Synthesis and two-photon absorption property of new π -conjugated donor–acceptor polymers carrying different heteroaromatics

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Abstract. In this communication, we report the synthesis of three newly designed fluorescent polymers **P1–P3**, starting from simple thiophene derivatives through precursor polyhydrazide route. The new polymers, carrying donor and acceptor heterocyclic moieties with different spacer groups were found to be thermally stable and good of nonlinear optical (NLO) materials with two photon absorption property. The structures of newly synthesized monomers and polymers were confirmed by FTIR, NMR spectral and elemental analyses. Further, polymers were characterized by GPC and TGA studies. Their linear optical and electrochemical properties were evaluated by UV-vis, fluorescence spectroscopic and cyclic voltammetric (CV) studies, respectively, whereas their NLO properties were studied by Z-scan technique using Nd: YAG laser at 532 nm with 7 ns pulse. The electrochemical band gap of **P1–P3** was determined to be 1.98, 1.91 and 2.05 eV, respectively. The NLO results reveal that polymers **P1–P3** show good optical limiting property with TPA coefficient values 2.9×10^{-11} m/W, 8.0×10^{-11} m/W and 1.4×10^{-11} m/W, respectively.

Keywords. Conjugated polymers; optical materials; NLO; D-A polymers.

1. Introduction

In recent times, there is tremendous increase in the usage of organic nonlinear optical (NLO) polymers in various applications like frequency doublers, optical storage devices, and electro-optic (EO) switches and modulators.¹⁻⁶ Out of various optical materials, organic polymers exhibit several advantages over inorganic materials, like large NLO effects, mechanical endurance, low driving voltage and ease of processing.⁷⁻¹¹ Amongst many organic polymers, conjugated polymers with their extended delocalization of π electrons have attracted much attention in optoelectronic studies. It has been established that conjugated polymers with π -excessive nature have greater tendency to transport holes than electrons, whereas polymers containing π -deficient heterocycles like pyridine, pyran, and oxadiazoles show greater tendency to transport electrons than holes.¹² Consequently, in order to have conjugated polymer with both hole and electron transporting groups in a single chain, the donoracceptor strategy is being widely used to tailor their electronic, mechanical and physical properties.

With regard to NLO properties, a strong delocalization of π -electrons in the polymer backbone is highly significant as it determines a very high molecular polarizability and thus giving rise to remarkable optical nonlinearity. Large molecular hyperpolarizabilities and low optical losses within the spectral region of interest are the basic requirements for NLO applications. A detailed literature review reveals that a general approach for obtaining materials with important NLO properties consists in synthesizing polymer framework involving electron-donor and electron-acceptor groups linked through a π -conjugated spacer.^{13–15} Such D–A systems exhibit a prominent intramolecular charge transfer (ICT) along the π -conjugated bridges, which is crucial in promoting large optical nonlinearities and ultra-fast responses due to instantaneous electronic polarization. Thus, an optimal combination of various factors such as π -delocalization length, donor-acceptor moieties, dimensionality, confirmation and orientation of molecular structure result in a large hyperpolarizability in the polymeric systems and hence it leads to achieve good nonlinearities in them.¹⁶⁻²³ Moreover, theoretical calculations further suggest that the electronic nature and location of heterocyclic rings in the system play a subtle role in the development of NLO properties of donor-acceptor compounds.²⁴⁻²⁶

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Presently, thiophene and oxadiazole based polymers are of special interest among the D-A type conjugated systems mainly due to their high thermal stability, readiness to accommodate functional groups and solubility in common organic solvents which offer great promise for practical device applications. Also, such conjugated polymers with different spacer groups like benzene, biphenyl, naphthalene, anthracene, pyridine, etc. were reported to possess good molecular hyperpolarizability.²⁷ Further, it was shown that incorporation of different five-membered heterocyclic rings as spacer groups of the polymeric system could lead to enhanced molecular hyperpolarizability. For instance, in certain polymers replacement of benzenoid moiety with heteroaromatic rings such as thiophene, furan effectively brought about increase in the electron delocalization,^{28,29} while in push-pull polyenes presence of benzene rings caused saturation in their molecular nonlinearity.²⁴ Against this background, several NLO chromospheres containing polarizable five-membered heteroaromatics with lower aromatic stabilization energy were developed as effective D–A type π -conjugative systems. Further, inclusion of electron withdrawing 1,3,4-oxadiazole offers an improved π -electron delocalization across the D-A links and provides significant electron transportation. Also, it was established that inclusion of electron deficient pyridine moiety in thiophene-based D-A type polymer increases the electron affinity that makes the polymer more resistant to oxidation and produces improved electron-transporting properties.

Keeping all these in view, we designed three new D-A type conjugated polymers (P1-P3) carrying 3,4*bis*(4-(decyloxy)-3-methoxybenzyloxy)thiophene unit as strong electron density donor and 1,3,4-oxadiazole as strong electron acceptor moieties. Additionally, different spacer groups, viz. phenyl (P1), thiophene (P2) and pyridine (P3) moieties were introduced as π conjugation bridges in between donor and acceptor groups in order to study their effect on electrochemical, linear and nonlinear optical properties. Accordingly, we synthesized the unknown polymers (P1-P3) starting from simple thiophene derivative through precursor polyhydrazide route. The structures of newly synthesized monomers and polymers were confirmed by FTIR, ¹H NMR, ¹³C NMR spectral methods followed by elemental analyses. Further, the molecular weight and thermal stability of polymers were evaluated by GPC and TGA studies, respectively. We have investigated their linear optical and electrochemical properties and determined their band gaps. Further, their NLO properties were studied by Z-scan technique using Nd: YAG laser at 532 nm with 7 ns pulse.

2. Experimental

2.1 Materials

The required starting material diethyl 3.4dihydroxythiophene-2,5-dicarboxylate (1), was synthesized according to the reported procedures.^{30,31} Tetrahydrofuran (THF) and acetonitrile (ACN), dried over CaH₂ were used. Thiodiglycolic acid, diethyloxalate and tetrabutylammoniumperchlorate (TBAPC) were purchased from Lanchaster (UK). Vanillin, sodium borohydride, phosporous tribromide, and lithium chloride were purchased from Aldrich and were used as received. All the solvents and reagents were of analytical grade, purchased commercially and used without further purification.

2.2 Instrumentation

Infrared spectra of all intermediate compounds, monomers and polymers were recorded on a Nicolet Avatar 5700 FTIR (Thermo Electron Corporation). The UV-visible and fluorescence spectra were taken in GBC Cintra 101 UV-visible and Perkin Elmer LS55 fluorescence spectrophotometers, respectively. ¹H NMR spectra were obtained with 400 MHz on Bruker NMR spectrometer using TMS/solvent signal as internal reference. Elemental analyses were performed on a Flash EA1112 CHNS analyzer (Thermo Electron Corporation). Electrochemical studies of the polymers were carried out using 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 weights of the polymers were determined with WATER's make Gel Permeation Chromatograph (GPC) against poly(styrene) standards with teterhydrofuran (THF) as an eluent. The thermal stability of polymers was studied by SII-EXSTAR6000-TG/DTA6300 thermogravimetric analyzer. O-Switched Nd: YAG laser was used for NLO studies.

2.3 Synthesis of monomers

The synthetic route towards the preparation of required intermediates and monomers is outlined in scheme 1. The alkylated vanillin (2), obtained from vanillin was reduced to corresponding alcohol (3) using sodium borohydride. The resulting alcohol was then bromomethylated using phosphorous tribromide.



(i) C₁₀H₂₁Br, DMF, K₂CO₃, (ii) NaBH₄, MeOH, (iii) PBr₃, DEE, (iv) DMF, K₂CO₃, (v) C₂H₅OH, NH₂NH₂. 2H₂O

Scheme 1. Synthesis of monomers.

The compound (4) was then condensed with 3,4dihydroxythiophene-2,5-dicarboxylate (5) to yield 3,4bis(4-(decyloxy)-3-methoxybenzyloxy)thiophene-2,5dicarboxylate (6), which was then converted to corresponding bishydrazide (7) using hydrazine hydrate. The procedures followed for their synthesis are given below.

2.3a Synthesis of 4-decyloxy-3-methoxybenzaldehyde (2): 1-Bromodecane (1.3 g, 1 mmol) was added to a mixture of 4-hydroxy-3-methoxybenzaldehyde (1 g, 6 mmol) and potassium carbonate (0.9 g, 1 mmol) in 25 mL of DMF. The reaction mixture was stirred at 60° C. The reaction mixture was then cooled and poured into water. The product was then extracted twice using 20 ml of diethyl ether. The organic layer was dried over sodium sulphate and solvent was removed under reduced pressure to yield the white semi-solid crystalline product.

Mp: 60–61°C, FTIR (cm⁻¹) 2916, 2849, 1679, 1583, 1458, 1128. ¹H NMR (DMSO-d^{6,} δ ppm): 9.79 (s, 2H, -CHO), 7.50–7.11 (m, 3H, Ar), 4.03–4.01 (t, 2H, -OCH₂-), 3.79 (s, 3H, -OCH₃), 1.73–1.21 (m, 16H, aliphatic), 0.83–0.80 (t, 3H, -CH₃). Element. Anal. Calcd. for C₁₈H₂₈O₃: C, 73.93%; H, 9.65%; Found: C, 73.90%; H, 9.59%.

2.3b Synthesis of (4-decyloxy-3-methoxyphenyl)methanol (3): To a solution of 3.42 mmol (1 g) of 4-decyloxy-3-methoxybenzaldehyde (2) in 15 mL methanol sodium borohydride (0.03 g, 0.85 mmol) was added pinch-wise during 15 min with stirring. After the complete addition of sodium borohydride, the reaction mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure; to this 20 mL of cold water was added and then solvent extracted using 15 mL of diethyl ether twice. The organic layer was dried over anhydrous sodium sulphate and then distilled under pressure to get white solid product, which was recrystalized using ethyl acetate.

Mp: 53–55°C. FTIR (cm⁻¹): 3349, 2915, 2850, 1512, 1458, 1236, 1133, 1024. ¹H NMR (DMSO-d⁶, δ ppm): 6.87–6.73 (m, 3H, Ar), 4.99–4.96 (t, 1H, -OH), 4.37–4.35 (d, 2H, Ar-CH₂), 3.7 (s, 3H, OCH₃), 1.67–1.21 (m, 16H, aliphatic), 0.80–0.83 (t, 3H, -CH₃). Element. Anal. Calcd. for C₁₈H₃₀O₃: C, 73.43%; H, 10.27%; Found: C, 73.38%; H, 10.12%.

2.3c Synthesis of 4-(bromomethyl)-1-ethoxy-2-The compound **3** methoxybenzene **(4**): (1 g. 3.40 mmol) was dissolved in diethyl ether; to this 0.3 mL of phosphorous tribromide (1 mmol) was added drop-wise and kept for stirring at room temperature for 5h. After completion of the reaction, the reaction mixture was poured into water and the organic layer was separated, dried over sodium sulphate and solvent was evaporated under reduced pressure to obtain white puffy solid. The product obtained was recrystalized using ethyl acetate. FTIR (cm⁻¹): 2915, 2850, 1511, 1458, 1254, 1087.

2.3d Synthesis of diethyl 3,4-bis(4-(decyloxy)-3methoxybenzyloxy)thiophene-2,5-dicarboxylate (6): To a mixture of compound 5 (1 g, 3.84 mmol) and potassium carbonate (1.16 g, 8.46 mmol) in DMF, solution of compound 4 in DMF was added drop-wise with stirring. The reaction mixture was refluxed for 8 h at 60°C, then cooled and poured into water to get creamish white solid. The product was recrystalized using ethyl acetate to get white crystalline solid.

Mp: 70–73°C. FTIR (cm⁻¹): 2914, 2848, 1711, 1467, 1234, 1143, 1040. ¹H NMR (DMSO-d^{6.} δ ppm): 6.97–6.83 (m, 6H, Ar), 5.06 (s, 2H, -OCH₂), 4.30–4.25 (q, 2H, -CH₂), 3.92–3.89 (t, 3H, -OCH₃), 3.65 (s, 3H, -OCH₃), 1.70–1.23 (m, 32H, aliphatic), 0.86–0.82 (t, 3H, -CH₃). Element. Anal. Calcd. for C₄₆H₆₈O₁₀S: C, 67.95%; H, 8.43%; S, 3.94%; Found: C, 67.91%; H, 8.33%; S, 3.78%.

2.3e Synthesis of 3,4-bis(4-(decyloxy)-3-methoxybenzyloxy) thiophene-2,5-dicarbohydrazide (7): One gram (1.23 mmol) of bisester (6) was added to a solution of 0.30 mL (6.15 mmol) of hydrazine hydrate in 25 mL of ethanol. The reaction mixture was refluxed for 5 h. Upon cooling, white precipitate was obtained. The product was then filtered, washed with alcohol and dried to get white solid. The product was recrystalized using chloroform.

Mp: 133–135°C. FTIR (cm⁻¹): 3386, 3325, 2919, 2857, 1664, 1513, 1466, 1306, 1247, 1137, 1025. ¹H NMR (DMSO-d⁶. δ ppm): 8.80 (s, 2H, -NH₂), 7.01–6.77 (m, 6H, Ar), 5.14 (s, 4H, -OCH₂), 4.54 (s, 1H,

-NH-), 4.30–4.24 (t, 3H, 3.93–3.90), 3.68 (s, 3H, -OCH₃), 1.69–1.24 (m, 32H, aliphatic), 0.82–0.86 (t, 3H, -CH₃). Element. Anal. Calcd. for $C_{42}H_{64}N_4O_8S$: C, 64.26%; H, 8.22%;N, 7.14%; S, 4.08%; Found: C, 64.12%; H, 8.02%; N, 6.98%, S, 3.89%.

2.3f Synthesis of diacid chlorides (9a-c): Excess of thionyl chloride (5 mL) was added to a flask containing corresponding diacid (8a-c) (0.3 g) and then a drop of DMF was added. The reaction mixture was refluxed for 5 h. The excess thionyl chloride was removed by distillation under reduced pressure. The residue was washed with methylene dichloride to remove trace amount of thionyl chloride.

2.4 Synthesis of polymers

The synthetic route towards the synthesis of polymers **P1–P3** from corresponding monomers is shown in scheme 2. The diacids were refluxed with excess thionyl chloride to obtain diacid chlorides, which on treatment with the dihydrazide 7, in the presence of



Scheme 2. Synthesis of polymers.

lithium chloride and pyridine underwent polycondensation to give required polyhydrazides **PH1–PH2** in good yield. The polyhydrazides on cyclodehydration with phosphorous oxychloride yielded target D–A type polymers. The experimental procedures for the synthesis of new polymers are as follows.

2.4a General procedures for the synthesis of polyhydrazides (**PH1–PH3**): To a stirred solution of 0.5 g of monomer (**7**) in 20 mL N-methylpyrrolidinone (NMP) containing LiCl (1 g) and 1–2 drops of pyridine, another monomer diacid chloride (**8a–c**) was added drop-wise. The reaction mixture was then heated to 80°C and stirred for 6 h. After cooling to room temperature, it was plunged into cold water and the separated precipitate was filtered and washed with ethanol to give corresponding polyhydrazide (**PH1–PH3**). Further, polymers were purified by soxhlet extraction technique using ethyl acetate and finally it was dried in vacuum oven at 40°C.

PH1: FTIR (cm⁻¹): 3298, 2918, 2851, 1621, 1453, 1274, 1021. ¹H NMR (DMSO-d^{6.} δ ppm): 10.94 (s, 1H, -NH), 9.16 (s, 1H, -NH), 7.22–6.98 (m, 6H, Aromatic), 5.71 (s, 4H, -OCH₂-Ar), 3.91 (s, 6H, -OCH₃), 3.37–3.35 (t, 6H, -OCH₂, alkyl), 1.66–1.22 (m, 34H, aliphatic), 0.83–0.81 (t, 6H, -CH₃).

PH2: FTIR (cm⁻¹): 3225, 2921, 2852, 1622, 1481, 1261, 1024. ¹H NMR (DMSO-d^{6.} δ ppm): 10.65 (s, 1H, -NH), 9.17 (s, 1H, -NH), 8.59–7.66 (m, 6H, Ar), 7.22–6.83 (m, 2H, Th), 5.72 (s, 4H, -OCH₂-Ar), 3.93–3.90 (t, 4H, -OCH₂-alkyl), 3.75 (s, 6H, -OCH₃), 1.68–1.23 (m, 34H, aliphatic), 0.85–0.82 (t, 6H, -CH₃).

PH3: FTIR (cm⁻¹): 3199, 2917, 2850, 1612, 1452, 1250, 1016. ¹H NMR (DMSO-d^{6.} δ ppm): 10.78 (s, 1H, -NH), 9.29 (s, 1H, -NH), 8.10–8.33 (m, 3H, pyridine), 8.01–7.79 (m, 6H, Ar), 5.76 (s, 4H, -OCH₂-Ar), 4.04–4.01 (t, 4H, -OCH₂-alkyl), 3.78(s, 6H, -OCH₃), 1.69–1.26 (m, 34H, aliphatic), 0.86–0.83 (t, 6H, -CH₃).

2.4b General procedure for the synthesis of polymers (*P1–P3*): Polyhydrazide (**PH1–PH3**, 0.3 g) was dispersed in 20 mL of phosphorus oxychloride. The reaction mixture was refluxed for 12 h. After cooling to room temperature, the reaction mixture was poured into ice cold water. The precipitate was collected by filtration and was washed with water, ethanol, followed by ethyl acetate and finally dried under vacuum at 40°C.

P1: FTIR (cm⁻¹): 2917, 2850, 1581, 1450, 1271, 1031. ¹H NMR (DMSO-d⁶. δ ppm): 7.49–7.31 (m, 6H, Aromatic), 5.70 (s, 4H, -OCH₂-Ar), 3.96–3.93 (t, 6H, -OCH₂-alkyl), 3.86 (s, 6H, -OCH₃), 1.66–1.21 (m, 34H, aliphatic), 0.84–0.82 (t, 6H, -CH₃). Weight average molecular weight (\overline{M}_w): 8121 g/mol, Number average molecular weight ($\overline{M}n$):3812 g/mol, Polydispersity index (PDI): 2.13.

P2: FTIR (cm⁻¹): 2924, 2854, 1597, 1469, 1248, 1021. ¹H NMR (DMSO-d^{6,δ} ppm): 8.15–7.69 (m, 6H, Ar), 7.22–6.98 (m, 2H, Th), 5.72 (s, 4H, -OCH₂-Ar), 1.66– 1.22 (m, 34H, aliphatic), 0.85–0.81(t, 6H, -CH₃). \overline{M}_w : 8198 g/mol, $\overline{M}n$: 4738 g/mol, PDI: 1.73.

P3: FTIR (cm⁻¹): 2916, 2852, 1580, 1449, 1264, 1023. ¹H NMR (DMSO-d^{6.}δ ppm): ¹H NMR (DMSO-d^{6.}δ ppm): 8.21–7.78 (m, 3H, pyridine), 8.13–7.67(m, 6H, Ar), 5.74 (s, 4H, -OCH₂-Ar), 4.05–4.03 (t, 4H, -OCH₂-alkyl), 3.79 (s, 6H, -OCH₃), 1.68–1.26 (m, 34H, aliphatic), 0.87–0.84 (t, 6H, -CH₃). \overline{M}_w : 6560 g/mol, \overline{Mn} : 3329 g/mol, PDI: 1.97.

3. Results and discussion

3.1 *Characterization of the new monomers and polymers*

Structures of newly synthesized intermediates, monomers and final polymers were confirmed by their FTIR, ¹H NMR and ¹³C NMR spectra, followed by elemental analysis. Formation of diester (2) from 4hydroxy-3-methoxybenzaldehyde (1) was confirmed by its FTIR, ¹H NMR spectral data and elemental analysis. Its FTIR spectrum showed sharp peaks at 2916 cm^{-1} and 2849 cm^{-1} indicating the presence of alkyl chain, and another sharp peak at $1679 \,\mathrm{cm}^{-1}$ that corresponds to aldehydic carbonyl group. Further, its ¹H NMR spectrum displayed a singlet at 9.79 ppm due to aldehyde proton, multiplet at 7.50-7.11 ppm for aromatic protons, and a triplet at 4.03–4.01 ppm for alkoxy -OCH₂. Furthermore, a singlet appeared at 3.79 ppm corresponds to methoxy group attached to benzene ring and peaks at 1.73-1.21 as multiplet and 0.83-0.80 as triplet correspond to alkyl chains and -CH₃ group. Structure of (4-decyloxy-3-methoxyphenyl)methanol (3) was confirmed by its FTIR, ¹H NMR spectral and elemental analyses. Its FTIR spectrum showed a broad peak due to OH group at 3349 cm⁻¹, sharp peaks at 2915 and $2850 \,\mathrm{cm}^{-1}$ corresponding to -CH- stretching. The ¹H NMR spectrum showed multiplet for aromatic protons at 6.87-6.73 ppm, and triplet at 4.99-4.96 ppm that corresponds to -OH group. Further, it displayed peaks at 4.37–4.35 ppm appeared as doublet for –CH₂ of benzyl group, a singlet at 3.7 ppm for methoxy attached at meta position, multiplet at 1.67-1.21 ppm for alkyl protons and triplet at 0.80-0.83 ppm that corresponds to methyl group at the end of alkyl chain.

Formation of compound 4-(bromomethyl)-1-ethoxy-2methoxybenzene (4) was confirmed by its FTIR spectrum, which showed the disappearance of -OH peak at 3349 cm^{-1} . Further, structure of **6** was confirmed by its IR, ¹H NMR, ¹³C NMR spectral data and elemental analysis. Its FTIR spectrum showed sharp peaks at 2914 and 2848 cm⁻¹ due to -CH- stretching and a sharp peak at 1711 cm⁻¹ which corresponds to carbonyl group of ester. Its ¹H NMR spectrum displayed a multiplet for aromatic protons at 6.97–6.83 ppm, a singlet at 5.06 for -OCH₂ of substituted benzyl group, a quatert at 4.30–4.25 ppm and triplet at 3.92–3.89 that corresponds to -CH₂- and -CH₃ of ester. A singlet appeared at 3.65 ppm is attributed to methoxy group attached to benzene. The peaks at 1.70-1.23 as multiplet and 0.86–0.82 as triplet correspond to aliphatic and end methyl group protons. Further, its ¹³C NMR showed a series of peaks at 159.85, 152.63, 148.73, 148.26, 128.62, 121.05, 119.20, 112.65, 112.53, 75.84, 68.17, 61.28, 55.33, 31.22, 30.61, 28.93, 28.88, 28.68, 28.61, 25.44, 22.01, 13.94, and 13.86 ppm confirming the presence of carbons of carbonyl, thiophene, benzyl, alkoxy and ester groups. The structure of monomer 7 was confirmed by its FTIR, ¹H NMR and elemental analyses. The FTIR spectrum showed sharp peaks at 3386 and 3325 cm⁻¹ that correspond to -NH and $-NH_2$, and peaks at 2919 and 2857 cm⁻¹ due to alkyl -CH- stretching. A strong peak appeared at 1664 cm⁻¹ implied the presence of carbonyl group of carbonyl hydrazide. Furthermore, ¹H NMR spectrum confirms the formation of compound 7 from compound 6, its spectrum showed broad singlet at 8.80 ppm for -NH₂ and multiplet at 7.01-6.77 ppm for aromatic protons. Oxymethylene protons of benzyloxy group appeared at 5.14 ppm as singlet and another -NH- appeared as singlet at 4.54 ppm. Alkoxy –OCH₂ appeared as triplet at 4.30-4.24 ppm and a singlet appeared at 4.54 ppm for mehoxy group attached to benzyl group. The peaks at 1.69–1.24 as multiplet and 0.82–0.86 as triplet for aliphatic and methyl protons.

The precursor polymer, i.e., polyhydrazide **PH1**, showed a peak at 3298 cm^{-1} that corresponds to -NH of amide and also a sharp peak appeared at 1621 cm^{-1} that shows the presence of carbonyl group. Further, ¹H NMR of precursor polyhydrazide **PH1** displayed peaks of amide protons at 10.94 ppm and 9.16 ppm and aromatic protons resonated as multiplets at 7.49–7.31 ppm. It also showed a singlet at 5.70 ppm due to the presence of $-\text{OCH}_2$ between attached to thiophene moiety. A singlet at 3.86 ppm appeared for $-\text{OCH}_3$ attached to bezyl ring, and a triplet at 3.96–3.93 ppm for $-\text{OCH}_2$ of alkyl chain appeared. Further, multiplet at 1.66–1.21 ppm and triplet at 0.84–0.82 ppm showed the pre-

sence of aliphatic protons of benzyl group attached to 3,4 positions of the thiophene. The cyclization of polyhydrazide **PH1** to target polymer **P1** was established by FTIR and ¹H NMR spectral data. The disappearance of peaks due to amide and carbonyl stretching frequencies and appearance of a new peak at 1581 cm⁻¹ due to >C=N group in FTIR spectrum of **P1** clearly indicated the formation of 1,3,4-oxadiazole ring. Further, ¹H NMR spectrum of **P1** showed no peaks due to amide group in the region of 9–10 ppm confirming the cyclization.

The newly synthesized D–A type polymers are soluble in common organic solvents such as chloroform, toluene, and chlorobenzene at room temperature. The weight average molecular weight of the polymer was determined by gel permeation chromatography (GPC) against polystyrene standards in THF. The weight average molecular weight (\overline{M}_w) and PDI of polymers **P1–P3** in THF solution was determined to be 8121 g/mol, 8198 g/mol, 6560 g/mol and 2.13, 1.73 and 1.97, respectively.

The thermogravimetric traces of the polymers **P1– P3** are as shown in figure 1. It revealed that the onset decomposition temperature of the polymer under nitrogen was $250-300^{\circ}$ C. The initial decrease in the mass of polymers continuously was attributed to the loss of the alkoxy side chain and the amount of this weight loss was found to increase with pendant chain length further. The second weight loss step took place that corresponds to the degradation of polymer backbone leaving behind a residue. Polymer **P1** underwent degradation faster than polymers **P2** and **P3** due to the presence of vinylene linkage in the polymer back bone.



Figure 1. Thermogravimetric traces of P1–P3.

Polymer	E_{oxd}	E _{red}	E _{oxd} (onset)	E _{red} (onset)	E _{HOMO} (eV)	$E_{LUMO} \left(eV \right)$	E _g ^a (eV)
P1	1.48	$-0.95 \\ -0.80 \\ -0.94$	1.35	-0.63	-5.75	-3.77	1.98
P2	1.37		1.27	-0.64	-5.67	-3.76	1.91
P3	1.50		1.22	-0.83	-5.62	-3.57	2.05

 Table 1.
 Electrochemical potentials, energy levels and electrochemical band gap of P1-P3.

^aElectrochemical band gap

3.2 Electrochemical studies

The electrochemical properties of the polymers were studied by cyclic voltammetry carried out in 0.1 M tetrabutylammonium perchlorate (TBAP). The cyclic voltammogram of polymers coated on a glassy carbon electrode was measured on AUTOLAB PGSTAT 30 electrochemical analyzer, using a Pt counter electrode and Ag/AgCl reference electrode at a scan rate of 25 mV/s. The electrochemically determined LUMO, HOMO energy levels and calculated band gaps are given in table 1.

The cyclic voltammograms of polymers **P1–P3** displayed distinct oxidation and reduction processes as shown in figures 2, 3 and 4. They showed reduction peaks at -0.95, -0.80 and -0.94 eV, respectively. These reduction potentials are lower than that of 2-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD), one of the most widely used electron transporting materials.^{12,32} In the anodic sweep, polymers **P1–P3** displayed small oxidation peaks at 1.48, 1.37 and 1.50 eV, respectively. The onset oxidation and reduction potentials were used to estimate energy levels of highest occupied molecular orbital (HOMO) and the lowest unoccupied

molecular orbital (LUMO). The equations $E_{\text{LUMO}} = -[E_{\text{Onset}}^{\text{Red}} - 4.4\text{eV}]$ and $E_{\text{HOMO}} = -[E_{\text{Onset}}^{\text{Oxd}} + 4.4\text{eV}]$ were used for the calculations. Here $E_{\text{Onset}}^{\text{Red}}$ and $E_{\text{Onset}}^{\text{Oxd}}$ are the onset potentials versus SCE for the oxidation and reduction processes.³³

Generally, band gap of any conjugated polymer is influenced by the extent of its conjugation, solid-state ordering, the presence of electron-withdrawing and electron-donating moieties in the polymer main chain. Also, many other factors such as the nature of (solubilizing) side-chains, the conformation of the polymer backbone and its chemical constituents normally influence their band gap. Consequently, one can tune the electrochemical behaviour of any conjugated polymer by varying the above properties. As a rule, the presence of electron-donating and withdrawing groups causes a partial charge separation along the polymer back bone and hence it lowers the band gap. It is evident that the effective conjugation length in a polymer can be easily controlled by incorporating proper electron-releasing and electron-withdrawing heteroaromatic/aromatic moieties while the torsion angle among the repeating units can be monitored by introducing the bulky alkoxy side chains which would bring about twisting the units out of plane.



Figure 2. Cyclic voltammetric waves of P1.



Figure 3. Cyclic voltammetric waves of P2.



Figure 4. Cyclic voltammetric waves of P3.

Figure 5 shows the energy level band diagram of the HOMO and LUMO levels of polymers **P1–P3**, PPV, ITO anode and Al cathode. The HOMO and LUMO energy levels of polymers **P1–P3** were determined to be -5.75, -5.67, -5.62 eV and -3.77, -3.76, -3.57 eV, respectively. These results indicate that the HOMO and LUMO energy levels of polymers and the work functions of ITO (-4.80 eV) and Al (-4.28 eV) with similar energy barrier (about 0.5 to 0.9 eV) match well. Thus, the obtained results of electrochemical studies suggest that polymers **P1–P3** are promising candidates for applications in electroluminescent devices.

3.3 Linear optical properties

The UV-vis absorption spectra of polymers **P1–P3** in dilute THF solution were recorded and their spectra are shown in figure 6. The absorption measurements were taken for dilute solutions (10^{-5} M) of polymers. It has been observed that absorption maxima of **P1**, **P2** and



Figure 5. Energy level band diagram of P1–P3.



Figure 6. UV-vis absorbance spectra of P1–P3.

P3 appeared at 360, 377 and 356 nm, respectively. The absorption maxima of **P2** has been red shifted compared to **P1** and **P3**. This is originated due to the presence of thiophene ring in the polymer **P2** which has enhanced the electron delocalization in the polymer. Further, the appearance of shoulder peak in polymer **P3** at 475 nm has been attributed to the intramolecular charge-transfer (ICT) transition between the thiophene and pyridine moieties,^{34,35} and its absorption maximum at 350 nm is due to the π - π * transition. The fluorescence emission spectra of polymers **P1**, **P2** and **P3** in THF showed emission peaks at 554, 566, and 552 nm, respectively as shown in figure 7. These data indicate that the polymers emit intense green light when photoexcited. The



Figure 7. Fluorescence emission spectra of P1–P3.

Polymer	Absorption maxima	Emission maxima	Quantum yield (%)
P1	360	554	34
P2	377	566	31
P3	356	552	29

 Table 2.
 Absorption maxima, emission maxima, quantum yield of P1–P3.

quantum yield of **P1–P3** is evaluated using 0.1 M quinine sulphate in H_2SO_4 as standard. The spectral data are summarized in table 2.

3.4 Nonlinear optical properties

The Z-scan is a widely used technique developed by Sheik Bahae et al. to measure the nonlinear absorption coefficient and nonlinear refractive index of materials.³⁶ The 'open aperture' Z -scan gives information about the nonlinear absorption coefficient. Here, a Gaussian laser beam is used for molecular excitation, and its propagation direction is taken as the z-axis. The beam is focused using a convex lens, and the focal point is taken as z = 0. Obviously, 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. 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 transmission. For a focused Gaussian beam, each z position corresponds to an input laser energy density of F(z) = $4\sqrt{\ln 2}E_{in}/\pi^{3/2}\omega(z)^2$, and intensity of $I(z) = F(z)/\tau$, where E_{in} is the input laser pulse energy, $\omega(z)$ is the beam radius, and τ is the laser pulse width. Thus the sample sees different laser intensity at each position, and hence, the measured position-dependent transmission gives information about its intensity-dependent transmission. From

the open aperture z-scan data, the nonlinear absorption coefficient of the material can be calculated.

In Z-scan set-up, we used a stepper-motor controlled linear translation stage to move the sample through the beam in precise steps. The samples were taken in 1 mm cuvettes. The transmission of the sample at each point was measured by means of two pyroelectric energy probes (Ri7620, Laser Probe Inc.). One energy probe monitors the input energy, while the other monitors the transmitted energy through the sample. The second harmonic output (532 nm) of a Q-switched Nd:YAG laser (Quanta Ray, Spectra Physics) was used for exciting the molecules. The laser pulse width is 7 nanoseconds. Laser pulse energy of approximately 190 microjoules was used for the experiments. The pulses were fired in the 'single shot' mode, allowing sufficient time between successive pulses to avoid accumulative thermal effects in the sample.

The nonlinear transmission behaviour of the present samples can therefore be modelled by defining an effective nonlinear absorption coefficient $\alpha(I)$, given by the equation:

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

where α_0 is the unsaturated linear absorption coefficient at the wavelength of excitation, *I* is the input laser intensity and is the saturation intensity (intensity at which the linear absorption drops to half its original



Figure 8. Z-scan and fluence curves of P1.



Figure 9. Z-scan and fluence curves of P2.

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,

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

was numerically solved. Here z' indicates the propagation distance within the sample. Figures 8, 9 and 10 show fluence open aperture and Z-scan curves obtained from the samples **P1**, **P2** and **P3**, respectively. Numerically, a two-photon absorption (TPA) type process is found to give the best fit to the measured Z-scan data. Samples **P1–P3** have a linear absorption of about 55, 68 and 50%, respectively at the excitation wavelength when taken in the 1 mm cuvette. Therefore, strong twostep excited state absorption would happen along with genuine TPA in the present case. The net effect is then known as an 'effective' TPA process. The data obtained are fitted to the nonlinear transmission equation (3) for a two-photon absorption process.

$$T(z) = \left[1 \middle/ \pi^{1/2} q(z)\right] \int_{-\infty}^{+\infty} \ln\left[1 + q(z) \exp\left(-\tau^2\right)\right] d\tau,$$
(3)

where T(z) is the sample transmission at position z, where I_0 is the peak intensity at the focal point, $L = [1 - \exp(-\alpha l)]/\alpha$, where l is the sample length and α is the linear absorption coefficient, and $z_0 = \pi \omega_0^2/\lambda$ is the Rayleigh range, where ω_0 is the beam waist radius at focus and λ is the light wavelength, and β is the effective TPA coefficient.

The numerically calculated values of the effective TPA coefficient are found to be 2.9×10^{-11} , 8.0×10^{-11} and 1.4×10^{-11} m/W for **P1–P3**, respectively. These observed values are comparable with those of good NLO materials. Under similar excitation conditions, Cu nanocomposite glasses were shown to possess effective TPA coefficient values of the order 10^{-10} to 10^{-12} m/W,³⁷ while bismuth nanorods and CdS quantum dots were shown to have 5.3×10^{-11} m/W, 1.9×10^{-9} m/W, respectively.^{38,39} From the results, it is evident that **P1–P3** are potential candidates for optical limiting devices.

The observed nonlinear behaviour of the polymers can be explained based on their structure. The alternate D–A arrangement in these polymers gives rise to high π -electron density along the polymeric chain and are easily polarizable which in turn results in enhanced delocalization of the electrons in the polymer



Figure 10. Z-scan and fluence curves of P3.

backbone. In the new polymers 3,4-bis(4-(decyloxy)-3-methoxybenzyloxy)thiophene acts as electron donor moiety, whereas 1,3,4-oxadiazole behaves as electron acceptor group. In polymer P1, the presence of benzene ring which functions as spacer as well as electron-rich group enhances the TPA coefficient when compared to P3. The higher TPA coefficient value of P2 than that of P1 and P3 is mainly ascribed to the presence of thiophene ring in between electron-donating 3.4-bis(4-(decyloxy)-3methoxybenzyloxy)thiophene and electron-accepting 1,3,4-oxadiazole rings. As expected, the presence of less aromatic thiophene ring as spacer group in polymer P2 has enhanced the electron delocalization in the main chain and also offers more effective π conjugation between donor and acceptor groups, in turn resulting in larger nonlinearities. However, in polymer P3 the TPA coefficient value is quite less, which is mainly due to the presence of pyridine ring next to the electron withdrawing 1,3,4-oxadiazole moiety. In **P1–P3**, the presence of 3.4-*bis*(4-(decyloxy)-3methoxybenzyloxy)thiophene group facilitates the solubility of the polymers due to the presence of long alkyl chain, while 1,3,4-oxadiazole ring imparts rigidity to the polymer chains. The spectra of intermediates, monomers and polymers are given in the supplementary information.

4. Conclusions

Three new donor-acceptor (D-A) type conjugated polymers (P1-P3) carrying 1,3,4-oxadiazole as electron withdrawing unit and 3,4-bis(4-(decyloxy)-3-methoxybenzyloxy)thiophene as electron-donating moiety with different spacer groups, viz. benzene, thiophene and pyridine rings were synthesized through precursor polyhydrazide route. They exhibit good thermal stability and their electrochemical band gap was found to be 1.98, 1.91 and 2.05 eV for P1, P2 and P3, respectively. They display low LUMO and low HOMO energy levels due to different D-A type arrangements. Further, their linear and nonlinear optical studies reveal that they possess good fluorescent and optical limiting properties. Polymer P2 shows the maximum TPA coefficient due to the presence of electron-donating thiophene as spacer group. The observed TPA coefficients indicate that the polymers are good optical limiting materials.

Supplementary information

The electronic supporting information can be seen in www.ias.ac.in/chemsci.

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