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PII: S0143-7208(19)32587-2

DOI: https://doi.org/10.1016/j.dyepig.2019.108181

Reference: DYPI 108181

To appear in: Dyes and Pigments

Received Date: 5 November 2019

Revised Date: 26 December 2019

Accepted Date: 31 December 2019

Please cite this article as: Kakekochi V, Nikhil P P, Chandrasekharan K, Kumar D U, Impact of donor–acceptor alternation on optical power limiting behavior of H–Shaped thiophene–imidazo[2,1-*b*] [1,3,4]thiadiazole flanked conjugated oligomers, *Dyes and Pigments* (2020), doi: https://doi.org/10.1016/j.dyepig.2019.108181.

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Impact of Donor–Acceptor Alternation on Optical Power Limiting Behavior of H–Shaped Thiophene–Imidazo[2,1-*b*][1,3,4]Thiadiazole Flanked Conjugated Oligomers

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Keywords

Thiophene; HOMO–LUMO energy; Density functional calculations; UV/Vis spectroscopy; Nonlinear optics; Two-photon absorption.

Highlights

- Four novel H-shaped donor-acceptor conjugated oligomers were designed and synthesized.
- Structure-property relationship of the synthesized oligomers was studied in detail.
- The influence of variation in the central core on third-order nonlinear optical properties was also discussed in detail.

TOC / Graphical Abstract



Schematic of two photon absorption (TPA) of H–shaped thiophene–imidazo[2,1*b*][1,3,4]thiadiazole flanked conjugated oligomer **TIPTz**, implying the effective optical limiting performance for sensors and eye protection.

Abstract

A new series of four D–A–D configured conjugated oligomers with H–type structure, possessing two thiophene–imidazo[2,1-*b*][1,3,4]thiadiazole branches and thiophene (**TIT**), thiophene–1,3,4-oxadiazole–thiophene (**TITO**), thiazolo[5,4-*d*]thiazole (**TITz**), phenyl–thiazolo[5,4-*d*]thiazole–phenyl (**TIPTz**) units as central core moieties were efficiently synthesized. These core moieties were specifically selected to increase the planarity, rigidity, stability, extend the π -conjugation and to understand the influence of central core on nonlinear absorption coefficient (β_{eff}) and optical limiting behavior of the synthesized oligomers. The structure-property relationships of these oligomers were established by the optical absorption (UV–Vis), electrochemical (CV) and theoretical (DFT) studies. The "effective two–photon absorption" of oligomers was confirmed by single–beam Z–scan analysis. The exceptional increase in nonlinear response was achieved with the oligomers **TITO** and **TIPTz** with nonlinear absorption coefficient (β_{eff}) of 1.62 and 2.71×10⁻¹⁰ m W⁻¹, and limiting thresholds of 6.02 and 3.14 J cm⁻², respectively, which suggest that these oligomers could be potent materials for practical applications in laser photonics.

1. Introduction

Recently, materials possessing nonlinear optical (NLO) properties have gained high importance because of their remarkable applications in bioimaging, telecommunication, optical memory storage, all-optical switching, dynamic holography and harmonic generators [1–8]. Among a wide category of NLO materials, π -conjugated organic molecules possess

specific advantages over the other materials such as, quick response, large molecular hyperpolarizabilities, large NLO absorption coefficients, exceptional photo-thermal stability, high structural flexibility, easy processing and low cost [9–12]. Moreover, the structures of organic compounds can easily be modified by tuning the electron donors and/or acceptors present in them, resulting in the desired NLO properties [13–16]. On the other hand, the extension of conjugation in organic molecules either by appropriate π –linker or by incorporating suitable donor/acceptor moieties enhances the intramolecular charge transfer (ICT) between the electron donor and acceptor units, which significantly improves the NLO response of organic materials [17,18].

Despite the numerous studies on impact of electron donors on optoelectronic properties, there is a paucity of work on the effect of strong electron acceptors on the performance of donor (D)–acceptor (A) (D–A) type materials. The one acceptor, that has immense applications in optoelectronic industry is 1,3,4–oxadiazole [19]. Lately, 2,5–diaryl–1,3,4–oxadiazoles have been explored as versatile electron transporting materials in optoelectronic field due to their electron–deficient nature, resistance to oxidative degradation, high thermal and hydrolytic stability. Further, they help in extending the conjugation when substituted in D–A type systems [20,21]. In addition, the organic molecules with the fused heterocycles have gained much interest as these molecules could increase the performance when applied in optoelectronics. For an instance, thiazolo[5,4-*d*]thiazole (tztz), a rigid, fused heterocyclic system having the coplanar structure with electron–withdrawing nitrogen atoms forming an imine (C=N-) backbone, also acts as an efficient electron acceptor [22,23]. The small molecules comprising tztz as an electron acceptor unit with either D–A–D or A–D–A structure are utilized as potent optoelectronic/ photovoltaic materials in the recent past [24–28]. However, the structure–property relationship of such molecules is yet to be understood.

In this regard, a series of four H–shaped conjugated oligomers **TIT**, **TITO**, **TITz** and **TIPTz** with thiophene, thiophene–1,3,4–oxadiazole–thiophene, tztz and phenyl–tztz–phenyl units as central cores, respectively and the thiophene–imidazo[2,1-*b*][1,3,4]thiadiazole (**Th–ITD**) moiety at the periphery (**Fig. 1**) are designed and synthesized. The optoelectronic and the third-order NLO properties of the peripheral **Th–ITD** moiety, were discussed in our previous communication [29]. Herein, an attempt has been made to study the effect of structural modifications on the optoelectronic properties of four new oligomers which differ in their central core moieties. In particular, the optical, electrochemical and theoretical studies of **TIT**, **TITO**, **TITz** and **TIPTz** are presented in the following sections.

2. Experimental information

2.1 Synthetic procedures

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

The intermediate (3) was synthesized following the procedure mentioned in the literature [29].

2.1.2 Synthesis of 2-(thiophen-2-yl)imidazo[2,1-b][1,3,4]thiadiazol-6-ol (5)

The intermediate (**5**) was synthesized following the procedure mentioned in the literature [29] using the precursors **3** (5 g, 27.28 mmol) and 4–hydroxy phenacyl chloride (5.58 g, 32.74 mmol). (off–white solid, 7.27 g, yield: 89%). ESI–MS (*m*/*z*) calcd. for C₁₄H₉N₃OS₂: 299.02, found: 300.00 [M+H]⁺; ¹H NMR (400 MHz, DMSO–*d*₆) δ (ppm): 9.51 (s, 1H, –OH), 8.49 (s, 1H, Ar–H), 7.91–7.89 (m, 1H, Ar–H), 7.83–7.82 (m, 1H, Ar–H), 7.66 (d, *J* = 8.0 Hz, 2H, Ar–H), 7.26–7.24 (m, 1H, Ar–H), 6.78 (d, *J* = 8.0 Hz, 2H, Ar–H); ¹³C NMR (100 MHz, DMSO–*d*₆) δ (ppm): 157.5, 155.3, 146.2, 143.9, 132.0, 131.5, 130.8, 129.1, 126.5, 125.0, 115.9, 109.4; Anal. calcd. for C₁₄H₉N₃OS₂: C, 56.17; H, 3.03; N,14.04; S, 21.42; found: C, 56.02; H, 3.15; N,14.16; S, 21.47.

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

The intermediate **5** (4 g, 13.36 mmol) and anhydrous potassium carbonate (5.53 g, 40.08 mmol) were added to N,N–dimethylformamide (DMF) (20 mL) and the mixture was stirred at room temperature (RT) for 0.5 h. Later, 1–bromodecane (4.15 mL, 20.04 mmol) was added slowly to the above mixture and heated at 80°C for 12 h. The reaction mixture was quenched using cold distilled water. The obtained solid was filtered and purified using column chromatography using a mixture of pet ether/ethyl acetate (9:1, v/v) as eluent to get (**6**) as a yellow solid (5.34 g, yield: 91%). ESI–MS (*m*/*z*) calcd. for C₂₄H₂₉N₃OS₂: 439.18, found: 440.10 [M+H]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.91 (s, 1H, Ar–H), 7.73 (d, *J* = 8.0 Hz, 2H, Ar–H), 7.54–7.52 (m, 2H, Ar–H), 7.15–7.13 (m, 1H, Ar–H), 6.94 (d, *J* = 8.0 Hz, 2H, Ar–H), 3.98 (t, *J* = 6.8 Hz, 2H, –OCH₂), 1.81–1.27 (m, 16H, –CH₂), 0.87 (t, *J* = 7.2 Hz, 3H, – CH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm):158.9, 155.1, 146.4, 144.3, 132.5, 129.6, 128.9, 128.0, 126.3, 126.0, 114.7, 108.4, 68.0, 31.8, 29.5, 29.5, 29.4, 29.3, 29.2, 26.0, 22.6, 14.1; Anal. calcd. for C₂₄H₂₉N₃OS₂: C, 65.57; H, 6.65; N,9.56; S, 14.58; found: C, 65.49; H, 6.67; N,9.52; S, 14.64.

2.1.4 Synthesis of 6–(decyloxy)–2–(thiophen–2–yl)imidazo[2,1–*b*][1,3,4]thiadiazole–5– carbaldehyde (7)

The intermediate (**7**) was synthesized following the procedure mentioned in the literature [29] using a freshly distilled DMF (1.05 mL, 13.64 mmol), phosphorus oxychloride (POCl₃) (1.27 mL, 13.64 mmol) and intermediate **6** (3 g, 6.82 mmol). (yellow solid, 2.74 g, yield: 86%). ESI–MS (*m*/*z*) calcd. for C₂₅H₂₉N₃O₂S₂: 467.17, found: 468.10 [M+H]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.09 (s, 1H,–CHO), 7.88 (d, *J* = 8.0 Hz, 2H, Ar–H), 7.64–7.59 (m, 2H, Ar–H), 7.18–7.16 (m, 1H, Ar–H), 7.01 (d, *J* = 9.2 Hz, 2H, Ar–H), 4.02 (t, *J* = 6.8 Hz, 2H, – OCH₂), 1.81–1.27 (m, 16H, –CH₂–), 0.87 (t, *J* = 7.2 Hz, 3H, –CH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 177.3, 160.7, 157.4, 155.8, 149.8, 131.6, 130.7, 130.4, 129.8, 128.1, 124.4, 123.6, 114.7, 68.1, 31.8, 29.5, 29.3, 29.1, 26.0, 22.6, 14.1; Anal. calcd. for C₂₅H₂₉N₃O₂S₂: C, 64.21; H, 6.25; N,8.99; S, 13.71; found: C, 64.30; H, 6.19; N,8.92; S, 13.78.

The procedures for the synthesis of intermediates 9–21 are provided in ESI (section S 2.1–S 2. 10).

2.1.5 2,5-bis((E)-2-(6-(4-(decyloxy)phenyl)-2-(thiophen-2-yl)imidazo[2,1b][1,3,4]thiadiazol-5-yl)vinyl)thiophene (TIT)

The intermediates **10** (0.5 g, 0.52 mmol) and **7** (0.49 g, 1.05 mmol) were dissolved in a mixture of chloroform and ethanol (1:1), to which, a freshly prepared solution of sodium ethoxide (89.3 mg, 8.11 mmol in 3 mL of ethanol) was added drop wise in argon atmosphere and the mixture was stirred at RT for 12 h. The excess of solvent was removed under reduced pressure and the residue was purified by column chromatography using a mixture of pet ether/ethyl acetate (8:2, v/v) to get the compound **TIT** as an orange colored solid (0.52 g, yield: 83%). MALDI–TOF–MS (*m*/*z*) calcd. for C₅₆H₆₂N₆O₂S₅: 1011.452, found: 1012.346 [M+H]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.89 (s,1H, Ar–H), 7.85 (s,1H, Ar–H), 7.68(d, *J* = 8.0 Hz, 4H, Ar–H), 7.60–7.56 (m, 4H, Ar–H), 7.19–7.16 (m, 2H, Ar–H), 7.11 (s, 1H, Ar–H), 7.07 (s, 1H, Ar–H), 7.05–7.03 (m, 6H, Ar–H), 4.03 (t, *J* = 8.0 Hz, 4H, –OCH₂), 1.86–1.81 (m, 4H, –CH₂–), 1.79–1.47 (m, 7H, –CH₂–), 1.34–1.28 (m, 21H, –CH₂–), 0.88 (t, *J* = 8.0 Hz, 6H, –CH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 159.0, 154.8, 145.2, 145.1, 142.2, 132.6, 129.7, 129.4, 129.0, 128.0, 127.1, 126.7, 121.7, 121.5, 114.8, 113.7, 68.1, 31.9, 29.6, 29.5, 29.4, 29.3, 26.1, 22.6, 14.1; Anal. calcd. for C₅₆H₆₂N₆O₂S₅: C, 66.50; H, 6.18; N, 8.31; S, 15.85; found: C, 66.58; H, 6.09; N, 8.43; S, 15.97.

2.1.6 2,5-bis(5-((E)-2-(6-(4-(decyloxy)phenyl)-2-(thiophen-2-yl)imidazo[2,1b][1,3,4]thiadiazol-5-yl)vinyl)thiophen-2-yl)-1,3,4-oxadiazole (TITO)

Similar procedure was followed for the synthesis of **TITO** in which intermediate **16** (0.5 g, 0.63 mmol) was reacted with intermediate **7** (0.59 g, 1.26 mmol) (0.52 g, yield: 85%). MALDI–TOF–MS (*m*/*z*) calcd. for C₆₂H₆₄N₈O₃S₆: 1160.343, found:1159.100 [M]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.89 (s, 1H, Ar–H), 7.85 (s, 2H, Ar–H), 7.80–7.60 (m, 3H, Ar–H), 7.57–7.48 (m, 2H, Ar–H), 7.42–7.39 (m, 3H, Ar–H), 7.22–7.15 (m, 3H, Ar–H), 7.14–7.00 (m, 3H, Ar–H), 6.96–6.93 (m, 2H, Ar–H), 6.89–6.78 (m, 2H, Ar–H), 6.75–6.72 (m, 1H, Ar–H), 4.06 (t, *J* = 8.0 Hz, 2H, –OCH₂), 3.95 (t, *J* = 8.0 Hz, 2H, –OCH₂), 1.86–1.83 (m, 4H, –CH₂–), 1.76–1.58 (m, 5H, –CH₂–), 1.50–1.42 (m, 4H, –CH₂–), 1.30–1.27 (m, 19H, –CH₂–), 0.88 (t, *J* = 8.0 Hz, 6H, –CH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 160.0, 159.9, 159.3, 158.9, 154.6, 148.3, 145.8, 144.8, 144.5, 132.6, 132.4, 130.4, 129.8, 129.5, 129.3, 128.9, 128.7, 128.5, 128.0, 127.8, 126.8, 126.3, 124.7, 121.1, 119.7, 118.0, 116.6, 114.9, 114.5, 68.1, 68.0, 31.8, 29.5, 29.3, 26.0, 22.6, 14.1; Anal. calcd. for C₆₂H₆₄N₈O₃S₆: C, 64.11; H, 5.55; N, 9.65; S, 16.56; found: C, 64.23; H, 5.42; N, 9.58; S, 16.67.

2.1.7 Synthesis of 2,5-bis(6-(4-(decyloxy)phenyl)-2-(thiophen-2-yl)imidazo[2,1b][1,3,4]thiadiazol-5-yl)thiazolo[5,4-d]thiazole (TITz)

The oligomer **TITz** was synthesized following the procedure for intermediate (**19**) (ESI), using the intermediate **7** (0.5 g, 1.06 mmol) and dithiooxamide (0.064 g, 0.53 mmol) (yellow crystals, 0.44 g, yield: 41%). MALDI–TOF–MS (*m/z*) calcd. for $C_{52}H_{56}N_8O_2S_6$: 1016.285, found: 1016.989 [M+H]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.96 (d, *J* = 8.0 Hz, 4H, Ar–H), 7.65 (d, *J* = 4.0 Hz, 2H, Ar–H), 7.60 (d, *J* = 8.0 Hz, 2H, Ar–H), 7.20–7.18 (m, 2H, Ar–H), 6.99 (d, *J* = 8.0 Hz, 4H, Ar–H), 4.03 (t, *J* = 8.0 Hz, 4H, –OCH₂), 1.84–1.80 (m, 5H, – CH₂–), 1.50–1.46 (m, 4H, –CH₂–), 1.38–1.28 (m, 23H, –CH₂–), 0.87 (t, *J* = 8.0 Hz, 6H, – CH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 159.7, 156.2, 155.8, 147.2, 145.4, 132.2, 130.4, 130.2, 129.4, 129.2, 128.1, 125.7, 118.7, 114.2, 68.0, 31.8, 29.5, 29.4, 29.2, 26.0, 22.6, 14.0; Anal. calcd. for C₅₂H₅₆N₈O₂S₆: C, 61.39; H, 5.55; N, 11.01; S, 18.91; found: C, 61.48; H, 5.51; N, 11.13; S, 18.86.

2.1.8 Synthesis of 2,5-bis(4-((E)-2-(6-(4-(decyloxy)phenyl)-2-(thiophen-2-yl)imidazo[2,1-b][1,3,4]thiadiazol-5-yl)vinyl)phenyl)thiazolo[5,4-d]thiazole (TIPTz)

The compound **TIPTz** was synthesized following the procedure mentioned for **TIT**, using intermediates **21** (0.5 g, 0.497 mmol) and **7** (0.46 g, 0.995 mmol) (0.49 g, yield: 82%). MALDI–TOF–MS (m/z) calcd. for C₆₈H₆₈N₈O₂S₆: 1221.706, found:1222.723 [M+H]⁺; ¹H

NMR (400 MHz, CDCl₃) δ (ppm): 7.97 (d, J = 8.0 Hz, 4H, Ar–H), 7.83 (s, 1H, Ar–H), 7.79 (s, 1H, Ar–H), 7.68 (d, J = 8.0 Hz, 4H, Ar–H), 7.60–7.58 (m, 7H, Ar–H), 7.40–7.36 (s, 3H, Ar–H), 7.20–7.18 (m, 2H, Ar–H), 7.04 (d, J = 8.0 Hz, 4H, Ar–H), 4.04 (t, J = 8.0 Hz, 4H, – OCH₂), 1.87–1.80 (m, 4H, –CH₂–), 1.52–1.46 (m, 5H, –CH₂–), 1.31–1.25 (m, 23H, –CH₂–), 0.89 (t, J = 8.0 Hz, 6H, –CH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 159.1, 145.4, 132.6, 129.6, 129.5, 128.9, 128.4, 128.0, 126.8, 126.6, 125.8, 121.8, 115.6, 114.7, 114.4, 68.1, 31.8, 29.6, 29.5, 29.3, 29.2, 26.0, 22.6, 14.0; Anal. calcd. for C₆₈H₆₈N₈O₂S₆: C, 66.85; H, 5.61; N, 9.17; S, 15.75; found: C, 66.93; H, 5.70; N, 9.06; S, 15.68.

The characterization details for the selected intermediates and final compounds are given in ESI.



Fig. 1. Chemical structures of four oligomers TITz, TIT, TITO and TIPTz.





Scheme 1. Synthetic pathways for the oligomers TITz, TIT, TITO and TIPTz. Reagents and reaction conditions: (a) POCl₃, 70°C, 0.5 h, yield: 94%; (b) C₂H₅OH, 80°C, 24 h, yield: 89%; (c) 1–Bromodecane, K₂CO₃, DMF, RT– 85°C, 12 h, yield: 91%; (d) POCl₃, DMF, 0– 60°C, 6 h, yield: 86%; (e) NBS, AIBN, Benzene, 75°C, 2 h, yield: 64–74%; (f) Triphenylphosphine, DMF, 85°C, 12 h, yield: 78–90%; (g) SOCl₂, 0°C– RT, 4 h, yield: 94%; (h) Hydrazine hydrate, triethylamine, NMP, RT, 8 h, yield: 94%; (i) POCl₃, 75°C, 3 h, yield: 78%; (j) DMF, 160°C, 5 h, yield: 41–55%; (k) C₂H₅ONa, CHCl₃, C₂H₅OH, RT, 12 h, yield: 82–85%.

3. Results and discussion

3.1 Synthesis

The thiophene substituted moiety, intermediate (5), obtained by the cyclization of intermediate (3) with 4–hydroxy phenacyl chloride, was alkylated to yield intermediate (6). In the alkylation step, the decyl chain was selected as alkylating agent to improve the solubility in different organic solvents. Later, which was formylated via well-known Vilsmeier-Haack reaction to achieve the intermediate (7). On the other hand, three different Wittig salts (10, 16 and 21) with the different conjugations were synthesized using multistep synthesis as mentioned in the Scheme 1. Finally, the intermediate (7) was reacted with dithiooxamide and the Wittig salts 10, 16 and 21 to yield TITz, TIT, TITO and TIPTz, respectively. All the intermediates and final molecules were characterized using ¹H NMR, ¹³C NMR and mass spectral analyses (ESI).

3.2 Optical properties

The normalized UV-vis and PL spectra of TIT, TITO, TITz and TIPTz are shown in Fig. 2 and the corresponding spectral data are listed in Table 1. As it is seen in Fig. 2, there are three absorption bands situated between 260–500 nm region for each of the four oligomers. The absorption bands observed at higher energy regions (260-340 nm) are attributed to the π - π * transitions of the aromatic conjugated skeleton, whereas, those at lower energy (400-460 nm) region are ascribed to the ICT from the electron donor to the acceptor moieties. The maximum absorption peaks (λ_{max}) of **TIT**, **TITO**, **TITz** and **TIPTz** are observed at 429, 451, 408 and 438 nm, respectively. Moreover, the introduction of 1,3,4-oxadiazole, a strong electron acceptor moiety, to the central core is considerably shifting the absorption maximum of **TITO** to higher wavelength region due to stronger donor-acceptor interaction [30] when compared to that of TIT, where, only thiophene moiety is present in the central core. Similarly, there is a considerable red shift in the absorption maximum of **TIPTz** compared to that of **TITz** due to the introduction of phenyl group (π -linker) to the central part, which increases the donor-acceptor interaction in TIPTz, causing the extension of conjugation. Further, the fluorescence emission spectra were recorded by exciting the oligomers at their excitation wavelengths. All the four oligomers exhibited single emission peak in the 500-540 nm region, with the green light emission in solution state. The optical band gaps (Eg) calculated from the intersection of normalized absorption and emission spectra were 2.63, 2.46, 2.66 and 2.55 eV for TIT, TITO, TITz and TIPTz, respectively. The extended π - conjugation in **TITO** and **TIPTz** has considerably reduced the E_g of **TITO** and **TIPTz** compared to that of **TIT** and **TITz**.



Fig. 2. Normalized UV–vis absorption and PL emission spectra of TIT, TITO, TITz and TIPTz in chloroform (10^{-5} M) .

 Table 1 Summary of optical, electrochemical and theoretical data of TIT, TITO, TITz and

 TIPTz.

Oligomers	$\lambda_{max}^{abs}(nm)$	λ^{pl}_{max} (nm)	E _g (eV)	E ^{ox} onset(V)	HOMO (eV)	LUMO (eV)
					h	2
TIT	429	512	2.63^{a}	0.54	-5.08°	-2.45°
			2 46 ^d		-4 52 ^d	-2.06^{d}
			2.40		4.52	2.00
ΤΙΤΟ	451	540	2.46 ^a	0.66	-5.20^{b}	-2.74°
			2.64 ^d		-4.84^{d}	-2.20^{d}
TITz	408	503	2.66 ^a	0.60	-5.14 ^b	-2.48°
			3.06 ^d		-5.08^{d}	-2.02^{d}
TIPTz	438	537	2.55 ^a	0.55	-5.09 ^b	-2.54 ^c
			2.64 ^d		-4.83 ^d	-2.19^{d}

^a Optical band gap calculated from the intersection of normalized absorption and emission spectra.

E^{ox}_{onset} Experimental onset oxidation potential vs SCE.

^b Experimental values from CV using equation (1) with Fc/Fc⁺ as internal standard.

^c Experimental values using equation (2).

^d Theoretical results.

3.3 Electrochemical studies

Cyclic voltammetry (CV) was carried out to determine the energy levels of the oligomers. **Fig. 3a–d** represent the cyclic voltammograms of **TIT**, **TITO**, **TITz** and **TIPTz**, respectively. The onset oxidation potentials of the oligomers are at 0.54, 0.66, 0.60 and 0.55 V vs saturated calomel electrode (SCE) for **TIT**, **TITO**, **TITz** and **TIPTz**, respectively. Using the equation (1), the highest occupied molecular orbital (HOMO) energy levels were determined to be -5.08, -5.20, -5.14 and -5.09 eV for **TIT**, **TITO**, **TITz** and **TIPTz**, respectively.

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

where, E_{onset}^{ox} and E_{FOC} are the onset of oxidation potentials of the oligomers and ferrocene ($E_{FOC} = 0.27$ V vs SCE (Fig. S28, ESI)), respectively, -4.8 eV is the HOMO energy level of ferrocene against vacuum.

Similarly, using the equation (2) the lowest unoccupied molecular orbital (LUMO) energy levels of the molecules were calculated to be -2.45, -2.74, -2.48 and -2.54 eV for **TIT**, **TITO**, **TITZ** and **TIPTZ**, respectively.

There is a slight increase in the HOMO energy levels of **TIT** and **TIPTz** when compared to that of **TITO** and **TITz**. This increment is attributed to the presence of thiophene in **TIT** and phenyl group in **TIPTz** in the central core as electron donor and π -linker, respectively [31], while, the decrease in the LUMO level of **TITO** compared to that of **TIT**, **TITz** and **TIPTz** is due to the presence of strong electron withdrawing 1,3,4–oxadiazole moiety in **TITO** [32]. The results of CV studies and the values of energy levels are summarized in **Table 1**.



Fig. 3. Cyclic voltammograms of (a)**TIT**, (b) **TITO**, (c) **TITz** and (d) **TIPTz** recorded in CH₃CN solutions containing 0.1 M Bu₄N(ClO₄) as supporting electrolyte at a scan rate of 100 mV s⁻¹ using SCE as reference electrode, Pt wire as counter electrode and material coated glassy carbon as working electrode. The inset shows enlarged image of the oxidation peak in the anodic region.

3.4 Theoretical studies

To gain further insight of the molecular orbital distribution and excited state transition, DFT and TD–DFT calculations were carried out. The long alkoxy chains were considered as methoxy groups in order to reduce the calculation time. As shown in the **Fig. 4**, both the HOMO and LUMO electrons are mainly populated on vinylic linkage and central part of the system in **TIT**, **TITO**, **TITz** and **TIPTz**. The HOMO distribution is further extended on the imidazole and decyloxy substituted phenyl ring of the terminal groups, whereas, the LUMO is mostly distributed on thiophene and imidazo[2,1-*b*][1,3,4]thiadiazole ring of the peripheral group and also, distribution suggests the balanced charge transfer process within the system [33]. The theoretical HOMO/LUMO values are given in **Table 1**. Further, the simulated absorption spectra of **TIT**, **TITO**, **TITz** and **TIPTz** are shown in the **Fig. 5**. There exist two absorption bands, the one at lower energy region corresponds to charge transfer transition and the other at higher energy region is due to π - π * transition. In general, the tiny discrepancy is

attributed to the theoretical overestimation. Nevertheless, the trend remains same and theoretical results are in good agreement with the experimental results.

The presence of long decyloxy chain causes the twisting of the decyloxy substituted phenyl group by an angle of ~32° from thiophene–imidazo[2,1-*b*][1,3,4]thiadiazole plane of peripheral **Th–ITD** moiety in all the four oligomers. The dihedral angle between the central core and the peripheral moiety is 9.8°, 9.5° and 10.4° in **TIT**, **TITO** and **TIPTz**, respectively. The presence of vinylic bond between the central core and the peripheral moiety in **TIT**, **TITO** and **TIPTz** reduces the steric hindrance between the central core and the peripheral moiety in **TIT**, **TITO** and **TIPTz** reduces the steric hindrance between the central core and the peripheral moiety in **TIT**, **TITO** and **TIPTz** reduces the steric hindrance between the central core and the peripheral moiety which is confirmed by the least dihedral angles (**Fig. S30**), whereas, in the case of **TITz** the two peripheral **Th–ITD** moieties are present orthogonal to each other with a dihedral angle of 36° between the central core and the peripheral moiety. This is due to the steric effects of imidazo[2,1-*b*][1,3,4]thiadiazole and tztz moieties, resulting from the direct bond present between them (**Fig. S31**). In all the four oligomers, the **Th–ITD** plane is present 90° to the plane of central unit, giving a H–shaped structure. As it is seen from the optimized geometry of **TITO** and **TIPTz**, the higher degree of conjugation decreases the twisting due to steric effects between the side groups and the central unit, providing a perfect H–shaped structure. The dihedral angles and the optimized geometries are shown in **Fig. S29**.







Fig. 5. Simulated absorption spectra of TIT, TITO, TITz and TIPTz.

3.5 Thermal properties

Thermo gravimetric analysis (TGA) was carried out to measure the thermal stability of the oligomers. **Fig. 6** represents the graph of weight loss as a function of temperature of **TIT**, **TITO**, **TITz** and **TIPTz**. As it is seen from the plot, the onset of decomposition temperature (T_d) corresponding to a 5% weight loss for **TIT** and **TITO** are 370 and 384°C, respectively and that corresponding to a 20% weight loss for **TITz** and **TIPTz** are 378 and 348°C, respectively. Further, there is a minor decomposition at 183 and 115°C observed for **TITz** and **TIPTz**, which is attributed to the decomposition of central units of **TITz** and **TIPTz**, respectively. Between **TIT** and **TITO**, **TITO** exhibits higher T_d , which is ascribed to the extended D–A–D structure with the presence of thermally stable 2,5–disubstituted–1,3,4– oxadiazole in the central unit. However, the higher T_d of **TITz** compared to that of **TIPTz** is due to the direct attachment of central tztz unit to the partially rigid imidazo[2,1-*b*][1,3,4]thiadiazole moiety of the terminal group in **TITz**, making the oligomer structurally more rigid compared to **TIPTz**. All the four oligomers exhibited good thermal stability, which revealed the suitability of these materials for practical application in optoelectronics.



Fig. 6. TGA plots of TIT, TITO, TITz and TIPTz.

3.6 Third–order NLO studies

3.6.1 Nonlinear absorption (NLA) properties

In the present study, Z-scan with the single-beam technique was used to investigate the third-order NLO coefficients of the synthesized thiophene-based oligomers[34]. The open aperture (OA) and the closed aperture (CA) Z-scan patterns of the oligomers in chloroform solution were measured at a wavelength of 532 nm laser beam with a pulse width of 7 ns. The oligomers were excited at an energy of 50 μ J (on-axis intensity of 1.386 GW cm⁻²) with a linear transmittance maintained at 70-72% (experimental details are given in ESI, section S4). The OA Z-scan traces of the oligomers TIT, TITO, TITz and TIPTz are shown in the Fig. 7a–d, respectively. As shown in the Fig. 7a–d, there is a decrease in the transmittance as the samples were moved near to the focus and reaches a minimum value at the focus, displaying a deep transmittance trough near the focal plane which is the signature of reverse saturable absorption (RSA). Further, on the nanosecond time scale this RSA is combined with two photon absorption (TPA) and excited state absorption (ESA), collectively called as "effective TPA" process [35,36]. The experimental results are matching well with the theoretical model for effective TPA process in all the samples. Thus, the effective nonlinear absorption coefficient ($\alpha(I)$), the nonlinear propagation equation (dI/dz), the normalized transmittance (T(z)) and finally, the imaginary part of third order nonlinear susceptibility (im $\chi^{(3)}$) for open aperture configuration were determined using the equations S1–S4,

respectively. The NLA parameters were obtained by fitting the experimental data to the theoretical model using equation S1 and S3. All the calculated NLA coefficients are listed in **Table 2**.

The numerically estimated effective TPA coefficient (β_{eff}) values are 0.52×10⁻¹⁰, 1.62×10⁻¹⁰, 1.55×10^{-10} and 2.71×10^{-10} m W⁻¹ for TIT, TITO, TITz and TIPTz, respectively. These obtained β_{eff} values are very much closer and predominantly higher than that reported in the literature (Table 2). For example, under the similar condition, in our previous communication, the Th-ITD based derivatives which exhibited excellent NLO properties with β_{eff} value of 1.55×10^{-10} m W⁻¹ for one of the molecules is reported [29]. The NLO properties of quinacridone derivatives were studied by Jia et al. [37], which showed notable NLO responses with β_{eff} of 0.76×10^{-10} m W⁻¹. Gowda *et al.* [38,39] synthesized 3,4ethylenedioxythiophene (EDOT) based bent-core and hockey stick like liquid crystals and studied the effect of metal nanoparticles (gold/silver), dispersed in phthalocyanine discotic liquid crystal matrix, which exhibited large optical nonlinear properties with β_{eff} of 0.56 and 2.5×10⁻¹⁰ m W⁻¹, respectively. Edappadikkunnummal et al. [40] synthesized phenothiazinegold nanoparticles by laser ablation method and studied the third-order NLO properties, which exhibited significant enhancement in NLA with β_{eff} of 1.7×10^{-10} m W⁻¹. Gopi *et al.* [41] synthesized new quinoxaline based push-pull molecules with 1,3-indandione as acceptor and investigated the NLO properties of the molecule, which showed an effective TPA with very high β_{eff} of 2.0×10⁻¹⁰ m W⁻¹. Zhang *et al.* [42] studied the NLO and optical limiting properties of graphene oxide-Fe₃O₄ hybrid material, which showed an enhanced β_{eff} of 2.6×10^{-10} m W⁻¹. Therefore, all the aforementioned studies involve uses of one or the other dopant for the enhancement of nonlinear response but the observed phenomenal increment in the nonlinear responses in the present study without any dopants, of the synthesized oligomers suggests that these oligomers would serve as effective optical limiters for sensors and eye protection.



Fig. 7. OA Z-scan curves of (a) TIT, (b) TITO, (c) TITz and (d) TIPTz at 50 µJ.

3.6.2 Optical limiting studies

An optical limiter (OL) is a material which exhibits linear transmittance at low input intensities and becomes slightly opaque at high input intensities. An optical limiter keeps the output transmitted fluence below some specified maximum value regardless of the magnitude of the input powers. The materials which exhibit at least one of the nonlinear optical processes viz., NLA, nonlinear refraction (NLR), nonlinear scattering (NLS), optically induced phase transitions and photo refraction (PR) show optical limiting action. The optical limiting devices found applications most importantly in the protection of human eyes and sensitive optical sensors/components from laser damage. Further, there are other potential applications such as laser power regulation, restoration of signal levels in optical data transmission and logic systems.

In order to explain the optical limiting properties of the present oligomers, graphs of input fluence versus the normalized transmission of pulse intensity of **TIT**, **TITO**, **TITz** and **TIPTz** were plotted and is shown **Fig. 8a–d**, respectively. The onset values of limiting action (the value of input fluence at which the transmission of output pulse intensity starts decreasing) are 0.349, 0.231, 0.270 and 0.151 J cm⁻² for **TIT**, **TITO**, **TITz** and **TIPTz**, respectively and the limiting threshold (LT) values (the value of input fluence at which the

output pulse intensity becomes half of the initial value) are 6.02, 4.51 and 3.14 J cm⁻² for **TITO**, **TITz** and **TIPTz**, respectively. Such a low onset and LT values of the synthesized oligomers infer that these materials would be powerful candidates in optical power limiting devices. The oligomer **TIT** did not show LT, as the output transmittance did not reach 50 % of its initial value at the input fluence used.



Fig. 8. Optical power limiting studies of (a) TIT, (b) TITO, (c) TITz and (d) TIPTz at 50

μJ.

Table 3 Comparison of NLA and NLR parameters of **TIT**, **TITO**, **TITz** and **TIPTz** with similar work reported.

Sample	$\frac{\beta_{eff} (\times 10^{-10}}{m W^{-1}})$	η ² (esu)	χ^{3} (esu) (10 ⁻¹²)	References
TIT	0.52	4.1637×10 ⁻¹¹	1.69375	This work
TITO	1.62	6.4593×10 ⁻¹¹	5.16077	This work
TITz	1.55	5.8669×10 ⁻¹¹	4.95886	This work
TIPTz	2.71	8.4294×10 ⁻¹¹	8.55506	This work



3.6.3 Nonlinear refraction (NLR) properties

The CA Z–scan was performed to determine both the magnitude and sign of the NLR. The pure NLR trace was obtained by dividing CA data by OA data to avoid the contribution of NLA and the corresponding plots of **TIT**, **TITO**, **TITz** and **TIPTz** are shown in **Fig. 9a–d**, respectively. All the four oligomers show negative nonlinearity and exhibit peak-valley pattern which are associated with the self-defocusing nature of the oligomers. The normalized transmittance (T) at CA condition, the real part of third order nonlinear susceptibility (real $\chi^{(3)}$) and the nonlinear refractive index (η_2) were fitted using equations S5–S7, respectively. The data of NLR coefficients are summarized in **Table 2**.



Fig. 9. CA Z-scan curves of (a) TIT, (b) TITO, (c) TITz and (d) TIPTz at 50 µJ.

In the present study, introduction of strong electron acceptor groups such as 1,3,4–oxadiazole (**TITO**) and thiazolo[5,4–d]thiazole (**TIPTz**), between the electron rich groups (thiophene in **TITO** and phenyl in **TIPTz**) at the central position of conjugated backbone ameliorated the planarity of the oligomers which extended the π –electron delocalization over the entire conjugated system and improved the effective charge transfer between the donor and acceptor groups which in turn increased the polarizability of the oligomers. And the cyclic groups (**ITD**) present at the peripheral position of the oligomers have improved the rigidity and strengthened the molecular backbone [43]. As a result, the oligomers **TITO** and **TIPTz** exhibited predominant increment in the NLO properties (enhanced β_{eff} of the order 10^{-10} , considerably low onset of limiting action and LT) compared to that of **TIT** and **TITz**. The enhanced conjugation facilitated by D–A–D framework of all the four oligomers substantially improved their NLO characteristics, as confirmed by Z–scan analysis.

4. Conclusion

In summary, four new D–A–D type, multi-heterocyclic conjugated oligomers were synthesized and characterized. The influence of incorporation of different donor–acceptor groups in the central unit on the optoelectronic properties and the energy levels of the molecules is confirmed. The red shift of the absorption and emission maxima of **TITO** and **TIPTz**, is due to the presence of 1,3,4–oxadiazole and thiazolo[5,4–*d*]thiazole units in **TITO** and **TIPTz**, respectively. Similarly, the increase in the HOMO level of **TIT** and **TIPTz**, is due to the electron rich thiophene and phenyl groups (π –spacer) present in the central position of the **TIT** and **TIPTz**, respectively. And all the four oligomers exhibited high thermal stability of >350°C. All the four oligomers exhibited an effective two photon absorption with tremendous increment in the β_{eff} of the order of 10^{-10} . The **TITO** and **TIPTz** exhibited improved ICT and high polarization with high β_{eff} of 1.62 and 2.71×10⁻¹⁰ m W⁻¹, very low onset of limiting of 0.231 and 0.151 J cm⁻² and limiting thresholds of 6.02 and 3.14 J cm⁻², respectively. The attractive NLO responses of the **TITO** and **TIPTz** proved that these oligomers could be excellent candidates for all-optical limiting and opto-electronic device applications.

Associated content

Supporting Information.

Includes materials and methods, synthetic procedures of intermediates 9-21, characterization details, spectral characterizations of selected intermediates and final oligomers, experimental set up of Z–scan measurements and the equations used for the theoretical fitting of Z–scan experimental data.

Conflicts of interest

None.

Acknowledgement

Authors are thankful to SERB (SB/FT/CS-145/2012), DST INDIA for financial support and department of Chemical Engineering, NITK, Surathkal for TGA facility.

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Please make the following change:

Please replace "Table 3" with Table 2 and the caption for Table 2 (which was written as Table 3 in page no:18, line:1059) is as follows

Table 2 Comparison of NLA and NLR parameters of **TIT**, **TITO**, **TITz** and **TIPTz** withsimilar work reported.

Sample	$\frac{\beta_{eff}(\times 10^{-10})}{mW^{-1}}$	η^2 (esu)	χ^3 (esu) (10 ⁻¹²)	References
TIT	0.52	4.1637×10 ⁻¹¹	1.69375	This work
ΤΙΤΟ	1.62	6.4593×10 ⁻¹¹	5.16077	This work
TITz	1.55	5.8669×10 ⁻¹¹	4.95886	This work
TIPTz	2.71	8.4294×10 ⁻¹¹	8.55506	This work
HOOC	1.55	6.57×10^{-11}	4.90	[29]
$\mathbb{C} - \langle \mathbb{C} \rangle - \langle \mathbb{C} \rangle$				
	0.76	6.27×10^{-19}	4.423	[37]
CH-O-ORO-OCH	0.56	-	-	[39]
Phenothiazine–Gold	1.74	8.0×10 ⁻¹¹	-	[40]
(Au) nanocomposite				
phthalocyanine–0.5%	2.5	-	-	[38]
matrix				
Ó, c. Ó, c. j. Ó c. Ó-c. j.o	2.0	-	-	[41]
Graphene oxide–	2.6	-	-	[42]

 Fe_3O_4

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Highlights

- Four novel H-shaped donor-acceptor conjugated oligomers were designed and synthesized.
- Structure-property relationship of the synthesized oligomers was studied in detail.
- The influence of variation in the central core on third-order nonlinear optical properties was also discussed in detail.

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Author statement

Viprabha Kakekochi: Designed the scheme, synthesized and characterized the compounds and prepared the original draft.

Nikhil P P and Keloth Chandrasekharan: Performed nonlinear optical analysis and carried out the theoretical fitting of NLO measurements.

Udaya Kumar D: Supervised and reviewed the original draft.

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

 \boxtimes The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

No conflict of interest.

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