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Effects of substituents on enriching optical limiting action of novel imidazo[2,1b][1,3,4]thiadiazole fused thiophene based small molecules

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Abstract

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Imidazo[2,1-*b*][1,3,4]thiadiazole (ITD) ring is a fused, planar aromatic heterocyclic system consisting of four heteroatoms with a bridgehead nitrogen atom. In this work, three new donor–acceptor–donor (D–A–D) type organic molecules (**ThITD1–ThITD3**) were designed and synthesized, wherein ITD is an electron acceptor unit and thiophene/ phenyl moieties are electron donor units that produce a D–A–D configuration. The thiophene–ITD core structure comprises three different groups *viz.*, thiophene–2–acetonitrile (**ThITD1**), phenylacetonitrile (**ThITD2**) and rhodanine–3–acetic acid (**ThITD3**) and the effect of substituents on the optical and electrochemical properties were discussed based on structural modifications. The third–order nonlinear optical (NLO) properties analyzed by Z–scan technique revealed that the molecules exhibit effective two photon absorption (TPA) with **ThITD3** possessing substantially higher effective TPA coefficient (β_{eff}) than that of **ThITD1** and **ThITD2**, which is comparable to β_{eff} values reported. The results unravel that ITD as an acceptor with an appropriate π –linker will be a promising entrant in the field of optoelectronics/photonics. Herein, the thiophene–ITD ring system for NLO applications is explored and reported for the first time.

Keywords

Thiophene, imidazo[2,1-*b*][1,3,4]thiadiazole, cyclic voltammetry, DFT, NLO, Z–scan.

1. Introduction

Organic semiconductors, especially π -conjugated small molecules, having well defined molecular structure along with π -conjugated polymers are being spotlighted since couple of decades ¹⁻³ for their application in many optoelectronic and electronic devices ^{4,5} such as organic photovoltaics, organic light emitting diodes (OLEDs) or electro chromic devices and Page 3 of 30

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optical limiters ⁶⁻¹⁴. The devices based on these materials have attracted widespread attention of the second attentis atten due to their flexibility, low cost and light weight compared to the conventional inorganic devices ^{15,16}. Simple modifications in synthetic route and functional groups lead to the variations in optical, electronic and charge transport properties in these systems. Most of the conjugated materials used in photovoltaic/optoelectronic industry are generally obtained by C-C coupling reactions viz., Suzuki, Heck, Stille and Kumada coupling reactions 9 17-20 which involve expensive transition metals as catalysts. Moreover, stringent reaction conditions and tedious purification methods are followed to achieve the target compounds which hinder the synthetic efficacy, thereby restricting the large-scale production and commercialization ²¹⁻²³. A clean, attractive, low-cost alternative route to synthesize conjugated materials is the condensation chemistry ^{24,25}, which can be performed without catalyst at ambient conditions and most of the condensation reactions result water as the byproduct, which makes the purification of the product easier ²⁶. Further, the reactions result in high yield compared to that of C-C coupling reactions. The introduction of olefinic bond as π -linker between the aromatic rings leads to the reduction in steric hindrance, improvement in planarity and hence extends the π -conjugation ²⁷. The presence of vinylic bond in conjugated materials modulates the electrochemical properties such as light emitting property, charge transfer ability, etc., ^{28–31}. Similarly, introduction of cyano group as electron withdrawing group lowers the lowest unoccupied molecular orbital (LUMO) level and also increases the electrochemical stability of the conjugated material, which is desirable to achieve high-performance optoelectronic devices ³². Despite of aforementioned benefits, compounds containing cyano groups also exhibited promising performances on their usage in various organic electronics such as organic filed effect transistors (OFETs), OLEDs and polymer ^{33–36} /small molecule photovoltaics ^{26,37}. However, the defined molecular weight, molecular structure, ease of synthesis and ease of purification of low molecular

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oligomers/small molecules make them superior to polymers ³⁸. A great number of similar of similar of similar molecular materials with thiophene unit either as a central core or as end/peripheral group, explored as active materials in organic electronics ^{39–43}.

Further, the meteoric rise of attention in the area of nonlinear optics leads to the development of novel materials with outstanding properties ⁴⁴. Since NLO effects could manipulate the high energy laser beam to new optical frequencies, they are very useful in this inspiring field. Organic molecular and polymeric materials have obtained considerable interest as good NLO materials, as they are cheap, biodegradable, have high damage threshold, excellent NLO responses, structural modification and ease of fabrication ^{45–47}. The presence of strong electron donor and acceptors increases the delocalization of π -electrons, making the material highly polarizable and thus causing remarkable optical nonlinearities in such system ⁴⁸. Due to these benefits, they are considered as potential candidates in various applications such as high density optical data storage, optical communications, optical limiters for eye and instrument safety and photo dynamic therapy for cancer treatment ^{49–54}.

Several organic materials with moderate to excellent NLO properties have been reported. Among them, thiophene derivatives are found to be good candidates because of their flexibility in structural modification and good semiconducting property when coupled with a suitable electron acceptor ^{28,55}. ITD is an efficient electron acceptor with a bridgehead nitrogen atom, along with three other heteroatoms and two condensed heterocycles with extended π -conjugations that make it planar and rigid heteroaromatic system ⁵⁶. These features anticipated to exhibit promising photo–physicochemical properties. There are plenty of literatures that describe the pharmacological importance of ITD but there are no reviews/literatures available which deal with the linear optical, electrochemical and NLO properties of this moiety. The present study discloses the optoelectronic properties and optical nonlinearity of three novel materials (**ThITD1–ThITD3**) containing thiophene as

electron donor and ITD as electron acceptor moiety with the expectation that t_1 it would dice online produce good performance when used in optoelectronic devices and also this present study focused on the evaluation of third order NLO properties such as nonlinear absorption coefficient (β_{eff}), nonlinear refractive index (η_2) and third order nonlinear susceptibility (χ^3) of the novel molecules.

2. Experimental

2.1 Materials and methods

All the reagents and starting materials used were procured from commercial vendors. The chemicals used are, thiophene–2–carboxylic acid (Sigma Aldrich, 99%), thiosemicarbazide (Alfa Aesar, 98%), phenacyl bromide (Spectrochem, 99%), thiophene–2–acetonitrile (Sigma Aldrich, 97%), phenylacetonitrile (Spectrochem, 98%) and rhodanine–3–acetic acid (Alfa Aesar, 98%). The solvents used were distilled and dried. All the reactions were carried out under inert condition and the progress of the reaction was monitored using thin layer chromatography (TLC) technique. All the intermediates and final compounds were purified by column chromatography using an appropriate eluent.

2.2 Synthesis

2.2.1 Synthesis of 5-(thiophen-2-yl)-1,3,4-thiadiazol-2-amine (3)

Thiophene–2–carboxylic acid (1) (9.0 g, 70.23 mmol) and thiosemicarbazide (2) (6.4 g, 70.23 mmol) were taken in a clean round–bottomed (RB) flask, followed by the addition of phosphorus oxychloride (POCl₃) (10.0 mL). The mixture was refluxed for 2 h, later which, the mixture was cooled to room temperature and quenched using ice cold water. It was then basified with 20% NaOH solution and thus, obtained solid was filtered and dried. The crude was purified by column chromatography (60–120 mesh silica) using dichloromethane as eluent to get compound (3) as white colored solid (12.08 g, yield: 94%). ESI–MS (m/z) calcd.

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for C₆H₅N₃S₂: 182.99, found: 184.0 [M+H]⁺; ¹H NMR (400 MHz, DMSO– d_6) δ (ppm): 7/60 for C₆H₅N₃S₂: 182.99, found: 184.0 [M+H]⁺; ¹H NMR (400 MHz, DMSO– d_6) δ (ppm): 7/60 for C₆H₅N₃S₂: 7.60 (d, J = 6.0 Hz, 1H, Ar–H), 7.42 (s, 2H, Ar–NH₂), 7.39–7.38 (d, J = 4.4 Hz, 1H, Ar–H), 7.11–7.09 (m, 1H, Ar–H); ¹³C NMR (100 MHz, DMSO– d_6) δ (ppm): 168.5, 151.0, 133.7, 128.4, 128.0; Anal. calcd. for C₆H₅N₃S₂: C, 39.33; H, 2.75; N, 22.93; S, 34.99; found: C, 39.29; H, 2.78; N, 22.89; S, 34.97.

2.2.2 Synthesis of 6-phenyl-2-(thiophen-2-yl)imidazo[2,1-b][1,3,4]thiadiazole (4)

To a solution of (3) (6.0 g, 32.74 mmol) in ethanol (20 mL), phenacyl bromide (7.8 g, 39.29 mmol) was added and refluxed for 24 h. Excess of ethanol was removed under reduced pressure, the resulting solid was suspended in water and refluxed for 4 h. After which, the product was neutralized with 10% Na₂CO₃. The obtained solid (4) was filtered, dried and purified by column chromatography using a mixture of petroleum ether (pet ether): ethyl acetate (8:2, v/v) as eluent (8.25 g, yield: 89%). ESI–MS (*m*/*z*) calcd. for C₁₄H₉N₃S₂: 283.02, found: 284.00 [M+H]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.01 (s, 1H, Ar–H), 8.00–7.98 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.83–7.81 (d, *J* = 8.0 Hz, 2H, Ar–H), 7.61–7.40 (m, 5H, Ar–H), 7.33–7.14 (m, 2H, Ar–H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 155.8, 146.1, 144.6, 133.1, 132.3, 129.9, 129.2, 128.8, 128.1, 127.8, 125.1, 109.4; Anal. calcd. for C₁₄H₉N₃S₂: C, 59.34; H, 3.20; N, 14.83; S, 22.63; found: C, 59.25; H, 3.31; N, 14.76; S, 22.71.

2.2.3 Synthesis of 6-phenyl-2-(thiophen-2-yl)imidazo[2,1-*b*][1,3,4]thiadiazole-5carbaldehyde (5)

A freshly distilled N,N–Dimethylformamide (DMF) (2.18 mL, 28.26 mmol) was taken in a two neck RB flask and cooled to 0 to -5° C. To this POCl₃ (2.64 mL, 28.26 mmol) was added in drop wise and stirred for 15 min to get Vilsmeier salt. The solution of **(4)** (4.0 g, 14.13 mmol) in DMF was added to the formed Vilsmeier salt and the mixture was heated at 65°C for 6 h, later which, the mixture was quenched using ice cold water. The obtained solid was filtered, dried and purified by column chromatography using a mixture of ethyl acetate and

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hexane (3:7, v/v) as eluent to obtain (**5**) as yellow solid (3.78 g, yield: 86%). ESI_{-MS} (m²/_{CSNJ01100E} calcd. for C₁₅H₉N₃OS₂: 311.02, found: 312.00 [M+H]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.11 (s, 1H, –CHO), 7.92–7.90 (m, 2H, Ar–H), 7.66–7.60 (m, 2H, Ar–H), 7.54–7.45 (m, 3H, Ar–H), 7.19–7.17 (m, 1H, Ar–H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 177.4, 163.0, 157.8, 155.9, 149.9, 132.2, 131.6, 130.9, 129.9, 129.1, 128.8, 128.2, 125.1, 124.2; Anal. calcd. for C₁₅H₉N₃OS₂: C, 57.86; H, 2.91; N, 13.50; S, 20.59; found: C, 57.79; H, 2.82; N, 13.62; S, 20.67.

2.2.4 Synthesis of (E)-3-(6-phenyl-2-(thiophen-2-yl)imidazo[2,1-b][1,3,4]thiadiazol-5-yl)2-(thiophen-2-yl)acrylonitrile (ThITD1)

To a freshly prepared solution of sodium ethoxide (89.3 mg, 8.11 mmol), thiophene–2– acetonitrile (0.40 mL, 3.85 mmol) was added slowly with stirring. After 15 min of stirring, compound **(5)** (1.0 g, 3.21 mmol) was added and the reaction mixture was stirred at room temperature for 5 h. The precipitated solid was collected by filtration, washed with ethanol and purified by column chromatography using a mixture of pet ether: ethyl acetate (9:1, v/v) as eluent to get **ThITD1** as yellow solid (0.97 g, yield: 73%). ESI–MS (*m/z*) calcd. for $C_{21}H_{12}N_4S_3$: 416.02, found: 417.10 [M+H]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.74–7.71 (m, 2H, Ar–H), 7.64–7.63 (m, 1H, Ar–H), 7.57–7.56 (d, *J* = 4.0 Hz, 1H, Ar–H), 7.51–7.47 (m, 2H, Ar–H), 7.44–7.41 (m, 3H, Ar–H), 7.34–7.33 (m, 1H, Ar–H), 7.17–7.15 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.12–7.09 (dd, *J* = 12.0 Hz, 1H, Ar–H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 155.4, 149.0, 147.3, 139.3, 130.5, 129.5, 128.9, 128.7, 128.3, 128.2, 128.1, 127.4, 126.6, 119.0, 116.3, 107.6; Anal. calcd. for C₂₁H₁₂N₄S₃: C, 60.55; H, 2.90; N, 13.45; S, 23.09; found: C, 60.61; H, 2.98; N, 13.36; S, 23.01.

2.2.5 Synthesis of (Z)-2-phenyl-3-(6-phenyl-2-(thiophen-2-yl)imidazo[2,1b][1,3,4]thiadiazol-5-yl)acrylonitrile (ThITD2)

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Compound ThITD2 was synthesized following the above procedure mentioned in section Additional Continues of the above procedure mentioned in section 2010 (1998) 101100 (1998) 10100 (1998) 10100 (1998) 10100 (1998) 10100 (1998) 10000 (1998) 1000 (1998) 1000 (1998) 1000 (1998) 100 2.2.4, in which the precursor used was phenylacetonitrile (0.44 mL, 3.85 mmol) with compound (5) (1.0 g, 3.21 mmol) (1.00 g, yield: 76%). ESI-MS (m/z) calcd. for C₂₃H₁₄N₄S₂: 410.07, found: 411.10 [M+H]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.73–7.71 (d, J = 8.0 Hz, 4H, Ar-H), 7.64-7.63 (m, 1H, Ar-H), 7.58-7.55 (m, 2H, Ar-H), 7.49-7.38 (m, 6H, Ar-H), 7.17–7.14 (m, 1H, Ar–H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 155.3, 149.0, 147.2, 134.2, 133.6, 132.3, 130.4, 129.4, 129.3, 129.1, 128.9, 128.6, 128.1, 126.2, 126.1, 119.5, 117.2, 113.5; Anal. calcd. for C₂₃H₁₄N₄S₂: C, 67.29; H, 3.44; N, 13.65; S, 15.62; found: C, 67.35; H, 3.53; N, 13.55; S, 15.51.

(E)-2-(4-0x0-5-((6-phenyl-2-(thiophen-2-yl)imidazo[2,1-b][1,3,4])2.2.6 **Synthesis** of thiadiazol-5-yl)methylene)-2-thioxothiazolidin-3-yl)acetic acid (ThITD3)

A mixture of intermediate (5) (1.0 g, 3.21 mmol) and rhodanine–3–acetic acid (0.61 g, 3.21 mmol) was taken in acetonitrile (10 mL). Piperidine (0.5 mL) was added to the mixture and refluxed for 8 h. After which, the solvent was evaporated and to the obtained residue distilled water (20 mL) was added and neutralized using 10% HCl. The suspended solid was filtered. dried and purified by column chromatography using a mixture of pet ether: ethyl acetate (6:4, v/v) as eluent to get (ThITD3) as orange solid (1.08 g, yield: 70%). ¹H NMR (400 MHz, DMSO- d_6) δ (ppm): 13.00 (s, 1H, -COOH), 8.03–8.02 (m, 1H, Ar–H), 7.96–7.95 (m, 1H, Ar-H), 7.76 (s, 1H, Ar-H), 7.69–7.67 (m, 2H, Ar-H), 7.58–7.49 (m, 3H, Ar-H), 7.31–7.29 (m, 1H, Ar–H), 4.70 (s, 1H, –CH₂). ¹³C NMR (100 MHz, DMSO– d_6) δ (ppm): 194.77, 167.93, 167.47, 157.83, 153.29, 149.74, 144.53, 133.24, 132.32, 131.45, 129.92, 129.50, 129.27, 119.44, 119.16, 118.31, 45.70; Anal. calcd. for C₂₀H₁₂N₄O₃S₄: C, 49.57; H, 2.50; N, 11.56; S, 26.46; found: C, 49.46; H, 2.58; N, 11.64; S, 26.38.

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Scheme 1. Synthetic route and molecular structures of molecules **ThITD1–ThITD3**. Reaction conditions: (i) POCl₃, 75°C, 2 h; (ii) Phenacyl bromide, ethanol, 85–90°C, 24 h; (iii) POCl₃, DMF 60–65°C, 6 h; (iv) 2-(thiophen-2-yl)acetonitrile, NaOC₂H₅, C₂H₅OH, RT; (v) 2-phenylacetonitrile, NaOC₂H₅, C₂H₅OH, RT; (vi) Rhodanine-3-acetic acid, piperidine, 80–85°C, 8 h.

2.3 Characterization details

ESI–Mass (Waters micro mass Q-Tofmicro), ¹H NMR (Bruker, 400 MHz) and ¹³C NMR (Bruker, 100 MHz) spectral techniques were utilized to elucidate the structures of all the intermediates and final compounds. A flash EA-112 CHNS analyzer (Thermo electron corporation) was used for the elemental analysis. The UV–Vis spectral data were collected from Analytik jena SPECORD S600 spectrometer and photoluminescence (PL) spectra were recorded using a Fluoromax Horiba Jobin Yuan spectrometer. IVIUM (Vertex-V55610) electrochemical work station was used to carryout cyclic voltammetric (CV) measurements of the molecules using three electrode system wherein the molecules were dissolved in chloroform and drop casted on glassy carbon electrode which was taken as working

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electrode, Platinum (Pt) wire as a counter electrode and saturated calomel electrode. (SCE) Astronome a reference electrode and the electrolyte used was 0.1 M solution of tetrabutylammonium perchlorate (TBAP) in acetonitrile. Ferrocene was used as an internal standard for all the electrochemical measurements and the scan rate used was set at 100 mV s⁻¹. Gaussian 09 software with B3LYP functional 6-311+G (d,p) level basis set was used for the density functional theory (DFT) and time-dependent density functional theory (TDDFT) studies of the molecules. Thermogravimetric analysis (TGA) were carried out using Seiko Instruments TGA/DTA Exstar 6300, Japan at a heating rate of 10°C min⁻¹ under argon atmosphere.

2.4 Z-scan analysis

To experiment the application of the samples in optoelectronics, NLO studies were performed by Z-scan technique under nano second excitation ⁵⁷. Using this technique both nonlinear absorption and nonlinear refractive index parameters were measured which finally provided χ^3 value. The nonlinear absorption (NLA) and optical limiting (OL) parameters were obtained from open aperture (OA) Z-scan analysis whereas nonlinear optical refraction (NLR) parameters were obtained from closed aperture (CA) Z-scan analysis. In OA Z-scan analysis the optical transmittance of the sample was recorded as a function of input intensity. The schematic representation of the Z-scan set up is shown in the Fig. S18 (ESI). The sample solutions were made to translate across the focus of a convex lens (focal length 150 mm) in the direction of laser beam (z axis from -z to +z) in predetermined steps using a translational stage which was controlled by a computer program.

The maximum intensity of the samples was observed at the focus which decreases equally on either side of the focus. The output transmittance from the sample at each position was collected by a detector which was then plotted against position of the samples. The NLA properties of the samples were measured by numerically fitting the recorded data to the theoretical model. To obtain the NLR parameters using CA Z–Scan, a small aperture was

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placed in front of the signal detector. Thus, obtained transmittance is affected by both NY dide Online as well as NLR and is susceptible to phase distortion. Division of CA output from OA output results in pure NLR part. All the experiments were carried out in the "single shot" mode. Sufficient time intervals were provided between successive pulses to avoid accumulative thermal effects in the sample. The NLO studies were performed using a Q– switched Nd– YAG laser Quanta Ray INDI–40 (Austin, USA) (7 ns pulse width) working at a wavelength of 532 nm with a frequency of 10 Hz. The linear transmittance of all the molecules was fixed between 70–80% at the excitation wavelength when taken in a 1 mm cuvette.

3. Results and discussion

3.1 Synthesis and structural characterization

The synthetic route and molecular structures of **ThITD1–ThITD3** are shown in the scheme 1. The synthesis of molecules **ThITD1–ThITD3** includes four steps. In the first step, the intermediate (**3**) was synthesized from the reaction between commercially available thiophene–2–carboxylic acid and thiosemicarbazide in the presence of POCl₃ with the yield of 94%. The intermediate (**4**) was synthesized by the reaction between (**3**) and phenacyl bromide followed by cyclization, which was then subjected to Vilsmeier–Hack formylation to obtain intermediate (**5**). In the final step, precursor (**5**) was subjected to well–known Knoevenagel condensation with active methylene compounds *viz.*, thiophene–2–acetonitrile, phenylacetonitrile and rhodanine–3–acetic acid to achieve the target compounds **ThITD1– ThITD3**, respectively. All the synthesized intermediates and final compounds were purified using either recrystallization or column chromatography. All the intermediates and final compounds were characterized using ¹H NMR, ¹³C NMR and mass spectroscopic techniques (see ESI for details).

3.2 Optical properties

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 Fig. 1 a and b show the absorption and PL spectra of **ThITD1–ThITD3**, respectively and the corresponding spectral data are listed in Table 1. All the spectra were recorded in solution state (1×10^{-5} M) in which chloroform was used as solvent. The absorption spectra exhibit two separate bands, one is around 250–270 nm which is ascribed to the π – π * electronic excitations and the other, in the range of 340–413 nm, is attributed to intramolecular charge transfer (ICT) from donor (thiophene, phenyl) to the acceptor (ITD) unit ⁵⁸. The large bathochromic shift in **ThITD3** compared to **ThITD1** and **ThITD2** is due to the strong electron withdrawing nature of rhodanine–3–acetic acid which is further leading to the extension of conjugation ^{59,60}. The absorption onset and the corresponding optical band gaps are summarized in Table 1. The determined optical band gaps to be 2.83, 2.95 and 2.72 eV for **ThITD1–ThITD3**, respectively. The emission spectra exhibit the maximum emission for **ThITD1–ThITD3** at 483, 480 and 509 nm, respectively upon exciting at their corresponding λ_{max} , establishing their luminescence property.



Fig. 1 (a) Normalized UV–vis absorption spectra (b) PL spectra of **ThITD1–ThITD3** in chloroform (1×10⁻⁵ M).

Table 1 UV–vis absorption and fluorescence emission data of molecules **ThITD1–ThITD3** in chloroform $(1 \times 10^{-5} \text{ M})$.

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Molecules	λ^{abs} (nm)	$\lambda^{pl}_{max}(nm)$	$\lambda^{c}_{edge}(nm)/E_{g}^{opt}(eV)$	View Article Online DOI: 10.1039/C9NJ01100E
ThITD1	264, 385 ^a	483	438/ 2.83	_
	371 ^b			
ThITD2	254, 338 ^a	480	419/ 2.95	
	360 ^b			
ThITD3	245, 411 ^a	509	455/ 2.72	
	430 ^b			

^a Experimentally determined values from UV-vis absorption spectra

^b values derived theoretically from TD–DFT studies

 $\lambda^{pl}_{max} = \lambda_{max}$ from PL spectra

^c Determined from the intersection between the tangent drawn to the absorption edge and the abscissa, the optical bandgap is calculated using the equation $E_g = 1240/\lambda_{edge}$.

3.3 Electrochemical studies

Cyclic voltammetric measurements were performed to investigate electrochemical properties, which further quantify the energies of molecular orbitals of the molecules. Fig. 2 a, b and c show the cyclic voltammograms of **ThITD1–ThITD3**, respectively. Considering the onset oxidation potential, energy of highest occupied molecular orbital (HOMO) level (E_{HOMO}) was calculated using the equation (1) ⁶¹,

$$E_{HOMO} = -\left[E_{onset}^{ox} + 4.8eV - E_{FOC}\right].$$
(1)

where, E^{ox}_{onset} and E_{FOC} are the onset oxidation potentials of the samples and ferrocene, respectively, -4.8 eV is the HOMO energy level of ferrocene against vacuum.

Further, LUMO levels were obtained from electrochemically measured HOMO energy and spectroscopically determined band gap, using the equation (2)

$$E_{LUMO} = E_{HOMO} + E_g....(2)$$

where, $E_g = 1240/\lambda_{edge}$.

The HOMO energy levels are at -5.66, -5.77 and -5.83 eV whereas LUMO energy levels are at -2.83, -2.82 and -3.11 eV for **ThITD1**, **ThITD2** and **ThITD3**, respectively. The significant reduction in the LUMO level is mainly attributed to the presence of strong

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electron withdrawing rhodanine –3 –acetic acid group in **ThITD3**, reducing the band view article Online compared to that of cyano groups in **ThITD1** and **ThITD2**. The experimentally obtained HOMO and LUMO values from CV are in agreement with the theoretically determined HOMO and LUMO values (Table 2).







Fig. 2 Cyclic voltammograms of (a) ThITD1, (b) ThITD2 and (c) ThITD3.

Table 2 Electrochemical and	d DFT data o	of ThITD1–	ThITD3
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Molecules	E ^{ox} _{onset} (V vs SCE)	HOMO (eV)	LUMO (eV)
ThITD1	1.18	-5.66ª	-2.83 ^a
		-5.96 ^b	-2.61 ^b
ThITD2	1.29	-5.77ª	-2.82 ^a
		-6.03 ^b	-2.54 ^b
ThITD3	1.35	-5.83ª	-3.11ª
		-6.21 ^b	-3.19 ^b

^a Experimentally determined values from CV, ^b values derived theoretically.

3.4 DFT studies

The electronic properties of the molecules **ThITD1–ThITD3** were investigated theoretically using DFT calculations. Fig. 3 depicts the optimized geometry and frontier orbital distribution of the molecules **ThITD1–ThITD3**. The estimated HOMO and LUMO energy levels are listed in Table 2 along with the experimental results. The HOMO and LUMO levels were obtained using Avogadro software (Version 1.2.0). The effect of thiophene functioning as electron donor appended with ITD and cyano/ rhodanine–3–acetic

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acid group as acceptor species governs the effective HOMO orbital distribution of the species online distribution is commonly observed in the three molecules **ThITD1–ThITD3**. The nature of electronic distribution in molecule **ThITD1** and **ThITD2** pertaining to LUMO portrays a π - π^* type of transition, whereas in **ThITD3** electron density is mostly localized on the ITD and rhodanine units. Such a type of distribution observed in the system effectively facilitates charge transfer transition between the acceptor group and the entire molecular network. The effect of rhodanine–3–acetic acid moiety which imparts stronger electron withdrawing nature in orbital distribution at LUMO level of **ThITD3**, were not observed in the case of **ThITD1** and **ThITD2**, possessing a cyano group as electron acceptor.

Also, the optimized structures of the compounds in Fig 3 reveal that after introducing double bonds the dihedral angle between ITD and thiophene -2-acetonitrile plane is 36.5° and that of ITD and benzene plane is 29.3° in **ThITD1** whereas dihedral angle between ITD and phenyl acetonitrile plane is 39.5° and that of ITD and benzene plane is 30.2° in **ThITD2** while dihedral angle between ITD and rhodanine–3–acetic acid plane is 23.0° and that of ITD and benzene plane is 42.4° in **ThITD3**. The steric hindrance caused by rhodanine moiety due to the lesser dihedral angle of 23.0° between ITD and rhodanine–3–acetic acid plane is caused by rhodanine moiety due to the lesser dihedral angle of 1TD and benzene plane in **ThITD3** to maintain the most stable conformation. The dihedral angles between ITD plane and the substituted groups, ITD plane and phenyl group are listed in Table S1 and the planes are represented in Fig S19.



Fig. 3 Ground state optimized geometry and molecular orbitals (HOMO and LUMO) of ThITD1–ThITD3.

TD-DFT calculations of **ThITD1–ThITD3** were carried out to estimate the electronic excited state transitions and to corroborate with the experimental absorption transitions. The simulated absorption spectra of **ThITD1–ThITD3** is shown in Fig 4. The theoretical absorption maxima (λ_{max}) for **ThITD1–ThITD3** are at 371, 360 and 430 nm, respectively (Table 1). The experimental and theoretical values differ by 14, 22 and 19 nm for **ThITD1, ThITD2** and **ThITD3**, respectively. This energy difference can be attributed to the fact that there exist many conformers in the solution state whereas such conformers may not be considered for the calculation ⁶². However, the results obtained by theoretical simulations are in concordant with the experimental results. Further, the spectral data exhibit two bands, wherein, the higher energy band corresponds to π - π * transition and the lower energy band corresponds to charge transfer transition. Overall, the trend remains the same for both theoretical and experimental calculations but the trifling inconsistencies observed in energy transition is due to the theoretical overestimation ⁶³.

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Fig. 4 Simulated absorption spectra of ThITD1-ThITD3.

3.5 Thermal properties

TGA were carried out to study the thermal stability of **ThITD1–ThITD3**. As shown in the Fig. 5, **ThITD1–ThITD3** showed satisfactory thermal stability. The decomposition temperatures (T_d) for **ThITD1**, **ThITD2** and **ThITD3** are 330, 357 and 346°C, respectively. The lower T_d of molecules **ThITD1** and **ThITD3** than that of **ThITD2** is due to the presence of heterocyclic rings attached with Th–ITD core moiety in **ThITD1** and **ThITD3**. The results showed that the molecules could be of relevant materials for electronic/photonic applications.



Fig. 5 TGA curves of ThITD1–ThITD3.

3.6 Third–order nonlinear optical properties

3.6.1 Nonlinear absorption studies

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Fig. 6 a, b and c show the open aperture Z–scan curves of the molecules **ThITD1– ThITD3**, respectively in DMF solutions. The molecules **ThITD1–ThITD3** were excited using the intensity of 1.386 GWcm⁻² (50 μ J). From the plots it is observed that the transmittance is minimum at the focus (z=0) and all the transmission curves are symmetric about the focus. Thus, the absorption is dependent on the excitation intensity. The molecules **ThITD1–ThITD3** showed two photon absorption (TPA) along with reverse saturable absorption (RSA), thereby the net effect becomes the "effective TPA" process ⁶⁴. The solid line indicates the theoretical fitting and the symbol indicates the experimental data. In all the cases, the data are found to be matching well with the theoretical model for excited state absorption (ESA). Thus, the effective nonlinear absorption coefficient $\alpha(I)$ (including both TPA and ESA) can be written as ⁶⁵,

$$\alpha(I) = \frac{\alpha_o}{1 + I/I_s} + \beta_{eff} I....(3)$$

where, α_0 is the linear absorption coefficient at the excitation wavelength, I_s is the saturation intensity, I is the input laser intensity, β_{eff} is the effective TPA coefficient.

The rate of change in the intensity of a beam as it passes through a medium is given by,

$$\frac{dI}{dz} = -\left(\frac{\alpha_o}{1+\frac{I}{I_s}}\right)I - \beta_{eff}I^2 \dots (4)$$

where, z is the propagation distance within the sample.

Dividing output intensity by input intensity and normalizing it with linear transmittance yielded the normalized transmittance ⁶⁶ and is given by the equation

$$T(z) = \frac{1}{\sqrt{\pi}q_0(z)} \int_{-\infty}^{\infty} \ln\left[1 + q_0(z)e^{-\tau^2}\right] d\tau....(5)$$

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where,
$$q_0(z) = \beta_{eff} I_0 L_{eff} / \left(1 + \frac{z^2}{z_0^2}\right)$$
 and $L_{eff} = \frac{\left(1 - e^{-\alpha_o L}\right)}{\alpha_0}$

As shown in the Fig. 6 a, b and c, the experimental data are in a good agreement with the theoretical simulation and thus the estimated β_{eff} values are 0.49×10^{-10} , 1.05×10^{-10} and 1.55×10^{-10} m W⁻¹ for molecules **ThITD1–ThITD3**, respectively. Under similar excitation conditions many NLO materials have shown effective NLA coefficient in the order of 10^{-10} m W⁻¹. The β_{eff} values obtained in the present study are comparable and better than that of many other organic NLO materials available in the literature (Table 3). Therefore, these materials could act as better optical limiters for high energy devices.



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Fig. 6 OA Z-scan curves of (a) ThITD1, (b) ThITD2 and (c) ThITD3 at 50 µJ.

3.6.2 Optical limiting studies

The optical limiters are the materials which exhibit constant transmission at lower input energy and reduced transmission at higher input energy. These materials find their importance in laser safety devices, mode locking, pulse compression etc. After certain critical value of the input energy, these materials show the limiting action because of NLA and NLR properties of the materials at the threshold value, which ultimately leads to the decrease in the transmittance. The optical limiting is due to the processes such as TPA, ESA, RSA, optically induced heating, nonlinear scattering and free carrier absorption that take place in these types of materials upon irradiation of laser beam ⁴⁴.

The graphs of transmittance versus input fluence which are shown in Fig. 7 a, b and c reveal the optical limiting studies of molecules **ThITD1–ThITD3.** The onset values (input fluence at which the transmittance starts decreasing) are at 1.60, 0.78 and 0.66 J cm⁻² for **ThITD1, ThITD2** and **ThITD3**, respectively. Thus, the molecules could act as protective layers in devices which involve intense laser beam.





Fig. 7 Optical limiting studies of (a) ThITD1, (b) ThITD2 and (c) ThITD3 at 50 µJ.

Table 3 NLO parameters of ThITD1-ThITD3 and few of	comparisons
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Sample	Is	β_{eff}	η_2	χ^3
	10 ¹² (Wm ⁻²)	10 ⁻¹⁰ (mW ⁻¹)	10 ⁻¹¹ (esu)	10 ⁻¹² (esu)

ThITD1	1.39	0.49	2.09	View Article Online 1.63OI: 10.1039/C9NJ01100E
ThITD2	1.50	1.05	5.40	3.29
ThITD3	1.59	1.55	6.57	4.90
(present study)				
Ref. 44	1.78	1.74	8.0	-
Ref. ⁶⁷	-	1.41	-	4.65
Ref. ⁶⁸	-	1.60	-	-
Ref. ⁶⁹	0.98	0.56	-	-

3.6.3 Nonlinear refraction studies

Fig. 8 a, b and c represent normalized closed by open Z–scan curves of the molecules **ThITD1–ThITD3**. The graphs show a change in the transmission with a characteristic peak, followed by a null and a valley as the sample is moved from the input lens towards the output lens through the focus. This is the signature of negative nonlinearity. Due to this effect the molecules **ThITD1–ThITD3** behave like diverging lens when the contact is made with the incoming beam which results in the defocusing of the beam.

The normalized transmittance (T) at closed aperture condition is given by the equation (6) ⁵⁷,

$$T(z,\Delta\Phi_o) = 1 + \frac{4\left(\frac{z}{z_o}\right)}{\left(\left(\frac{z}{z_o}\right)^2 + 1\right)\left(\left(\frac{z}{z_o}\right)^2 + 9\right)}\Delta\Phi_o....(6)$$

where $\Delta \varphi_0$ is the on-axis phase shift at *z*=0.

The real part of third order nonlinear susceptibility is given by,

 $\operatorname{Re} al \chi^{(3)} = 2n_o^2 \varepsilon_o c n_2.$

where n_0^2 is the linear refractive index, *c* velocity of light, ε_0 is the permittivity of free space and the nonlinear refractive index is thus given by,





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Fig. 8 CA Z-scan curves of (a) ThITD1, (b) ThITD2 and (c) ThITD3 at 50 µJ.

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In the present study, the introduction of imidazo[2,1-*b*][1,3,4]thiadiazole as acceptor unit the online between high electron donating thiophene and phenyl moieties improve the rigidity and planarity of the molecules thereby has increased the strength of D–A–D backbone which in turn enhanced the extent of delocalization in the entire molecule. Thus, the synthesized molecules **ThITD1–ThITD3** exhibited substantially improved optical nonlinearity when subjected to the Z–scan analysis, which is due to the presence of donor–acceptor arrangement and π –delocalization in them ^{70,71}.

Further, the stronger electron accepting nature and polarity of rhodanine–3–acetic acid moiety in **ThITD3** than that of cyano groups in **ThITD1** and **ThITD2** increased the rigidity, hyperpolarizability and conjugation length in **ThITD3**, which resulted in larger NLO properties and improved β_{eff} and χ^3 values of **ThITD3** compared to those of **ThITD1** and **ThITD2**. The comparison of obtained NLO parameters of **ThITD1–ThITD3** with a few of the similar works reported is presented in Table 3 and it is understood that the molecules studied would be of potential candidates for optical limiters in photonic devices.

4. Conclusions

Three novel conjugated molecules (**ThITD1–ThITD3**) with thiophene as the donor and imidazo[2,1-*b*][1,3,4]thiadiazole as an acceptor unit were designed and synthesized via simple Knoevenagel condensation reaction. The chemical structures of **ThITD1–ThITD3** were confirmed by ¹H NMR, ¹³C NMR and mass spectroscopic techniques. The high absorption maxima and low LUMO level of **ThITD3** compared to that of **ThITD1** and **ThITD2** are due to the strong electron withdrawing ability of rhodanine–3–acetic acid present in **ThITD3**. The third–order nonlinear optical studies confirmed the effective two photon absorption of the molecules, exhibiting a large third–order nonlinearity with high β_{eff} of the order of 10⁻¹⁰ m W⁻¹ and optical limiting property. The higher β_{eff} value of **ThITD3** compared to that of **ThITD1** and **ThITD2** is confirmed to be originated from the strong New Journal of Chemistry Accepted Manuscript

electron accepting nature of rhodanine– 3–acetic acid moiety which also resulted in rigidity $\beta_{\rm HJ01100E}$ and enhanced π –delocalization in **ThITD3**. The results unveiled that the molecule **ThITD3** could provide a good choice of optical limiters in laser photonics and also advance its development in other optoelectronic/photovoltaic devices.

Associated content

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Supporting Information

¹H NMR, ¹³C NMR and ESI-MS characterizations of molecules **ThITD1–ThITD3** and experimental set up of Z–scan measurements.

Conflicts of interest

There are no conflicts to declare.

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TOC / Graphical Abstract



Depicting optical limiting action of novel imidazo[2,1-*b*][1,3,4]thiadiazole based small molecule (ThITD3), which blocks high irradiance and transmits low–intensity (less harmful) light.