

Novel poly(3,4-dialkoxythiophene)s carrying 1,3,4-oxadiazolyl-biphenyl moieties: synthesis and nonlinear optical studies

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Abstract

Two new donor–acceptor types of polymer, poly{2-(biphenyl-4-yl)-5-[3,4-dialkoxy-5-(1,3,4-oxadiazol-2-yl)thiophen-2-yl]-1,3,4-oxadiazole}s, were synthesized starting from 2,2'-sulfanediyl diacetic acid and diethyl ethanedioate through multi-step reactions. The polymerization was carried out via the polyhydrazide precursor route. The optical and charge-transporting properties of the polymers were investigated using UV-visible and fluorescence emission spectroscopic and cyclic voltammetric studies. The polymers showed bluish-green fluorescence in solutions. The electrochemical band gaps of the polymers were determined to be 2.16 and 2.22 eV. The nonlinear optical properties of the polymers were investigated at 532 nm using the single-beam Z-scan technique with nanosecond laser pulses. The polymers showed strong optical limiting behaviour due to effective three-photon absorption. The values of the three-photon absorption coefficients for the polymers were found to be 9×10^{-24} and $17 \times 10^{-24} \text{ m}^3 \text{ W}^{-2}$, which are comparable to those of good optical limiting materials.

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Keywords: conjugated polymers; 3,4-dialkoxythiophene; 1,3,4-oxadiazole; nonlinear optical (NLO) properties; Z-scan; three-photon absorption

INTRODUCTION

Polymeric materials with significant third-order nonlinear optical (NLO) properties play an important role in integrated components for the efficient manipulation of optical information. Recently, many polymers containing extended conjugation have been shown to exhibit an electro-optic effect, i.e. the change in refractive index of a medium with an applied electric field.^{1–3} Because of their good NLO response, they have been shown to be potential candidates for use in certain applications such as optical switching, modulation, optical computing, optical limiting, data storage, etc. A thorough literature survey reveals that many conjugated polymers have been shown to display remarkable third-order nonlinearities, because of the fact that they possess a strong delocalization of π -electrons in their polymeric backbone that imparts very high molecular polarizability. However, the investigation of the relationship between polymer structure and the resulting third-order nonlinearities is still continuing in order to establish an understanding of the dependence of nonlinear behaviour on structure. In this context, the study of the linear and nonlinear optical coefficients is fundamental for the ability to tune NLO properties by appropriate design of polymer systems at the molecular level.^{4–7}

Thiophene-based polymers are currently under active investigation in terms of their third-order NLO properties due to their easy processability, chemical stability, ease of functionalization, good film-forming characteristics, solubility, optical transparency and adequate mechanical strength.^{8–12} According to recent reports,^{13–15} in polythiophenes NLO properties can be synthetically tuned by introducing electron-releasing and electron-accepting segments in the polymer chain, which re-

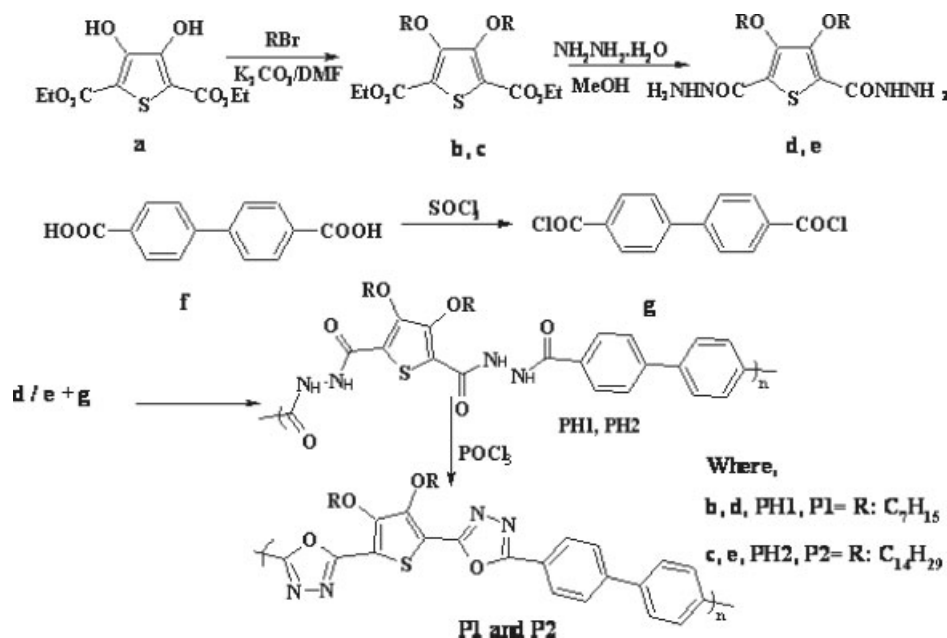
sults in improved delocalization in the molecule and hence an enhancement of their NLO properties. Thus, new molecular designs with various types of donor and acceptor moieties in the polymer backbone would lead to an increase in conjugation length and also the polarizability of resulting polymeric materials.

Two new donor–acceptor types of polymer have been designed, i.e. poly{2-(biphenyl-4-yl)-5-[3,4-dialkoxy-5-(1,3,4-oxadiazol-2-yl)thiophen-2-yl]-1,3,4-oxadiazole}s (**P1** and **P2**; Scheme 1), wherein additional electron-withdrawing biphenyl moieties are incorporated between 3,4-dialkoxy-substituted thiophen-2-yl-oxadiazole systems in order to enhance the electron-accepting nature within the polymer chain. It is predicted that the new design will reduce the steric repulsion between the bulky alkoxythiophene groups and increase the planarity which is expected to enhance the delocalization. It is hoped that the resulting conjugated polymers will exhibit good NLO properties. In this report, we describe the synthesis and characterization of **P1** and **P2**. Further, we report an investigation of their NLO properties using the Z-scan technique with nanosecond laser pulses at 532 nm.

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

EXPERIMENTAL

Materials

Dimethylformamide (DMF) and acetonitrile (both analytical reagent grade) were purchased from Merck, and were dried over CaH₂ prior to use. Thiodiglycolic acid, diethyl oxalate, tetrabutylammonium perchlorate and *n*-bromoalkanes were purchased from Lancaster (UK) and were used as received. 4,4'-Biphenyldicarboxylic acid (**f**) was purchased from Aldrich and was used as received. All solvents and reagents were of analytical grade, purchased from Merck and used without further purification.

Instrumentation

Fourier transform infrared (FTIR) spectra of all intermediate compounds and the polymers were recorded with a Nicolet Avatar 5700 FTIR (Thermo Electron Corporation). UV-visible and fluorescence emission spectra of the polymers were obtained with PerkinElmer Lambda 750 and PerkinElmer LS55 spectrophotometers, respectively. ¹H NMR spectra were obtained with an AMX 400 MHz FT-NMR spectrophotometer using tetramethylsilane/solvent signal as internal reference. Elemental analysis was performed with a Flash EA1112 CHNS analyser (Thermo Electron Corporation). Electrochemical studies of the polymers were carried out using an Autolab PGSTAT30 electrochemical analyser. Molecular weights of the polymers were determined with a Waters gel permeation chromatography instrument using polystyrene standards and tetrahydrofuran (THF) solvent. The thermal stability of the polymers was studied using an SII-EXSTAR6000-TG/DTA6300 thermogravimetric analyser.

Z-scan measurements

The Z-scan technique developed by Sheik-Bahae *et al.*¹⁶ is ideal for measuring the nonlinear optical refraction and absorption coefficients of materials. The 'open-aperture' Z-scan is used for measuring 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

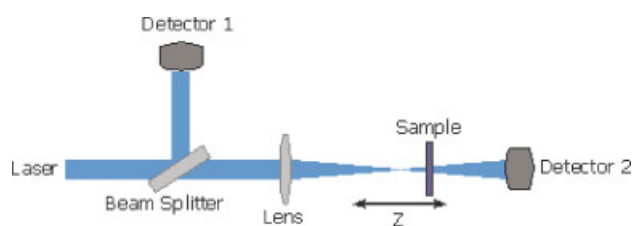


Figure 1. Open-aperture Z-scan set-up.

convex lens, and the focal point is taken as $z = 0$. The experiment is done by placing a 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 on either side of it, for positive and negative values of z . Hence the sample is subject to 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 (532 nm) from a Q-switched Nd:YAG laser (Quanta Ray, Spectra Physics) was used for the measurements. The beam had a nearly Gaussian spatial intensity profile. The laser pulse width was 7 ns, and a laser pulse energy of 90 μJ was used for the experiments. The sample was 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.). Figure 1 shows the typical open-aperture Z-scan set-up. One energy probe monitored the input energy and the other recorded the transmitted energy through the sample. The pulses were produced in the single-shot mode, allowing sufficient time between successive pulses to prevent accumulative thermal effects in the sample.

Synthesis of polymers

The polymers were synthesized from diethyl-3,4-alkoxythiophene-2,5-carboxylates (**b, c**) following the reaction sequence

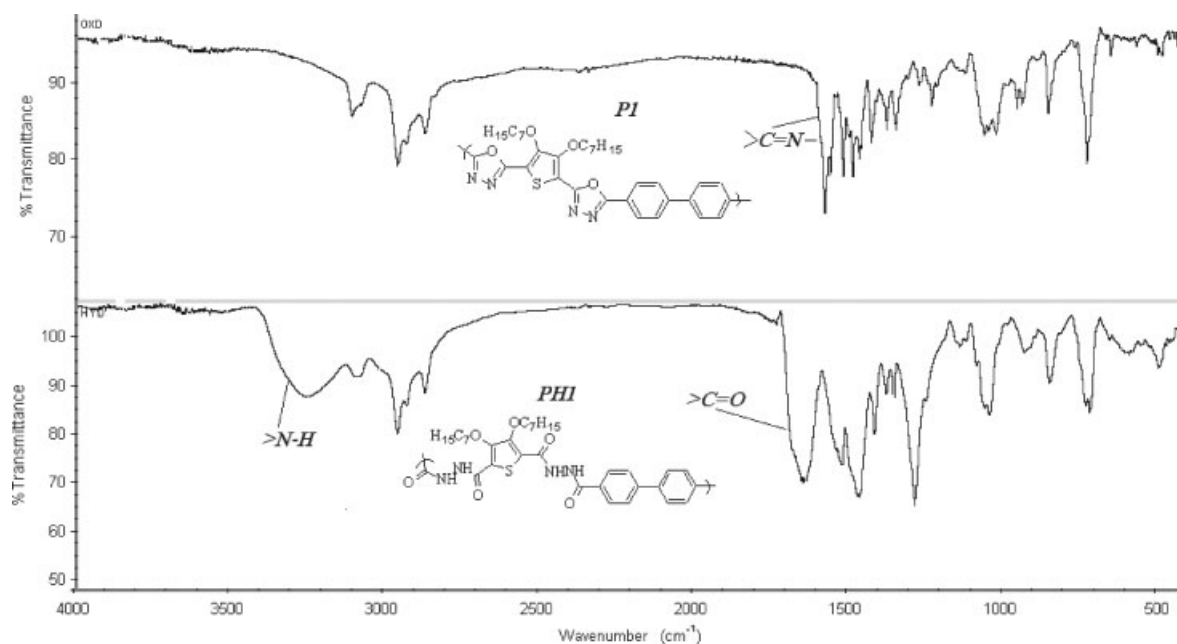


Figure 2. FTIR spectra of polyhydrazide **PH1** and polymer **P1**.

shown in Scheme 1. Compounds **b** and **c** and diethyl-3,4-ditetracycloxythiophene-2,5-dicarbohydrazide (**d**) were synthesized according to the reported literature procedure.^{17–20} 4,4'-Biphenylcarboxylic acid (**f**) was converted into 4,4'-biphenyldicarbonyl chloride (**g**) by the reaction with excess of thionyl chloride in the presence of a few drops of DMF.

Preparation of polyhydrazides **PH1** and **PH2**

To a mixture of 1 eq. of **d/e**, 4 eq. of anhydrous aluminium chloride and 0.1 mL of pyridine, 1 eq. of **g** was added slowly at room temperature with stirring, the stirring being continued for 4 h. It was then heated at 80 °C for a further 20 h. After cooling to room temperature, the reaction mixture was poured into ice-cold water and the precipitate that separated was collected by filtration. It was washed with water followed by acetone and finally dried in vacuum. The products were the polyhydrazides **PH1** and **PH2**.

PH1. Yield: 82%. FTIR (KBr; ν , cm^{-1}): 3255 ($-\text{N}-\text{H}$), 1647 ($< \text{C}=\text{O}$). Elemental analysis: calcd for $\text{C}_{34}\text{H}_{38}\text{N}_4\text{O}_6\text{S}$: C, 68.20%; H, 6.40%; N, 9.36%; S, 5.36%; found: C, 68.31%; H, 6.27%; N, 9.17%; S, 5.19%.

PH2. Yield: 80%. FTIR (KBr; ν , cm^{-1}): 3322 ($-\text{N}-\text{H}$), 1704 ($< \text{C}=\text{O}$). Elemental analysis: calcd for $\text{C}_{48}\text{H}_{66}\text{N}_4\text{O}_6\text{S}$: C, 72.51%; H, 8.37%; N, 7.05%; S, 4.03%; found: C, 72.39%; H, 8.20%; N, 7.00%; S, 3.92%.

Synthesis of polymers **P1** and **P2**

A mixture of polyhydrazide (**PH1/PH2**, 0.5 g) and 20 mL of phosphorus oxychloride was heated at 100 °C for 8 h with stirring. The reaction mixture was then cooled to room temperature and poured into excess ice. The resulting precipitate was collected by filtration, washed with excess of water followed by acetone and dried in a vacuum oven. The final products were the polymers **P1** and **P2**.

P1. Yield: 70%. FTIR (KBr; ν , cm^{-1}): 2932, 2863, 2755, 1578, 1453, 1060. ^1H NMR (400 MHz, $\text{DMSO}-d_6$; δ , ppm): 0.92 (t, 6H, $-\text{CH}_3$),

0.82–1.58 (m, 20H, alkyl), 3.46 (t, 4H, $-\text{OCH}_2$), 7.63–7.90 (m, 8H, biphenyl). Analysis: calcd for $\text{C}_{34}\text{H}_{38}\text{N}_4\text{O}_4\text{S}$: C, 68.20%; H, 6.40%; N, 9.36%; S, 5.36%; found: C, 68.07%; H, 6.26%; N, 9.44%; S, 5.21%. Molecular weight: $M_w = 4280 \text{ g mol}^{-1}$, $M_n = 3892 \text{ g mol}^{-1}$, polydispersity (PD) = 1.10.

P2. Yield: 70%. FTIR (KBr; ν , cm^{-1}): 2944, 2852, 2758, 1588, 1472, 1044. ^1H NMR (400 MHz, $\text{DMSO}-d_6$; δ , ppm): 0.82 (t, 6H, $-\text{CH}_3$), 1.02–1.85 (m, 48H, alkyl), 4.20 (t, 4H, $-\text{OCH}_2$), 7.6–8.10 (m, 8H, biphenyl). Analysis: calcd for $\text{C}_{48}\text{H}_{66}\text{N}_4\text{O}_4\text{S}$: C, 72.51%; H, 8.37%; N, 7.05%; S, 4.03%; found: C, 72.22%; H, 8.02%; N, 7.44%; S, 4.28%. Molecular weight: $M_w = 5430 \text{ g mol}^{-1}$, $M_n = 4452 \text{ g mol}^{-1}$, polydispersity (PD) = 1.22.

RESULTS AND DISCUSSION

Synthesis and characterization of polymers

As shown in Scheme 1, the precursor polyhydrazides were synthesized by polycondensation of 3,4-dialkoxythiophene-2,5-carbonyldihydrazides with 4,4'-biphenyldicarbonyl chloride in the presence of anhydrous aluminium chloride and pyridine. The polyhydrazides (**PH1** and **PH2**) were cyclized to polyoxadiazoles using phosphorus oxychloride. The formation of precursor **PH1** was confirmed from FTIR spectral and elemental analyses. The FTIR spectrum of the polyhydrazide exhibits sharp peaks at 3255 and 1647 cm^{-1} corresponding to $< \text{N}-\text{H}$ and $< \text{C}=\text{O}$ groups, respectively, as shown in Fig. 2. The successful conversion of polyhydrazide into polyoxadiazole (**P1**) was confirmed from the FTIR spectrum. The disappearance of the $< \text{C}=\text{O}$ and $< \text{N}-\text{H}$ stretching absorption bands and the appearance of a sharp peak at around 1578 cm^{-1} due to the imine of the oxadiazole ring indicate the cyclization (Fig. 2).

The chemical structure of **P1** was further confirmed using ^1H NMR spectral and elemental analyses. The ^1H NMR spectrum of **P1** (Fig. 3) shows a multiplet at 7.50–8.05 ppm, due to the eight protons of the biphenyl ring. Peaks corresponding to the protons of the alkoxy ($-\text{OCH}_2-$) groups at 3- and 4-positions of the thiophene ring appear as a triplet at 4.12 ppm. A set of

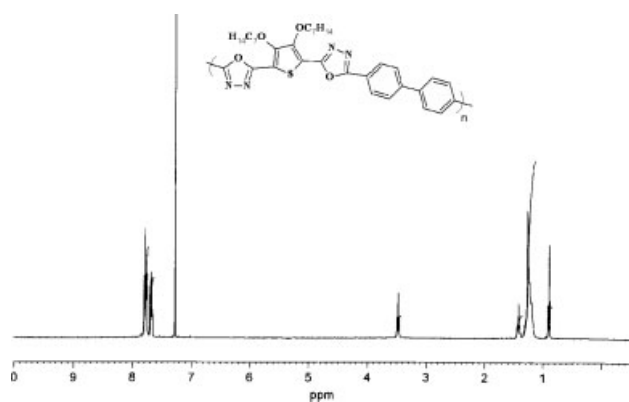


Figure 3. ^1H NMR spectrum of polymer P1.

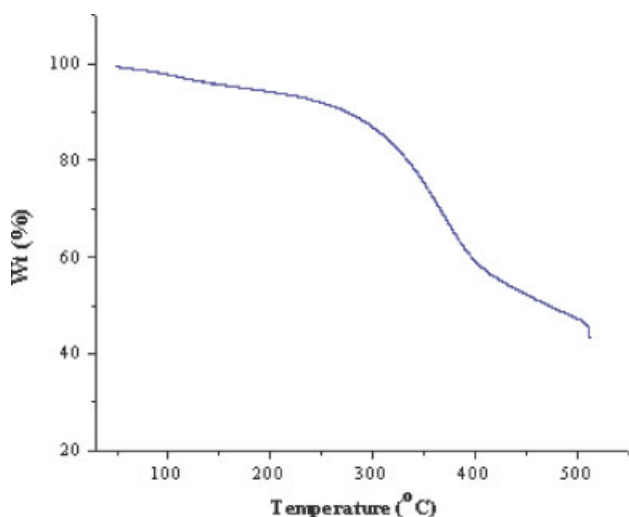


Figure 4. Thermogravimetric trace of polymer P1.

multiplet peaks corresponding to $-(\text{CH}_2)_{10}$ (alkyl chain) appear at 1.08–1.78 ppm. The end methyl protons ($-\text{CH}_3$) of the alkoxy substituent resonate as a triplet at 0.92 ppm.

The results of the elemental analysis of the polymer are in agreement with its expected empirical formula. The THF-soluble part of the polymer was taken for molecular weight analysis. The weight-average (M_w) and number-average (M_n) molecular weights of P1 are found to be 4280 and 3892 g mol^{-1} , respectively. Its polydispersity is estimated to be 1.10. The polymer is found to be thermally stable up to about 310 °C. The thermogravimetric trace of P1 is shown in Fig. 4.

Electrochemical studies

Cyclic voltammetry was employed to determine the redox potentials of the new polymers and then to estimate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), which is of importance in determining the band gap. The cyclic voltammograms of the polymers coated on a glassy carbon electrode were measured using an Autolab PGSTAT30 electrochemical analyser, with a platinum counter electrode and an Ag/AgCl reference electrode, immersed in an electrolyte of 0.1 mol L^{-1} (*n*-Bu) $_4\text{NClO}_4$ in acetonitrile at a scan rate of 25 mV s^{-1} . Electrochemical data for P1 are summarized in Table 1.

Table 1. Electrochemical potentials and energy levels of polymers P1 and P2

Polymer	E_{oxd} (V)	E_{red} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
P1	1.21, 1.74	−0.85	−5.86	−3.70	2.16
P2	1.66	−1.04	−5.84	−3.62	2.22

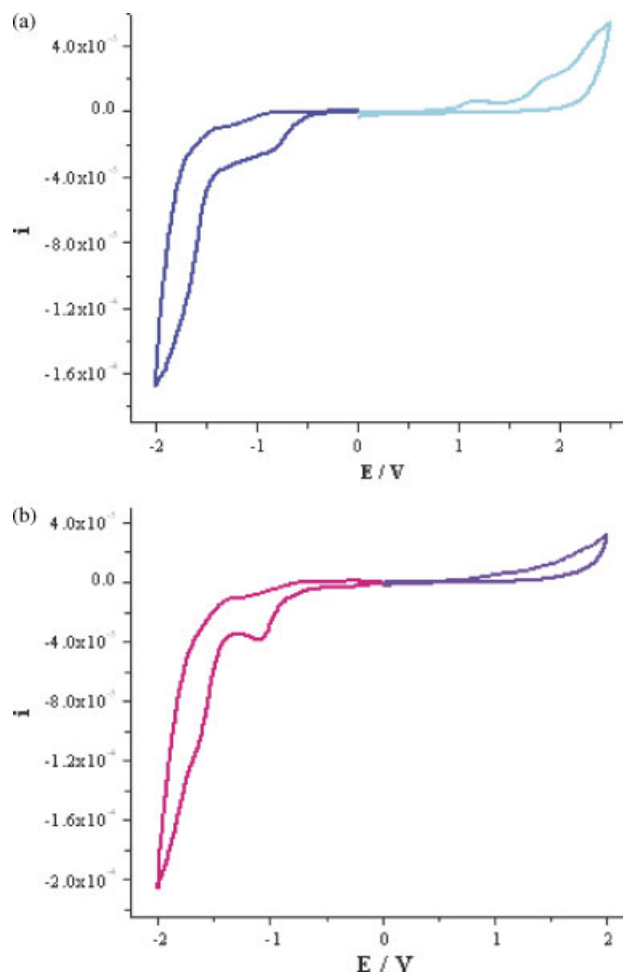


Figure 5. Oxidation and reduction cyclic voltammetric waves: (a) P1; (b) P2.

While sweeping cathodically, polymers P1 (Fig. 5(a)) and P2 (Fig. 5(b)) show reduction peaks at -0.85 and -1.04 V, respectively. These reduction potentials are lower than those of 2-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, one of the most widely used electron-transporting materials. For the anodic sweep, polymer P1 shows oxidation peaks at 1.21 and 1.74 V, while polymer P2 shows a weak reduction peak at 1.66 V, comparable with some donor–acceptor types of polymers containing oxadiazole moieties reported in the literature. The onset potentials of *n*- and *p*-doping processes can be used to estimate the HOMO and LUMO of the polymers. The equations reported in the literature,^{20–22} $E_{\text{HOMO}} = -(E_{\text{onset}}^{\text{oxd}} + 4.40 \text{ eV})$ and $E_{\text{LUMO}} = -(E_{\text{onset}}^{\text{red}} - 4.40 \text{ eV})$, were used for the calculations, 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 polymer.

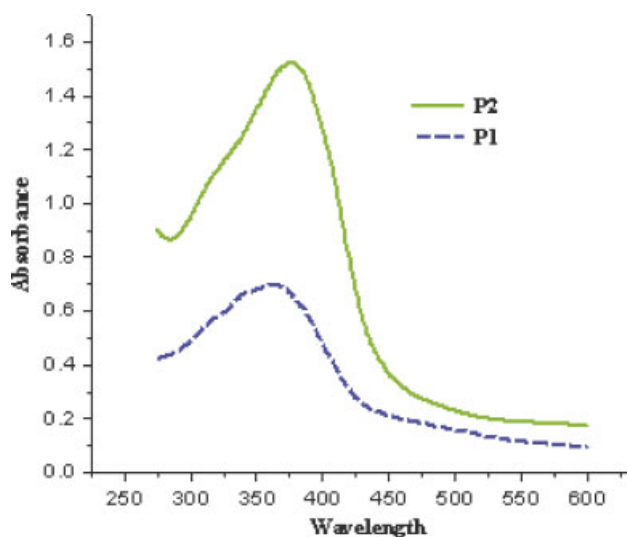


Figure 6. UV-visible absorption spectra of the polymers in DMF solution.

The HOMO energy levels of **P1** and **P2** are estimated to be -5.86 and -5.84 eV, respectively. In the cyclic voltammogram of **P1** (Fig. 5(a)), a main peak at 1.74 V is observed along with a shoulder peak at 1.21 V. This may be attributed to the oxidation process assigned to two different heteroaromatic rings present in the polymer chain.^{21,22} For our calculation of energy levels, oxidation onset of the main peak was considered. The HOMO energy levels are comparable with those of cyano-polyphenylenevinylene and some reported polyoxadiazoles. The LUMO energy levels (-3.70 and 3.62 eV) are lower than those of polyphenylenevinylene and some other p-type conjugated polymers indicating the polymers have better electron-transporting properties. Further, it is noted that the LUMO levels are lower than those of some reported polyoxadiazoles. This may be attributable to the introduction of additional electron-withdrawing biphenyloxadiazole rings within the polymer backbone. The very high electron affinity of these polymers may be attributed to the incorporation of electron-deficient biphenyloxadiazole rings in the polymer backbone. From the onset potentials of oxidation and reduction processes, the band gaps of **P1** and **P2** are estimated to be 2.16 and 2.22 eV, respectively.

Linear optical properties

The UV-visible absorption and fluorescence spectra of the polymers were recorded in dilute DMF solution. As shown in Fig. 6, the absorption maxima of the polymers in dilute DMF solution are at 368 and 376 nm for **P1** and **P2**, respectively. The fluorescence emission spectra of these polymers in solution are shown in Fig. 7. The emission maxima (excitation wavelength of 360 nm) of the polymers in dilute DMF solution are at 392 and 398 nm for **P1** and **P2**, respectively. It is observed that the increase in the length of the alkoxy side chain of the thiophene ring does not cause any significant change in the optical properties. These results indicate that the polymers emit intense bluish-green light on irradiation with UV light.

Nonlinear optical properties

The linear absorption spectra of the polymers show that the excitation wavelength of 532 nm is close to one of the absorption edges. The linear absorption coefficients (α) of the polymers are

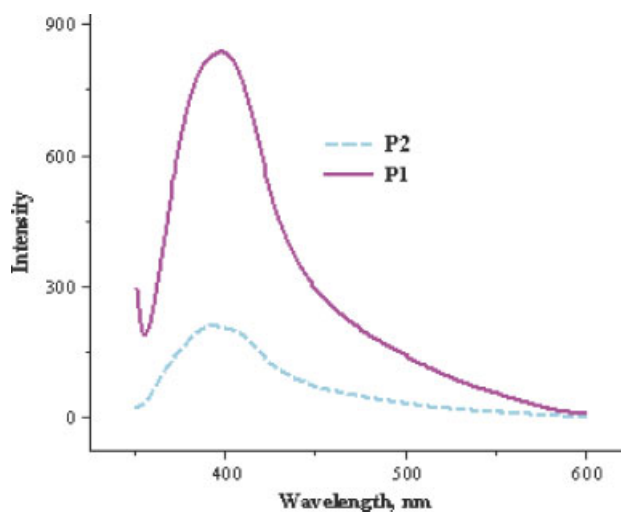


Figure 7. Fluorescence emission spectra of the polymers in DMF solution.

Sample	Linear optical properties		Nonlinear optical properties (Z-scan)
	n_0^a	α^b (m^{-1})	γ ($\times 10^{-24} m^3 W^{-2}$)
P1	1.432	510	9.0
P2	1.433	494	17

^a Refractive index.
^b Absorption coefficient.

given in Table 2. As is evident from Fig. 8, the polymers show strong optical limiting behaviour, where the transmittance decreases when the pump fluence is increased. A three-photon absorption (3 PA)-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 3 PA process, given by the equation¹

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

where T is the transmission of the sample, R is the Fresnel reflection coefficient at the sample-air interface, α is the linear absorption coefficient and L is the sample length. Parameter p_0 is given by $[2\gamma(1 - R)^2 I_0^2 L_{\text{eff}}]^{1/2}$, where γ is the 3 PA coefficient and I_0 the incident intensity. L_{eff} is given by $[1 - \exp(-2\alpha L)]/2\alpha$. The 3 PA coefficients obtained from the curve fitting are $9.0 \times 10^{-24} m^3 W^{-2}$ for **P1** and $17 \times 10^{-24} m^3 W^{-2}$ for **P2**. While doing the calculation the pulse-to-pulse energy fluctuations of the laser are also taken into account, and hence the simulated curve is not fully smooth.

The values reported in the literature for similar polymeric materials refer mainly to a two-photon-like absorption process. For example, the reported effective two-photon absorption coefficient value for polymers containing alternating 3,4-dialkoxythiophene and (1,3,4-oxadiazolyl)benzene units²³ was $1.996 \times 10^{-10} m W^{-1}$. For polyoxadiazoles containing 3,4-dialkoxythiophenes, an

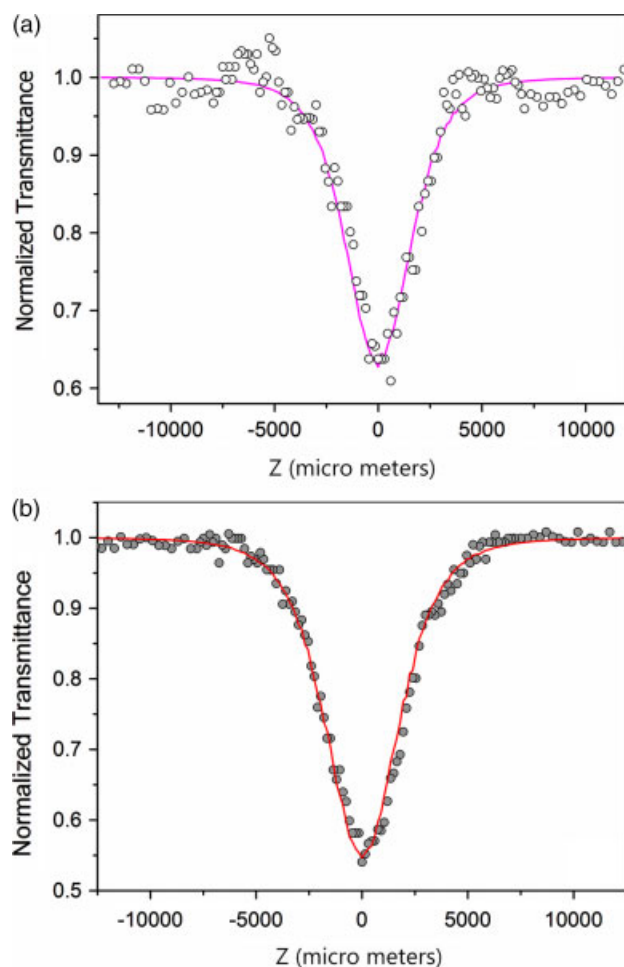


Figure 8. Open-aperture Z-scan curves for (a) **P1** and (b) **P2**. Circles are data points and solid curves are numerical fits obtained using Eqn (1).

effective two-photon absorption coefficient of $6.36 \times 10^{-10} \text{ m W}^{-1}$ was reported²⁴ and for a new thiophene-based conjugated polymer an effective two-photon absorption coefficient of $2.81 \times 10^{-10} \text{ m W}^{-1}$ was reported.²⁵ In the present work we find that a 3 PA process fits well to the data obtained. The values obtained for the effective 3 PA coefficients are of the order of $10^{-23} \text{ m}^3 \text{ W}^{-2}$.

In view of the absorption spectra of the polymers and considering that pure 3 PA cross-sections are generally very low, it seems that the observed nonlinearity arises from sequential 3 PA involving excited states. Two-photon absorption followed by excited-state absorption is another possibility. Therefore the nonlinearity can be considered as an 'effective' 3 PA process. Such absorptive nonlinearities involving real excited states have been reported previously in C_{60} (fullerenes), semiconductors, metal nanoclusters, phthalocyanines and some fluorine derivatives.^{1,26–33} In a 3 PA process, absorption is proportional to the cube of the incident intensity. This feature may help to obtain higher contrast and resolution in imaging, since 3 PA provides a stronger spatial confinement. With the availability of ultrafast pulsed lasers, there has been significant progress in 3 PA-based applications including three-photon pumped lasing and 3 PA-based optical limiting and stabilization.²⁶

In π -conjugated polymeric systems electrons can move in large molecular orbitals that result from the linear superpo-

sition of the carbon p_z atomic orbitals. This leads to a very significant optical nonlinearity, which increases with the conjugation length.²⁷ The polymers studied in the present work consist of a thiophene ring substituted with alkoxy groups pendant at 3- and 4-positions as the electron-donating unit and 1,3,4-oxadiazolylbiphenyl moiety along with unsubstituted thiophene moieties as electron-withdrawing groups. This leads to the formation of a donor–acceptor type of arrangement in the polymer backbone. The enhanced third-order nonlinearity in the polymer arises due to the high density of the π -electrons 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 groups not only enhances the delocalization electrons in the polymer, but also acts as a solubilizing group. The length of the alkoxy side chains at the 3- and 4-positions of the thiophene ring does not influence the optical nonlinearity to any great extent.

CONCLUSIONS

Two new conjugated polymers (**P1** and **P2**) consisting of alternate 3,4-dialkoxythiophene (donor) and 1,3,4-oxadiazolylbiphenyl (acceptor) moieties have been designed and synthesized using the polyhydrazide precursor route. Their structures have been confirmed using FTIR, ^1H NMR spectral and elemental analyses. They possess well-defined structures and exhibit good thermal stability. Their M_w values were determined to be 4280 and 5430 g mol^{-1} for **P1** and **P2**, respectively. Their UV-visible absorption spectra in solution showed maxima at 368 and 376 nm, and they displayed bluish-green fluorescence in solution. The band gaps were determined to be 2.16 and 2.22 eV for **P1** and **P2**, respectively. The polymers exhibited effective 3 PA, the absorptive nonlinearity observed being of the optical limiting type, which means they can have potential applications in optical limiters. As predicted, the newly designed molecules exhibited good NLO properties. This is mainly attributed to the greater extent of delocalization and hence the increased hyperpolarizability in the molecules.

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