

Synthesis and characterization of a new NLO-active donor–acceptor-type conjugated polymer derived from 3,4-diphenylthiophene

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Abstract A new donor–acceptor-type conjugated polymer (P1) carrying 3,4-diphenylthiophene, 2,5-dihexyloxybenzene, and 1,3,4-oxadiazole units was synthesized through multi-step reactions. The polymer was prepared using a polyhydrazide precursor route. The polymer has a well-defined structure and exhibits good thermal stability, with a decomposition onset temperature in nitrogen of 300 °C. Cyclic voltammetry experiments revealed that the polymer has low-lying LUMO (−3.68 eV) and high-lying HOMO (−5.78 eV) energy levels. The electrochemical band gap was found to be 2.10 eV. The UV-visible absorption spectrum of the polymer presented a maximum at 373 nm, and it displayed bluish-green fluorescence in dilute chloroform solution. The nonlinear optical properties of the new polymer were investigated at 532 nm using the Z-scan technique with nanosecond laser pulses. The polymer exhibited strong optical limiting behavior due to

excited state absorption, which was phenomenologically similar to a three-photon absorption (3PA) process. The 3PA coefficient γ was found to be $7 \times 10^{-22} \text{ m}^3/\text{W}^2$. The studies show that the new polymer (P1) is a promising material for developing efficient photonic devices.

Keywords Donor–acceptor conjugated polymers · 3,4-Diphenylthiophene · 1,3,4-Oxadiazole · Electrochemical properties · NLO · 3PA

Introduction

Organic materials exhibiting strong nonlinear optical (NLO) properties have received considerable attention due to their potential applications in optical communications, optical switching, optical data storage, and eye and sensor protection [1–3]. According to NLO studies conducted in several media, organic materials are attractive, due mainly to their versatility, high nonlinearities, ultrafast responses and their flexibility in terms of being able to tune the optical properties. Recently, conjugated polymeric systems have emerged as a promising class of NLO materials, characterized by large third-order susceptibilities along the direction of the polymer chain. These macromolecules offer good flexibility at both the molecular and the bulk level, so structural modifications that are needed to optimize them for specific device applications are possible. Since the nonlinear responses of these systems are determined primarily by their chemical structures, it is possible to design unique molecular structures and synthesize compounds with enhanced nonlinear responses by introducing suitable substituent groups.

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In general, if there is strong π -electron delocalization in the molecular structure, its NLO properties will be enhanced. Recently, Cassano et al. [4] reported a new strategy for tuning the linear and nonlinear optical properties of conjugated polymers. According to them, incorporating alternate electron-acceptor and electron-donor units into the polymer backbone would enhance the NLO properties, mainly due to hyperpolarizability.

NLO-related uses aside, conjugated polymers also find application in devices such as light emitting diodes (LEDs), field effect transistors, electrochemical cells, and organic photovoltaic cells. Some newly developed polymers—poly(1,4-phenylenevinylene) (PPV) [5], poly(*p*-phenylenes) (PPs) [6], polyfluorenes (PFs) [7] and polythiophenes (PTs) [8]—have been the foci of such investigations recently.

The third-order optical nonlinearity of thiophene-based polymers is currently under investigation mainly because of their chemical stability, their easy processibility, and their ease of functionalization [9–11]. Good film-forming properties, solubility, and adequate mechanical properties have made them better choices for device fabrication than their inorganic counterparts. For example, nonlinear optical properties can be synthetically tuned in polythiophenes by introducing electron-releasing and electron-accepting segments into the polymer chain, resulting in increased delocalization in the molecule. Shi et al. have reported the synthesis of thermally stable polyoxadiazoles with Schiff base structures [12]. Following a similar strategy, Adhikari and coworkers synthesized a few donor–acceptor-type polythiophenes and studied how their NLO properties depend on their structure [13–15]. They found that the introduction of electron-releasing and electron-accepting groups onto the polymer backbone is a promising method of enhancing the third-order NLO properties.

In this context, we planned to incorporate a 3,4-diphenylthiophene moiety in-between the 2,5-dialkoxy substituted benzene and the oxadiazole system in our synthetic design in order to enhance the electron-accepting nature of the polymer chain, with the expectation that the resulting molecule would exhibit improved NLO properties. Further, it has been predicted that the presence of 3,4-diphenyl thiophene units should reduce the steric repulsion between the bulky alkyl groups and increase the planarity of the polymer chain, which could help to reduce the band gap. In this communication, we report the synthesis of a hitherto-unknown polymer carrying 2-[2,5-dihexyloxy-4-(1,3,4-oxadiazol-2-yl)phenyl]-5-(3,4-diphenylthiophen-2-yl)-1,3,4-oxadiazole units, and investigation of its electrochemical and optical properties. Further, we report the results of third-order NLO absorption studies of this new polymer, as performed by the Z-scan technique.

Experimental part

Materials

Thiodiglycolic acid, benzil, diethyldihydroxy terephthalate, 1-bromohexane, and tetrabutylammoniumperchlorate (TBAPC) were purchased from Lancaster (Newgate, UK). All of the solvents and reagents were of analytical grade. They were purchased commercially and used without further purification.

Instrumentation

Infrared spectra of all intermediate compounds and polymers were recorded on a Nicolet Avatar 5700 FT-IR (Thermo Electron Corporation, Waltham, MA, USA). The UV-visible and fluorescence emission spectra were measured in GBC (Dandenong, Australia) Cintra 101 UV-visible and PerkinElmer (Waltham, MA, USA) LS55 spectrophotometers, respectively. ^1H NMR spectra were obtained with a Bruker (Karlsruhe, Germany) AMX 400 MHz FT-NMR spectrophotometer using the TMS/solvent signal as internal reference. Elemental analyses were performed on a Flash EA1112 CHNS analyzer (Thermo Electron Corporation). The thermal stability of the polymer was analyzed using a TG/DTA 6300 thermogravimetric analyzer (TGA; Seiko Instruments, Tokyo, Japan). The electrochemical study of the polymer was carried out using an Eco Chemie (Utrecht, The Netherlands) Autolab PGSTAT30 electrochemical analyzer. Cyclic voltammograms were recorded using a three-electrode cell system, with a glassy carbon button used as the working electrode, a platinum wire as the counter electrode and an Ag/AgCl electrode as the reference electrode. The molecular weight of the polymer was determined on a Waters (Milford, MA, USA) gel permeation chromatography (GPC) system using polystyrene standards in THF solvent.

Z-scan measurement

The z-scan technique developed by Sheik-Bahae et al. [16] is widely used to measure the nonlinear absorption coefficients and nonlinear refractive indices of materials. In the “open aperture” z-scan, which provides information about the nonlinear absorption coefficient, 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 beam has maximum energy density at the focus, and the energy density drops symmetrically on either side of the focus (i.e., for positive and negative values of z). In the experiment (Fig. 1), the sample is placed in the beam at different positions with respect to the focus (different values of z),

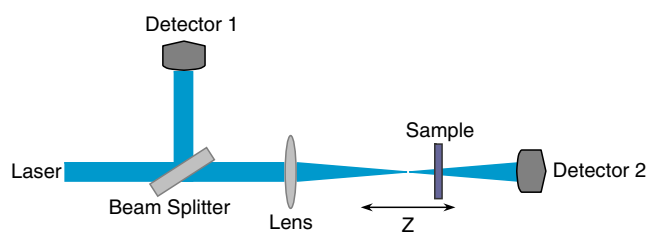


Fig. 1 The open-aperture z-scan setup

and the corresponding transmission is measured. The sample sees a different laser intensity at each position, and so its intensity-dependent transmission will be position dependent. The nonlinear absorption coefficient can be calculated from this nonlinear transmission information.

We used a stepper-motor-controlled linear translation stage in our setup to move the sample through the beam in precise steps. The sample was placed in a 1 mm cuvette. The transmission of the sample at each point was measured using two pyroelectric energy probes (Rj7620, Laser Probe Inc., Utica, NY, USA). One energy probe monitored the input energy while the other monitored the energy transmitted through the sample. The second harmonic output (532 nm) of a Q-switched Nd:YAG laser (Quanta Ray, Spectra Physics, Mountain View, CA, USA) was used to excite the molecules. The temporal width (FWHM) of the laser pulses was 7 ns. A pulse energy of 16 μJ 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.

Synthesis of 3,4-diphenylthiophene-2,5-dicarboxylic acid (**2**)

The 3,4-diphenylthiophene-2,5-dicarboxylic acid (**2**) was synthesized according to the reported procedure [17]. The formation of the required compound was confirmed by FT-IR and mass spectroscopic studies followed by elemental analyses. The experimental results matched the reported data.

Synthesis of 3,4-diphenylthiophene-2,5-dicarbonyl chloride (**3**)

The 3,4-diphenylthiophene-2,5-dicarbonyl chloride (**3**) was synthesized according to the reported procedure [18, 19], by the action of thionyl chloride (SOCl_2) on 3,4-diphenylthiophene-2,5-dicarboxylic acid (**2**). The structure of the essential monomer (**3**) was confirmed by FTIR and elemental analyses. Yield: 70%. FT-IR (KBr, cm^{-1}): ν 1670 (C=O). Anal. calcd. (%) for ($\text{C}_{18}\text{H}_{10}\text{N}_4\text{Cl}_2\text{O}_2\text{S}$) (361.2): C, 59.85; H, 2.79; S, 8.88. Found: C, 60.02; H, 2.98; S, 8.66.

Synthesis of 2,5-dihexyloxybenzene-1,4-dihydrazide (**4**)

The 2,5-dihexyloxybenzene-1,4-dihydrazide (**4**) was synthesized according to the reported procedure [20]. The structure was confirmed by FT-IR, ^1H NMR, and elemental analysis. The experimental results are in agreement with the reported data.

Synthesis of the polyhydrazide precursor (PH1)

To a mixture of 1 equivalent of dihydrazide (**4**), 2 equivalents of anhydrous aluminum chloride, and 0.1 mL of pyridine in 30 mL of *N*-methyl pyrrolidone (NMP), 1 equivalent of diacid chloride (**3**) was added slowly at room temperature with stirring, and stirring was continued for 5 h. It was then heated at 80 $^\circ\text{C}$ for 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 excess water followed by acetone and finally dried in a vacuum to get the polyhydrazide (PH1) with a 75% yield. FT-IR (KBr, cm^{-1}): ν 3320 (N–H), 1725 (C=O). Anal. calcd. for repeating unit ($\text{C}_{38}\text{H}_{42}\text{N}_4\text{O}_6\text{S}$) (682.8): C, 66.84; H, 6.20; N, 8.21; S, 4.70. Found: C, 66.45; H, 6.66; N, 8.54; S, 4.85.

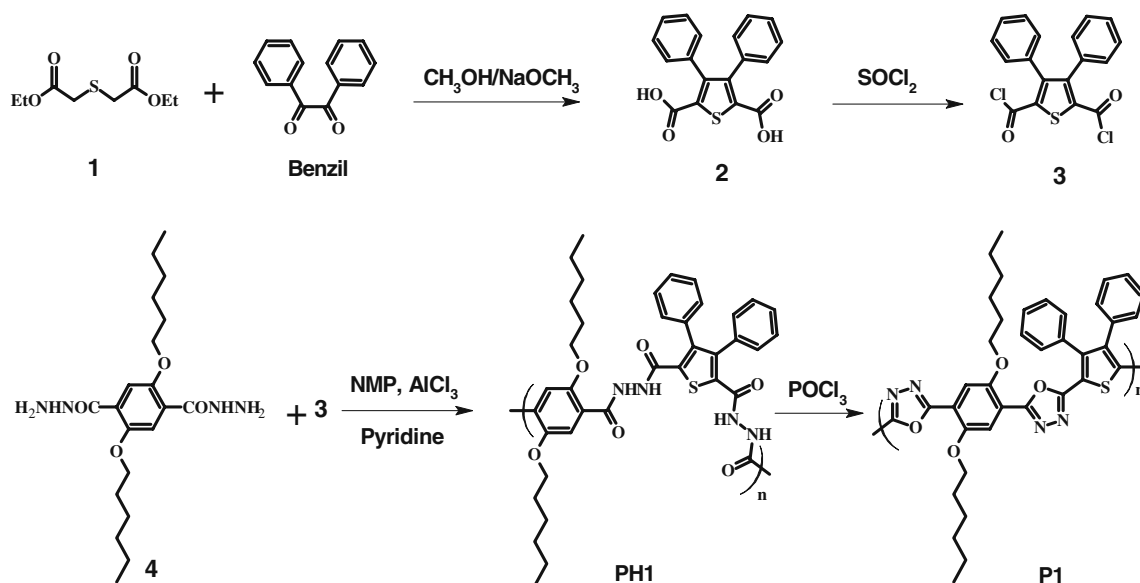
Synthesis of polymer (P1)

A mixture of polyhydrazide (0.5 g) and 20 mL phosphorus oxychloride was heated at 100 $^\circ\text{C}$ for 8 h with stirring under a nitrogen atmosphere. The reaction mixture was then cooled to room temperature and poured onto an excess of ice cold water. The resulting precipitate was collected by filtration, washed with water followed by acetone, and dried in a vacuum oven to get the polymer (P1) with an 80% yield. FT-IR (KBr, cm^{-1}): ν 2920, 2848 (C–H), 1595 (C=N), 1467 (aromatic), 1060 (=C–O–C= stretching of ether bond). ^1H NMR (400 MHz CDCl_3 , ppm): δ 7.3–8.0 (m, 12H, aromatic), 4.10 (t, 4H, $-\text{OCH}_2-$), 1.96–1.28 (m, 16H, $-(\text{CH}_2)_4-$), 0.88 (t, 6H, $-\text{CH}_3$). Anal. calcd. for repeating unit ($\text{C}_{38}\text{H}_{38}\text{N}_4\text{O}_4\text{S}$) (646.8): C, 70.56; H, 5.92; N, 8.66; S, 4.96. Found: C, 70.92; H, 6.32; N, 8.38; S, 5.03.

Results and discussion

Synthesis and characterization of the polymer

Scheme 1 shows the designed synthetic route for the preparation of monomers and the polymer (P1). The required 3,4-diphenylthiophene-2,5-dicarboxylic acid (**2**) was synthesized by condensing 1,2-diphenylethane-1,2-dione (benzil) with diethyl thiodiglycolate (**1**), which was treated with



Scheme 1 Designed scheme for the synthesis of the polymer (**P1**)

excess thionyl chloride to obtain 3,4-diphenylthiophene-2,5-dicarbonyl chloride (**3**). The 2,5-dihexyloxybenzene-1,4-dihydrazide (**4**) was synthesized according to the reported procedure [20]. The precursor polyhydrazone (**PH1**) was synthesized by the polycondensation of 2,5-dihexyloxybenzene-1,4-dihydrazide (**4**) with 3,4-diphenylthiophene-2,5-dicarbonyl chloride (**3**) in the presence of anhydrous aluminum chloride and pyridine. The polyhydrazone was converted into the target polymer (**P1**) through cyclization using phosphorus oxychloride as a dehydrating agent.

The structures of newly synthesized compounds were confirmed by their FT-IR, ^1H NMR, mass spectroscopic

studies, and elemental analyses. The formation of precursor polyhydrazone (**PH1**) was demonstrated by FT-IR and elemental analyses. The FT-IR spectrum of **PH1** exhibited sharp peaks at 3320 and 1725 cm^{-1} (Fig. 2), assigned to $>\text{N-H}$ and $>\text{C=O}$ groups, respectively. The successful conversion of polyhydrazone (**PH1**) into polyoxadiazole (**P1**) was confirmed by its FT-IR spectrum. In its IR spectrum, the disappearance of the $>\text{C=O}$ and $>\text{N-H}$ stretching absorption bands and the appearance of a sharp peak at around 1595 cm^{-1} due to the imine of the oxadiazole ring indicate the occurrence of cyclization (Fig. 3). The chemical structure of the polymer was

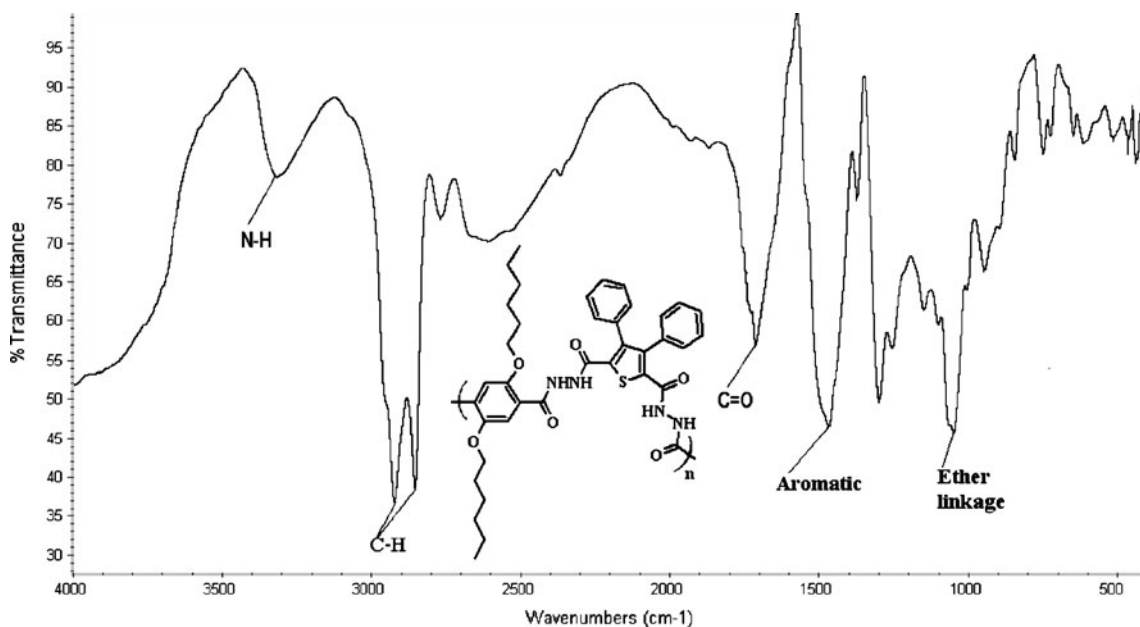


Fig. 2 FTIR spectrum of the polyhydrazone (**PH1**)

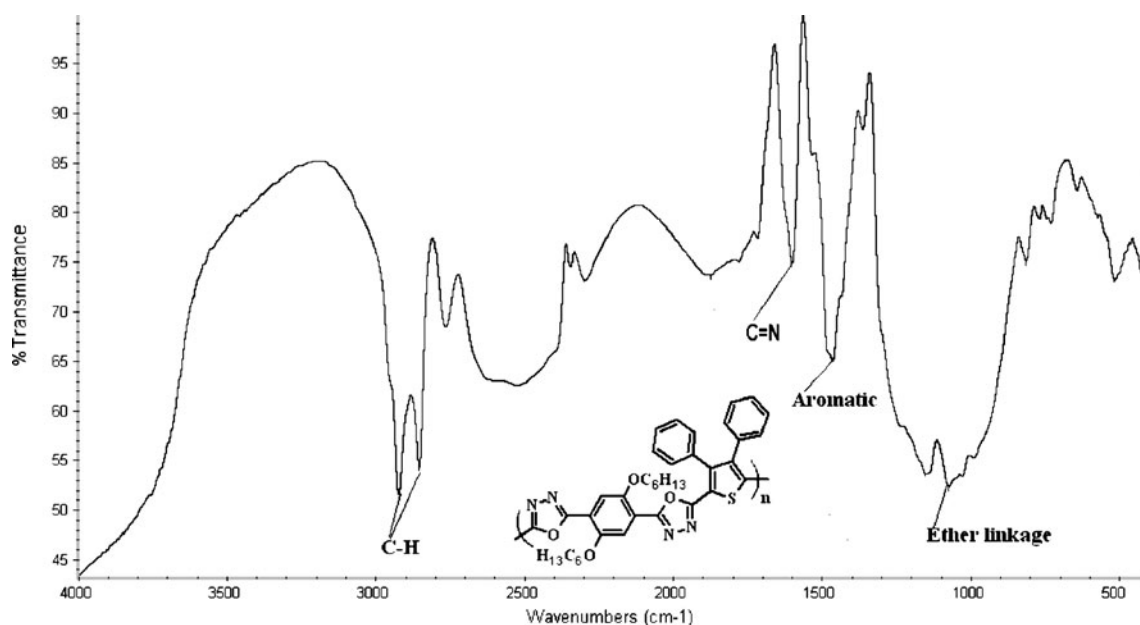


Fig. 3 FTIR spectrum of the polymer (P1)

confirmed by FT-IR, $^1\text{H-NMR}$ spectroscopy, and elemental analysis. The FTIR spectrum of P1 showed characteristic absorption peaks at 2920 , 2848 cm^{-1} (C–H stretching aliphatic segments), 1590 cm^{-1} (1,3,4-oxadiazole), 1467 cm^{-1} (aromatic), 1060 cm^{-1} (=C–O–C=stretching of the ether bond). The $^1\text{H-NMR}$ spectrum of polymer P1 showed a multiplet at δ 7.30 to 8.00 ppm due to the protons of the two phenyl rings at the 3- and 4-positions of the thiophene unit and the hexyloxy benzene moiety. Peaks corresponding to the protons of the alkoxy ($-\text{OCH}_2-$) groups at the 2- and 5-positions of the benzene ring appeared at δ 4.10 ppm. A set of multiplet peaks corresponding to $-\text{CH}_2-$ appeared at δ 1.28–1.96 ppm. The methyl protons ($-\text{CH}_3$) of the alkoxy substituent resonated as a triplet at δ 0.88 ppm. The results from the elemental analysis of this polymer were in agreement with its expected empirical formula. The weight-average molecular weight of the polymer (THF-soluble part) was found to be 3846. The molecular weight and polydispersity data for polymer P1 are summarized in Table 1. Thermogravimetric analysis (TGA) of the polymer was carried out under a nitrogen atmosphere at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. As shown in Fig. 4, the polymer is found to be thermally stable up to $300\text{ }^\circ\text{C}$.

Electrochemical properties

Cyclic voltammetry (CV) was employed to determine the redox potentials of the new polymer and then to estimate the HOMO and LUMO energy levels, which are important for determining the band gap. The cyclic voltammogram of the polymer coated on a glassy carbon electrode was measured on an Autolab PGSTAT 30 electrochemical analyzer, using a Pt counter electrode and a Ag/AgCl reference electrode immersed in the electrolyte $[0.1\text{ M } (n\text{-Bu})_4\text{NClO}_4$ in acetonitrile] at a scan rate of 25 mV/s . Electrochemical data for the polymer P1 are summarized in Table 1.

While sweeping cathodically (Fig. 5), the polymer showed a reduction peak at -1.02 V . This reduction potential is much lower than that of 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) [21, 22], one of the most widely used electron-transporting material. In the anodic sweep (Fig. 5), the polymer showed an oxidation peak at 1.72 V , which is comparable with some donor–acceptor-type polymers containing oxadiazole moieties [23–25]. The onset potentials for the n- and p-doping processes can be used to estimate the HOMO and LUMO of the polymer. According to research reports [26–28], $E_{\text{HOMO}} = -[E_{\text{onset}}^{\text{oxd}} + 4.4\text{ eV}]$

Table 1 Molecular weight data, electrochemical potentials, and energy levels for polymer P1

Polymer	M_n^a	M_w^b	PD ^c	$E_{\text{oxd}}^{\text{onset}}$	$E_{\text{red}}^{\text{onset}}$	E_{oxd}	E_{red}	HOMO (eV)	LUMO (eV)	E_g^d (eV)
P1	2725	3846	1.41	1.45	−0.65	1.72	−1.02	−5.78	−3.68	2.10

^a Number-average molecular weight; ^b weight-average molecular weight; ^c polydispersity; ^d electrochemical band gap

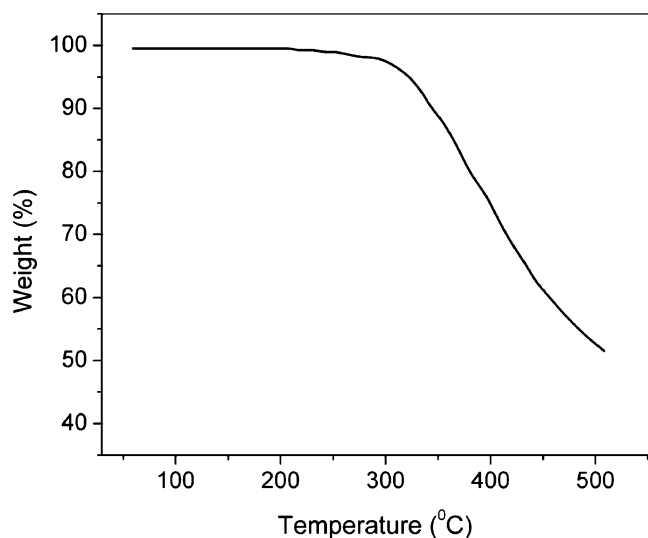


Fig. 4 TGA trace of the polymer (P1)

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 polymer.

The HOMO energy level for the polymer P1 was estimated to be -5.78 eV . The HOMO energy level is comparable with that of CN-PPV and some reported polyoxadiazoles [23–25]. The LUMO energy level (-3.68 eV) is lower than those of PPV and some other conjugated p-type polymers, indicating that it has much better electron-transporting properties. Further, its LUMO energy value is lower than those of some reported polyoxadiazoles [20–22], showing that this polymer possesses better electron injection abilities. From the onset potentials of the oxidation and reduction processes, the band gap of the polymer is estimated to be 2.10 eV . Based

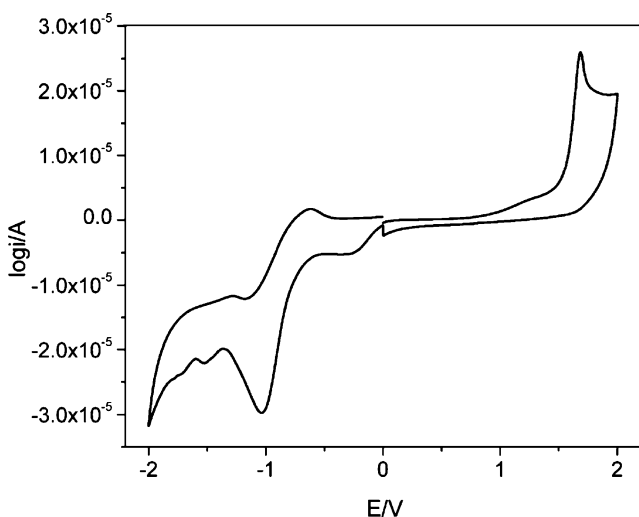


Fig. 5 Oxidation and reduction cyclic voltammetry traces for the polymer

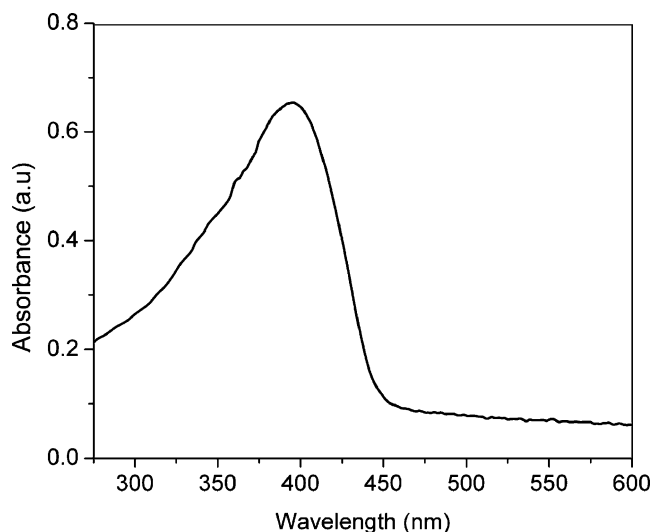


Fig. 6 UV-vis absorption spectrum for the polymer in CHCl_3

on the results of the electrochemical studies, improved charge-carrying properties are expected for the new polymer P1.

Linear optical properties

The UV-visible absorption and fluorescence emission spectra for the polymer were recorded in chloroform solution. As shown in Fig. 6, the polymer exhibits an absorption maximum at 373 nm . The fluorescence emission spectrum of the polymer (Fig. 7) shows an emission maximum (for an excitation wavelength of 380 nm) at 473 nm . A small peak observed at 380 nm is due to the excitation wavelength. These results clearly indicate that the polymer emits intense bluish-green light under UV irradiation.

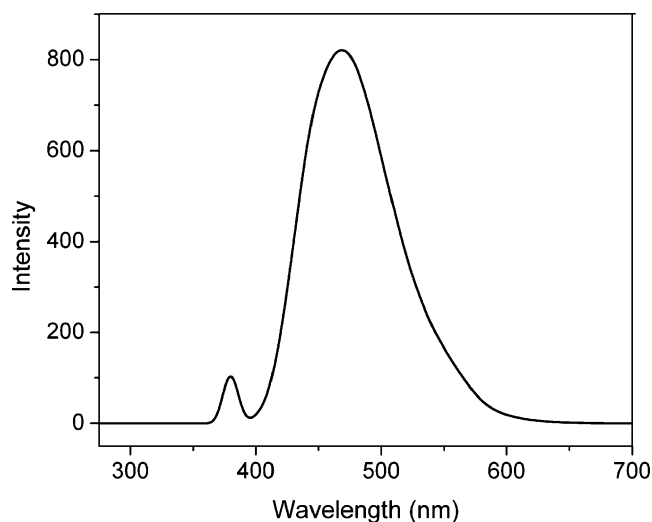


Fig. 7 Fluorescence emission spectrum for the polymer in CHCl_3

Nonlinear optical (NLO) properties

The absorption spectrum of the polymer shows that the excitation wavelength of 532 nm is close to one of the absorption edges. The linear absorption coefficient (α) for the polymer at 532 nm is 186.33 m^{-1} . When placed in a 1 mm cuvette, the sample has a linear transmission of 83% at 532 nm. As seen from Fig. 8, this sample shows strong optical limiting behavior, since the transmittance decreases when the pump intensity is increased. A three-photon absorption (3PA)-type process gives the best fit to the obtained experimental data. The intensity versus normalized transmission curves derived from the z-scan data are therefore numerically fitted to the nonlinear transmission equation for a three-photon absorption process, as given by the equation

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

where T is the transmission of the sample, R is the Fresnel reflection coefficient at the sample–air interface, α is the absorption coefficient, and L is the sample length. Here p_0 is given by $[2\gamma(1 - R)^2 I_0^2 L_{\text{eff}}]^{1/2}$, where γ is the three-photon absorption coefficient and I_0 is the incident intensity. The term L_{eff} is given by $[1 - \exp(-2\alpha L)]/2\alpha$. The value of the 3PA coefficient (γ) obtained by curve fitting is found to be $7 \times 10^{-22} \text{ m}^3/\text{W}^2$.

Considering the absorption spectrum for the polymer and recalling that pure three-photon absorption cross-sections

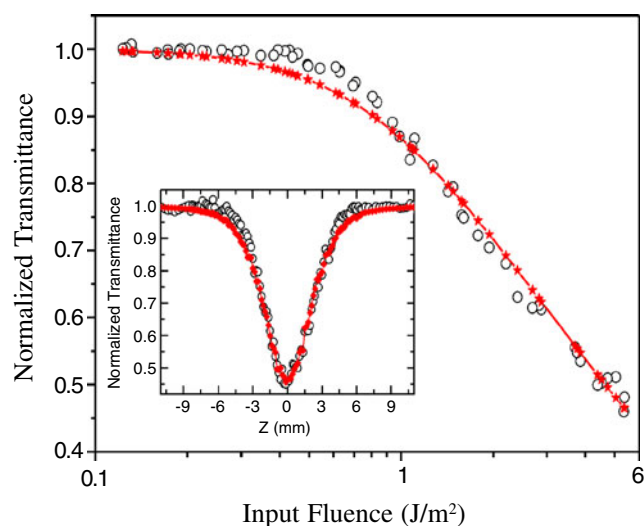


Fig. 8 Input fluence versus the normalized transmittance for the polymer. *Inset* shows the z-scan curve. *Hollow circles* show the data points, and the *filled stars/squares* give the best 3PA fit to the data

are generally very low, it appears that the observed nonlinearity arises from sequential three-photon absorption involving excited states. Two-photon absorption followed by excited-state absorption is another possibility. Therefore, the nonlinearity can be considered an “effective” three-photon absorption process. During the 3PA process, the excitation is proportional to the cube of the incident intensity. This feature could be used to obtain higher contrast and resolution in imaging, since 3PA provides stronger spatial confinement. With the availability of ultrafast pulsed lasers in recent years, significant progress in 3PA-based applications has been made, including in the fields of three-photon pumped lasing and 3PA-based optical limiting and stabilization [29].

In π -conjugated polymeric systems, electrons can move in large molecular orbitals resulting from the linear superposition of the carbon p_z atomic orbitals, leading to very high optical nonlinearity that increases with conjugation length [30]. The polymer studied in the present work consists of a benzene ring with hexyloxy pendants substituted at the 2- and 5-positions as electron-donating groups, and 1,3,4-oxadiazole along with 3,4-diphenylthiophene units substituted as electron-withdrawing segments. This leads to the formation of a donor–acceptor-type arrangement on the polymer backbone. The enhanced third-order nonlinearity in the polymer arises due to the high π -electron density along the polymeric chain; these electrons are easy to polarize as a result of the alternating donor–acceptor-type arrangement. The substitution of the electron-donating alkoxy group not only enhances the delocalization of electrons in the polymer, but it also acts as a solubilizing group. Such absorptive nonlinearities involving real excited states have been reported previously in C_{60} (fullerenes), semiconductors, metal nanoclusters, phthalocyanines, and some fluorine derivatives [31–36].

Conclusions

A novel conjugated polymer (P1) carrying [2,5-dihexyloxy-4-(1,3,4-oxadiazol-2-yl)phenyl]-5-(3,4-diphenylthiophen-2-yl)-1,3,4-oxadiazole units with donor and acceptor moieties in the molecular architecture has been successfully synthesized through multistep reactions. The newly synthesized monomers and the polymer were characterized by spectroscopic techniques. The electrochemical properties showed that the polymer possesses high-lying HOMO (-5.78 eV) and low lying LUMO (-3.68 eV) energy levels. This is attributed to the presence of alternate donor and acceptor conjugated units along the polymer backbone. An analysis of its optical properties revealed that the polymer emits bluish-green fluorescence under irradiation from light. The nonlinear optical properties of the polymer were studied

using the z-scan technique. The polymer exhibited effective three-photon absorption (3PA), which suggests that it would be useful in optical telecommunications and biological applications. The value of the three-photon absorption coefficient (γ) was calculated. The absorptive nonlinearity observed in this polymer is of the optical limiting type, which could have potential applications in devices.

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