Synthesis, physicochemical properties and computational study of donor–acceptor polymer for optical limiting application

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Abstract

A new donor–acceptor configured π -conjugated polymer P1 with alkoxy pendant groups having cyclic diimide and thiophene core moieties in polymer backbone were efficiently synthesized via polycondensation reaction. The incorporation of cyclic diimide in polymer increased the rigidity and thermal stability of polymer backbone aided by its high T_g value. These chromophores assisted in reducing the steric interaction of bulky alkoxy pendants which supported lowering the bandgap. The donor and acceptor moieties along with π spacers were particularly chosen to enhance the π -conjugation length in the polymer thereby increasing its nonlinear optical absorption i.e. two-photon absorption. The various structure–property relationships of the polymer were characterized by UV–Vis absorption, fluorescence emission, cyclic voltammetry, and density functional theory studies. The molecular nonlinear properties were theoretically evaluated through the calculation of polarizabilities and hyperpolarizabilities using time-dependent Hartree–Fock method. The polymer showed enhanced effective two-photon absorption with an absorption coefficient (β_{eff}) of 2.031×10^{-10} m/W obtained from open aperture Z-scan analysis which is in good agreement with theoretical study.

Keywords Conjugated polymer · NLO materials · Optical limiting · Donor–acceptor polymer · DFT method

1 Introduction

Conjugated polymers have proven to be potential candidates for nonlinear optical (NLO) applications due to their synthetic flexibility, charge transport, and fast nonlinear response [1]. Recently lot of effort has been dedicated to exploiting the nonlinear optical absorption (NLA) i.e. two-photon absorption process in π -conjugated polymers which makes them suitable for optical limiting and switching applications [2]. Polymers with donor–acceptor (D–A) structure containing optically active chromophores are of greater interest [3] as they display fast nonlinear response by delocalization of π -electrons along the conjugated

backbone [4]. The donor and acceptor moieties improve the conjugation length in the polymer which enhances the intramolecular charge transfer by decreasing the charge recombination and magnifying the asymmetric electronic distribution, leading to low bandgap polymers with elevated nonlinear optical response [5]. Also polymer with enhanced conjugation length in the backbone displayed enhanced nonlinear absorption properties [6]. A heteroaromatic electron-donating unit such as thiophene moiety originates as an excellent substituent for enhancing the donor–acceptor nature in the polymer backbone due to its efficient electron-donating capability. Hence conjugated polymers with enhanced donor nature show

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increased hyperpolarizabilities [7]. Further, the steric interactions and stability of conjugated polymers greatly impact the bandgap [8] and processability of the polymer. In this regard, cyclic polyimides are recognized as potential candidates for the NLO process [9, 10] since they are effective NLO chromophores with electron-accepting character and possess high glass transition temperature (T_g) [11]. The higher thermal stability of cyclic polyimides arises from polar interactions and charge transfer complexation that aid for stabilization of dipole alignment at higher temperatures. To overcome the drawback of insolubility in organic solvents, cyclic polyimides are generally introduced with various flexible pendant groups [12], among which alkoxy groups yield better solubility and processability of polymers. Also, the fusion of heterocycles such as oxadiazole and thiadiazole in D–A polymers greatly enhances the optoelectronic performance of the polymer [13, 14].

Here, we report the design and synthesis of cyclic diimide and dialkoxythiophene based π -conjugated polymer P1 for potential optical limiting applications. The D–A structured polymer has dialkoxythiophene as electron-donating moiety and cyclic diimide as NLO chromophore as well as an electron-accepting unit. The polymer P1 was substituted with bulky alkoxy pendant groups that aided for increasing the processability of the polymer. Polymer P1 showed high thermal stability resulting from high T_g value of NLO chromophore in the polymer backbone. The structural conformation of polymer P1 was evaluated through various spectral techniques. Further, the incorporation of thiophene moiety as an electron donor in the D–A structure showed an increase in the conjugation path length thus yielding a low HOMO–LUMO bandgap polymer which was characterized through electrochemical studies. The addition of oxadiazole heterocycles in the polymer P1 also aided for enhancing the D–A nature of the polymer which resulted in increased hyperpolarizabilities. The NLO properties of the polymer were obtained through open aperture Z-scan studies developed by Sheik-Bahae et al. [15], which is a standard tool for the measurement of NLO properties of polymers due to its high selectivity and sensitivity. The two-photon absorption coefficient (β_{eff}) of polymer P1 was calculated from Z-scan traces by curve fitting method.

In addition, theoretical calculations contribute to a greater extent in understanding the structure–property relationship in D–A polymers [16, 17]. Thus, the charge transfer characteristics in the D–A system (P1) that lead to enhanced nonlinear optical properties are explored using density functional theory (DFT) through partial charge analysis and frontier molecular orbital analysis. Furthermore, the theoretical spectral studies of P1 were performed utilizing the time-dependent density functional theory (TD-DFT). The molecular NLO properties of P1 were

evaluated through the interpretation of dipole moment, polarizabilities and hyperpolarizabilities computed using time-dependent Hartree–Fock (TDHF) method. The results were compared with experimental data and their agreement is briefly discussed.

2 Materials and methods

2.1 Materials

3,4-Dialkoxythiophene-2,5-dicarboxylate was synthesized according to the reported procedure [18]. The raw materials for the synthesis of monomers and polymers were directly procured from Sigma Aldrich. Analytical grade solvents are used for synthesis and study.

2.2 Material synthesis

2.2.1 Synthesis of diamine monomer

In the preparation of diamine monomer, dihydrazide 1 was treated with nitro benzoyl chloride to obtain dicarbohydrazide 2, the resulting molecule reacted with phosphorous oxychloride. POCl_3 induced the cyclization of oxadiazole to yield corresponding dinitro derivative 3. The resulting dinitro compound was reduced to diamine monomer M1 using hydrazine hydrate in ethanolic media without any metal catalyst. The synthesis of diamine monomer M1 is depicted in Fig. 1 and the synthetic procedure is explained in the supplementary information.

2.2.2 Synthetic design of polymer

As outlined in Fig. 1, polymer P1 was synthesized by condensing the conjugated diamine monomer M1 with cyclic dianhydride monomer M2. Polymerization was carried out using a two-step reaction involving amidation followed by oxidative. In the first step, amine reacts with anhydride to form a polyamide which upon heating converts into corresponding cyclized polymer. Since cyclic anhydrides are rigid in their structure, they undergo polymerization reaction slowly. Therefore, the reaction was carried out at a high temperature, i.e. 120 °C in an inert atmosphere.

2.3 Procedure for synthesis of polymer P1

The diamine monomer M1 (1 g, 1.20 mmol) was added to a clear solution of dianhydride monomer M2 (0.26 g, 1.20 mmol) in NMP (N-methyl pyrrolidinone) solvent. The addition was done at 0 °C under controlled inert atmosphere (reaction mass was purged with nitrogen to ensure the inertness). After the addition, the resulting mixture

Fig. 1 Synthesis of diamine monomer M1 and polymer P1

slowly stirred at room temperature for about 2 h. Then the reaction temperature is raised to 120 °C and stirring was continued for about 12 h. After the successful completion of the reaction, the temperature was reduced to room temperature and poured to crushed ice. Then it was filtered and washed with cold ethanol to remove any unreacted materials. The obtained solid polymer was purified by soxhlet extraction using hexane, ethyl acetate, methanol, and finally, chloroform soluble fraction was precipitated in excess of methanol and dried in vacuum.

Polymer P1: Yield 66%. FTIR (cm^{-1}): 2920, 2847, 1675, 1640, 1486, 1372, 1305. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.52–7.90 (m, aromatic), 6.82–6.74 (m, aromatic), 4.37–4.26 (t, 4H, $-\text{OCH}_2-$, $J=8$ Hz), 11.89–1.24 (m, 48H, $-\text{CH}_2-$), 0.86 (t, 6H, $-\text{CH}_2\text{CH}_3$, $J=8$ Hz). Element. Anal. Calcd. (%) for $\text{C}_{65}\text{H}_{72}\text{N}_6\text{O}_9\text{S}$: C, 70.12; H, 6.52; N, 7.55; S, 2.88. Found: C, 70.02; H, 6.32; N, 7.49; S, 2.71. The weighted average molecular weight (M_w) is 12,500 with a polydispersity index of 2.1.

2.4 Computational methods

The geometry of polymer P1 ($n=1$) (Fig. 2) was optimized in ORCA 4.0.1 program [19] employing density functional theory [DFT] using Becke's three-parameter hybrid functional with the Lee et al. [20] correlation functional (B3LYP) using the Pople basis set, 6-31G(d), in THF solvent [21].

Default convergence criteria and gradient techniques were used for all the calculations. The absence of considerable imaginary frequencies calculated at the same level of theory by neglecting the zero-point energy corrections indicated that the optimized structure is at its local minima. Further, the charge transfer character of the molecule was studied through atomic point charges and frontier molecular orbital analysis. The spectral properties of the molecule were computed using time-dependent DFT with cc-pVTZ basis set in THF solvent ($\epsilon=7.25$) utilizing the CPCM solvent model. To study the third-order NLO activity, the time-dependent Hartree–Fock [TDHF] method in Firefly QC package (version 8.2.0), which is partially based on the GAMESS(US) [21] source code was utilized. The implemented TDHF method offered a good compromise between accuracy and computational cost. Hence, TDHF method was used for calculating static and frequency-dependent linear polarizabilities [22–24], first and second hyperpolarizabilities. The frequency-dependent $\alpha(-\omega;\omega)$, $\beta(-2\omega;\omega,\omega)$ and $\gamma(-3\omega;\omega,\omega,\omega)$ computations were considered at $\omega=0.08563$ a.u. ($\lambda=532$ nm) using the aforementioned method in the gas phase (Fig. 2).

Fig. 2 Monomer structure of P1 considered for quantum calculations along with atoms numbering

3 Results and discussion

3.1 Experimental

3.1.1 Structure analysis

^1H NMR spectrum of dinitro derivative 3 showed no peaks due to amidic protons but showed a de-shielding effect of protons attached to aromatic ring indicating the construction of oxadiazole ring. Further, in its FTIR spectrum, it showed the absence of amidic carbonyl absorption bands and the appearance of $-\text{C}=\text{N}-$ stretching absorption peaks indicating the cyclization. Similarly, the formation of conjugated diamine monomer M1 was confirmed by its FTIR spectrum wherein it showed strong absorption bands that correspond to the primary amine ($3341, 3217\text{ cm}^{-1}$). Also, its ^1H NMR displayed the appearance of a broad singlet at δ 4.09 ppm which confirms the presence of a primary amine. Furthermore, the aromatic protons of the benzene ring attached to the amine functionality shielded to a great extent and hence they resonated at δ 6.75 ppm confirming the conversion.

The structure of polymer P1 was established using FTIR and ^1H NMR spectral data. In the FTIR spectrum of polymer P1, an absorption band was observed at 1650 cm^{-1} due to two cyclicamidic carbonyl groups. Further, its ^1H NMR spectrum showed no peaks due to primary amine confirming the formation of the polymer. Thermal stability of polymer was studied using Thermogravimetric analysis (TGA). The cyclic imide containing conjugated polymer P1 showed good thermal stability up to 310°C (Fig. 3). The enhanced thermal stability is due to the incorporation of cyclic diimide units in the polymer backbone. The observed degradation after 310°C is attributed to the

Fig. 3 Thermogravimetric trace of polymer P1

decomposition of flexible alkyl side chains in the polymer. These results indicate that polymer can be used in high-temperature applications. Also, this thermal stability is one of the major parameters in our study because the polymer will be exposed to high energy laser during nonlinear absorption studies. Further we observed reproducible results in nonlinear absorption studies even after exposure to high energy pulsating laser for same sample in different trials. Molecular weight of the polymer was determined using Waters make Gel permeation chromatography. Weight average molecular weight ($\bar{M}_w$) for polymer P1 was found to be 12,500 with a polydispersity index of 2.1.

The determined electrochemical data of polymer P1 showed good resemblance to the imide containing polymers, reported in the literature [25]. This observation

indicates that the imide's carbonyl group in the polymers acts as an electro-active site. Further, the appearance of a reversible reduction peak indicates that the carbonyl group is responsible for reversible redox reaction in the polymers. The reduction potential of P1 appeared at a more negative potential than that of imide containing polymers reported in the literature, indicating that the reduction potential relates to the electron affinity of the additional carbonyl group present in P1. The observed bandgap of the polymer was 2.22 eV which is quite low compared to the polyamides reported in the literature [26, 27]. This may be attributed to the enhancement of conjugation path-length and D–A type arrangement in the polymer backbone. Also, the introduction of cyclic imides in the polymeric backbone has resulted in the reduction of steric interaction of bulky alkoxy pendants, which leads to a decrease in the bandgap of the resulting polymer. The details of onset oxidation and HOMO and LUMO levels have been depicted in Table 1. Also, a trace of cyclic voltammogram is given in Fig. 4.

3.1.2 Linear optical properties analysis

UV–Vis absorption spectra of polymer P1 was recorded using GBC Cintra double beam spectrometer with Tetrahydrofuran (THF) as solvent. The polymer P1 showed broad absorption with absorption maxima of 383 nm. This is due to the presence of strong D–A nature induced by the 3,4-dialkoxythiophene and 1,3,4-oxadiazole moieties along with conjugated diimide backbone. Also, polymer P1 displayed higher absorption maxima when compared to that of cyclic amide containing polymers in the literature [26, 27], which is attributed to the enhancement in conjugation path length brought about by the additional phenyl and carbonyl functionality attached to phenyl in the polymer back bone. Introduction of the bulky alkyl side group along the polymer backbone increased the hydrophobicity of the polymer and hence increased the solubility of the polymer in common organic solvents (Fig. 5).

Further, this polymer was found to be strongly emissive with high quantum yield. This could be attributable to the rigid structure of the polymeric backbone tendered by the introduction of cyclic imides. This resulted in the reduction of non-radiative (e.g., thermal) relaxation process from the excited state, thereby increasing the fluorescence quantum yield. Stokes shift is generated by electronic or geometrical structure relaxation of the photoexcited

Fig. 4 Cyclic voltammogram of polymer P1

molecule. This information suggests a significant conformational difference between an absorbing ground state and the emitting excited state. If the Stokes shift is too small, the emission and absorption spectra will overlap more. Then the emitting light will be self-absorbed and the luminescence efficiency will decrease in the devices. Here the synthesized polymer exhibited well Stokes shift values along with solvatochromic behaviour (Fig. 6) which indicates that the polymer is a potential candidate for the electroluminescent application also. The optical properties of the polymer are represented in Table 2.

3.1.3 Nonlinear optical (NLO) properties using the Z-scan technique

The “open aperture” Z-scan technique was used for the measurement of nonlinear optical properties of polymer P1. This technique is particularly useful when the nonlinear refraction is accompanied by nonlinear absorption. In this experiment, the optical limiting behavior of the materials was identified in the solution state using Q-switched Nd:YAG nanosecond laser. The laser used had a nominal pulse width of 7 ns and a laser pulse energy of 15 micro joules was used for the experiments. The output of the laser possessed almost a Gaussian Intensity profile. The sample was taken in a 1 mm cuvette. The transmission of the sample at each point was measured through two pyroelectric energy probes (Rj7620, Laser Probe Inc.). One energy probe monitored the input energy, while the other

Table 1 Electrochemical characterization data of polymer P1

Polymer	E_{oxd} (V)	E_{red} (V)	E_{oxd} onset	E_{red} onset	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
P1	1.86	−0.85	1.64	−0.58	−6.04	−3.82	2.22

Fig. 5 UV–Vis absorption and emission spectra of polymer P1 in THF solution

Fig. 6 Fluorescence emission spectra (solatochromism) of polymer in various organic solvents

monitored the transmitted energy through the sample. The pulses were fired in the “single-shot” mode, allowing sufficient time between successive pulses to avoid accumulative thermal effects in the sample [15]. All NLO measurements were carried out in the solutions state at room temperature. The polymer was dissolved in NLO inactive organic solvent (THF) and used for the study. Polymer was highly soluble in THF hence scattering effect was not observed. The enhanced solubility of the polymer is due to introduction of long alkyl chains. The concentration of the samples set to a linear transmission of about 60–70% at the excitation wavelength.

Figure 7 shows the fluence curve Z-Scan curves of polymer P1 in THF solution. In our studies we have observed two photon absorption (TPA). NLO activity of any polymeric system can be explained by wavelength of the laser, laser pulse intensity, and duration of laser pulse. This TPA process can be explained by two different transitions from

Table 2 Linear optical characterization data of polymer P1

Sl. no	Polymer	UV–visible absorption maxima in THF (in nm)	Fluorescence emission maxima in THF (in nm)				Quantum yields* (in THF)
			THF	CHCl ₃	DMF	DMSO	
1	P1	383	501	499	547	551	31%

*Quantum yield relative to quinine sulfate (10^{-5} M quinine sulfate in 0.1 M H₂SO₄)

Fig. 7 Open aperture Z-scan traces of polymer P1

ground state S_0 to their excitation state S_n along with its first singlet excitation state S_1 to higher excitation state S_n . These two processes are known as excited state absorption. If their cross-sections are larger than the ground state, linear absorption then it is known as reverse saturable absorption. The nonlinear transmittance of the studied polymer was modelled by defining effective nonlinear absorption coefficient $\alpha(I)$, given by Eq. 1.

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

where α_0 is the unsaturated linear absorption coefficient, and I_s is the saturation intensity of the laser light. β is the effective two photon absorption coefficient. For the calculation of output laser intensity with respect to a given input intensity, we numerically simulate the output intensity from polymer sample for each input intensity by solving following Eq. 2 as given by Runge–Kutta method [15].

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

Input intensities of the of laser beam in each sample position was calculated by considering input laser energy and irradiation area of the laser. Then propagation direction is represented as “z”. Normalized transmittance was calculated by the ratio of output intensity with input intensity with normalization. The obtained transmittance values were compared with standard theoretical values then effective TPA coefficient (β) was calculated by curve fitting method.

In present study, the intensity of the light coming out from the polymeric solution at various laser intensities were plotted against the position of the sample which gives the open aperture Z-scan traces. Furthermore, these values were fitted to the theoretical equations to obtain effective TPA coefficients (β). There was good agreement between the experimental data and numerical simulation for polymer P1. The approximate energy of the laser was maintained around 100 mJ. Polymer under study showed reverse saturable absorption with a two-photon absorption process. Generally, while performing Z-scan studies of different materials there will be localized heating due to intense laser beam. If the material is not stable to light/heat then it degrades and the results will not be reproducible. But during the measurement the optical limiting behaviour of polymer P1, reproducible results were obtained even after many exposures of the sample to pulsating laser beam.

The experimentally measured two-photon absorption (TPA) coefficient β of the polymer P1 was found to be 2.031×10^{-10} m/W by curve fitting method (Fig. 7). The nonlinearity of this polymer is mainly attributed to the increase in the conjugation path length due to the presence of sterically rigid cyclic imides and the occurrence of D–A nature in the polymeric backbone. These cyclic imides reduced the steric strain between bulky alkoxy side chains of the polymer backbone. Further, the presence of highly electron-withdrawing oxadiazole unit enhanced molecular hyperpolarizability which in-turn increased the optical limiting behaviour of the resulting polyimides.

3.2 Quantum chemical calculations

3.2.1 Optimized geometry

The ground state optimized geometry of P1 was obtained by DFT/B3LYP with 6-31G(d) basis set in THF solvent. To simplify the calculations, the single repeating unit of the polymer was considered for calculations and all the branched alkyl chains were replaced with propyl chains (Fig. 2), respective optimized structure is shown in Fig. 8. The calculated C–O bond lengths of the molecule ranged from 1.2150 to 1.4634 Å and the bond angles of cyclic imide were found to be 125.53° (N₃₄–C₄₁–O₄₃) and 125.64° (N₃₄–C₄₂–O₄₄) which facilitated for reduction of steric interaction in alkoxy pendant group. Further, analytical vibrational frequencies were calculated at the same level of theory to confirm the local minima of the structure, which showed no imaginary frequencies. Hence the above optimized geometry was used for further quantum chemical calculations.

3.2.2 Charge transfer analysis

a. Atomic charges

Partial atomic charges play an important role in altering the electronic properties of the molecule such as dipole moment, polarizability, etc. and define the reactivity of the molecule. Since the partial atomic charges are not physical observables and have no unique quantum mechanical definition, the charge distribution of P1 was computed using different models [28] at B3LYP/6-31G(d) level of theory using Multiwfn 3.7 wavefunction analyser [29]. The models considered for charge population analysis include Mulliken population analysis based on orbital wavefunctions, Hirshfeld method based on deformation density partition, CM5

Fig. 8 Optimized structure of P1 molecule at B3LYP/6-31G(d) level

atomic charges which are corrected Hirshfeld charges, and CHELPG electrostatic potential (ESP) fitting charge model. The computed charge values are depicted in Fig. 9. The partial atomic charges derived from different charge models showed similar behaviour to that of Mulliken charges. The results displayed both positive and negative charge values for carbon atoms due to substituent effects thus indicating the probable path of charge delocalization through carbon atoms. Additionally, the hydrogen atom H₇₇ showed higher positive charge value as compared to other hydrogen atoms which displayed almost equal charge values. Further, Atoms C₂, C₂₀ and N₅₄, O₄₄ showed highest positive and negative ESP fitted charges respectively indicating potential reactive sites in the molecule.

b. Frontier molecular orbital (FMO) analysis

Nonlinear optical activity exhibited by a molecule is dependent on the charge transfer character in the molecular system. In a π -conjugated system, the electron cloud movement from donor to acceptor moieties causes charge transfer in the molecule [30, 31]. Hence, analyzing the HOMO (nucleophile) and LUMO (electrophile) orbitals of the molecule and its corresponding bandgap is essential in understanding the same, as they are considered to be main contributors to intramolecular charge transfer (ICT). The orbital distribution of HOMO and LUMO of the P1 molecule are visualized in Fig. 10. The calculated HOMO and LUMO energy levels were found to be –5.98 eV and –3.12 eV which are close to the experimental energy levels of –6.04 eV and –3.82 eV respectively. The theoretical optical energy gap of P1 was 2.86 eV (experimental electrochemical bandgap 2.22 eV). The deviation from the experimental value may be attributed to the length of the side chain [32] and monomer structure considered since the narrowing of bandgap takes place in polymers due to molecular orbital hybridization of each monomer [33]. The orbital density of HOMO is predominantly distributed over dialkoxythiophene moiety extending to oxadiazole and benzene rings, whereas the LUMO is localized over cyclic diimide moiety. This suggests the existence of intramolecular charge transfer through the system upon HOMO–LUMO excitation. Further, the lower value of energy gap of the molecule indicates that it can be easily polarized, resulting in enhanced NLO properties.

Furthermore, the global reactivity descriptors were calculated according to Koopman theorem [17] using HOMO and LUMO energy values obtained from DFT calculations. Which include hardness (η), chemical potential (μ), softness (S), electronegativity (χ), electrophilicity index (ω) as shown below.

Fig. 9 Partial atomic charge distribution of P1 estimated at B3LYP/6-31G(d) level

$$\eta = \frac{I - A}{2} \quad \mu = -\frac{(I + A)}{2} \quad S = \frac{1}{2\eta} \quad \chi = \frac{I + A}{2} \quad \omega = \frac{\mu^2}{2\eta}$$

The ionization potential (I) and electron affinity (A) of the molecule can be expressed through HOMO and LUMO orbital energies as $I = -\text{HOMO}$ and $A = -\text{LUMO}$. The calculated values of global reactivity descriptors for the P1 molecule are presented in Table 3. The results showed a higher value of electron affinity (A) indicating the higher accepting capability of P1. The lower values of η and μ implied that the molecule possesses lower stability and better reactivity which is also described by the higher value of softness (S). These findings explain the suitability of polymer P1 for charge transfer reactions [34].

3.2.3 UV–Vis analysis

The absorption spectral properties of the P1 molecule were calculated employing TDDFT/B3LYP/cc-pVTZ in THF solvent using the optimized ground state geometry. The theoretical absorption spectrum of molecule P1 is shown in Fig. 11. The theoretical results indicate that the $S_0 \rightarrow S_1$ excitation is dominated by one electron transition from HOMO to LUMO (95%). Although the major orbital contribution to the absorption peak is displayed from the

transition of $\text{HOMO} \rightarrow \text{LUMO} + 2$ (81%) having the highest oscillator strength of $f = 1.6445$. Accordingly, the theoretical absorption peak of P1 was located at 387.4 nm arising due to $\pi \rightarrow \pi^*$ transition. The calculated absorption wavelength, additional dominant molecular orbital contributions, oscillator strengths, and corresponding excitation energies are detailed in Table 4. The calculated absorption bands showed good agreement with the experimental values.

3.2.4 Molecular NLO properties

The static and dynamic nonlinear optical response of the molecule were evaluated by calculating average static dipole moment (μ), linear polarizability (α_0), the anisotropy of polarizability ($\Delta\alpha_0$), first hyperpolarizability (β_{tot}) and average second-order hyperpolarizability ($\langle\gamma\rangle$) using the equations that are defined mathematically in supplementary information. The tensor components of both static and frequency dependant polarizabilities and hyperpolarizabilities were analytically computed using time-dependent Hartree–Fock (TDHF) method with 6-31G(d,p) basis set implemented in Firefly QC package. The obtained polarizabilities values were converted to electrostatic units

Fig. 10 The orbital distribution and HOMO–LUMO energy of P1 at B3LYP/cc-pVTZ level of theory in THF solvent (isovalue = 0.02)

Table 3 GCRD of P1 molecule

I (eV)	A (eV)	η (eV)	μ (eV)	S (eV ⁻¹)	χ (eV)	ω (eV)
5.98	3.12	1.429	-4.550	2.092	4.550	7.244

(esu) from atomic units (a.u.) (α : 1 a.u. = 0.1482×10^{-24} esu; β : 1 a.u. = 8.6393×10^{-33} esu; γ : 1 a.u. = 5.0367×10^{-40} esu).

The computed components of the static dipole moment (μ) are listed in Table 5. Accordingly, the dipole moment of P1 molecule was found to be 5.1479 Debye, which is 1.0708 times of urea molecule. The higher value of dipole moment indicates a relatively higher polarization in the molecule [35–37] which is in line with the computed static linear polarizability (α) value of $81.8382 (\times 10^{-24})$ esu. The dynamic second-harmonic generation $\beta(-2\omega; \omega, \omega)$ and third-harmonic generation $\gamma(-3\omega; \omega, \omega, \omega)$ values were computed at a frequency of $\omega = 0.08563$ a.u., analogous to the Nd:YAG

laser wavelength of 532 nm that was used for experimental Z-scan study. Corresponding static and dynamic tensor components of linear polarizability, first hyperpolarizability, and second-order hyperpolarizability are detailed in Tables 6, 7. The computed static β_{tot} and γ value of polymer P1 was found to be $44.9892 (\times 10^{-31})$ esu and $17.6834 (\times 10^{-35})$ esu. These estimated values are higher and are comparable with various diimide derivatives and other previously reported materials [38–42]. In particular the static γ value of the polymer P1 was comparable with structurally similar molecules having aromatic diimides reported in the literature [43]. Further, compared to static value, the dynamic

Fig. 11 Theoretical UV-visible absorption spectrum of P1

linear polarizability $\alpha_0(-\omega;\omega)$ of the polymer was increased by 11.41%. Similarly, the frequency dependant value of $\beta_{tot}(-2\omega;\omega, \omega)$ was increased by 92.51% when compared to static value. In both cases, the polymer displayed enhanced hyperpolarizability values. This can be attributed to its lower energy gap between HOMO and LUMO and enhanced ICT character in D–A structure [42, 43]. The non-zero values of hyperpolarizabilities confirm the nonlinear optical behavior of polymer P1. Also, the positive values of second-order hyperpolarizability tensor components indicate that the polymer displays microscopic third-order nonlinear optical activity, which is consistent with the open aperture Z-scan findings. Further, the delocalization of electron cloud along the polymer direction (x-axis) was indicated by the high magnitude of β_{xxx} and γ_{xxxx} components of hyperpolarizabilities. Additionally, the polymer P1 showed enhanced first hyperpolarizability (β_{tot}) and second-order hyperpolarizability (γ) by 14 and 48 times, compared to urea molecule in the gas phase, thus making it a promising material for third-order NLO applications.

Table 5 Calculated static dipole moment and dipole moment components of P1 [Debye]

μ_x	μ_y	μ_z	μ
−3.3639	−3.2232	−2.1901	5.1479

Table 6 Calculated components of static linear polarizability, first hyperpolarizability, and second hyperpolarizability ($\omega=0$) by TDHF method [esu]

$\alpha(0;0)(\times 10^{-24})$		$\beta(0;0,0)(\times 10^{-31})$		$\gamma(0;0,0,0)(\times 10^{-35})$	
α_{xx}	126.5127	β_{xxx}	40.8290	γ_{xxxx}	52.3499
α_{yy}	84.8828	β_{xyy}	6.4929	γ_{yyyy}	9.6815
α_{zz}	37.7895	β_{xzz}	−3.3184	γ_{zzzz}	0.1471
α_{xy}	15.6867	β_{yyy}	−15.4265	γ_{xxyy}	12.3632
α_{xz}	−3.4959	β_{xxy}	24.2439	γ_{xxzz}	0.5877
α_{yz}	−1.9407	β_{yzz}	0.4870	γ_{yyzz}	0.1678
α_0	83.0616	β_{zzz}	6.0429	γ	17.6834
$\Delta\alpha_0$	81.8382	β_{xxz}	−10.8321		
		β_{yyz}	3.7138		
		β_{tot}	44.9892		

4 Conclusion

In summary, a thermally stable donor–acceptor type conjugated polymer based on dialkoxythiophene and cyclic diimide was successfully synthesized via polycondensation reaction and characterized using various techniques. Linear optical studies indicated that the polymer is a good fluorescent material with solvatochromic behaviour. The GCRD values indicated that the polymer P1 has more accepting capability and reactivity, thus making it a potential candidate for charge transfer reactions. Further, NLO studies revealed that the resulting polymer showing good thermal stability towards laser light and exhibited good optical limiting property with two-photon absorption (2PA) coefficient of the order of 2.031×10^{-10} m/W. Theoretical studies on the polymer showed non-zero values of hyperpolarizabilities thus confirming the enhanced NLO behaviour

Table 4 Photophysical properties of P1 molecule calculated using TDDFT

Major transition*	Energy (cm ⁻¹)	Osc. strength (f)	λ_{abs} (nm) exp. cal		Symmetry
H ₁ → L + 2 (81%) H ₁ - 1 → L (10%)	25,815.5	1.6445	383	387.4	Singlet
H ₁ - 1 → L (62%)	22,455.0	0.1190	–	445.3	Singlet
H ₁ → L (95%)	13,519.1	0.0209	–	739.7	Singlet

*H denotes HOMO and L denotes LUMO

Table 7 Calculated components of frequency dependant linear polarizability, first hyperpolarizability, and second hyperpolarizability ($\omega = 0.08563$ a.u) by TDHF method [esu]

$\alpha(-\omega; \omega) (\times 10^{-24})$		$\beta(-2\omega; \omega, \omega) (\times 10^{-31})$		$\gamma(-3\omega; \omega, \omega, \omega) (\times 10^{-35})$	
α_{xx}	145.4733	β_{xxx}	− 295.6011	γ_{xxxx}	− 857.5599
α_{yy}	93.4946	β_{xyy}	376.9256	γ_{yyyy}	23.5431
α_{zz}	38.6636	β_{xzz}	− 6.2827	γ_{zzzz}	0.4149
α_{xy}	22.6218	β_{yyy}	− 189.1771	γ_{xxyy}	− 32.3327
α_{xz}	− 4.1096	β_{xxy}	137.4503	γ_{xxzz}	− 6.4896
α_{yz}	− 2.3339	β_{yzz}	8.8747	γ_{yyzz}	0.9393
α_0	92.5438	β_{zzz}	8.0237	γ	− 181.8735
$\Delta\alpha_0$	100.7993	β_{xxz}	− 25.7745		
		β_{yyz}	11.9361		
		β_{tot}	86.6105		

with microscopic third-order NLO phenomena, which are consistent with the experimental results. Additionally, the polymer showed elevated first and second-order hyperpolarizabilities in theoretical calculations compared to the standard urea molecule. Thus, it can be concluded that the incorporation of cyclic diimide along with alkoxythiophene may give thermal stability to the polymer along with the increase in the optical limiting behaviour of the polymer, hence making this polymer a potential optical limiting material which may find applications in optical switching devices.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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