

## Polymer Communication

# Synthesis, electrochemical and optical studies of new cyanopyridine based conjugated polymers as potential fluorescent materials

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## ABSTRACT

In this communication we describe the design and synthesis of four new conjugated polymers (**P1–P4**) carrying cyanopyridine in their backbone via Wittig condensation technique. Their structures were well established by FTIR, <sup>1</sup>H NMR, elemental analysis and gel permeation chromatographic techniques. They exhibited good thermal stability with the onset decomposition temperature around 300–350 °C in nitrogen atmosphere. Further, their electrochemical, linear and third-order non-linear optical properties have been investigated. The polymers showed low electrochemical band gaps in the range of 1.77–1.99 eV and displayed very good fluorescence emission property in various polar solvents. The fluorescence quantum yields of polymers **P1–P4** in tetrahydrofuran (THF) were found to be 35, 42, 38 and 34%, respectively. The effective two-photon absorption coefficients ( $\beta$ ) for the polymers were determined by Z-Scan technique and were found to be  $1.34 \times 10^{-11}$ ,  $1.24 \times 10^{-11}$ ,  $3.04 \times 10^{-11}$  and  $1.85 \times 10^{-11}$  m/W for polymers **P1–P4**, respectively.

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## 1. Introduction

In recent years, a great deal of interest has been focused on the synthesis of novel  $\pi$ -conjugated polymers, because of their intriguing properties such as electrical conductivity [1], electroluminescence [2], third-order non-linear optical properties [3] and chemical sensing [4]. These polymers easily form relatively stable radical cations (holes) and also possess high-charge carrier mobilities. As a result, they achieve high thermal as well as photochemical stability.

Pyridine, being an interesting thermally stable n-type of heterocyclic system, has attracted much attention of many researchers, particularly for designing new conjugated polymers [5–8]. In addition, pyridine ring is a highly electron-withdrawing moiety, which displays good electron-transporting abilities and optical properties when it is introduced into the polymer main chain. In fact, the optical properties of such polymers can be tailored, via protonation, because of the localized, lone pair of  $sp^2$  orbital electrons of the nitrogen atom in the pyridine ring [7,8]. Keeping this in view, Koleva's group established a relationship between molecular structure and optical properties of pyridinium compounds [9,10]. Additionally, presence of the nitrile (CN) substituent on the pyridine ring can further promote its electron-transporting nature and hence incorporation of

cyanopyridine ring into polymer chain would lead to enhancement of charge carrying properties of the resulting polymer [11]. Because of fluorescent nature of cyanopyridine, its presence in polymer chain would increase the optical properties. Also, the literature study reveals that conjugated polymers carrying cyanopyridine possess very good optical limiting property [12]. Similarly carbazole is an attractive heterocyclic tricyclic system that has been extensively used in the synthesis of many polymers because of the fact that it has good photo-conducting and high electron donating properties. It has been reported that carbazole based polymers possess good thermal stability and interesting electro-optical, and photochemical properties [13]. Further, introduction of 3,6-disubstituted carbazole induces a bent conformation for the resulting macromolecular chain, which in turn enhances thermal stability, solubility, extended glassy nature and moderately high oxidation potential of polymers [14].

It has been well established that many conjugated polymeric systems carrying five membered aromatic heterocyclic rings exhibit an increased hyperpolarizability when compared to those carrying benzenoid systems [15,16]. This is because the delocalization energy of heteroaromatics is lower than that of benzenoid systems. Aromatic heterocycles such as thiophene [17], thiazole, benzothiazole [18] and benzoxazole [19] or their derivatives containing chromophores are among the most studied systems. Further, oligothiophenes have been shown to possess better electron relay properties and hence they are very good non-linear materials. Besides the electron transmission efficiency,

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oligothiophenes possess inherent stability [20]. An extensive literature survey reveals that 3,4-dialkoxythiophene based conjugated polymers show facile dopability and low band gap ascribe to the electron donating nature of the alkoxy moiety [21].

Phenothiazine is another interesting tricyclic heterocycle which contains nitrogen and sulphur as hetero atoms in its structure. It possesses stronger electron donating property than that of carbazole [22]. Therefore, its incorporation to polymer chain enhances hole-transportation properties. Since the size of sulphur atom is larger than that of nitrogen, there is enhancement in  $\pi$ -electron overlap along the polymer main chain. Also, phenothiazine chromophore is much more effective in lowering the ionization potential and band gap when compared to other hole-transporting chromophores such as carbazole, diphenyl amine and triphenyl amine.

In recent times optical limiting (OL) materials have been under intensive investigations because of their potential applications in protection of optical sensors and human eyes from high intensity laser beams. An ideal optical limiter should be transparent in low energy laser pulse and it must absorb high energy laser pulse. In the literature, many smart materials like fullerene (C60) [23], carbon nanotubes [26], organometallics [27] and metallophthalocyanine complexes [24] were shown to possess very good optical limiting properties. However, these materials show poor solubility and hence have difficulties in fabricating the devices. Interestingly, polymers containing fused heterocyclic nuclei were found to be equally efficient optical limiting materials [25]. As polymers possess good processability and stability, they are potential candidates for future non-linear optical materials. Hence, there is a need for design and development of new polymers for such applications.

Against this background, we have designed four new Donor–Acceptor (D–A) type conjugated polymers (**P1–P4**) carrying strongly electron accepting cyanopyridine as a core moiety and fairly good electron donating moieties, viz. phenyl, carbazole, dialkoxythiophene and phenothiazine rings. In the new design, cyanopyridine ring would act as very good electron-transporting medium because of the presence of nitrile group attached to the electron deficient pyridine ring. Also, vinylene linkages have been incorporated between donors and acceptors in order to enhance the conjugation path length, which may lead to increase in optical limiting behaviour. The newly designed four new cyanopyridine based conjugated polymers **P1–P4** carrying respectively phenyl, carbazole, dialkoxythiophene and phenothiazine moieties has been synthesized from their monomers in good yield through Wittig condensation technique. The structures of these polymers have been established by spectral techniques. Further their electrochemical, linear and third-order non-linear optical properties have been evaluated in order to investigate the influence of their structure on the various optical and optoelectronic properties.

## 2. Experimental section

### 2.1. Materials and methods

3,4-Dialkoxythiophene-2,5-dicarboxylate **5** was synthesized according to the reported procedure [21]. All the chemicals used in present work procured from Sigma Aldrich and Lanchaster (UK). All the solvents are of analytical grade. They were purchased and used as such without any further purification.

### 2.2. Instrumentation

Infrared spectra of all intermediate compounds and polymer were recorded on a Nicolet Avatar 5700 FTIR (Thermo Electron Corporation). The UV–visible and fluorescence spectra were taken in GBC Cintra 101 and Perkin Elmer LS55 fluorescence spectrophotometers respectively.  $^1\text{H}$  NMR spectra were obtained with Bruker–400 MHz FT-NMR spectrometer using TMS/solvent signal as internal reference. Elemental analyses were performed on a Flash EA1112 CHNS analyzer (Thermo Electron Corporation). Mass spectra were recorded on a Jeol SX-102 (FAB) Mass Spectrometer. The electrochemical studies were carried out using AUTOLAB PGSTAT-30 electrochemical analyzer. Molecular weights were determined with WATER's make Gel Permeation Chromatograph (GPC) against polystyrene standards with THF as an eluent.

### 2.3. Synthesis of intermediates, monomers and polymers

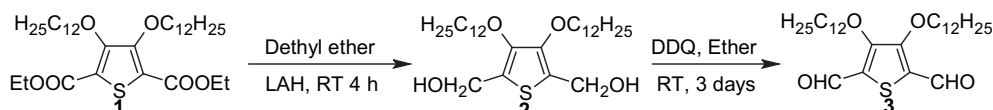
All the required monomers and polymers **P1–P3** were synthesized according to the standard procedures. Monomers **10** and **13** were prepared as per the reported procedures [28]. Synthetic methods and characterization data of monomers **10** and **13** were included in the Supporting Information.

#### 2.3.1. Synthesis of (3,4-didodecyloxythiophene-2,5-diyl)dimethanol **2**

To a clear solution of 0.5 g (0.008 mol) of diethyl 3,4-didodecyloxythiophene-2,5-dicarboxylate (**5**) 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 4 h at room temperature. The completion of the reaction was monitored by TLC. The reaction mixture was then poured into cold dilute sulphuric acid solution to remove 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: 0.35g (81%). M.p: 46–48 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 4.68 (s, 2H, –OH), 4.01 (t, 4H, –OCH<sub>2</sub>–), 1.74–1.27 (m, 40H, –(CH<sub>2</sub>)<sub>10</sub>–), 0.89 (t, 6H, –CH<sub>3</sub>). FABHRMS:  $m/z$ , 513 (Calculated: 512.82) IR (ATR,  $\text{cm}^{-1}$ ): 3345(–OH), 2917(Ar–H), 2851(Aliphatic –C–H). Element. Anal. Calcd. For  $\text{C}_{30}\text{H}_{56}\text{O}_4\text{S}$ : C, 70.26; H, 11.01; S, 6.25. Found: C, 77.08; H, 10.88; S, 6.37.

#### 2.3.2. Synthesis of 3,4-didoecyloxythiophene-2,5-dicarbaldehyde **3**

A mixture of 0.5 g (0.001 mol) of 3,4-didodecyloxythiophene-2,5-diyl)dimethanol (**6**), 0.88 g (0.004 mol) of dicyanodichloroquinine (DDQ) and 15 mL of dry diethyl ether was stirred for 72 h 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 (**7**) and was recrystallized from ethanol. Yield: 0.41g (80%). M.p: 36–37 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 10.12 (s, 2H, –CHO), 4.27 (t, 4H, –OCH<sub>2</sub>–), 1.84–1.31 (m, 40H, –(CH<sub>2</sub>)<sub>10</sub>–), 0.89 (t, 6H, –CH<sub>3</sub>). FABHRMS:  $m/z$ , 509 (Calculated: 508.79). IR (ATR,  $\text{cm}^{-1}$ ): 1690(>C=O). Element. Anal. Calcd. For  $\text{C}_{30}\text{H}_{52}\text{O}_4\text{S}$ : C, 70.82; H, 10.30; S, 6.30. Found: C, 70.99; H, 10.52; S, 6.17 (Scheme 1).



Scheme 1. Synthetic scheme for monomer **3**.

### 2.3.3. Synthesis of 1,3-bis(4-methylphenyl)prop-2-en-1-one **4**

A mixture of tolaldehyde (5 g, 41.6 mmol) and 4-methyl acetophenone (5.5 g, 41.6 mmol) were dissolved in 50 ml of ethanol and stirred in presence of potassium hydroxide solution (2.3 g in 5 ml water) at room temperature. After 4 h, obtained solid was filtered, and it was recrystallized from chloroform methanol system to get yellow needle shaped solid. Yield 8.9g (90%). IR (ATR,  $\text{cm}^{-1}$ ): 1644, 1591, 1169, 987, 805, 726, Element. Anal. Calcd. For  $\text{C}_{17}\text{H}_{16}\text{O}$ : C, 86.40; H, 6.82; Found C 86.41; H, 6.84.

### 2.3.4. Synthesis of 2-methoxy-4,6-bis(4-methylphenyl)pyridine-3-carbonitrile **5**

Compound **1** (5 g, 21.1 mmol) was added slowly to a freshly prepared sodium alkoxide solution (223.3 mmol of sodium in 100 mL of methanol) during stirring. Malononitrile (1.39 g, 21.1 mmol mol) was then added with continuous stirring at room temperature until the precipitate separates out. The solid separated was collected by filtration and recrystallized from hot ethanol and chloroform. Yield: 4.5 g (67%). M.p.: 142–144 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 8.00 (m, 2H, Ar–H), 7.55(m, 2H, Ar–H), 7.44 (s, 1H, Ar–H (pyridine)), m 7.34–7.28(m, 4H, Ar–H), 4.19 (s, 3H, –O–CH<sub>3</sub>), 2.43 (s, 6H, Ar–CH<sub>3</sub>), IR (ATR,  $\text{cm}^{-1}$ ): 2907, 2217, 1658, 1554, 1366, 1139, 818. Element. Anal. Calcd. For  $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}$ : C, 80.23; H, 5.77; N, 8.91; Found: C, 80.25; H, 5.75; N, 8.93.

### 2.3.5. Synthesis of 4,6-bis[4-(bromomethyl)phenyl]-2-methoxypyridine-3-carbonitrile **6**

A mixture of compound **2** (3g, 9.5 mmol), N-bromosuccinimide (1.38 g, 19.1 mmol), 5 mg of benzoyl peroxide in 30 mL of carbon tetrachloride was refluxed for 8 h. After the solvent was removed, 20 mL of water was added with stirring for 1 h. The resulting crude product was recrystallized from ethyl acetate/chloroform mixture to get pure white coloured solid. Yield: 3.5 g (77%). M.p.: 202–205 °C  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 8.00 (m, 2H, Ar–H), 7.99–7.55(m, 4H, Ar–H), 7.5–7.3(m, 2H, Ar–H), 7.29 (s, 1H, Ar–H (pyridine)), 4.81 (s, 6H, Ar–CH<sub>2</sub>–Br), 4.13 (3H, –O–CH<sub>3</sub>), IR (ATR,  $\text{cm}^{-1}$ ): 2993, 2219, 1580, 1546, 1359, 1139, 1007, 821,600. Element. Anal. Calcd. For  $\text{C}_{21}\text{H}_{16}\text{Br}_2\text{N}_2\text{O}$ : C, 53.42; H, 3.42; N, 5.93. Found: C, 53.46; H, 3.45; N, 5.94.

### 2.3.6. Synthesis of [4,6-bis[44-triphenyl phosphonium methyl)phenyl]-2-methoxy, 3-cyanopyridine]dibromide **7**

A solution of dibromide compound **3** (1g, 6.3 mmol) and triphenyl phosphine (3.34 g, 12.7 mmol) in 5 mL of DMF was refluxed with stirring for 8 h. The reaction mixture was cooled to room temperature and poured into 50 mL of ethyl acetate. The resulting mixture was sonicated for about 30 min to get precipitate. The obtained white coloured amorphous solid was filtered off, washed with excess of ethyl acetate and dried at 40 °C for 10 h. Yield: 82%. M.p.: above 300 °C  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 8.14–8.12 (m, 2H, Ar–H), 7.99–7.50(m, 33H, Ar–H), 7.16–7.12(m, 4H, Ar–H), 5.26 (s, 4H, Ar–CH<sub>2</sub>), 4.13 (s, 3H, –O–CH<sub>3</sub>), IR (ATR,  $\text{cm}^{-1}$ ): 3365, 3051, 2853, 2211, 1658, 1430, 1103, 728, 682, 495. Element. Anal. Calcd. For  $\text{C}_{57}\text{H}_{46}\text{Br}_2\text{N}_2\text{O}_2$ : C, 68.68; H, 4.65; N, 2.81. Found: C, 68.66; H, 4.68; N, 2.84.

### 2.3.7. General procedure for synthesis of polymers **P1–P4**

Compound **4** (0.5 g, 0.5 mmol) and compound **14** (0.067 g, 0.5 mmol) were dissolved in a mixture of 5 mL of chloroform and 15 mL of ethanol. Sodium ethoxide (0.020 g, 1 mmol in 10 mL of ethanol) was added to the reaction mass at room temperature under nitrogen atmosphere. Then, reaction mixture turned into yellow colour. It was stirred for 12 h at room temperature. After the completion of the reaction, solvent was removed off under reduced pressure. Then the crude reaction mass was poured into excess of

methanol and stirred for about 30 min. The obtained polymer was filtered and then washed thoroughly with acetone, re-dissolved in chloroform and poured into excess of methanol to remove oligomers. The resulting precipitate was filtered off and dried at 40 °C under vacuum for 24 h to give fluorescent deep greenish yellow coloured powder. On the similar lines, polymers **P2–P4** were prepared (Scheme 2). The characterization data of **P1–P4** are given below.

**P1:**  $^1\text{H}$  NMR, (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 7.90–7.18(m, 13H, Ar–H), 6.78–6.74 (m, 2H, –CH=CH–), 4.21 (s, 3H, –O–CH<sub>3</sub>). IR (ATR,  $\text{cm}^{-1}$ ): 2220, 1573, 1540, 1445, 1356, 1009, 832. Element. Anal. Calcd. For  $\text{C}_{30}\text{H}_{24}\text{N}_2\text{O}$ : C, 4.08; H, 5.65; N, 6.54. Found: C, 83.89; H, 5.54; N, 6.36. Weight average molecular weight ( $M_w$ ): 12900.

**P2:**  $^1\text{H}$  NMR, (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 8.32–6.91(m, 15H, Ar–H), 6.65–6.00 (m, 2H, –CH=CH–), 4.28–4.15(m, 5H, –O–CH<sub>3</sub> and –NCH<sub>2</sub>–), 2.41–1.25 (m, 24H, aliphatic), 0.85 (t, 3H, –CH<sub>3</sub>), IR (ATR,  $\text{cm}^{-1}$ ): 2919, 2853, 2215, 1576, 1540, 1478, 1448, 1353, 1135, 1010, 807. Element. Anal. Calcd. For  $\text{C}_{50}\text{H}_{57}\text{N}_3\text{O}$ : C, 83.87; H, 8.02; N, 5.87. Found: C, 83.59; H, 7.85, N, 5.64. Weight average molecular weight ( $M_w$ ): 6400.

**P3:**  $^1\text{H}$  NMR, (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 8.13–6.56(m, 9H, Ar–H), 6.8–6.68 (m, 2H, –CH=CH–), 4.68–4.32(m, 7H, –O–CH<sub>3</sub> and –OCH<sub>2</sub>–), 1.78–1.26 (m, 48H, aliphatic), 0.85 (t, 6H, –CH<sub>3</sub>)IR (ATR,  $\text{cm}^{-1}$ ): 2918, 2849, 2218, 1579, 1539, 1452, 1359, 1260, 1014, 850, 811. Element. Anal. Calcd. For  $\text{C}_{56}\text{H}_{78}\text{N}_2\text{O}_3\text{S}$ : C, 78.27; H, 9.15; N, 3.26; S, 3.73. Found: C, 78.08; H, 8.98; N, 3.12; S, 3.58. Weight average molecular weight ( $M_w$ ): 9500.

**P4:**  $^1\text{H}$  NMR, (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 8.08–6.70(m, 15H, Ar–H), 6.55–6.53 (m, 2H, –CH=CH–), 4.25–4.10(m, 5H, –O–CH<sub>3</sub> and –NCH<sub>2</sub>–), 2.44–1.24 (m, 24H, aliphatic), 0.875 (t, 3H, –CH<sub>3</sub>), IR (ATR,  $\text{cm}^{-1}$ ):2917, 2848, 2217, 1574, 1540, 1506, 1462, 1403, 1355, 1244, 1010, 812. Element. Anal. Calcd. For  $\text{C}_{50}\text{H}_{57}\text{N}_3\text{OS}$ : C, 80.28; H, 7.68; N, 5.62; S, 4.29. Found: C, 80.12; H, 7.59; N, 5.55; S, 4.18. Weight average molecular weight ( $M_w$ ): 18700.

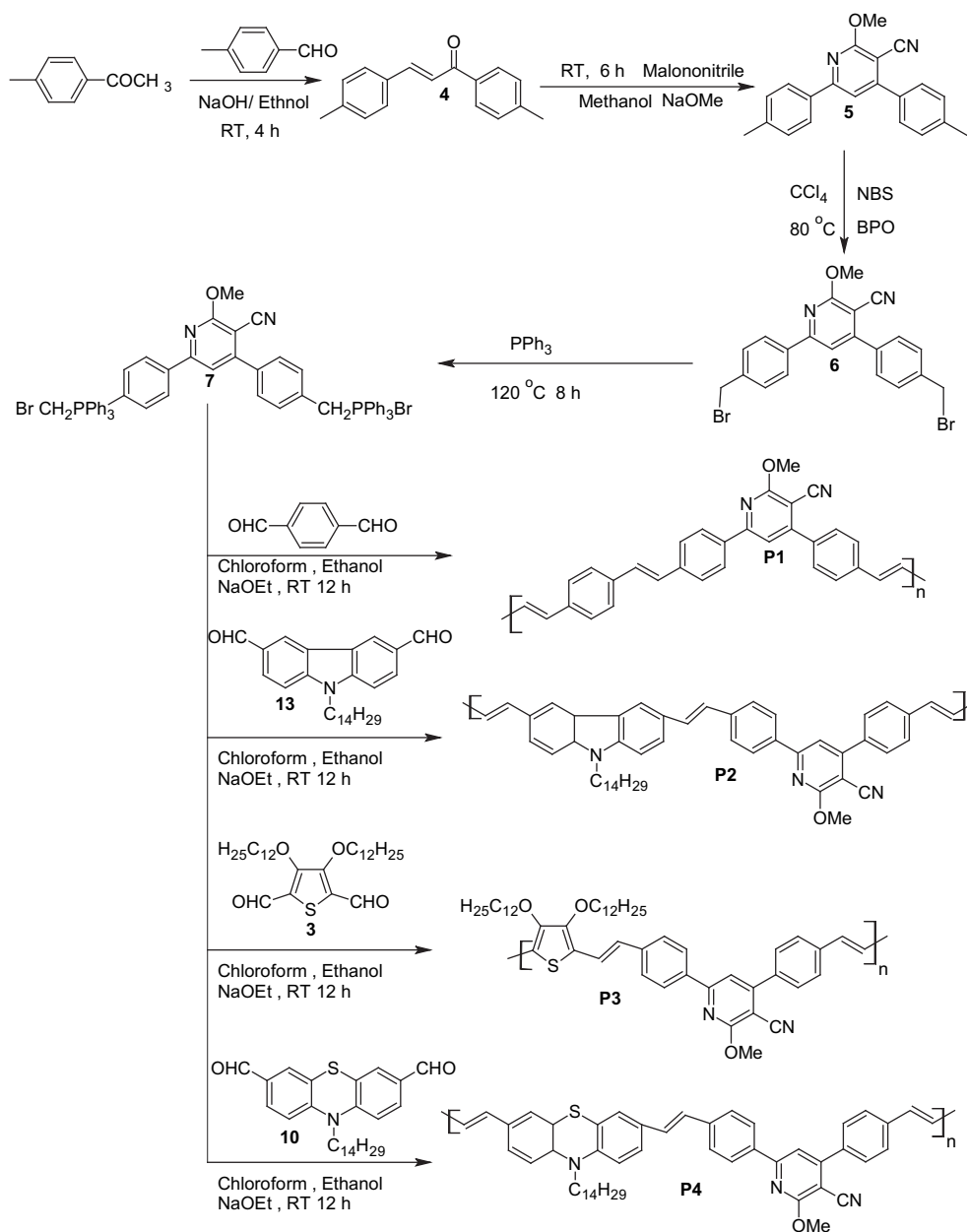
## 3. Results and discussion

### 3.1. Synthetic design

In the present article four new conjugated polymers **P1–P4** based on cyanopyridine were synthesized through Wittig condensation method. The required chalcone **4** was prepared from tolaldehyde and 4-methyl acetophenone using Claisen–Schmidt reaction. It was then cyclized to cyanopyridine **5** by reacting it with malononitrile in presence of sodium methoxide. Further, two methyl groups of **5** were brominated **6** by Wholzigler method using NBS and BPO. The resulting dibromo derivative was conveniently converted to phosphonium Wittig salt **7**, which on treatment with different dialdehydes in ethanol-chloroform medium yielded final polymers **P1, P2, P3** and **P4**.

### 3.2. Characterization

Structures of the intermediates as well as target polymers were established by elemental analysis and spectroscopic techniques. The spectral characteristics of chalcone **4** matched with the reported data. Cyclisation of chalcone to cyanopyridine **5** was confirmed by its  $^1\text{H}$  NMR spectrum wherein it showed a signal at  $\delta$  4.19 which corresponds to –OCH<sub>3</sub> protons of the pyridine ring. In its IR spectrum, it displayed a sharp peak at 2217  $\text{cm}^{-1}$  indicating the presence of cyano group. Formation of compound **6** was



**Scheme 2.** Synthetic scheme for monomer and polymers **P1–P4**.

confirmed by its  $^1\text{H}$  NMR spectrum, where it showed a signal at  $\delta$  4.81 that corresponds to methylene protons, which is deshielded to a greater extent when compared to compound **5**. Further, the structure of monomer **7** was evidenced by its  $^1\text{H}$  NMR data. In its spectrum, methyl protons of phosphonium salt resonated at  $\delta$  5.26, being largely deshielded when compared to that of compound **6**. The  $^1\text{H}$  NMR spectrum of compound **2** showed a peak at  $\delta$  4.68 and its IR spectrum displayed a broad peak at  $3345\text{ cm}^{-1}$  confirming the presence of OH group. Structure of compound **3** was confirmed by its  $^1\text{H}$  NMR spectrum wherein it showed a peak at  $\delta$  10.12 due to an aldehydic proton; its IR spectrum displayed a sharp peak at  $1690\text{ cm}^{-1}$  showing the presence of CHO group. The spectral data of compounds **10** and **13** are in good agreement with those of reported values [28]. Structures of the polymers were confirmed by IR and  $^1\text{H}$  NMR spectroscopy. IR spectroscopy of all the polymers showed a peak around  $2220\text{ cm}^{-1}$ , which indicates

the presence of cyano group in the polymer. Also except polymer **P1** all the polymer showed two intense band around  $2919\text{ cm}^{-1}$ ,  $2853\text{ cm}^{-1}$  which corresponds to the long alkyl/alkoxy side chain.  $^1\text{H}$  NMR spectrum of **P1** showed multiplet at  $\delta$  4.2 which corresponds to  $-\text{O}-\text{CH}_3$  on the cyanopyridine ring. **P2**, **P3** and **P4** showed a multiplet around  $\delta$  4.2 corresponds to  $-\text{OCH}_2-$  and  $-\text{NCH}_2-$  protons in the polymers.

The synthesized polymers were soluble in common solvents such as chloroform, dichloromethane, and dimethylsulfoxide. Thermogravimetric analysis (TGA) reveals good thermal stability of the polymers up to  $300\text{ }^\circ\text{C}$  (See Supporting Information). The degradation temperatures of the polymers were found to be  $340$ ,  $320$ ,  $325$  and  $330\text{ }^\circ\text{C}$  for polymers **P1**, **P2**, **P3** and **P4**, respectively. The gradual weight loss beyond  $300\text{ }^\circ\text{C}$  may be attributed to the degradation of the attached alkoxy chains on the thiophene rings. Similar behaviour was observed for substituted polythiophenes in



earlier reports. The weight loss that took place in the temperature range of ca. 300–900 °C corresponds to the degradation of polymer backbone leaving behind a residue content of less than 25%. Further, at higher temperature of TGA scan, there may be occurrence of cross-linking in polymer across longer side chain or degradation of side chains [29–31]. Among these polymers, **P1** showed the highest onset decomposition temperature. This is because of the fact that the polymer strand does not contain any alkyl/alkoxy side chain. The molecular weights of the polymers were estimated by gel permeation chromatography using polystyrene standard. Weight average molecular weight ( $M_w$ ) of these polymers were found to be 12900, 6400, 9500, 18700 with polydispersity (PD) 2.01, 1.56, 1.98, 2.03, for polymers **P1**, **P2**, **P3** and **P4**, respectively.

### 3.3. Linear optical properties

The solution-phase UV–vis absorption and fluorescence emission spectra of newly synthesized polymers were recorded at room temperature in dilute solutions with different polar solvents (Figs. 1–5). All spectral data of measurements are summarized in Table 1. Polymers showed almost identical electronic properties in solution. From the absorption spectra it was observed that the absorption maxima of polymer **P2** is greater than that of **P1** because of the presence of carbazole unit in the polymer **P2**. It was established that carbazole is a good electron donating moiety which possesses interesting electro-optical and photochemical properties as well as high thermal stability due to its bent structure [13]. Also, polymer **P3** showed the highest absorption maxima in this series because of strong electron donating nature of thiophene units. The electron releasing nature of the thiophene ring is further enhanced by the incorporation of the long alkoxy units which also increases the solubility of the resulting polymer in common organic solvents. Polymer **P4** displayed comparable absorption maxima to that of polymer **P3**, because it contains good electron donating tricyclic phenothiazine ring, which is stronger electron donating moiety than carbazole because it contains two hetero atoms in its tricyclic structure. Because of this **P4** showed 16 nm red shift when compared to that **P2** [22].

Fluorescence studies of the polymers **P1–P4** were carried out in different polar solvents. They displayed very good fluorescence in different solvents when irradiated with UV light, as shown in Fig. 6. The PL (Photoluminescence) spectra were obtained by irradiative

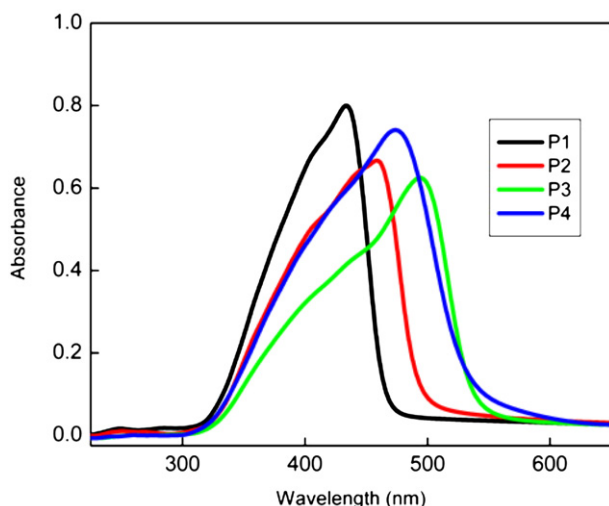


Fig. 1. UV absorption spectra of **P1–P4** in THF solution.

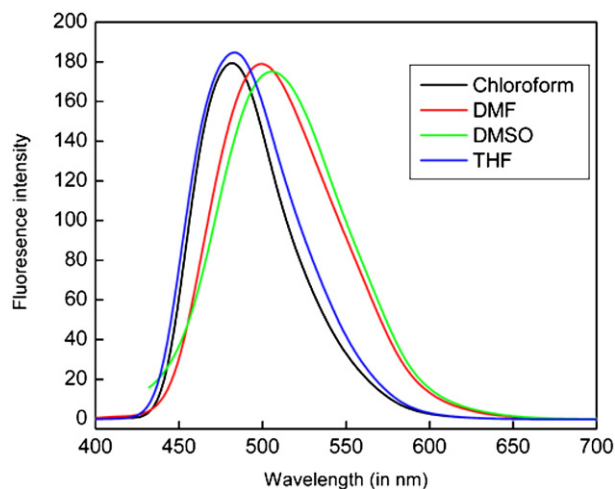


Fig. 2. Fluorescence emission spectra of **P1** in different solvents.

excitation at the wavelength of the absorption maxima. The fluorescence emission spectra of the polymers exhibited a strong solvatochromism effect in different polar solvents [32,33]. From these studies it was observed that the emission maxima of the polymers were red shifted as the polarity of the solvent was increased. In highly polar solvents the emissive S1 state of intra molecular charge transfer (ICT) character is strongly solvated and hence its energy is dramatically lowered. As a result, the energy gap  $\Delta E$  (S1, S2) is enlarged so that the coupling of S1 and S2 states is blocked, whereas the radiation less coupling of S1 state to the ground state stays opened. Consequently, the intersystem crossing from the S1 to T state is enhanced [34,35]. The high electron releasing character of electron donating moieties such as carbazole, thiophene and phenothiazine moieties leads to a red shift (lower energy) of the emission relative to the absorption is caused by energy losses due to dissipation of vibrational energy during the decay. This is influenced by interaction between the fluorophore and the solvent molecules around the excited dipole, hydrogen bonding and formation of charge complexes. In addition, introduction of the pyridinyl moiety in the polymer backbone not only increases the electron affinity of the polymer, which makes the polymer more resistant to oxidation and also gives the polymer better electron-transporting properties, but also avoids fluorescence

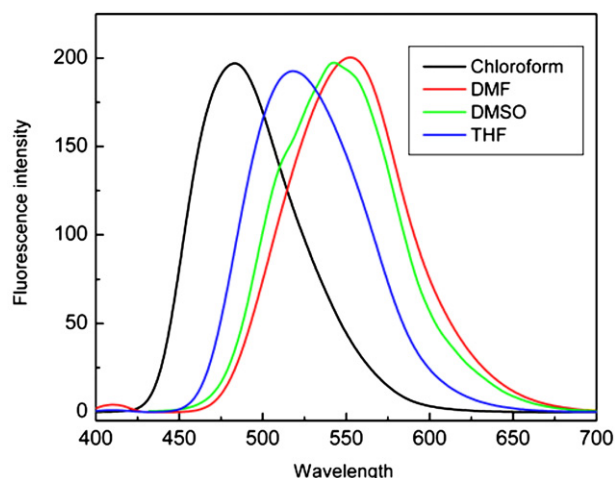


Fig. 3. Fluorescence emission spectra of **P2** in different solvents.

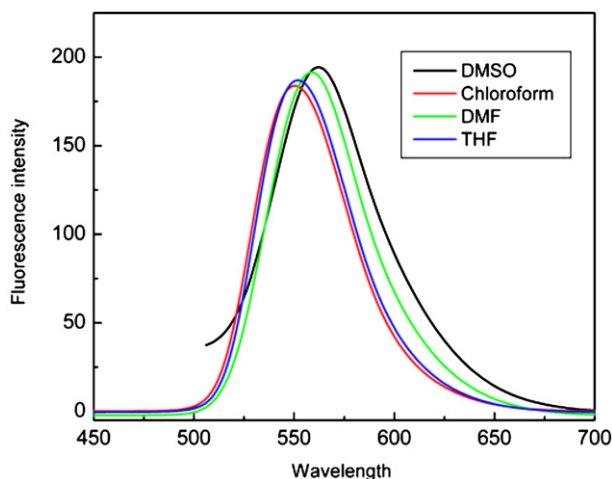


Fig. 4. Fluorescence emission spectra of **P3** in different solvents.

quenching due to the intersystem crossing (ISC) effect of heavy atom [36].

In the present study polymer **P2** showed enhanced solvatochromic behaviour compared to other polymers. The enhanced solvatofluorochromism behaviour is due to the existence of photoinduced intramolecular charge transfer (ICT) phenomenon from the donor (N-alkyl-carbazole) to the acceptor (cyanopyridine) in its structure, which in turn enhances the donor–acceptor nature of the macromolecular system [37,38]. Also, presence of bulky alkyl/alkoxy groups in between cyanopyridine–phenylenevinylene spacers would facilitate to attain trans form which in turn enhances the extent of planarity and rigidity in the resulting polymer chains. Consequently, the polymers possess improved optical properties. The quantum yield for emission in solution was determined according to the method described by Davey et al. [39] relative to quinine sulphate in 0.1 M H<sub>2</sub>SO<sub>4</sub>. Polymers **P1–P4** were found to be strongly emissive with high quantum yields. This could be attributable to the rigid structure of the polymer with the effect that relaxation from the excited state through non-radiative (e.g., thermal) processes will be reduced with consequently higher fluorescence quantum yield [40]. The UV absorption and fluorescence emission spectra of the polymers are given below.

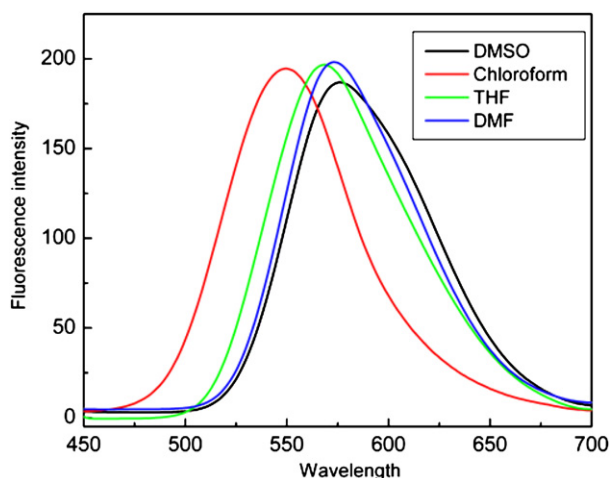


Fig. 5. Fluorescence emission spectra of **P4** in different solvents.

**Table 1**  
Optical characterizations data.

Polymer	UV (nm) in THF	Fluorescence in different solvents (nm)				Quantum yields
		CHCl <sub>3</sub>	THF	DMF	DMSO	
<b>P1</b>	434	481	484	499	505	36%
<b>P2</b>	458	484	517	541	552	42%
<b>P3</b>	494	550	551	558	562	38%
<b>P4</b>	474	549	567	573	575	41%

### 3.4. 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)<sub>4</sub>N<sup>+</sup>(ClO<sub>4</sub>)<sup>-</sup> in acetonitrile] at a scan rate of 25 mV/S [41].

All the measurements were calibrated using ferrocene as standard [42]. As shown in Fig. 7, the newly synthesized polymers were electroactive either in the cathodic region or in the anodic region. From the figures onset oxidation potentials were estimated, which were found to be 1.050, 1.069, 0.98 and 1.022 eV for **P1**, **P2**, **P3** and **P4**, respectively. This *p*-doping potentials are comparable to other oxadiazole-containing light-emitting polymers [43]. For the *n*-doping (reduction) process, the onset potentials for the polymers appeared at −0.905, −0.821, −0.791 and −0.650 eV for **P1**, **P2**, **P3** and **P4**, respectively. These onset reduction values are even lower than that of 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) [44], the most widely used electron-transporting material in PLEDs. In these polymers, reversibility of the *p*-doping process is poorer than that of its *n*-doping. 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 polymers. The equations,  $E_{\text{HOMO}} = -[E_{\text{onset}}^{\text{oxd}} + 4.4\text{eV}]$  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 standard calomel electrode (SCE) for the oxidation and reduction of the material referred, were used for the calculation. Electrochemical potentials and energy levels of the polymer are tabulated in Table 2. The HOMO energy levels of the polymers were estimated to be −5.450, −5.469, −5.385, and −5.422 eV; the LUMO energy levels were found to be −3.495, −3.579, −3.609 and −3.750 eV for **P1**, **P2**, **P3** and **P4**, respectively. The HOMO energy levels of **P3** and **P4** are almost same as that of poly (cyanoterphthalylidene) (CN-PPV), indicating that the polymers have similar hole-injection ability to CN-PPV when they are used in PLEDs. However, all these values are

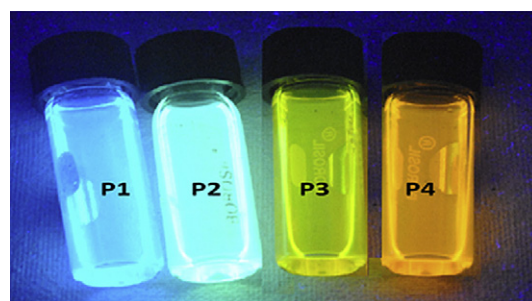


Fig. 6. Polymer solutions (**P1–P4**) in THF under UV irradiation.

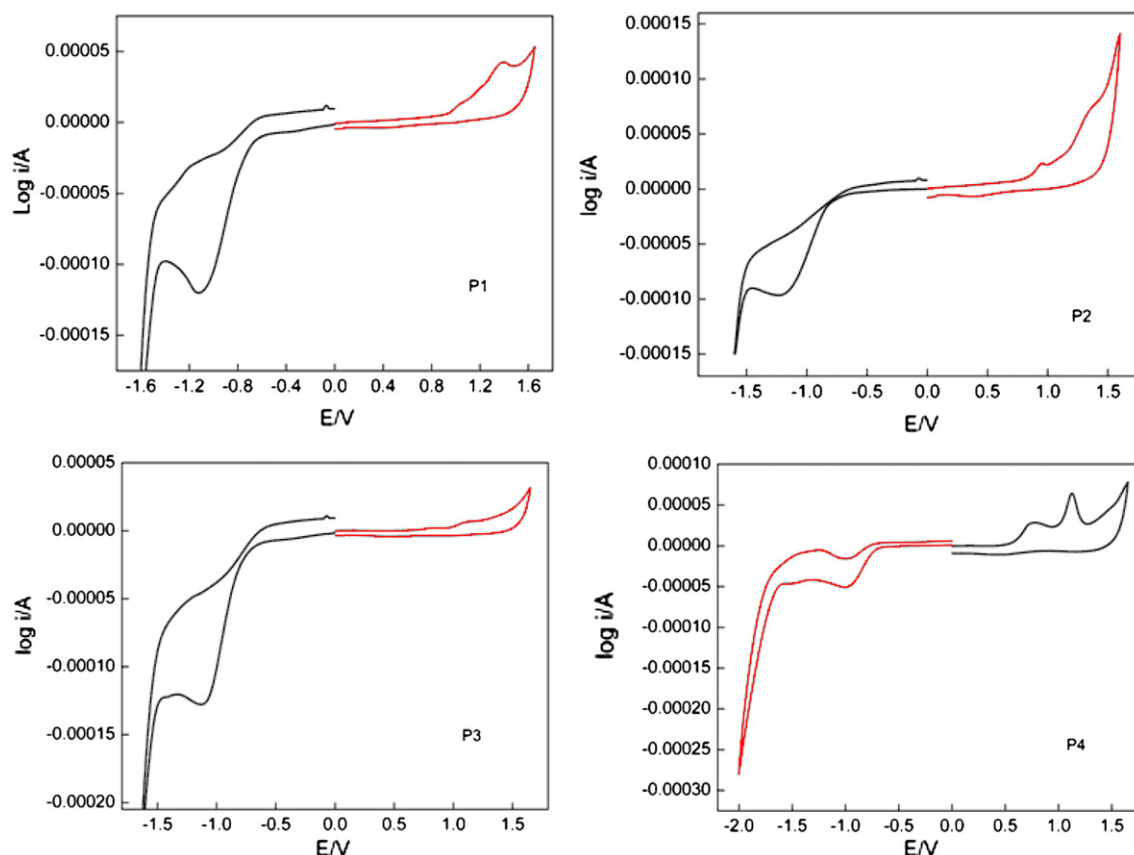


Fig. 7. Cyclic voltammetric trace of **P1–P4**.

higher than those of PPV [45] and other p-type conjugated polymers; this could be due to the introduction of cyanopyridine units along the polymer backbone. The LUMO energy levels of polymers are lower than those of PPV and other conjugated polythiophenes. Further, the values are lower than those of CN-PPV, and some poly (aromatic oxadiazole)s [46], indicating that these polymers have better electron-injection ability when they are used in PLEDs. The electrochemical band gaps of these polymers were found to be 1.955, 1.890, 1.779, and 1.672 eV, respectively. In conclusion, the high electron affinities of polymers **P1–P4** may be attributed to the presence of electron deficient cyanopyridine moiety and also the alternating p- and n-type arrangement along the polymer backbone [47,48].

The observed electrochemical behaviour in **P1–P4** can be well explained on the basis of their structure–property relationship. In general, when electron-withdrawing substituents are attached to the conjugated molecules, the electron density in the  $\pi$ -system of the conjugated molecule will be decreased. Consequently, the molecule will be stabilized and its oxidation potential will be increased. This results in a shift of the HOMO energy level to lower energy. Similarly, presence of carbazole and phenothiazene units influences the HOMO energy level due to their high electron

donating ability. Usually, the band gap of any conjugated polymer can be influenced by conjugation length, solid-state intermolecular ordering and the presence of electron-withdrawing or donating moieties. By varying these properties, optical and electrochemical behaviour of such polymers can be tuned. The effective conjugation length, which is dependent upon the torsion angle between the repeating units along the polymer backbone, can be controlled by introduction of sterically hindered bulky alkoxy side chains in order to twist the units out of plane [49]. In this context, carbazole carrying bulky alkyl substituent has a major role in enhancement of oxidation potentials [50]. Normally, incorporation of  $\pi$ -excessive thiophene units into the D–A type conjugated polymer main chain decreases its band gap because of increase in effective conjugation length. Also insertion of phenothiazine chromophores is much more effective in lowering the ionization potential and band gap of the polymer.

In Fig. 8 energy levels corresponding to different HOMO and LUMO of **P1–P4** are summarized along with energy levels of aluminium cathode and ITO anode. Thus, the results of their electrochemical studies indicate that **P1–P4** are promising candidates for their applications in electroluminescent devices.

### 3.5. Third-order non-linear optical activity

#### 3.5.1. Z-scan studies

A very convenient and fast experimental method to assess materials for NLO (including optical limiting) is the Z-scan experiment [51]. This measure the magnitude of both the non-linear refraction (NLR) and non-linear absorption (NLA) as a function of incident laser intensity while the sample is gradually moved through the focus of a lens (along the z-axis). In the experiment, the

**Table 2**  
Electrochemical characterization data.

Polymer	$E_{\text{Oxd}}$	$E_{\text{Red}}$	$E_{\text{Oxd}}$ (onset)	$E_{\text{Red}}$ (onset)	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$E_g$ (eV)
P1	1.389	−1.369	1.050	−0.905	−5.450	−3.495	1.955
P2	1.344	−1.211	1.069	−0.821	−5.469	−3.579	1.890
P3	1.103	−1.115	0.985	−0.791	−5.385	−3.609	1.779
P4	1.120	−0.963	1.022	−0.650	−5.422	−3.750	1.672

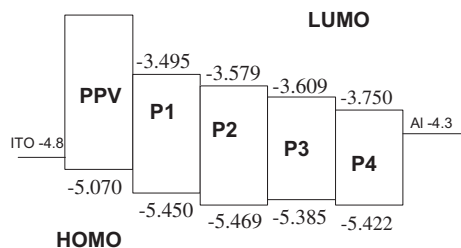


Fig. 8. Band diagram of P1–P4.

sample is placed in the path of high intense laser beam at different positions with respect to the focus (different values of  $z$ ), and the corresponding transmission is measured. Then the sample exposes to different laser intensity at each position, and therefore its position-dependent transmission will give information on its intensity-dependent transmission as well. The effective non-linear absorption coefficients were calculated by fitting theory. 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) was used to excite the molecules. The temporal width (FWHM) of the laser pulses was 7 ns. The pulses were fired in the “single shot” mode, allowing sufficient time between successive pulses to avoid accumulative thermal effects in the sample.

Figs. 9 and 10 shows the open aperture Z-scan curves of the polymers in THF solutions. In each case we have observed two-photon absorption (TPA). The non-linear activity of the polymer can be explained by considering pulse duration, pump intensity and wavelength. It can be explained by the transitions (a) ground state  $S_0$  to higher excited singlet states  $S_n$  (two-photon or multi-photon

excitation) (b) the first excited singlet state  $S_1$  to higher excited states  $S_n$ , and (c) the  $T_1$  to  $T_n$  states in the triplet manifold. The last two processes are known as excited state absorption (ESA), and if their cross-sections are larger than that of the ground state linear absorption, then these are referred to as reverse saturable absorption (RSA). The net effect is then known as an “effective” TPA process.

The non-linear transmission behaviour of the present sample can therefore be modelled by defining an effective non-linear absorption coefficient  $\alpha(I)$ , given by

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

where  $\alpha_0$  is the unsaturated linear absorption coefficient at the wavelength of excitation, and  $I_s$  is the saturation intensity (intensity at which the linear absorption drops to half its original value).  $\beta$  is the effective TPA coefficient. For calculating the output laser intensity for a given input intensity, first we numerically evaluate the output intensity from the sample for each input intensity by solving the propagation equation,

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

using the fourth order Runge-Kutta method. Input intensities for the Gaussian laser beam for each sample position in the Z-scan are calculated from the input energy, laser pulse width and irradiation area. Here ‘ $z$ ’ indicates the propagation distance within the sample. The normalized transmittance is then calculated by dividing the output intensity with the input intensity and normalizing it with the linear transmittance. As seen from Figs. 9 and 10, there is good agreement between the experimental data and numerical simulation. The numerically estimated values the effective TPA coefficients are  $1.34 \times 10^{-11}$ ,  $1.24 \times 10^{-11}$ ,  $3.04 \times 10^{-11}$  and

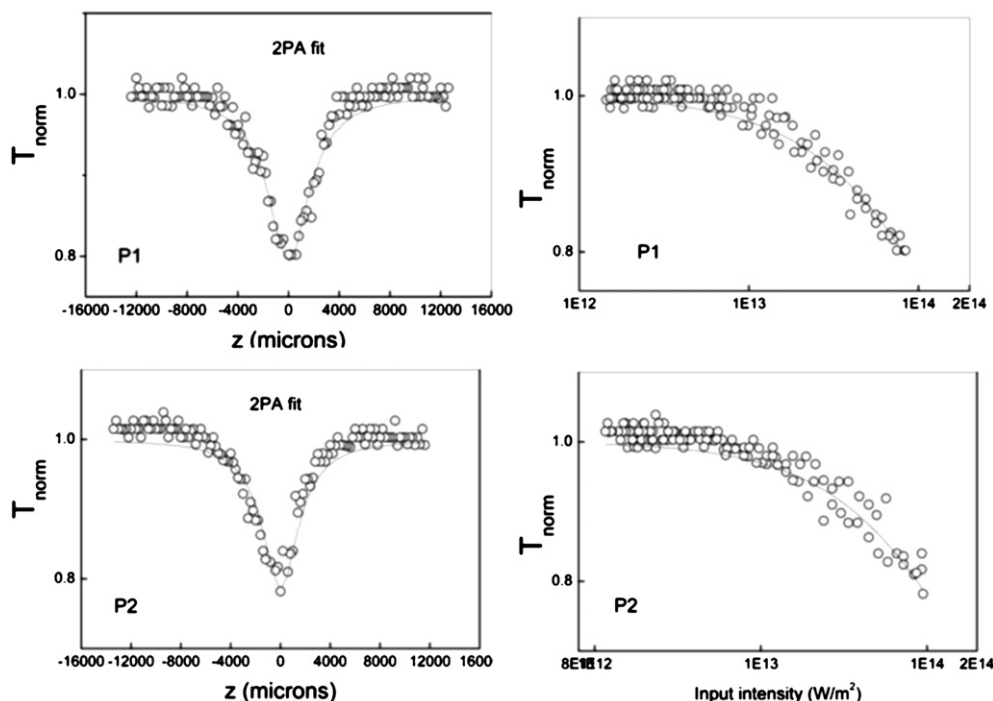


Fig. 9. Z-scan and fluence curves of P1 and P2.



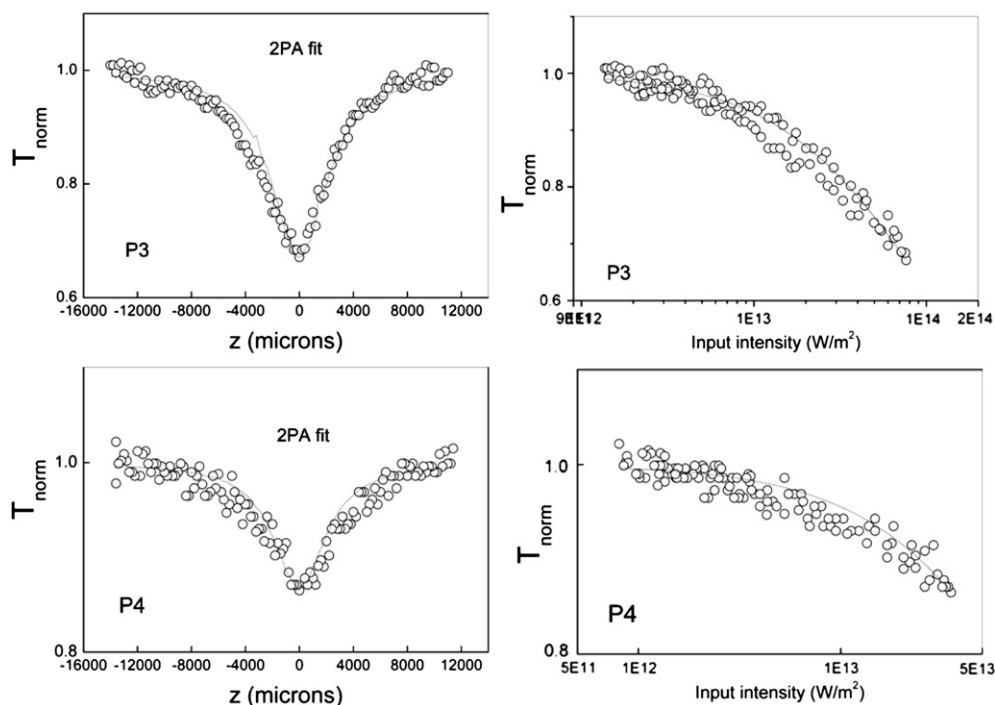


Fig. 10. Z-scan and fluence curves of **P3** and **P4**.

$1.85 \times 10^{-11}$  m/W, for Polymers **P1**, **P2**, **P3** and **P4**. For comparison, under similar excitation conditions, NLO materials like Cu nano-composite glasses showed effective TPA coefficient values of  $10^{-10}$  to  $10^{-12}$  m/W [52], functionalised carbon nanotubes showed  $3 \times 10^{-11}$  m/W [53] Bismuth nanorods gave  $5.3 \times 10^{-11}$  m/W [54] and CdS quantum dots exhibited  $1.9 \times 10^{-9}$  m/W [55]. These values show that the present sample has an optical nonlinearity comparable to good optical limiters reported in literature, so that it can find potential applications in optical limiting devices.

As discussed earlier, introduction of electron deficient cyanopyridine in between highly electron donating moieties, viz. phenyl, carbazole, thiophene and phenothiazene rings has enhanced the D–A nature of the resulting polymers, in turn increased the extent of delocalization in the polymer strands. As a result, the optical nonlinearity of **P1–P4** has increased considerably.

It is well-known that increase in planarity and rigidity of polymer chain helps to enhance third-order susceptibilities as it optimizes the overlap of  $\pi$ -orbitals, resulting in enhanced electron delocalization [56]. Also, the third-order optical nonlinearity can be enhanced by increasing  $\pi$ -delocalized electron density and the carrier transport [57]. In the present study **P2** and **P3** showed promising optical limiting behaviour. The enhanced behaviour of **P2** is mainly due to the presence of highly electron donating alkyl substituted carbazole ring, which brings about rigid structure and bent shape to the resulting polymer [58]. The maximum NLO property of **P3** is mainly attributed to the presence of highly electron donating 3,4-dialkoxythiophene and a strong electron accepting cyanopyridine unit in the newly designed D–A architecture. Further, presence of extended conjugation, easy polarizability of the molecule due to D–A type arrangement and chromophores are responsible for enhanced optical nonlinearity in **P3**.

#### 4. Conclusion

In summary, four new donor–acceptor type conjugated polymers **P1–P4** carrying highly electron deficient cyanopyridine

system and large electron donating moieties, viz. phenyl, carbazole, thiophene and phenothiazene rings, were successfully synthesized and characterized using various techniques. Linear optical studies indicated that these polymers are excellent fluorescent materials. Results of the electrochemical measurements revealed that the band gap of the polymer can be reduced by increasing the donor strength. Z-scan study showed that the new polymers are promising non-linear materials. Amongst **P1–P4**, the thiophene based polymer **P3** emerged as good optical limiting material. It can be concluded that cyanopyridine based polymers have excellent solubility, high quantum yield and good thermal stability which could meet the basic requirements for their applications in optoelectronics and photonics.

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#### AppendixSupplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.polymer.2011.07.012.

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