

# A novel narrow band gap red light-emitting cyanovinylene polymer derived from 3,4-dialkoxy thiophene for optoelectronic applications

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Received: 21 July 2009 / Accepted: 24 September 2009 / Published online: 14 October 2009  
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**Abstract** A novel donor–acceptor type narrow band gap cyanovinylene poly{3,3'-(3,4-ditetradecyloxythiophene-2,5-diyl) bis[2-(thiophen-2-yl)prop-2-enenitrile]} has been designed and synthesized through multistep reactions. All the newly synthesized compounds were characterized by using FTIR and  $^1\text{H}$  NMR spectroscopy followed by elemental analyses. The polymer **P** is found to be thermally stable up to 300 °C under nitrogen atmosphere. The optical and charge-transporting properties of the polymer were investigated by UV–visible, fluorescence emission spectroscopic and cyclic voltammetric studies. The monomer (**M**) emits intense green-light in solution state and the polymer (**P**) exhibited intense red-fluorescence both in solution and solid state. The fluorescence quantum yield of the polymer is determined to be 43%. Cyclic voltammetric studies reveal that the polymer possesses good charge carrying property. The electrochemical band-gap is estimated to be 1.8 eV. The studies reveal that the new cyanovinylene polymer **P** is a promising material for the development of efficient optoelectronic devices.

## 1 Introduction

Conjugated polymers are currently the subject of an intense research effort because of their potential applications in electronic and electrochemical devices such as light emitting diodes (LEDs), photovoltaic devices (PVDs) and field

effect transistors (FETs). Amongst various newly developed polymers, poly(1,4-phenylenevinylene) (PPV) [1], poly(*p*-phenylene) (PPPs) [2], polyfluorenes (PFs) [3], and polythiophenes (PTs) [4] were in the focus of investigations. Presently, one of the main research objectives in this field is to develop light emitting polymers with both high thermal stability and emitting efficiency that are directly related to the performance and reliability of polymer light emitting devices (PLEDs) [5, 6]. The development of more effective electron transporting polymers (*n*-type) which facilitate the use of air-stable cathodes such as aluminium is one of the challenges to develop efficient PLEDs [7]. Generally, in PLEDs, polymers such as polypyridines [8], polyquinoxalines [9], polyquinolines [10], polyoxadiazoles [11] containing electron-affinitive molecules have been widely used as electron transporting materials. An ideal electron transport polymer should permit efficient electron injection into it from an air-stable metallic electrode [12]. Also it must possess high mobility of electrons and effective transfer of electrons to the emissive polymer at the polymer/polymer interface.

In order to achieve high efficiency of PLED devices, it is necessary to balance the injection rate of electrons and holes. It has been reported that in most of the existing conjugated polymers the barrier between the Lowest Occupied Molecular Orbital (LUMO) of the polymers and the work function of the cathode is much larger than that between the Highest Occupied Molecular Orbital (HOMO) of the polymer and the work function of the anode. This causes an imbalance of the injection between electrons and holes, resulting in low efficiency of the PLED devices. Generally, there are two strategies to improve the efficiency of the PLEDs. The first approach is to utilization of the low work function metals like Ca, Li as cathode [13]. Insertion of an electron transporting/hole blocking layer

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between the emitter and cathode [14] is the second strategy. Main disadvantages of these two approaches are reduction in the durability of devices due to reactive cathodes and difficulty involving in the fabrication of double layers PLEDs.

The latest approach involves the modification of chemical structure of emitting polymer molecules, i.e., design of new conjugated polymers with desired HOMO and LUMO levels. To achieve this, the polymer backbone must involve both donor and acceptor segments. In this context, it is necessary to incorporate electron rich and electron deficient units in the polymer chain during the synthetic design. In the structural design, selection of *p*- and *n*-type segments plays an important role on their balanced charge transporting property. An especially interesting class of conjugated polymer is the narrow band gap polymers. Such polymers offer broad range of attractive features for use in a variety of device architectures, such as ease of oxidation reduction and potential for high electron and hole mobility (LEDs). Also, narrow band gap polymers are particularly desirable for photovoltaic device applications due to their spectral absorption which matches the solar terrestrial radiation. Based on this, synthesis of few narrow band gap conjugated donor–acceptor type cyanovinylene polymers have been reported and shown to possess unique electrochemical and optical properties [15, 16]. In such type of polymers cyano-containing chromophore play principle role in ground dipole moments which determine an efficiency of the LED emission determining by the transport of the carriers [17]. Literature survey reveals that 3,4-dialkoxy substituted poly(thiophene)s show facile dopability and lower band gap ascribe to the electron donating nature of the alkoxy moiety. It has been also reported that introduction of long alkoxy pendants at 3- and 4- positions of the thiophene ring improves the solvent processibility and hole carrying ability of the corresponding polymer [18, 19].

Against this background, it has been thought of designing the synthesis of new donor–acceptor type conjugated cyanovinylene polymer containing 3,4-dialkoxy thiophene units with both electron and hole transport architecture. It is hoped that the resulting polymer would show low band gap nature and balanced charge carrying property. Further, it is predicted that the new polymer would act as efficient light emitting material for the development of PLEDs. In this communication, we hereby report the synthesis of new cyanovinylene polymer (**P**) carrying 3,3'-(3,4-ditetradecyloxythiophene-2,5-diyl)bis[2-(thiophen-2-yl)prop-2-enenitrile] unit in its backbone structure and investigation of its optical (absorption as well as emission) and electrochemical (redox) properties.

## 2 Experimental section

### 2.1 Materials

Diethyl 3,4-ditetradecyloxythiophene-2,5-dicarboxylate (**1**) was synthesized according to literature procedure [20, 21] starting from thiodiglycolic acid and diethyl oxalate. Thiodiglycolic acid, diethyl oxalate, tetrabutylammoniumperchlorate (TBAPC) and 1-bromotetradecane were purchased from Lanchaster (UK). Lithium aluminium hydride ( $\text{LiAlH}_4$ ) 2,3-dichloro-5,6-dicyano benzoquinone (DDQ) and anhydrous ferric chloride ( $\text{FeCl}_3$ ) were purchased from Sigma–Aldrich. All the solvents and reagents were of analytical grade. They were purchased commercially and used without further purification.

### 2.2 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 emission spectra were measured in GBC Cintra 101 UV–visible and Perkin Elmer LS55 spectrophotometers, respectively.  $^1\text{H}$  NMR spectra were obtained with AMX 400 MHz FT-NMR spectrophotometer using 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 by SII EXSTAR6000-TG/DTA6300 Thermo Gravimetric Analyzer (TGA). The electrochemical study of the polymer was carried out using an AUTOLAB PGSTAT30 electrochemical analyzer. Cyclic voltammograms were recorded using a three-electrode cell system, with glassy carbon button as working electrode, a platinum wire as counter electrode and an Ag/AgCl electrode as the reference electrode. Molecular weight of the polymer was determined on Waters make Gel Permeation Chromatography (GPC) using polystyrene standards in THF solvent.

### 2.3 Synthesis of (3,4-ditetradecyloxythiophene-2,5-diyl) dimethanol (**2**)

To a solution of 2 mmol of diester (**1**) in 50 mL of dry diethyl ether, 6 mmol of lithium aluminium hydride ( $\text{LiAlH}_4$ ) was added carefully. The reaction mixture was stirred for 1 h at room temperature. The progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, the solvent was removed and the solid residue obtained was acidified with 1:1 sulfuric acid. Then, the aqueous layer was extracted three times with methylene dichloride (30 mL each). The organic layer was dried using anhydrous sodium sulphite

and then evaporated using rotary evaporator. Finally, the obtained solid crude product was recrystallized using *n*-hexane. Yield: 80%, m.p: 42–44 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 4.65 (s, 2H, –OH), 4.05 (t, 4H, –OCH<sub>2</sub>–, *J* = 6.7 Hz), 1.78–1.22 (m, 40H, –(CH<sub>2</sub>)<sub>10</sub>–), 0.90 (t, 6H, –CH<sub>3</sub>, *J* = 6.8 Hz). IR (KBr, ν): 3,348 (–OH), 2,919, 2,854 cm<sup>–1</sup>. Elemental. Calcd for C<sub>34</sub>H<sub>64</sub>O<sub>4</sub>S: C, 71.78; H, 11.34; S, 5.64%, Found: C, 71.99; H, 11.52; S, 5.57%.

#### 2.4 Synthesis of 3,4-ditetradecyloxythiophene-2,5-dicarbaldehyde (**3**)

To a solution of 2 mmol of bisalcohol (**2**) in 50 mL diethyl ether, 8 mmol of 2,3-dichloro-5,6-dicyano benzoquinone (DDQ) was added while stirring. After stirring the reaction mixture for 2 h at room temperature additional 2 mmol of DDQ and 30 mL of diethyl ether were added. The stirring was continued for 72 h at room temperature. Then, the solvent was evaporated using rotary evaporator. The solid residue obtained was redissolved in 50 mL of *n*-hexane and filtered. Finally, the organic layer was evaporated and the solid crude product obtained was recrystallized using ethanol. Yield: 62%, m.p: 34–35 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 10.10 (s, 2H, –CHO), 4.28 (t, 4H, –OCH<sub>2</sub>–, *J* = 6.6 Hz), 1.85–1.31 (m, 48H, –(CH<sub>2</sub>)<sub>12</sub>–), 0.89 (t, 6H, –CH<sub>3</sub>, *J* = 6.7 Hz). IR (KBr, ν): 1,692 (>C=O) cm<sup>–1</sup>. Elemental Calcd For C<sub>34</sub>H<sub>60</sub>O<sub>4</sub>S: C, 72.29; H, 10.71; S, 5.68, Found: C, 72.39%; H, 10.52%; S, 5.47%.

#### 2.5 Synthesis of cyano monomer 3,3'-(3,4-ditetradecyloxythiophene-2,5-diyl)bis[2-(thiophen-2-yl)prop-2-enenitrile] (**M**)

To a mixture of 1 equivalent of dialdehyde (**3**) and 2 equivalent of thiophene-2-acetonitrile (**4**) in 30 mL of ethanol was added 5 equivalent of potassium tertiary butoxide (Bu<sup>t</sup>OK). The reaction mixture was stirred for 2 h at room temperature. The precipitated solid was filtered, dried and recrystallized using ethanol to get the monomer (**M**) as dark-red shiny solid. Yield: 63%, m.p: 68–70 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 7.62 (s, 2H, Olefinic proton), 7.38 (d, 2H, Thiophene proton), 7.32 (d, 2H, Thiophene proton), 7.05 (t, 2H, Thiophene proton), 4.14 (t, 4H, –OCH<sub>2</sub>–, *J* = 6.6 Hz), 1.80–1.23 (m, 48H, –(CH<sub>2</sub>)<sub>12</sub>–), 0.90 (t, 6H, –CH<sub>3</sub>, *J* = 6.7 Hz). FABHRMS: *m/z*, 775. IR (KBr, ν): 2,211 (–CN) cm<sup>–1</sup>. Elemental Calcd For C<sub>46</sub>H<sub>66</sub>N<sub>2</sub>O<sub>2</sub>S<sub>3</sub>: C, 71.27; H, 8.58; N, 3.61; S, 12.41%, Found: C, 71.45; H, 8.38; N, 3.54; S, 12.56%.

#### 2.6 Synthesis of polymer (**P**)

To a solution of four equivalents of anhydrous ferric chloride in 20 mL of chloroform, one equivalent of

monomer (**M**) in 10 mL of chloroform was added slowly for 30 min. The reaction mixture was stirred at room temperature for 24 h. The progress of the reaction was monitored by TLC. After the completion of the reaction, the chloroform was removed by rotary evaporator under vacuum. The solid product obtained was washed with excess of methanol to remove the ferric chloride. The last trace of ferric chloride was removed by Soxhlet extraction technique using methanol as solvent. The polymer (**P**) was obtained as bluish-black powder. Yield: 66%, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 7.64 (s, 2H, Olefinic proton), 7.33 (d, 2H, Thiophene proton), 7.22 (d, 2H, Thiophene proton), 4.12 (t, 4H, –OCH<sub>2</sub>–, *J* = 6.8 Hz), 1.83–1.20 (m, 48H, –(CH<sub>2</sub>)<sub>12</sub>–), 0.90 (t, 6H, –CH<sub>3</sub>, *J* = 6.7 Hz). IR (KBr, ν): 2,925, 2,852 (>C–H), 2,210 (–CN), 1,468 (Aromatic), 1,058 (=C–O–C=stretching of ether bond) cm<sup>–1</sup>. Elemental Calcd for C<sub>46</sub>H<sub>64</sub>N<sub>2</sub>O<sub>2</sub>S<sub>3</sub>: C, 71.45; H, 8.34; N, 3.62; S, 12.44%, Found: C, 71.22; H, 8.10; N, 3.91; S, 12.11%.

### 3 Results and discussion

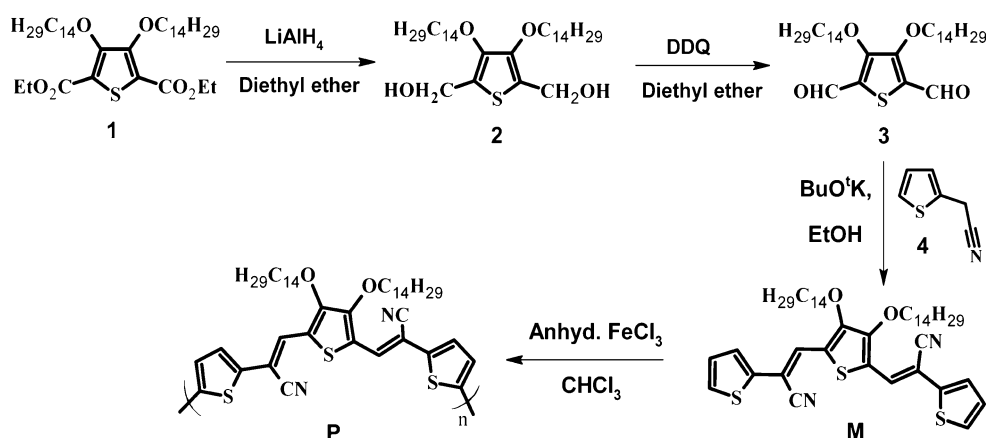
#### 3.1 Synthetic plan

The scheme 1 outlines the designed synthetic route for the preparation of cyanovinylene monomer **M** and the polymer **P**. Required (3,4-ditetradecyloxythiophene-2,5-diyl)dimethanol (**2**) was prepared by the reduction of diethyl 3,4-ditetradecyloxythiophene-2,5-dicarboxylate (**1**) using lithium aluminium hydride (LiAlH<sub>4</sub>) as reducing agent. The compound **2** was readily converted into 3,4-ditetradecyloxythiophene-2,5-dicarbaldehyde (**3**) by the action of mild oxidizing agent, 2,3-dichloro-5,6 dicyano benzoquinone (DDQ) in diethyl ether medium. Then, the novel monomer 3,3'-(3,4-ditetradecyloxythiophene-2,5-diyl)bis[2-(thiophen-2-yl)prop-2-enenitrile] (**M**) was prepared by the Knoevenagel condensation of thiophene-2-acetonitrile (**4**) with dialdehyde (**3**) in the presence of Bu<sup>t</sup>OK. Finally, the monomer **M** was polymerized via chemical polymerization technique using anhydrous ferric chloride (FeCl<sub>3</sub>) as polymerization catalyst. This is a good synthetic protocol for new cyanovinylene polymers.

#### 3.2 Characterization of the polymer

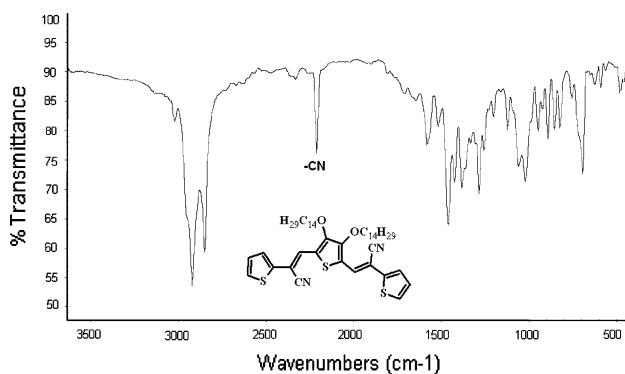
The structures of newly synthesized compounds were confirmed by their spectral and elemental analyses. Formation of (3,4-ditetradecyloxythiophene-2,5-diyl)dimethanol (**2**) from diester (**1**) was evidenced by its IR and <sup>1</sup>H NMR spectral data. Its IR spectrum showed sharp peak at 3,348 cm<sup>–1</sup> indicating the presence of –OH groups. <sup>1</sup>H NMR spectra of it displayed peak at δ value 4.65 (s, 2H)

**Scheme 1** Designed synthetic route for the preparation of thiophene based cyanovinylene polymer

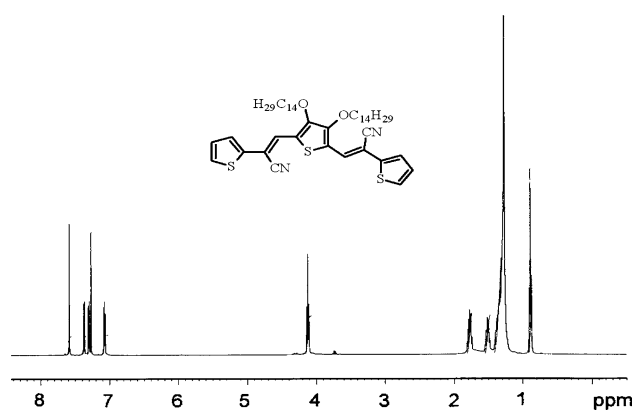


corresponding to  $\text{-OH}$  protons. Conversion of bisalcohol (**2**) to dicarbaldehyde (**3**) was confirmed by its IR and  $^1\text{H}$  NMR spectral studies. Its IR spectrum exhibited sharp peak at  $1,692\text{ cm}^{-1}$  for  $>\text{C}=\text{O}$  group.  $^1\text{H}$  NMR spectrum of it showed two aldehyde protons as singlet at  $\delta$  value  $10.10\text{ ppm}$ . Condensation of thiophene-2-acetonitrile to dicarbaldehyde (**3**) was established by IR and  $^1\text{H}$  NMR spectral data. Its IR spectrum (Fig. 1) showed absorption peak at  $2,211\text{ cm}^{-1}$  due to  $\text{-CN}$  group. Further, in its  $^1\text{H}$  NMR spectrum (Fig. 2) showed a singlet at  $\delta$   $7.62$  due to olefinic protons and multiple peaks at  $\delta$  value  $7.38\text{--}7.05\text{ ppm}$  due to free thiophene protons.

Polymerization of the monomer **M** was evidenced by  $^1\text{H}$  NMR spectrum. In its  $^1\text{H}$  NMR disappearance of one doublet peak and conversion of one triplet into a doublet peak clearly confirms the polymerization of the monomer **M** to polymer **P**. The chemical structure of the polymer **P** was confirmed by FTIR,  $^1\text{H}$  NMR spectroscopy and elemental analysis. FTIR spectrum of **P** showed characteristic absorption peaks at  $2,925, 2,852\text{ cm}^{-1}$  ( $\text{C-H}$  stretching aliphatic segments),  $2,210\text{ cm}^{-1}$  ( $\text{-CN}$ ),  $1,468\text{ cm}^{-1}$  (aromatic). The  $^1\text{H}$ -NMR spectra of polymer **P** showed a singlet at  $\delta$   $7.64\text{ ppm}$  due to the olefinic protons of the polymer chain and two doublets at  $\delta$   $7.33$  and  $7.22\text{ ppm}$  due to thiophene protons at position 3 and 4. A peak corresponds to



**Fig. 1** FTIR spectrum of cyano monomer **M**



**Fig. 2**  $^1\text{H}$  NMR spectrum of cyano monomer **M**

the protons of the alkoxy ( $\text{-OCH}_2\text{-}$ ) groups at 3 and 4-positions of the thiophene ring appeared at  $\delta$   $4.12\text{ ppm}$ . A set of multiplet peaks which corresponds to  $\text{-CH}_2\text{-}$  protons appeared at  $\delta$   $1.20\text{--}1.83\text{ ppm}$ . The methyl protons ( $\text{-CH}_3$ ) of the alkyl chain resonated as a triplet at  $\delta$   $0.90\text{ ppm}$ . The elemental analysis results of the polymer **P** were in agreement with their expected empirical formula. The weight average molecular weight of THF soluble part of the polymer was found to be  $4,920$ . The molecular weight data is summarized in Table 1. Thermogravimetric analysis of the polymer **P** was carried out under nitrogen atmosphere at heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ . As shown in Fig. 3, the polymer **P** is found to be thermally stable up to  $300\text{ }^\circ\text{C}$ .

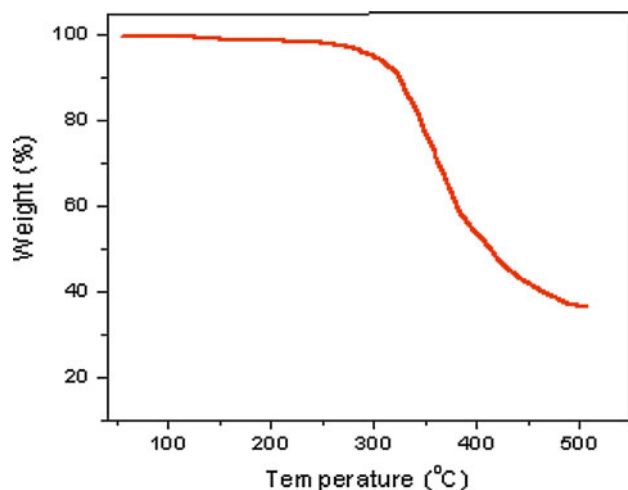
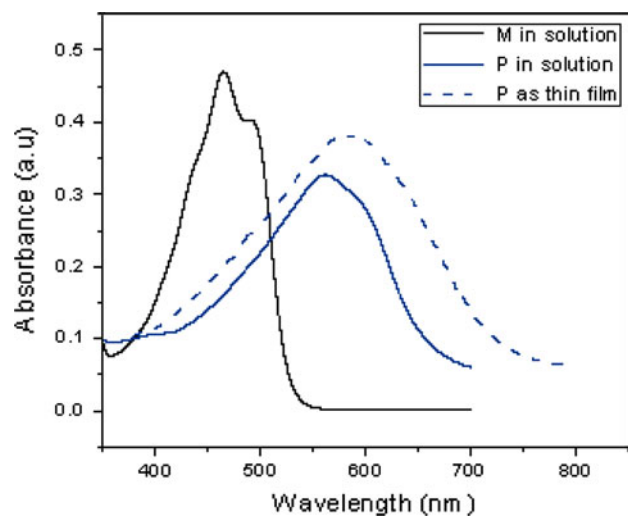
### 3.3 Optical properties

The UV-Visible absorption and fluorescence emission spectrum of the monomer **M** was recorded in dilute chloroform solution and for the polymer **P** they were recorded both in solution and in thin film form. The corresponding spectral data are summarized in Table 1. As shown in Fig. 4, absorption maximum for the monomer in dilute chloroform solution is  $468\text{ nm}$ . The absorption spectrum of the polymer (Fig. 4) in dilute chloroform solution showed

**Table 1** Molecular weight, UV–vis absorption maximum, emission maximum and fluorescence quantum yield of the polymer **P**

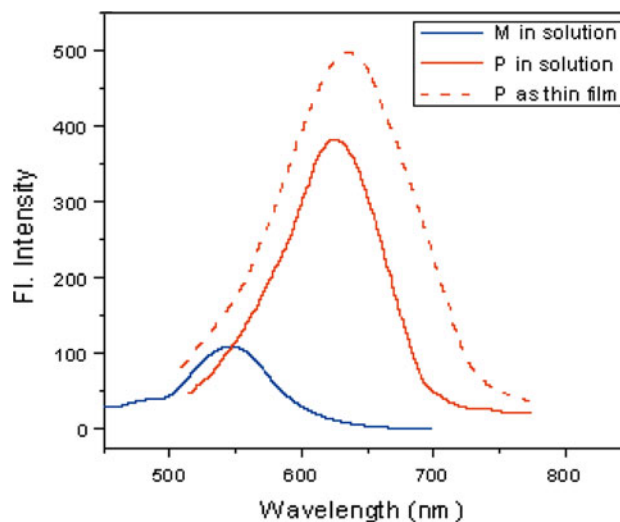
Polymer	$M_n^a$	$M_w^b$	PD <sup>c</sup>	Absorption, $\lambda_{max}$ (nm)		Emission, $\lambda_{max}$ (nm)		Optical band gap $E_g$ (eV)	Quantum yield <sup>d</sup> (%)
				Solution	Film	Solution	Film		
P	3,032	4,920	1.62	572	600	630	647	1.70	43

<sup>a</sup> Number average molecular weight, <sup>b</sup> weight average molecular weight, <sup>c</sup> polydispersity, <sup>d</sup> quantum yield relative to quinine sulfate ( $10^{-5}$  M quinine sulfate in 0.1 M  $H_2SO_4$ )

**Fig. 3** TGA trace of the polymer **P****Fig. 4** UV–visible absorption spectra of the monomer **M** in solution and the polymer **P** both in solution and thin film form

$\lambda_{max}$  at 572 nm. A red shift of 28 nm was observed in the absorption spectra of the polymer in thin film state (Fig. 4) with respect to that obtained from its solution indicating the presence of inter-chain interactions in the solid state. Band-gap of the polymer was calculated by taking absorption edge of the spectrum and is found to be 1.7 eV.

As shown in Fig. 5, the emissive maximum (excitation wavelength 470 nm) of the monomer in dilute solution is

**Fig. 5** Fluorescence emission spectra of the monomer **M** in solution and the polymer **P** both in solution and thin film form

548 nm. This clearly indicates that the monomer **M** emits intense green-light under the irradiation of light. The fluorescence emission spectrum of the polymer in solution state (Fig. 5) shows maximum at 630 nm (excitation wavelength 570 nm). However, in the emission spectrum of the polymer thin film (Fig. 5) 17 nm bathochromic shift was observed with respect to that obtained from its solution. The polymer **P** emits intense red-fluorescence both in solution and solid state. The Stokes shift is found to be 47 nm. A large shift in the absorption and emission maxima for the polymer **P** when compared to its monomer also confirms the presence of extended conjugation in the polymer. The fluorescence quantum yield of the polymer in solution was determined using quinine sulfate as a standard and it is found to be 43%. These results clearly indicated that the newly synthesized polymer is a potential candidate for its applications in polymer LEDs. Further, organic narrow band-gap polymers are particularly desirable for photovoltaics due to their spectral absorption which matches the solar terrestrial radiation [16]. Hence, it is predicted that the polymer **P** would act as a good material for photovoltaic device applications. The device fabrication and their characterization are in progress.

In recent years, it has been shown that conjugated polymers are promising class of third-order nonlinear



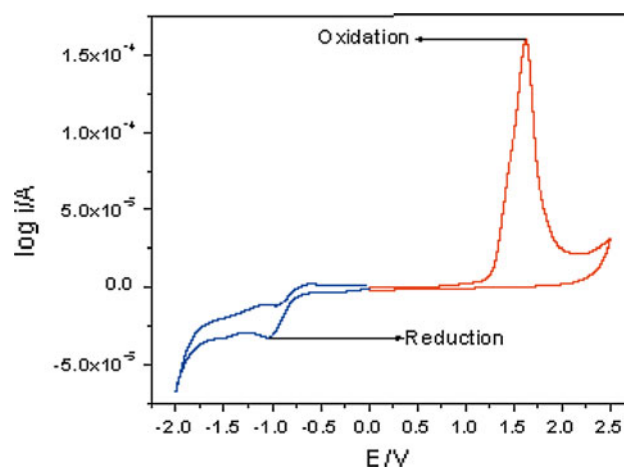
optical (NLO) materials because of their potentially large third-order susceptibilities associated with fast response time. Further, their processibility and thermal stability are added features for their selection. Conjugated systems consisting of electron donor and electron acceptor units were shown to possess enhanced third-order optical non-linearity [22]. Hence we expect that polymer **P** with conjugated donor–acceptor arrangement would show good third-order NLO properties. Preliminary studies on this polymer using Nd:YAG as laser source by Z-scan and degenerate four wave mixing (DFWM) techniques showed promising results. The detailed study of NLO properties of the polymer **P** will be discussed elsewhere.

### 3.4 Electrochemical properties

Cyclic voltammetry (CV) was employed to determine redox potentials and then to estimate the HOMO and LUMO energy of the polymer, which are of crucial importance to the selection of cathode and anode materials for PLED devices. The cyclic voltammogram of the polymer coated on a glassy carbon electrode was measured on AUTOLAB PGSTAT 30 electrochemical analyzer, using a Pt counter electrode and a Ag/AgCl reference electrode, immersed in the electrolyte [0.1 M (*n*-Bu)<sub>4</sub>N-ClO<sub>4</sub> in acetonitrile] at a scan rate of 25 mV/S. Electrochemical data of polymer **P** are summarized in Table 2.

When the polymer was swept cathodically, it showed reduction peak at  $-1.00$  V (Fig. 6) with onset reduction potential at  $-0.60$  V. This reduction potential is lower than that of 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) [23, 24], one of the most widely used electron transporting material, and is comparable with those of some good electron transporting materials. While sweeping anodically, (Fig. 6) polymer showed an oxidation peak at  $1.64$  V with onset oxidation potential at  $1.20$  V. The onset potentials of oxidation and reduction processes are used to estimate the HOMO and LUMO energy levels of the polymer.

According to the equations reported in the articles [25–27], i.e.,  $E_{\text{HOMO}} = -[E_{\text{onset}}^{\text{oxd}} + 4.4\text{eV}]$  and  $E_{\text{LUMO}} = -[E_{\text{onset}}^{\text{red}} - 4.4\text{eV}]$ , where  $E_{\text{onset}}^{\text{oxd}}$  and  $E_{\text{onset}}^{\text{red}}$  are the onset potentials versus SCE for the oxidation and reduction processes of a polymer, respectively. The HOMO and LUMO energy levels of the polymer **P** were estimated to be  $-5.53$  and  $-3.73$  eV, respectively. These values are



**Fig. 6** Oxidation reduction cyclic voltammetric traces of the polymer **P**

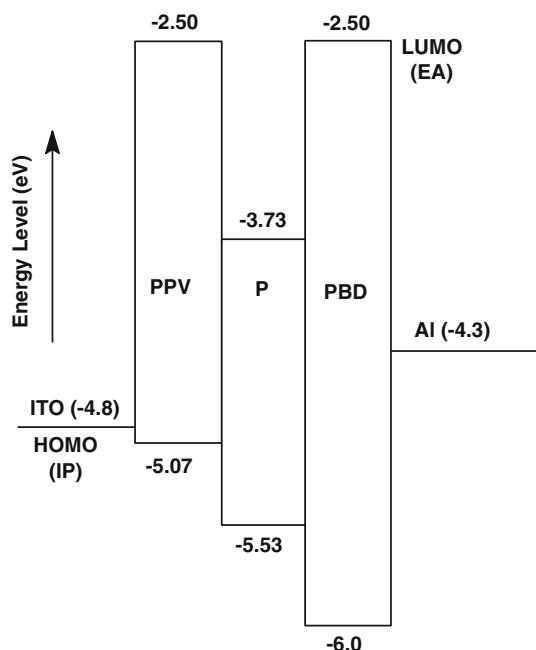
comparable with some reported similar type of cyano polymers [15, 16]. The low lying LUMO energy level clearly indicates that the polymer has better electron injection ability. The high electron affinity of the polymer is attributed to the presence of electron deficient  $-\text{CN}$  groups along the polymer backbone. The band-gap of the polymer is estimated to be  $1.8$  eV which is quite close to that obtained by optical method.

The energy barriers between the emitting polymer and electrodes can be estimated by comparing the work functions of the electrodes with the HOMO and LUMO energy levels of emitting polymers. Thus the hole-injection barrier is  $\Delta E_{\text{h}} = E_{\text{HOMO}} - 4.8$  eV, where  $4.8$  eV is the work function of the ITO anode and the electron-injection barrier is  $\Delta E_{\text{e}} = 4.3 - E_{\text{LUMO}}$  eV, where  $4.3$  eV is the work function of aluminium cathode. The difference between the electron and hole-injection barriers ( $\Delta E_{\text{e}} - \Delta E_{\text{h}}$ ) is a useful parameter for evaluating the balance in electron and hole injection. Lower ( $\Delta E_{\text{e}} - \Delta E_{\text{h}}$ ) values indicate improved injection balance of electrons and holes from the cathode and anode, respectively. The band structure of the polymer is depicted in Fig. 7 and the barrier energies are listed in Table 2. As shown in Table 2, the  $\Delta E_{\text{e}}$  value of this polymer is lower than PPV ( $1.8$  eV) and some other *p*-type polymers indicating that the cyano group in the polymer backbone tend to decrease barrier for electron-injection and thus enhances the electron transporting properties of the corresponding polymer. The  $\Delta E_{\text{h}}$  values of the polymer is higher than PPV ( $0.3$  eV) [28] due to the introduction of

**Table 2** Electrochemical potentials and energy levels of the polymer

Polymer	$E_{\text{oxd}}$ (onset)	$E_{\text{red}}$ (onset)	$E_{\text{oxd}}$	$E_{\text{red}}$	HOMO (eV)	LUMO (eV)	$E_{\text{g}}^{\text{a}}$ (eV)	$\Delta E_{\text{h}}^{\text{b}}$ (eV)	$\Delta E_{\text{e}}^{\text{c}}$ (eV)	$\Delta E_{\text{e}} - \Delta E_{\text{h}}$ (eV)
P	1.20	-0.60	1.64	-1.00	-5.53	-3.73	1.80	0.73	0.57	-0.16

<sup>a</sup> Electrochemical band gap, <sup>b</sup>Energy barrier between HOMO and work function of ITO anode, <sup>c</sup>Energy barrier between LUMO and work function of Al cathode



**Fig. 7** Band diagram of **P** as determined from the electrochemical data. The band structures of **PPV** and **PBD** also given for comparison

the cyano groups along the polymer backbone. Further, the value is lower than those of PBD [29] and tris (8-hydroxyquinoline) aluminium ( $\text{Alq}_3$ ) [30], which are widely used as electron transport hole blocking materials. The barrier energy difference ( $\Delta E_c - \Delta E_h$ ) for the polymer **P** is  $-0.16$  eV. This value is lower than those of some reported cyanovinylene polymers [16]. The low value of  $\Delta E_c - \Delta E_h$  clearly indicates that the new polymer has good charge carrying property which is one of the requirements for the development of efficient PLEDs. Preliminary studies on light emitting device preparation and their characterization are on progress.

#### 4 Conclusions

A novel narrow band gap cyanovinylene polymer carrying 3,3'-(3,4-ditetradecyloxythiène-2,5-diyl)bis[2-(thiophen-2-yl)prop-2-enenitrile] unit has been successfully synthesized via multistep reactions and newly synthesized compounds have been characterized. The new polymer is found to be thermally stable up to  $300^\circ\text{C}$ . The optical properties revealed that the polymer emits intense red fluorescence under the irradiation of light with fairly good quantum yield of 43%. The optical band gap is observed to be 1.7 eV. The electrochemical properties showed that the polymer **P** possesses high-lying HOMO energy level ( $-5.53$  eV) and low lying LUMO level ( $-3.73$  eV). The energy barrier between the emitting polymer (**P**) and electrodes is estimated to be  $-0.16$  eV. From the results of

electrochemical studies it can be concluded that the new polymer possesses good charge carrying property. The light emitting and charge carrying properties revealed that the polymer **P** is a promising material for the development of efficient photonic/optoelectronic devices.

**Acknowledgments** The authors are grateful to the CDRI, Lucknow, NMR research centre, IISc Bangalore, and RRL, Trivandrum, for providing instrumental analyses.

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