6, δ ppm): 10.92 (s, 1H, -NH), 9.97 (s, 1H, -NH), 7.41-8.0 (m, 14H, naphthyl), 5.25 (s, 4H, -OCH$_2$- naphthyl), 4.29 (s, 4H, -OCH$_2$- hexyl), 1.36–2.63 (m, 16H, -C_8H_{16}). Element. Anal. Calcd. for $C_{46}H_{48}N_4O_8S_2$: C, 65.07%; H, 5.70%; N, 6.60%; S, 7.55%. Found: C, 64.49%; H, 5.58%; N, 6.48%; S, 7.42%.

Synthesis of Polymers (P1 and P2)

A mixture of polyhydrazide (**6a-b**, 0.5 g) and 20 mL of phosphorus oxychloride was heated at 90°C for 8 h with stirring. The reaction mixture was then cooled to room temperature and poured to excess of ice-cold water. The resulting orange-red precipitate was collected by filtration, washed with water followed by ethyl acetate, and finally dried in a vacuum oven at 40°C.

P1: Yield: 78%, FTIR (KBr, υ, cm^{-1}): 2838, 2654 (>C-H), 1580 (>C=N), 1450, 1064 (Aromatic –CH=CH). ^{1}H NMR (DMSO-d^6, δ ppm): 6.87–7.98 (m, 14H, naphthyl), 5.27 (s, 4H, -OCH$_2$- naphthyl), 4.93 (s, 4H, -OCH$_2$-, dodecyl), 1.18–1.36 (m, 40H, -$C_{20}H_{40}$), 0.87 (t, 6H, -CH$_3$). Element. Anal. Calcd. for

$C_{58}H_{68}N_4O_6S_2$: C, 70.99%; H, 6.98%; N, 5.71%; S, 6.54%. Found: C, 69.79%; H, 6.74%; N, 5.61%; S, 6.43%. Molecular weight, Mw = 14517, Mn = 10519 polydispersity (PD) = 1.38.

P2: Yield: 73%, FTIR (KBr, υ, cm^{-1}): 2845, 2674 (>C-H), 1583 (-C=N), 1458, 1061 (Aromatic –CH = CH). ^{1}HNMR (DMSO-d^6, δ ppm): 7.09–8.18 (m, 14H, naphthyl), 5.31 (s, 4H, -OCH_2- naphthyl), 4.97 (s, 4H, -OCH_2-, hexyl), 1.22–1.36 (m, 16H, -C_8H_{16}), 0.9 (t, 6H, -CH_3). Element. Anal. Calcd. for $C_{46}H_{44}N_4O_6S_2$: C, 67.96%; H, 5.46%; N, 6.89%; S, 7.89%. Found: C, 66.74%; H, 5.36%; N, 6.78%; S, 7.74%. Molecular weight, Mw = 8655, Mn = 6182 polydispersity (PD) = 1.4.

RESULTS AND DISCUSSION

Characterization of the New Monomers and Polymers

The molecular structures of newly synthesized intermediates, monomers, precursors, and the final polymers were confirmed by their FTIR, ^{1}H NMR, and elemental analyses. The structure of 3,4-bis(naphthalen-2-ylmethoxy)-thiophene-2,5-dicarboxylic acid (**3**) was confirmed by its ^{1}H NMR, FTIR, and elemental analysis. ^{1}H NMR of the diacid (**3**) showed singlet peak at δ, 13.6 ppm that corresponds to the protons of the carboxylic acid. A set of multiplet peaks between δ values 7.27–8.16 ppm was observed for the protons corresponding to the naphthalene segment, while the methoxy protons resonated at δ, 5.59 ppm.

Formation of precursor polyhydrazide **6a** was evidenced by FTIR spectrum, wherein it exhibited sharp peaks at 3000 and 1638 cm^{-1} accounting for amine (>NH) and carbonyl (>C=O) groups, respectively. The successful conversion of polyhydrazide **6a** to polyoxadiazole **P1** was confirmed by FTIR spectrum. Disappearance of amine (>NH) and carbonyl (>C=O) stretching absorption bands and appearance of sharp peak at around 1558 cm^{-1} due to imine (>C=N-) of the 1,3,4-oxadiazole ring clearly indicates the cyclization. The chemical structures of the polymers were further confirmed by FTIR, ^{1}H NMR spectral, and elemental analysis data. FTIR spectrum of polymer **P1** showed characteristic absorption peaks at 2854 and 2756 cm^{-1}, accounting for C-H stretching of aliphatic segments. The absorption band corresponding to >C–O–C< stretching of 1,3,4-oxadiazole was observed at 1064 cm^{-1}. The ^{1}HNMR spectrum of polyhydrazide **6a** displayed two sharp peaks at δ values, 9.9 to 10.8 ppm due to hydrazide protons (>NH), as shown in Figure 3. Naphthalene protons were resonated at δ values 7.45–8.19 ppm as multiplet and alkoxy protons appeared at 5.27 ppm as singlet. Further, alkyl protons resonated at 1.31–2.51 ppm as multiplet. ^{1}HNMR spectra of polymer **P1** showed disappearance of amine (>NH) peaks at δ value, 9.9 to 10.8 ppm confirms the formation of 1,3,4-oxadiazole in the polymer backbone. ^{1}HNMR

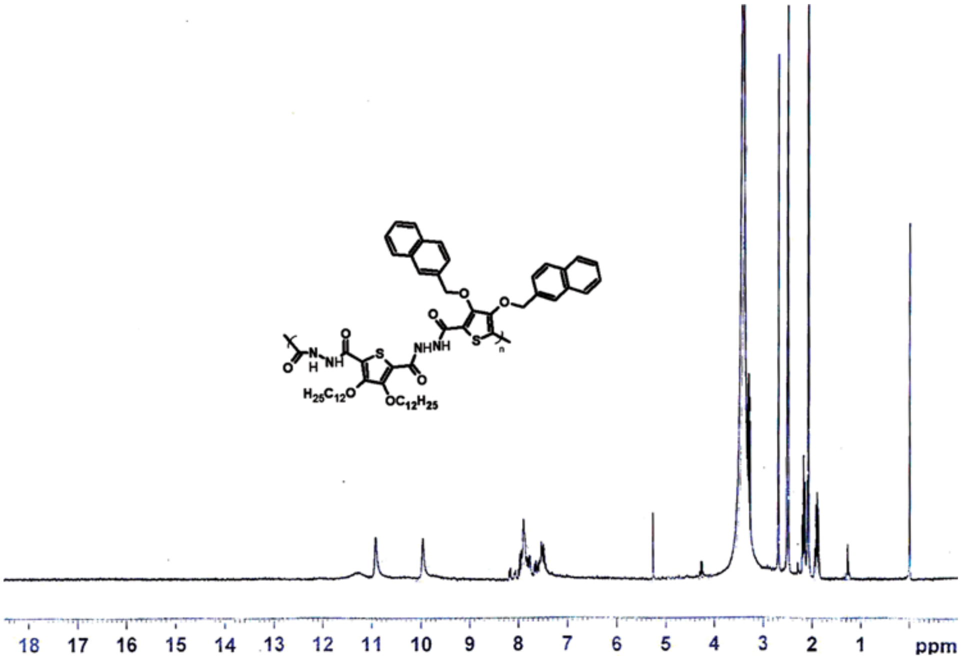


Figure 3: ^{1}H NMR spectrum of polyhydrazide **6a**. (*Figure is provided in color online.*)

spectrum of **P1** displayed a set of multiplet peaks at δ 6.87–7.98 ppm (Figure 4) due to protons of the two naphthyl rings on 3,4-position of the thiophene ring. The observed peaks at δ value 4.97 and 5.26 ppm correspond to the oxymethylene (-OCH$_2$) group attached to the alkyl and naphthyl ring, respectively. The protons of dodecyl chain substituted at 3,4 positions of the thiophene ring were resonated at δ values in the region of 0.90 to 2.40 ppm as multiplet peaks.

The results of elemental analysis of polymers were in agreement with the expected empirical formula. The THF soluble part of the polymer was taken for molecular weight determination. The weight average molecular weight ($\overline{M}_w$) of the polymer **P1** was determined to be 14517 and its polydispersity (PD) was found to be 1.38. The thermogravimetric trace of polymer **P1** is shown in Figure 5. From the trace it is clear that the polymer is thermally stable up to about 300°C.

Electrochemical Studies

Cyclic voltammetry (CV) was employed to determine redox potentials of new polymers and then to estimate the HOMO and LUMO energy of the polymers, which are of importance to determine the band gap of the new polymers. The cyclic voltammogram of the polymer coated on a glassy carbon electrode

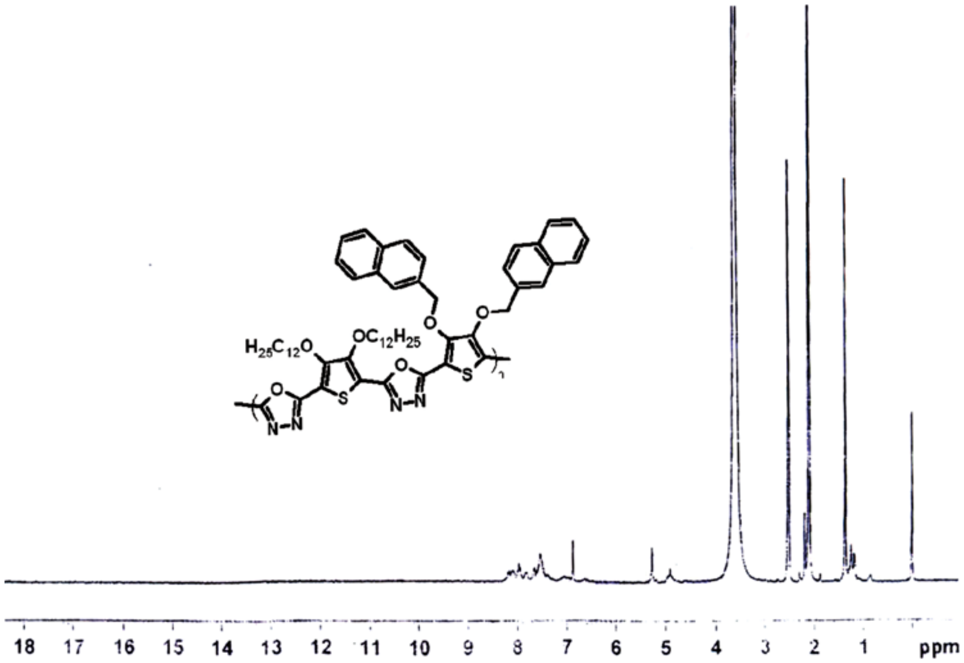


Figure 4: ^{1}H NMR spectrum of polymer **P1**. (*Figure is provided in color online.*)

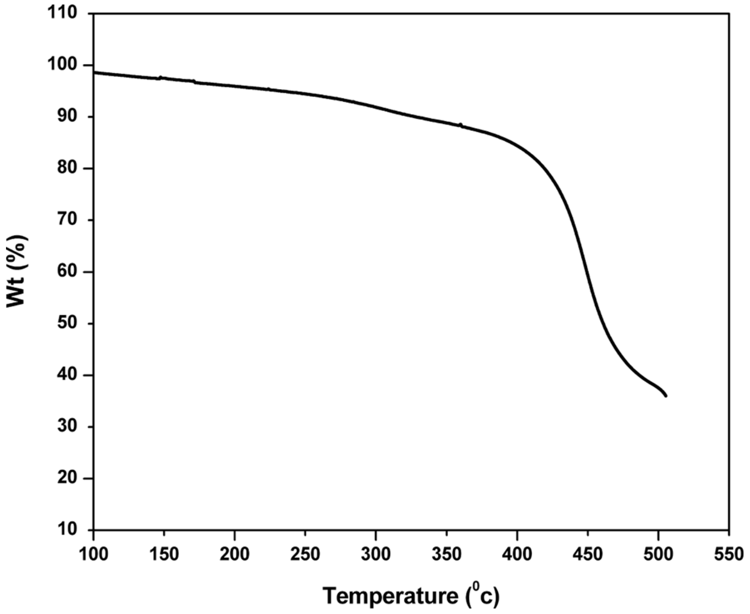
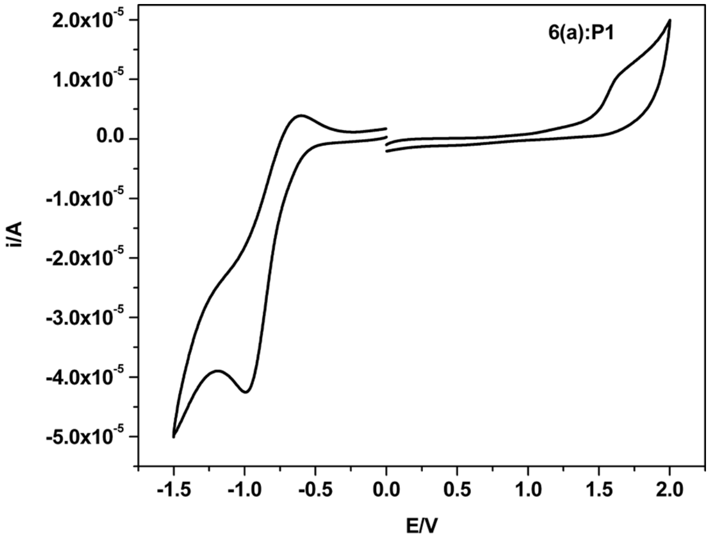


Figure 5: Thermogravimetric trace of the polymer **P1**.

Table 1: Electrochemical potentials, energy levels, and electrochemical band gap of polymers **P1** and **P2**

Polymer	E_{oxd}	E_{red}	E_{oxd} (onset)	E_{red} (onset)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g[a] (eV)
P1	1.63	−0.99	1.49	−0.74	−5.89	−3.66	2.23
P2	1.44	−1.57	1.05	−1.32	−5.45	−3.08	2.37

[a] Electrochemical band gap.



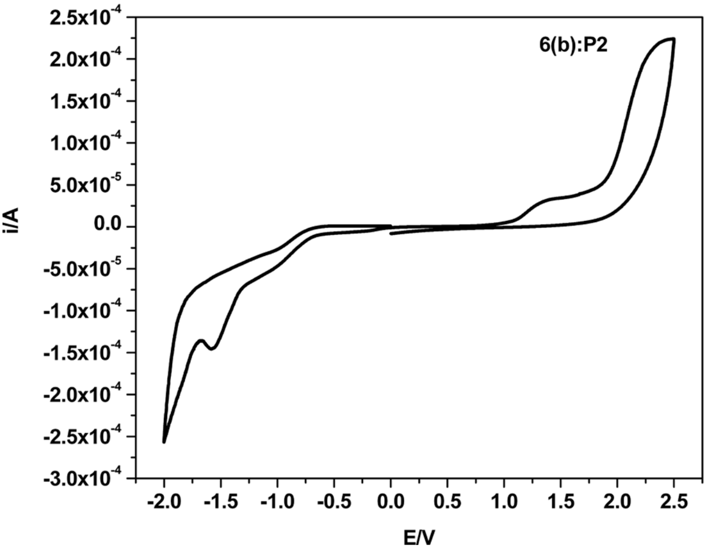


Figure 6: (a) and (b) Cyclic voltammetric waves of the polymers **P1** and **P2,** respectively.

was measured on an AUTOLAB PGSTAT 30 electrochemical analyzer, using a Pt counter electrode and a Ag/AgCl reference electrode, immersed in the electrolyte [0.1 M $(n\text{-Bu})_4NClO_4$ in acetonitrile] at a scan rate of 25 mV/s. Electrochemical data of **P1** and **P2** are summarized in Table 1.

The cyclic voltammograms of the polymer **P1** and **P2** display distinct oxidation and reduction processes, as shown in Figure 6(a) and (b). In cyclic voltammetric redox sweep the polymers P1 and **P2** displayed reduction peak at around −0.99 eV and −1.57 eV, respectively. These reduction potentials are lower than that of 2-(4-tirt-butylphenyl)-1,3,4-oxadiazole (PBD) [56,57], one of the most widely used electron transporting materials. In the anodic sweep, polymers **P1** and **P2** showed small oxidation peak at 1.63 eV and 1.44 eV, respectively. These values are comparable with those of reported D-A-type polymers containing thiophene and 1,3,4-oxadiazole moieties [53]. The onset oxidation and reduction potentials are used to estimate highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). In equations $E_{LUMO} = -[E^{Red}_{Onset} - 4.4\,eV]$ and $E_{HOMO} = -[E^{Oxd}_{Onset} + 4.4\,eV]$, E^{Red}_{Onset} and E^{Oxd}_{Onset} were used for the calculations. Here E^{Red}_{Onset} and E^{Oxd}_{Onset} are the onset potentials versus SCE for the oxidation and reduction process [58]. The calculated HOMO, LUMO, and band gap of the polymers are summarized in Table 1.

Linear Optical Properties

The linear photophysics of the polymer solution in THF solution was investigated using UV-visible and fluorescence spectral studies. The

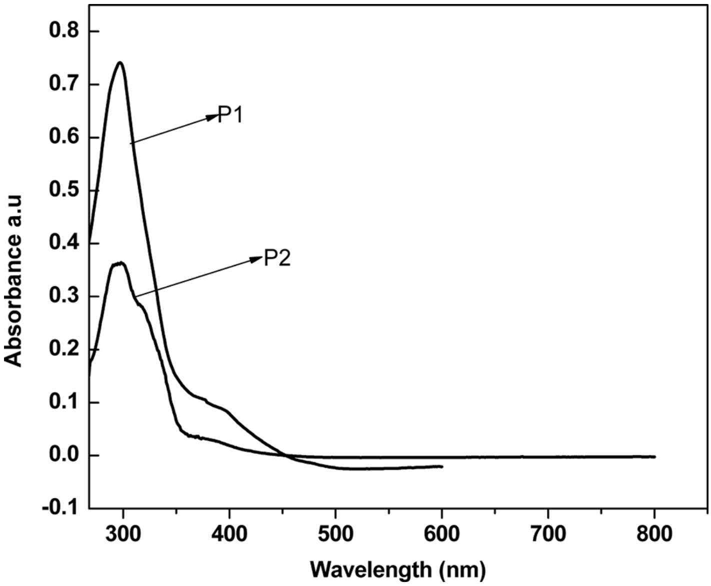


Figure 7: UV-vis absorption spectra of the polyhydrazides **6a**-**b** in THF.

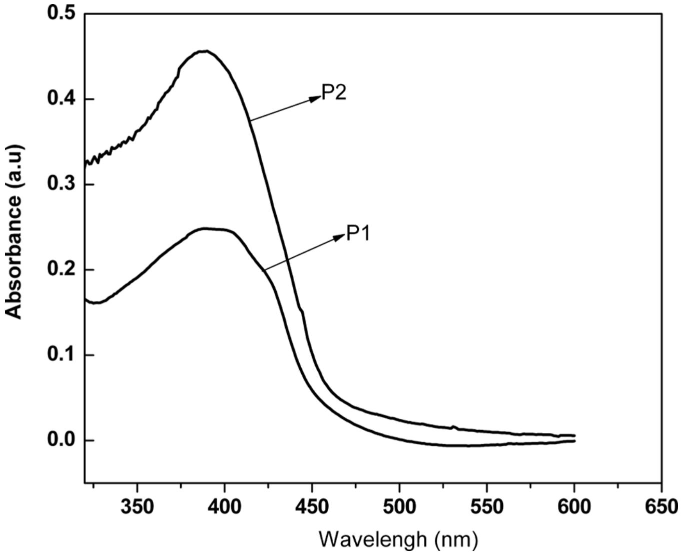


Figure 8: UV-vis absorption spectra of the polymers **P1** and **P2**.

absorption maxima of the precursor polymers **6a-b**, appeared at 297 nm and 293 nm undergo a red shift to 395 nm and 388 nm, respectively, due to the cyclization of precursor polyhydrazide to polyoxadiazole (Figures 7 and 8). This is caused by increased conjugation along the polymer chain with the for-

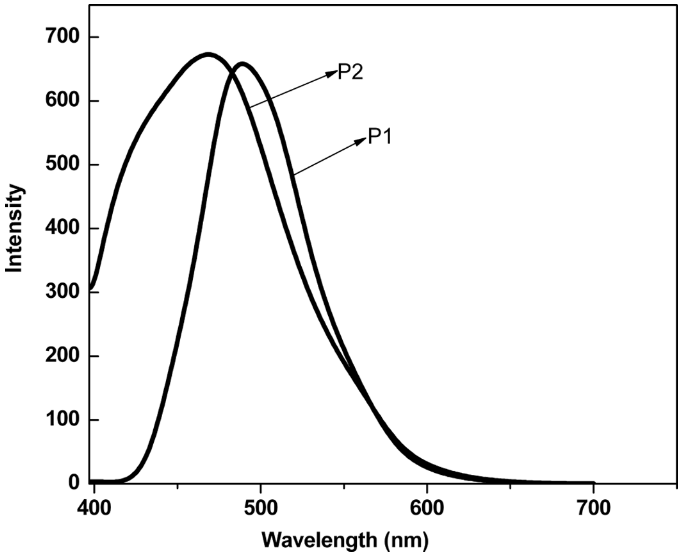


Figure 9: Photoluminiscence spectra of polymers **P1** and **P2**.

mation of 1,3,4-oxadiazole ring. The fluorescence emission spectra of the polymers **P1** and **P2** in THF showed emission peaks at 489 nm and 468 nm, respectively (excitation wavelength 380 nm), as shown in Figure 9. These data indicate that the polymers emit intense bluish-green light when photoexcited.

Nonlinear Optical Properties

Z-Scan

We have investigated third-order nonlinear optical properties of conjugated polymers **P1** and **P2**, with the interest in fundamental structure – property relations. The open aperture z-scans and optical limiting curves obtained from the samples P1 and P2 are given in Figures 10, 11, 12, and 13. It was found that numerically, a TPA-type process gives the best fit to the measured z-scan data. Both samples have a linear absorption of about 48% at the excitation wavelength in the 1 mm cuvette and hence strong two-step excited state absorption also will happen along with genuine TPA in the present case. The net effect is then known as an "effective" TPA process. The data obtained are fitted to the nonlinear transmission equation for a two-photon absorption process, given by [59].

$$T(z) = [1/\pi^{1/2} q(z)] \int_{-\infty}^{+\infty} \ln[1 + q(z)\exp(-\tau^2)]d\tau \qquad (1)$$

where T (z) is the sample transmission at position z. $q(z) = \beta I_0 L/[1 + (z/z_0)^2]$,

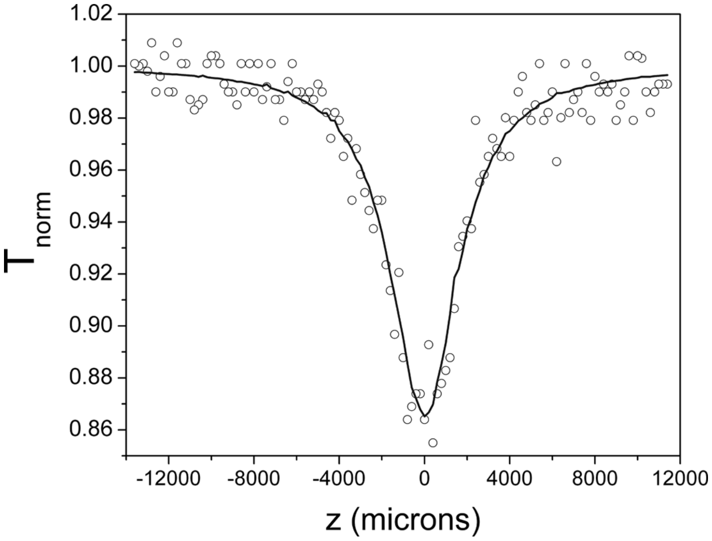


Figure 10: Open aperture Z-scan curve for polymer **P1**. Circles are data points while the solid curve is a numerical fit to the data using equation (1).

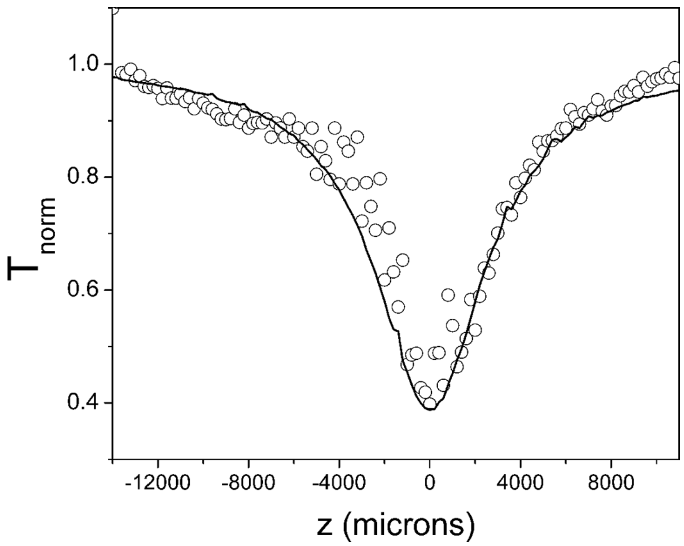


Figure 11: Open aperture Z-scan curve for polymer **P2**. Circles are data points while the solid curve is a numerical fit to the data using equation (1).

where I_0 is the peak intensity at the focal point, $L = [1 - \exp(-\alpha l)]/\alpha$, where l is the sample length and α is the linear absorption coefficient, and $Z_0 = \pi\omega_0^2/\lambda$ is the Rayleigh range, where ω_0 is the beam waist radius at focus and λ is the light wavelength, β is the effective TPA coefficient. The numerically calculated values of the effective TPA coefficient are 6.8×10^{-11} m/W for **P1** and 9.4×10^{-11} mW^{-1} for **P2**. For comparison, under

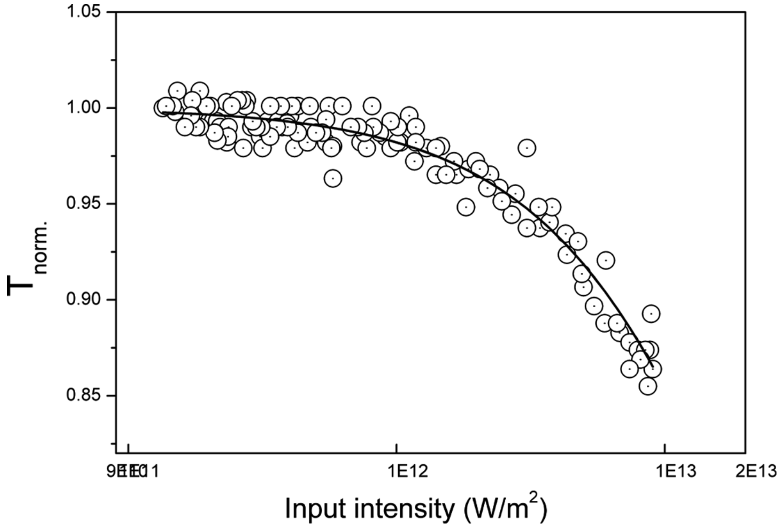


Figure 12: Optical limiting curve of polymer **P1**.

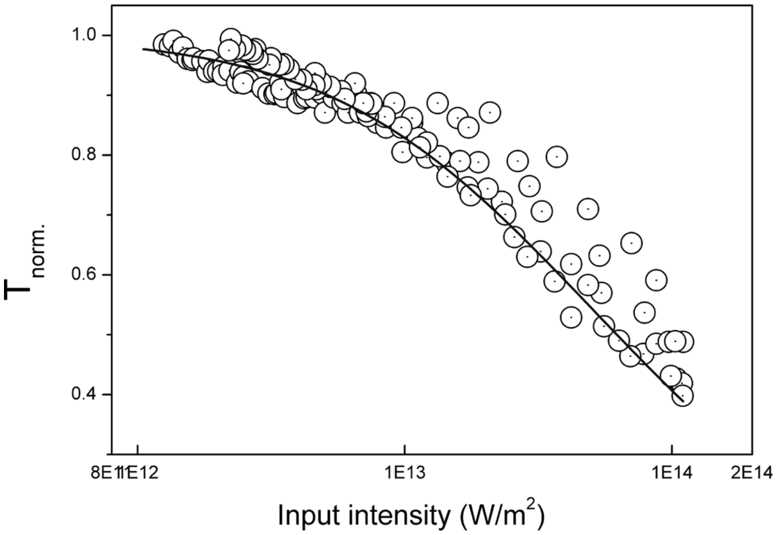


Figure 13: Optical limiting curve of polymer **P2**.

similar excitation conditions, NLO materials like Cu nanocomposite glasses had given effective TPA coefficient values of 10^{-10} to 10^{-12} m/W [51,60], bismuth nanorods gave 5.3×10^{-11} m/W, and CdS quantum dots gave 1.9×10^{-9} m/W, respectively [61]. These values show that the present samples

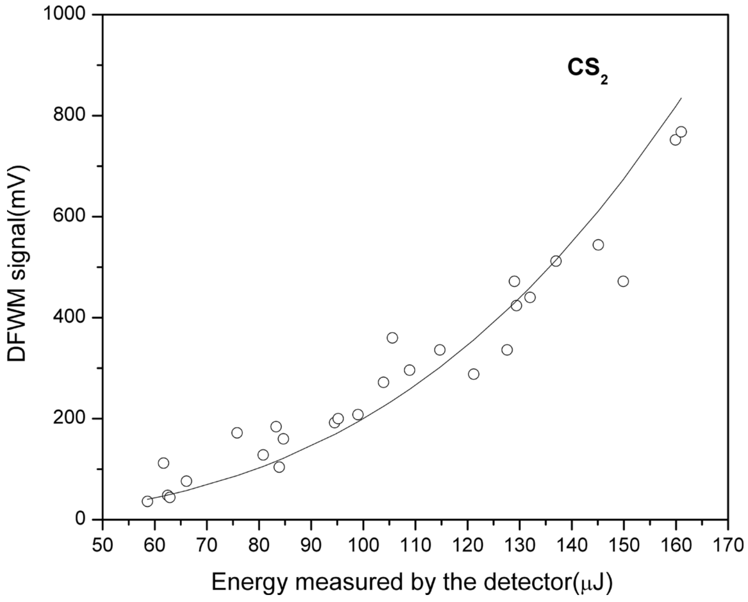


Figure 14: DFWM signal obtained in $\mathbf{CS_2}$. Circles are data points while the solid line is a cubic fit to the data.

have an optical nonlinearity comparable to good optical limiters reported in the literature, and hence they can find potential applications in optical-limiting devices.

DFWM

The DFWM signal as a function of pump intensity for $\mathbf{CS_2}$, polymers **P1**, and **P2** are shown in Figures 15 and 16, respectively. Here CS_2 is the reference sample for measurement. The signal is proportional to the cubic power of the input intensity, as given by (2),

$$I(\omega)\alpha\left(\frac{\omega}{2\varepsilon_O c n^2}\right)\left|\chi^{(3)}\right|^2 l^2 I_0^3(\omega) \tag{2}$$

where $I(\omega)$ is the DFWM signal intensity, $I_o(\omega)$ is the pump intensity, l is the length of the sample, and n is the refractive index of the medium. The solid curves in the figures are the cubic fits to the experimental data. The third-order non-linear optical susceptibility $\chi^{(3)}$ can be calculated from equation (3).

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

where the subscript "R" refers to the standard reference CS_2. "$\chi_R^{(3)}$" is taken to be 4.0×10^{-13} esu [61]. The figure of merit F, given by $\chi^{(3)}/\alpha$, is then calculated.

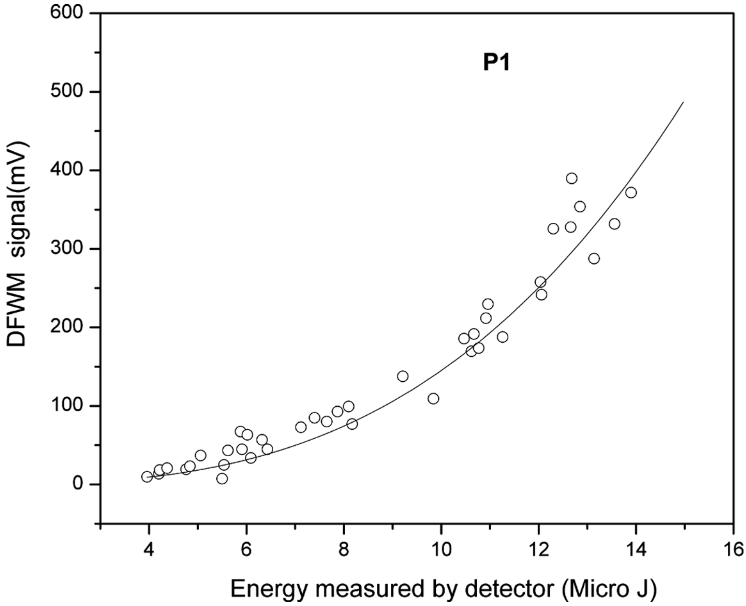


Figure 15: DFWM signal obtained in polymer **P1**. Circles are data points while the solid line is a cubic fit to the data.

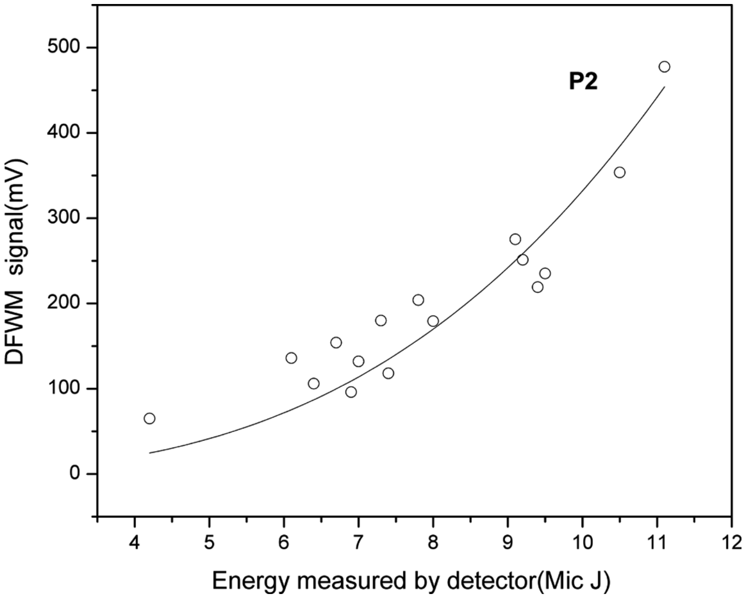


Figure 16: DFWM signal obtained in polymer **P2**. Circles are data points while the solid line is a cubic fit to the data.

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 materials when they are resonantly excited (as in the present case). The $\chi^{(3)}$ values obtained for **P1** and **P2** are 1.2×10^{-11} esu and 2.7×10^{-11} esu, respectively, and the *F* values are 6.0×10^{-12} esu cm^{-1} and 6.8×10^{-12} esu cm^{-1}, respectively. It is interesting to note that the F values obtained are an order of magnitude better than those of phthalocyanine compounds reported previously [62,63], which are materials known to have a high optical nonlinearity. Their enhanced nonlinear behavior can be explained based on their structure. In the polymers alkyloxy and naphthyloxy pendants substituted at the 3 and 4 positions of the thiophene ring behave as donor moieties, whereas 1,3,4-oxadiazole behaves as strong acceptor moiety. This alternate D-A arrangement gives rise to high π-electron density along the polymeric chain and is easily polarizable, which in turn results in enhanced delocalization of the electrons in the polymer backbone. Moreover, the alkoxy and naphthyloxy groups act as a solubilizing group, thereby facilitating the solubility of the polymers. All these factors collectively favored the nonlinear absorption of the polymers as a whole. The enhancement is well perceived as the resulting third-order nonlinear susceptibility has increased ten-fold when compared to the results of some of the D-A type polymers already reported [51,64,65].

CONCLUSIONS

We have synthesized two new D-A type conjugated polymers (**P1** and **P2**) consisting of 3,4-dialkoxythiophene/3,4-dinaphthyloxythiophene (donor) and 1,3,4-oxadiazoe (acceptor) moieties following the precursor polyhydrazide route. The structures of the new polymers have been confirmed by FTIR, ^{1}H NMR spectral, GPC, and elemental analyses. They possess well-defined structure and exhibit good thermal stability. The weight average molecular weights are determined to be 14517 g/mole and 8655 g/mole for **P1** and **P2**, respectively. Their UV-visible absorption spectra in solution show maxima at 395 nm and 388 nm, respectively, and display bluish-green fluorescence in solution state. The band gaps are determined to be 2.23 eV and 2.37 eV for **P1** and **P2**, respectively. The nonlinear optical properties of the polymers have been studied using the Z-scan and DFWM techniques. The polymers display strong absorptive nonlinearity due to an effective two-photon absorption process. Values of the effective two-photon absorption coefficients, third-order nonlinear susceptibilities, and figures of merit have been calculated and found to be better than those of the reported compounds. Their improved nonlinear behavior has been explained on the basis of their structure. The results indicate that the polymers possess high optical nonlinearity and hence they are potential materials for photonic applications.

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