A new donor–acceptor type conjugative poly{2-[4-(1-cyanoethenyl)phenyl]-3-(3,4-didodecyloxythiophen-2-yl)prop-2-enenitrile}: Synthesis and NLO studies

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ABSTRACT

This research article describes a technique to synthesize a new donor–acceptor type conjugated polymer carrying cyanophenylenevinylene and 3,4-didodecyloxy thiophene moieties, as an effective optical limiting material. It also includes the evaluation of its linear and nonlinear optical properties and electrochemical studies. The new polymer, viz., poly{2-[4-(1-cyanoethenyl)phenyl]-3-(3,4-didodecyloxythiophen-2-yl)prop-2-enenitrile} (**P1**) has been synthesized starting from 2,2′-sulfanediyldiacetic acid and diethyl ethanedioate through multistep reactions. In the final step, the polymerization was brought about by Knovenagel condensation. The newly synthesized intermediate, monomer and the polymer (**P1**) have been characterized by different spectroscopic techniques followed by elemental analysis. Its optical and electrochemical properties are investigated by UV–vis, fluorescence spectroscopy and cyclic voltammetric studies, respectively. The red colored polymer has a well defined structure, good thermal stability and a band gap of 1.78 eV. It emits green fluorescence both in solution and in film state. The third-order nonlinear optical property (NLO) of the polymer was studied by the Z-scan technique. The measurements were performed at 532 nm with 5 ns laser pulses using samples in solution form. An absorptive nonlinearity of the optical limiting type was found in this polymer, which is due to the combined action of saturable absorption and excited state absorption processes. These studies revealed that polymer **P1** is a promising material for optical limiting applications.

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1. Introduction

During the past 10 years there has been considerable progress in the design of organic materials for optical power limiting. Among the new materials, the more promising are reverse saturable absorbers (RSA), which derive their limiting capability from the photo-generation of highly absorbing charge states. Interestingly, new approaches have been followed for designing new molecules with large two-photon cross-sections which gives access to highly absorbing charge states. Extensive literature survey reveals that over the past few years many research groups have addressed the problem of photo-generated charge state formation in conjugated polymers [1,2].

While two-photon absorption has been studied for a number of years, detailed structure–property relationships which might per-

mit the design of new chromophores with enhanced two-photon cross-sections have been lacking [3–5]. However, in the recent past a few groups have attempted to address the requirement of such design paradigms. Among them, Reinhardt et al. have projected some important design parameters and proposed a series of general rules for increasing the molecular two-photon cross-sections in the new targets. According to them (i) the presence of extended conjugation length, (ii) change in the identity of the conjugated bridge, (iii) increase in the π-donor strength, (iv) incorporation of more polarizable double bonds and (v) increase in the planarity of the polymer backbone, would lead to rise in two-photon absorption characteristics of the molecules.

Thiophene based polymers are currently under active investigations for third-order NLO properties due to their easy processability, chemical stability, readiness of functionalities, good film forming characteristics, solubility, optical transparency and adequate mechanical strength [6–12]. According to the recent reports [13–15], 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
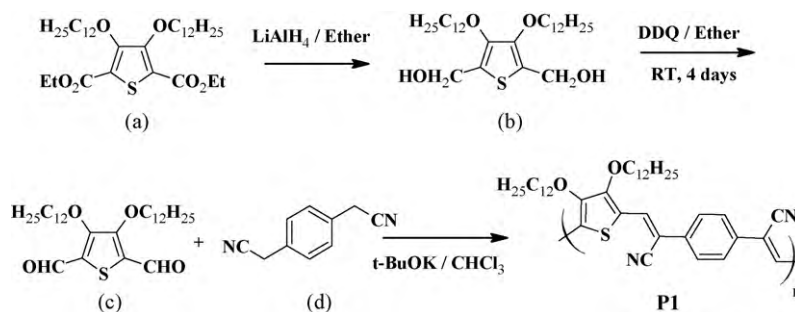
Scheme 1. Synthetic route for the preparation of polymer **P1**.

improved delocalization in the molecule and hence the enhancement of their NLO properties. According to these reports, donor and acceptor groups along the polymer backbone would be a promising molecular design for enhancing the third-order NLO properties.

By applying the design concept proposed by Reinhardt et al., we have designed a new donor–acceptor type conjugative polythiophene wherein cyanophenylenevinylene moiety is incorporated inbetween 3,4-didodecyloxy substituted thiophene moieties in the polymer backbone. It is expected that the new polymer would show enhanced molecular two-photon cross-sections and hence exhibit better *reverse saturable absorption* properties. In this paper, we describe the synthesis and characterization of hitherto unknown polymer containing 3,4-didodecyloxythiophene group as an electron rich n-type segment, cyano-vinylene moiety as electron deficient p-type segment and phenyl ring, as a conjugative spacer as well as a conjugated bridge in the chain. Further, it has been predicted that the introduction of cyanophenylenevinylene moiety reduces the lowest unoccupied molecular orbital (LUMO) level which is expected to increase the linear and nonlinear optical responses [16]. The paper also describes the measurement of nonlinear optical absorption of the polymer using the open aperture Z-scan technique, employing 5 ns laser pulses at 532 nm from a frequency-doubled Nd:YAG laser.

2. Experimental

2.1. Materials

Diethyl 3,4-didodecyloxythiophene-2,5-dicarboxylate (**a**) was synthesized according to the reported literature procedure [17–19]. Dimethylformamide and acetonitrile were dried over CaH_2. 2,2′-Sulfanediyldiacetic acid, diethyl ethanedioate, n-bromoalkanes, lithium aluminium hydride, dichlorodicyanoquinone (DDQ) and tetrabutylammoniumperchlorate (TBAPC) were purchased from Lanchaster (UK) and were used as received. 1,4-Phenylene diacetonitrile was purchased from Aldrich and it was used as received. All the solvents and reagents were of analytical grade. They were purchased commercially and used without further purification.

2.2. Instrumentation

Infrared spectrum of all intermediate compounds and the polymer was recorded on a Nicolet Avatar 5700 FTIR (Thermo Electron Corporation). The UV–vis and fluorescence emission spectra of the polymer were measured in GBC Cintra 101 UV-visible and Perkin–Elmer LS55 spectrophotometers respectively. ^{1}H 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 polymer 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. The thermal stability of the polymer was studied by SII-EXSTAR6000-TG/DTA6300 thermogravimetric analyzer.

2.3. Z-scan measurements

The Z-scan is a well known experimental technique developed by Sheik-Bahae et al. [20] for measuring the nonlinear optical refraction and absorption coefficients of material. 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 at $z = 0$. 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 transmissions. 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 experiences different laser intensity at each z position. A graph drawn between the z position and sample transmission is known as the open aperture Z-scan curve. From this curve, the nonlinear absorption parameters of the sample can be calculated.

The second harmonic output from a Q-switched pulsed Nd:YAG laser (MiniLite, Continuum) was used for the measurements. The laser pulses had a nominal width of 5 ns, and energy of 190 μJ. Pulse-to-pulse energy fluctuation was less than 2%. The laser beam had a Gaussian spatial 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 monitored the input energy, while the other monitored 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.

2.4. Synthesis of polymer, **P1**

The polymer, **P1** was synthesized from 3,4-didodecyloxythiophene 2,5-carboxylate following the reaction sequence as described in Scheme 1.

2.4.1. Preparation of (3,4-didodecyloxythiene-2,5-diyl)dimethanol (**b**)

To a clear solution of 0.5 g (0.0008 mol) of diethyl 3,4-didodecyloxythiophene-2,5-dicarboxylate (**a**) in 10 mL of dry

diethyl ether, 0.13 g (0.004 mol) of anhydrous lithium aluminium hydride was added portion-wise, while stirring. The stirring was continued for 30 min at room temperature. The completion of the reaction was monitored by TLC. The reaction mixture was then poured into cold dilute sulfuric acid solution to decompose the excess lithium aluminium hydride. The organic layer was separated and washed with saturated sodium bicarbonate solution. After the evaporation of the solvent, the obtained solid was filtered and recrystallized from hexane. Yield: 80%, m.p.: 46–48 °C. ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 4.68 (s, 2H, –OH), 4.01 (t, 4H, –OCH$_2$–), 1.74–1.27 (m, 40H, (–CH$_2$)$_{10}$–), 0.89 (t, 6H, –CH$_3$). FAB HRMS: m/z, 513 (calculated: 512.82) IR (KBr, cm^{-1}): 3345(–OH), 2917, 2851. Element. Anal. Calcd. for C$_{30}$H$_{56}$O$_4$S: C, 70.26; H, 11.01; S, 6.25. Found: C, 77.08; H, 10.88; S, 6.37.

2.4.2. Synthesis of 3,4-didoecyloxythiophene-2,5-dicarbaldehyde (c)

A mixture of 0.5 g (0.001 mol) of 3,4-didodecyloxythiene-2,5-diyl)dimethanol (b), 0.88 g (0.004 mol) of dicyanodichloroquinine (DDQ) and 15 mL of dry diethyl ether was stirred for four days at room temperature under nitrogen atmosphere. After the completion of the reaction (monitored by TLC) the mixture was filtered. The filtrate was evaporated to get the solid dial, viz., 3,4-didodecyloxythiophene-2,5-dicarbaldehyde (c) and was recrystallized from ethanol. Yield: 60%, m.p.: 36–37 °C. ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 10.12 (s, 2H, –CHO), 4.27 (t, 4H, –OCH$_2$–), 1.84–1.31 (m, 40H, –(CH$_2$)$_{10}$–), 0.89 (t, 6H, –CH$_3$). FAB HRMS: m/z, 509 (calculated: 508.79). IR (KBr, cm^{-1}): 1690 ($>$C=O). Element. Anal. Calcd. for C$_{30}$H$_{52}$O$_4$S: C, 70.82; H, 10.30; S, 6.30. Found: C, 70.99; H, 10.52; S, 6.17.

2.4.3. Synthesis of poly{2-[4-(1-cyanoethenyl)phenyl]-3-(3,4-didodecyloxythiophen-2-yl)prop-2-enenitrile} (P1)

In an inert atmosphere, to a stirred solution of dialdehyde (c) (0.4 g, 0.0008 mol) and 1,4-phenylene diacetonitrile (0.12 g, 0.0008 mol) in dry chloroform (10 mL), was added 100 mg potassium tertiary butoxide. The yellow suspension immediately turned to dark red purple. The stirring was continued for 40 min. The reaction mixture was then cooled to room temperature and treated with methanol. The solid separated was filtered and washed thoroughly with methanol to remove the unreacted starting materials. The polymer was further purified by dissolving it in chloroform and re-precipitation by adding methanol. It was finally dried in vacuum at 40–50 °C. P1 yield: 62%. IR (cm^{-1}): 2924, 2853, 2208 (–C≡N), 1581, 1458, 1267, 1041, 825. ^{1}H NMR (400 MHz, CDCl$_3$). δ (ppm): 7.70 (s, 2H, olefinic proton), 7.62 (d, 2H, aromatic protons), 7.25 (d, 2H, aromatic protons), 4.32 (t, 4H, –OCH$_2$–), 1.80–1.33 (m, 40H, –(CH$_2$)$_{10}$–), 0.92 (t, 6H, –CH$_3$). Anal. Calcd. for the repeating unit (C$_{40}$H$_{58}$N$_2$O$_2$S): C, 76.14; H, 9.27; N, 4.44, S, 5.08. Found: C, 76.42; H, 9.55; N, 4.27; S, 5.21.

3. Results and discussion

3.1. Synthesis and characterization of the polymer, P1

The synthetic route for the preparation of polymer P1 is shown in Scheme 1. As mentioned in the scheme, 3,4-didodecyloxythiene-2,5-diyl)dimethanol (b) was obtained by the reduction of diethyl 3,4-didodecyloxythiophene-2,5-dicarboxylate (a) by lithium aluminium hydride. The bis-alcohol (b) was then treated with dicyanodichloroquinine (DDQ) to get 3,4-didodecyloxythiophene-2,5-dicarbaldehyde (c). In the final step, the polymerization was carried out by the condensation of the monomer, dial (c) with 1,4-phenylene diacetonitrile (d), using Knoevenagel's reaction, under basic condition.
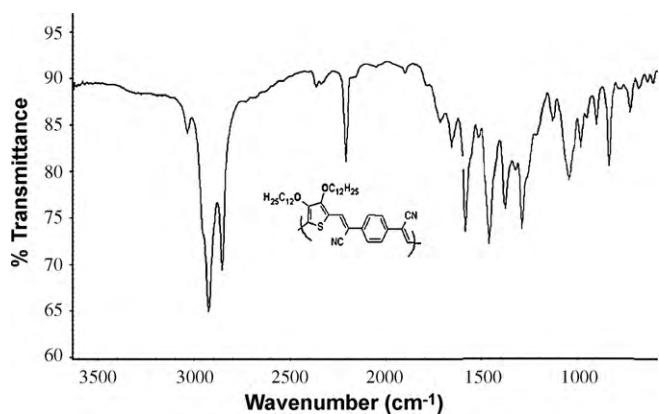

Fig. 1. FTIR spectrum of the polymer P1.

The intermediate dimethanol (b) and the monomer dicarbaldehyde (c) were characterized by their FTIR, ^{1}H NMR, mass spectral and elemental analyses. The FTIR spectrum of (b) showed broad peak at 3345 cm^{-1} corresponding to the –OH stretching frequency. The ^{1}H NMR spectrum of (b) showed peaks at δ (ppm) 4.68 (s, 2H, –OH), 4.01 (t, 4H, –OCH$_2$–), 1.74–1.27 (m, 40H, (–CH$_2$)$_{10}$–) and 0.89 (t, 6H, –CH$_3$) which confirms the structure of the dimethanol. Formation of the compound (b) from its ester (a) was further confirmed by its mass spectrum. In its mass spectrum, the compound displayed molecular ion peak at m/z 513 (M+1), which is in agreement with the molecular formula C$_{30}$H$_{56}$O$_4$S. The elemental analysis of the dimethanol was in agreement with its expected empirical formula.

The FTIR spectrum of (c) showed a sharp peak at 1658 cm^{-1} which corresponds to the stretching frequency of $>$C=O of the aldehydic group. The ^{1}H NMR spectrum of (c) showed δ (ppm) 10.12 (s, 2H, –CHO), 4.27 (t, 4H, –OCH$_2$–), 1.84–1.31 (m, 40H, –(CH$_2$)$_{10}$–) and 0.89 (t, 6H, –CH$_3$). The proton count matches with the expected structure. In its mass spectrum, the compound displayed molecular ion peak at m/z 509, which is in agreement with the molecular formula, C$_{30}$H$_{52}$O$_4$S. The elemental analysis of the dial was in agreement with its expected empirical formula.

The chemical structure of the new polymer was further confirmed by its ^{1}H NMR spectroscopy, elemental analysis and molecular weight by gel permeation chromatography (GPC). The FTIR spectrum of the polymer (Fig. 1) P1 exhibits 2208 cm^{-1} accounting for the nitrile ($>$C≡N) group of the polymer chain. The ^{1}H NMR spectrum of the polymer P1 showed (Fig. 2) olefinic pro-

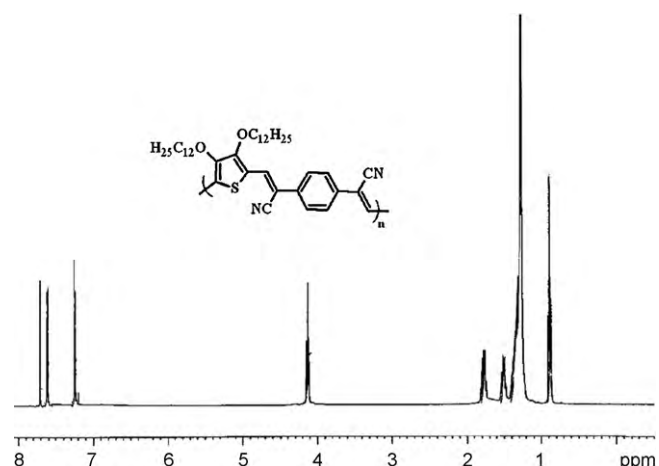Fig. 2. ^{1}H NMR spectrum of the polymer P1.

Table 1
Electrochemical potential and energy levels of the polymer **P1**.

Polymer	E_{oxd}	E_{red}	E_{oxd} (onset)	E_{red} (onset)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
P1	1.50	−1.10	1.16	−0.62	5.50	−3.72	1.78

tons resonated at δ (ppm) 7.70 (s, 2H), aromatic protons appeared at 7.62 (d, 2H), 7.25 (d, 2H), peaks corresponding –OCH_2– observed at 4.32 (t, 4H), the peaks of alky chain –$(CH_2)_{10}$– observed as multiplet at 1.80–1.33 (m, 40H) and peak of methyl protons are seen at 0.92 (t, 6H). The result of elemental analysis of polymer was in agreement with its expected empirical formula. The molecular weight of the new polymer was determined by light scattering method and it was found to be 34,340. The polymer was found to be thermally stable up to about 320 °C under thermogravimetric experimental condition. The thermogravimetric trace of the polymer is shown in Fig. 3.

3.2. Electrochemical studies

Cyclic voltammetry (CV) was employed to determine redox potentials of new polymer and then to estimate the HOMO and LUMO levels, which is of importance to determine the band gap. The cyclic voltammogram of the polymer coated on a glassy carbon electrode was obtained by 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)$_4$NClO$_4$ in acetonitrile] at a scan rate of 25 mV/s. Electrochemical data of **P1** is summarized in Table 1.

The cyclic voltammograms of the polymer **P1** display distinct oxidation and reduction processes as shown in Fig. 4. The onset oxidation and reduction potentials were used to estimate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the copolymer **P1** [21]. The equations reported by de Leeuw et al., $E_{HOMO} = -\left[E_{onset}^{oxd} + 4.44\,eV\right]$ and $E_{LUMO} = -\left[E_{onset}^{red} - 4.44\,eV\right]$, where E_{onset}^{oxd} and E_{onset}^{red} are the onset potentials versus SCE for the oxidation and reduction of this polymer, were referred for the calculations. Electrochemical potentials and energy levels of the polymer are tabulated in Table 1. The HOMO energy level of the polymer is estimated to be −5.50 eV and the LUMO energy level is found to be −3.72 eV for **P1**. The HOMO energy levels are comparable with some of the good photonic materials reported in the literature [22,23]. The LUMO value is lower than those of cyano-PPV (reported, −3.02) and some aromatic poly(oxadiazole)s (reported, −2.8 to −2.9 eV) reported in the
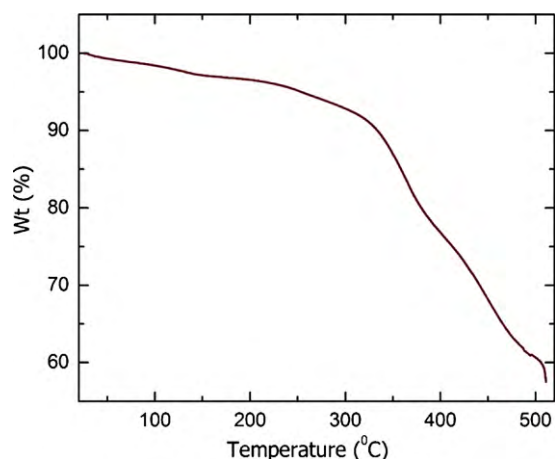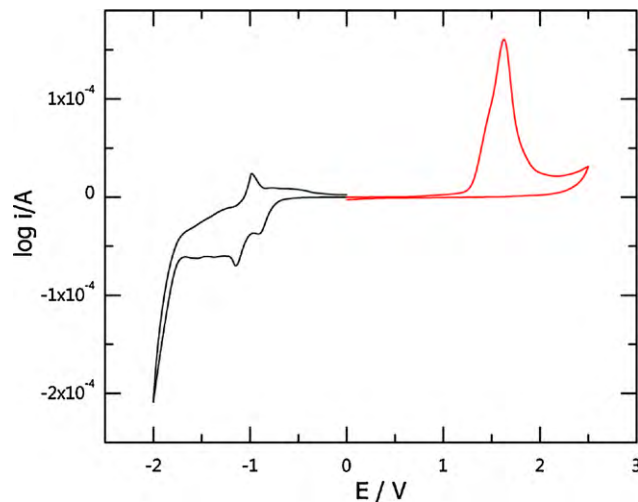

Fig. 4. Cyclic voltammetric trace of the polymer **P1**.

literature. The electrochemical band gap (E_g) of the polymer **P1** is estimated to be 1.78 eV.

3.3. Linear optical properties

Optical properties of the polymer were studied by UV–vis and fluorescence spectroscopic measurements. The UV–vis absorption and fluorescence emission spectra were recorded in thin films as well as in dilute chloroform solution. The absorption maximum of the polymer in dilute solution was observed at 515 nm. The spectrum in thin film form showed red shift (around 10 nm) indicating the presence of inter-chain interactions in the solid state. The optical band gap (E_g) was found to be 1.68 eV for **P1**. The polymer emits intense green fluorescence with emission peak at 574 nm in solution. The absorption and fluorescence spectra of the polymer in dilute solution are shown in Figs. 5 and 6, respectively.
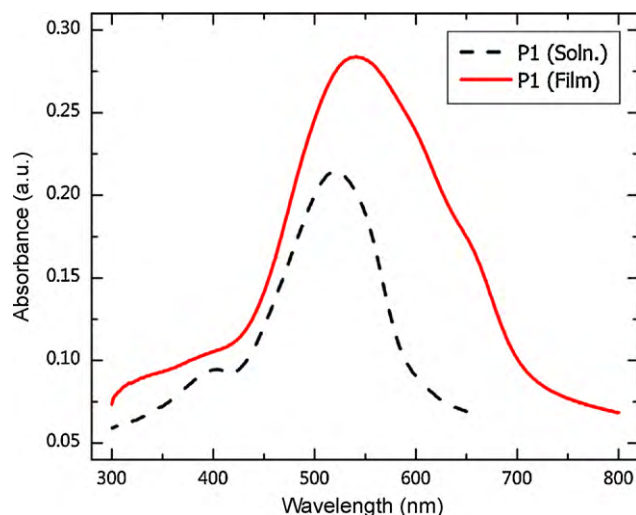

Fig. 3. The thermogravimetric trace of the polymer **P1**.

Fig. 5. UV–vis absorption spectra of the polymer in solution and in thin film.
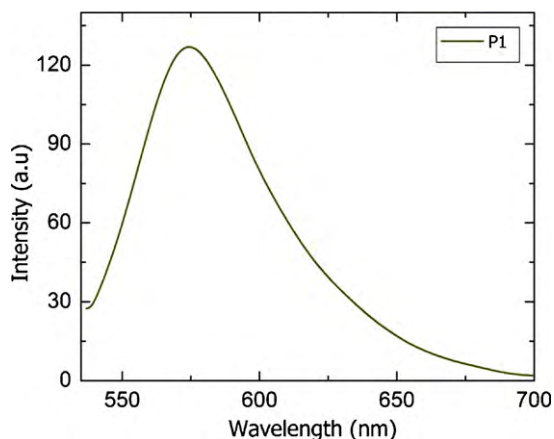
Fig. 6. Fluorescence emission spectrum of the polymer **P1** in solution.

3.4. Nonlinear optical properties

3.4.1. Z-scan

The linear absorption spectrum of the polymer shows that the excitation wavelength of 532 nm is close to the absorption peak, which is a favorable situation for absorption saturation. However, as shown in Fig. 7 the polymer **P1** shows strong optical limiting behavior, where the transmittance decreases when the pump fluence is increased. This is apparently a counter-intuitive result, but from numerical calculations it was found that this nonlinear transmittance arises from a combined action of saturable absorption and excited state absorption at the excitation wavelength. This conclusion was arrived by considering an effective nonlinear absorption coefficient $\alpha(I)$, given by [24].

$$\alpha(I) = \left(\frac{\alpha_0}{1 + \left(\frac{I}{I_s} \right)} \right) + \beta I \qquad (1)$$

where α_0 is the unsaturated linear absorption coefficient at the wavelength of excitation, I is the input laser intensity and I_s is the saturation intensity (intensity at which the linear absorption drops to half of its original value). $\beta I = \sigma N$ is the excited state absorption (ESA) coefficient, where σ is the ESA cross-section and $N(I)$ is the intensity-dependent excited state population density. For calculating the transmitted intensity for a given input intensity, the
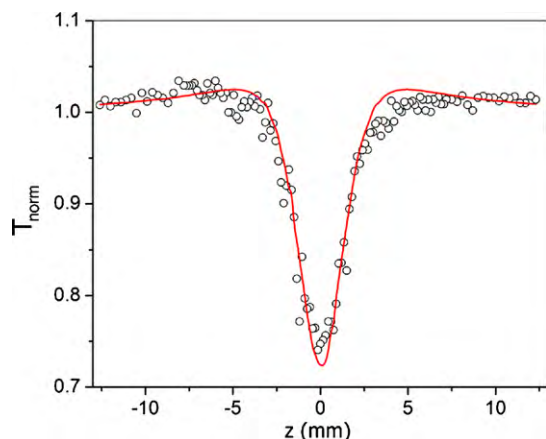
propagation equation

$$\frac{dI}{dz'} = - \left[\left(\frac{\alpha_0}{1 + \frac{I}{I_s}} \right) + \beta I \right] I \qquad (2)$$

was numerically solved. Here z' indicates the propagation distance within the sample. By determining the best-fit curve for the experimental data, the value of I_s is found to be 2.6×10^{13} W/m^2, and that of β is 1.3×10^{-11} m/W.

As mentioned above, when the optical excitation is at or near an absorption peak, a saturation of absorption will take place for moderate input light intensities. This occurs when the ground state and excited state populations become equal. At still higher intensities absorption from the excited state becomes prominent, leading to a net decrease in the optical transmission. In this region the polymer sample behaves as an optical limiter, as seen from Fig. 7 for polymer **P1**.

In π-conjugated polymeric systems electrons move in large molecular orbitals, which result from the linear superposition of the carbon p_z atomic orbitals. This brings about a high optical nonlinearity, which increases with the conjugation length [25]. The polymer studied in the present work consists of thiophene ring substituted with dodecyloxy pendant at 3,4-position as electron donating group and cyano-vinylene moiety as an electron accepting moiety. This leads to the formation of a donor–acceptor type of arrangement in the polymer backbone. Further the phenyl ring acts as a conjugation bridge in the polymeric backbone. The π-electrons along the polymeric chain are easily polarizable and they have a high density, so that the third-order nonlinearity gets enhanced. In addition to enhancing the delocalization electrons in the polymer, the substitution of the electron donating didodecyloxy group also acts as a solubilizing group.

4. Conclusions

In conclusion, we have described a method for the synthesis of a new donor–acceptor type conjugative polymer containing cyanophenylenevinylene and 3,4-didodecyloxy thiophene moieties in the polymer architecture. The newly synthesized intermediate, monomer and the polymer have been characterized by different spectroscopic techniques and elemental analysis. Further the polymer was analyzed for GPC and thermogravimetric studies. The electrochemical and optical band gaps of the polymer were found to be 1.78 eV and 1.68 eV, respectively. The polymer showed very good optical limiting property for 5 ns laser pulses at the excitation wavelength of 532 nm. The optical limiting behavior is due to combined action of saturable absorption and excited state absorption at the wavelength used. Because of the strong nonlinearity, polymer **P1** can have potential applications in the fabrication of optical limiting devices.

Fig. 7. Open aperture Z-scan trace of polymer **P1** at 532 nm. Circles are data points and the solid curve is a numerical fit based on Eqs. (1) and (2).

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