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Facile synthesis and exploration of excited state assisted two-photon property of D-A-D type thiophene-pyridine derivatives

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Keywords

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Pyridine; HOMO–LUMO energy; Density functional calculations; UV/Vis spectroscopy; thermal stability; two–photon absorption; Nonlinear optics.

Abstract

A series of trigonal-shaped molecules (**TPyT** and **TPyP**) and polymer (**P2TPy**) with donor– acceptor–donor (D–A–D) structural arrangement was designed with thiophene and 2,4,6trisubstituted pyridine as the backbone i.e., 4-(4-(decyloxy)phenyl)-2,6-di(thiophen-2yl)pyridine core structure, for the first time and synthesized via microwave assisted one pot reaction. The extension of conjugation of the system by substituting thiophene acrylonitrile (**TPyT**) and phenyl acrylonitriles (**TPyP** and **P2TPy**) via low cost condensation reactions improved the linear optical, electronic and thermal properties of the synthesized compounds. Further, the nonlinear absorption (NLA) was also enriched appreciably by increasing the conjugation. The three compounds showed "effective two–photon absorption" phenomenon with the NLA coefficient (β_{eff}) of the order of 10⁻¹⁰ m W⁻¹. The suitability to be utilized in the fabrication of all-optical limiting devices is best achieved by polymer **P2TPy** as it exhibits substantially higher β_{eff} (7.02×10⁻¹⁰ m W⁻¹) and extremely low optical limiting thresholds (1.42 J cm⁻²).

1. Introduction

In the past couple of decades, the third-order nonlinear optical (NLO) phenomena have gather poolarge much attention in the fields of engineering and materials science due to their tremendous utilization in the fundamental technologies of photonics and optoelectronics^{1,2}. In recent years, considerable efforts have been made for the development of more efficient NLO materials, of those, organic conjugated molecules and polymers have emerged as forefront candidates, in addition to more traditional inorganic/semiconductor materials^{3–5}. The fast response time, large optical nonlinearity⁶, low cost, easy purification and variable molecular design⁷ of organic π conjugated molecules and polymers, make them more relevant materials in photonic fields such as optical switching^{8,9}, optical limiting¹⁰, tele-communication¹¹, signal processing, laser medicine¹², etc. Generally, NLO properties of organic materials are determined by their nonlinear absorption (NLA). Among the various mechanisms of NLA, the excited state absorption (ESA) and two-photon absorption (TPA) are considered to be more appropriate^{10,13} in the fields of energy up-conversion¹⁴, 3D optical data storage¹⁵, microfabrication¹⁶, twophoton photodynamic therapy¹⁷ and bioimaging¹⁸. In order to synthesize organic materials with larger TPA or ESA cross sections and to scale up the applications, various design strategies such as donor-*n*-acceptor (D-*n*-A), donor-acceptor-donor (D-A-D) and acceptor-donoracceptor (A–D–A) have been established by many research groups^{19,20}. In addition, proper selection of D and A building blocks, distance between D and A moieties, suitable π -linkers to connect D and A units and the symmetry of the molecule play key roles in fine tuning the optical nonlinearity of the system¹³. Further, the intramolecular charge transfer (ICT) resulting from the strong delocalization of π -electrons between the D and A units in a conjugated system provides very high molecular polarizability and enhances the third-order nonlinearities²¹.

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Among the various electron donors, thiophene is found to be a well-known, ever attractive electron donor moiety due to its good electron donating property, electronic tunability and high chemical and environmental stability^{22,23}. On the other hand, pyridine ring, is an electron deficient and a highly electron withdrawing moiety. The electro-optical properties of pyridine derivatives can be tuned by substitution of pyridine at different positions and also, by coordination of different guest units to the nitrogen atom of the pyridine group²⁴.

Given that, in the present study, a new class of trigonal-shaped molecules (**TPyT** and **TPyP**) and polymer (**P2TPy**) with D–A–D structural arrangement have been designed with 2,4,6-trisubstituted pyridine (served as electron acceptor) and thiophene (served as electron donor) backbone and synthesized via microwave assisted one pot reaction. The thiophene acetonitrile (**TPyT**) and phenyl acetonitrile groups (**TPyP** and **P2TPy**) were added as side groups via simple Knoevenagel condensation reactions in order to expand the π -conjugation. The effect

of conjugation on the fundamental photophysical, electrochemical and third order of the Photophysical and third order of the Photophysical and third order of the Photophysical and the Photophysical

properties were studied. To the best of the knowledge, the thiophene-pyridine based D-A-D Accepted Manuscript type trigonal-shaped materials for NLO applications are reported here for the first time. The chemicals are commercially available and used as received without further purification unless specially stated. The chemicals used were, 2-acetylthiophene (Avra Synthesis Pvt. Ltd, 95%), 4-hydroxybenzaldehyde (Loba Chemie, 98%), ammonium acetate (Merck, 97%), 1bromodecane (Sigma Aldrich, 98%), potassium carbonate (K₂CO₃) (Loba Chemie, 99%), thiophene-2-acetonitrile (Sigma Aldrich, 97%), phenylacetonitrile (Spectrochem Pvt. Ltd, 98%) and 1,4-phenylenediacetonitrile (Alfa Aesar, 97%). Organic solvents were purified according to the standard procedures. The progress of the reaction was monitored by thin layer chromatography (TLC) using pre-coated aluminum sheets with 60 F254 silica gel (Merck KGaA). The intermediates and final compounds were purified by silica gel column

2.2 Synthesis

2. Experimental Section

2.1 Materials and methods

2.2.1 Synthesis of 4-(4-(hydroxy)phenyl)-2,6-di(thiophen-2-yl)pyridine (3)

chromatography (60-120 mesh) using suitable solvent mixtures.

In a single-necked round-bottomed (RB) flask 4-hydroxybenzaldehyde (5.0 g, 40.94 mmol), 2acetylthiophene (8.84 mL, 81.88 mmol) and ammonium acetate (63.12 g, 818.86 mmol) were taken. The mixture was subjected to microwave irradiation (400 W) at 120°C for 30 min, then the residue was quenched using ice-water (60 mL) and the obtained solid was filtered. The solid was washed several times with ice cold distilled water to remove unreacted ammonium acetate and purified by column chromatography using a mixture of petroleum ether (pet ether)/ethyl acetate (8:2, v/v) as mobile solvent to get (3) as a white solid (9.32 g, yield: 68%). ESI-MS (m/z) calcd. for C₁₉H₁₃NOS₂: 335.04 found: 336.21 [M+H]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.72 (s, 2H, Ar–H), 7.65–7.60 (m, 4H, Ar–H), 7.44 (d, J = 8.0 Hz, 2H, Ar– H), 7.17–7.14 (m, 2H, Ar–H), 6.97 (d, J = 8.4 Hz, 2H, Ar–H), 5.29 (s, 1H, –OH); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 156.64, 152.55, 149.54, 144.89, 130.95, 128.45, 127.91, 127.70, 124.77, 116.01, 114.59; Anal. calcd. for C₁₉H₁₃NOS₂: C, 68.03; H, 3.91; N, 4.18; S, 19.12; found: C, 67.86; H, 4.17; N, 3.97; S, 19.66.

2.2.2 Synthesis of 4-(4-(decyloxy)phenyl)-2,6-di(thiophen-2-yl)pyridine (4)

A mixture of (3) (4.00 g, 11.92 mmol) and K_2CO_3 (4.94 g, 35.77 mmol) was taken in anhydrous N,N-dimethylformamide (DMF) (10 mL) and stirred at room temperature (RT) for 0.5 h. Later, 1-bromodecane (3.77 mL, 17.88 mmol) was added slowly and the mixture was refluxed at 80°C

for 10 h. Then, the reaction mixture was cooled to RT and quenched using ice-cold distributed on the reaction mixture was cooled to RT and quenched using ice-cold distributed by the reaction of the reaction

water. The obtained solid was filtered and dried. Further, the solid was purified by column chromatography using a mixture of pet ether/dichloromethane (DCM) (9:1, v/v) as eluent to yield intermediate (**4**) as an off-white colored solid (5.10 g, yield: 90%). ESI–MS (*m/z*) calcd. for C₂₉H₃₃NOS₂: 475.20 found: 476.34 [M+H]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.72 (s, 2H, Ar–H), 7.67–7.65 (m, 4H, Ar–H), 7.44 (d, *J* = 4.8 Hz, 2H, Ar–H), 7.17–7.14 (m, 2H, Ar–H), 7.04 (d, *J* = 8.8 Hz, 2H, Ar–H), 4.04 (t, *J* = 6.8 Hz, 2H, –OCH₂), 1.88–1.81 (m, 2H, – CH₂–), 1.52–1.49 (m, 2H, –CH₂–), 1.37–1.29 (m, 12H, –CH₂–), 0.93 (t, *J* = 6.8 Hz, 3H, –CH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 160.17, 152.49, 149.60, 145.00, 130.37, 128.16, 127.92, 127.67, 124.70, 115.03, 114.48, 68.18, 31.91, 29.59, 29.41, 29.43, 29.22, 26.04, 22.70, 14.15; Anal. calcd. for C₂₉H₃₃NOS₂: C, 73.22; H, 6.99; N, 2.94; S, 13.48; found: C, 73.88; H, 6.18; N, 2.55; S, 13.87.

2.2.3 Synthesis of 5,5'-(4-(4-(decyloxy)phenyl)pyridine-2,6-diyl)bis(thiophene-2carbaldehyde) (5)

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Freshly distilled DMF (11.66 mL, 151.35 mmol) was taken in a dry two-necked RB flask and cooled to 0 to -5°C. Phosphorus oxychloride (POCl₃) (14.10 mL, 151.35 mmol) was added to this drop wise and stirred for 30 min to get Vilsmeier salt. Then, solution of (4) (4.0 g, 8.40 mmol) in DMF (10 mL) was added to the formed Vilsmeier salt and the mixture was refluxed at 95°C for 48 h. The reaction mass was quenched using ice-cold water and subsequently, basified using NaOH solution (5 M). The precipitated solid was collected by filtration and the crude product was purified by column chromatography using a mixture of pet ether/ethyl acetate (8:2, v/v) as eluent to obtain (5) as a yellow solid (2.2 g, yield: 49%). ESI-MS (m/z) calcd. for $C_{31}H_{33}NO_3S_2$: 531.19 found: 532.43 [M+H]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.88 (s, 2H, -CHO), 7.72-7.69 (m, 6H, Ar-H), 7.57 (d, J = 8.8 Hz, 2H, Ar-H), 6.99 (d, J = 8.4 Hz, 2H, Ar-H), 4.00 (t, J = 6.8 Hz, 2H, -OCH₂), 1.84–1.77 (m, 2H, -CH₂-), 1.48–1.43 (m, 2H, $-CH_2$ -), 1.32–1.26 (m, 12H, $-CH_2$ -), 0.87 (t, J = 6.8 Hz, 3H, $-CH_3$); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 183.01, 160.63, 153.18, 151.32, 150.22, 144.45, 136.50, 129.06, 128.10, 125.50, 116.54, 115.19, 68.22, 31.82, 29.50, 29.32, 29.24, 29.13, 25.96, 22.60, 14.03; Anal. calcd. for C₃₁H₃₃NO₃S₂: C, 70.02; H, 6.26; N, 2.63; S, 12.06; found: C, 70.47; H, 6.52; N, 2.09; S, 12.17.

2.2.4 Synthesis of (2E,2'E)-3,3'-((4-(4-(decyloxy)phenyl)pyridine-2,6-diyl)bis(thiophene-5,2-diyl))bis(2 (thiophen-2-yl)acrylonitrile) (TPyT)

Freshly prepared solution of sodium ethoxide (89.3 mg, 8.11 mmol) was added drop wise to the solution of thiophene–2–acetonitrile (0.12 mL, 1.18 mmol) in ethanol (10 mL). Then, after

15 min, compound (**5**) (0.3 g, 0.56 mmol) was added and stirred at RT for 4 h. The precipitate column solid was collected by filtration, washed several times with ethanol and purified by column chromatography using a mixture of pet ether: ethyl acetate (9:1, v/v) as eluent to get **TPyT** as a yellow solid (0.29 g, yield: 71%). MALDI–TOF–MS (*m/z*) calcd. for C₄₃H₃₉N₃OS₄: 741.20 found: 742.194 [M+H]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.77–7.76 (m, 2H, Ar–H), 7.73–7.72 (m, 4H, Ar–H), 7.67 (d, *J* = 8.8 Hz, 2H, Ar–H), 7.48 (s, 2H, Ar–H), 7.38–7.37 (m, 2H, Ar–H), 7.32–7.30 (m, 2H, Ar–H), 7.09–7.07 (m, 2H, Ar–H), 7.04 (d, *J* = 8.8 Hz, 2H, Ar–H), 4.04 (t, *J* = 6.4 Hz, 2H, –OCH₂), 1.79–1.75 (m, 2H, –CH₂–), 1.49–1.47 (m, 2H, –CH₂–), 1.28–1.25 (m, 12H, –CH₂–), 0.88 (t, *J* = 6.8 Hz, 3H, –CH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 160.46, 151.59, 149.79, 148.29, 138.99, 138.90, 134.83, 132.86, 132.36, 131.60, 130.10, 129.54, 129.28, 128.76, 128.17, 127.12, 127.00, 126.09, 125.89, 125.67, 124.60, 116.92, 115.80, 115.13, 103.31, 68.24, 68.14, 38.72, 31.86, 30.34, 29.64, 29.54, 29.37, 29.28, 29.21, 28.90, 26.01, 23.74, 22.93, 22.64, 14.06; Anal. calcd. for C₄₃H₃₉N₃OS₄: C, 69.60; H, 5.30; N, 5.66; S, 17.28; found: C, 69.42; H, 5.71; N, 5.52; S, 17.33.

2.2.5 Synthesis of (2Z,2'Z)-3,3'-((4-(4-(decyloxy)phenyl)pyridine-2,6-diyl)bis(thiophene-5,2-diyl))bis(2-phenylacrylonitrile) (TPyP)

TPyP was synthesized following the above-mentioned procedure for **TPyT** using the precursors (**5**) (0.3 g, 0.56 mmol) and phenylacetonitrile (0.13 mL, 1.18 mmol) (0.27 g, yield: 68%). MALDI–TOF–MS (*m/z*) calcd. for C₄₇H₄₃N₃OS₂: 729.28 found: 730.221 [M+H]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.79 (s, 2H, Ar–H), 7.75 (s, 2H, Ar–H), 7.69–7.67 (m, 6H, Ar–H), 7.47–7.44 (m, 4H, Ar–H), 7.40–7.37 (m, 4H, Ar–H), 7.05 (d, *J*= 8.8 Hz, 2H, Ar–H), 6.99 (s, 2H, Ar–H), 4.04 (t, *J* = 6.4 Hz, 2H, –OCH₂), 1.77–1.75 (m, 2H, –CH₂–), 1.50–1.47 (m, 2H, –CH₂–), 1.30–1.25 (m, 12H, –CH₂–), 0.88 (t, *J* = 6.8 Hz, 3H, –CH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 160.47, 151.72, 148.39, 139.40, 133.92, 133.84, 132.69, 129.65, 129.08, 129.00, 128.23, 125.87, 125.72, 118.10, 115.78, 115.17, 108.58, 68.24, 31.86, 29.54, 29.37, 29.27, 29.20, 26.01, 22.64, 14.05; Anal. calcd. for C₄₇H₄₃N₃OS₂: C, 77.33; H, 5.94; N, 5.76; S, 8.78; found: C, 77.17; H, 5.76; N, 5.89; S, 8.92.

2.2.6 Synthesis of poly [(Z)-2-(4-(1-cyanovinyl)phenyl)-3-(5-(4-(4-(decyloxy)phenyl)-6-(thiophen-2-yl)pyridin-2-yl)thiophen-2-yl)acrylonitrile] (P2TPy)

The intermediate (**5**) (0.3 g, 0.56 mmol) and 1,4-phenylenediacetonitrile (0.096 g, 0.62 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 under argon atmosphere and the mixture was stirred at RT for 12 h. The reaction mixture was

poured slowly into 50 mL methanol and the precipitated polymer **P2TPy** was filtered. The Article Online obtained polymer was re-dissolved in chloroform and precipitated in methanol several times. The obtained orange colored solid polymer **P2TPy** after filtration was vacuum dried. Mw = 10426, PD = 4.34; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.63–7.39 (m, 7H, Ar–H), 7.20–6.99 (m, 15H, Ar–H), 4.00 (t, *J* = 6.8 Hz, 2H, –OCH₂), 1.80 (m, 2H, –CH₂–), 1.29–1.24 (m, 14H, – CH₂–), 0.88 (t, *J* = 6.8 Hz, 3H, –CH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 128.12, 125.85, 115.04, 68.12, 31.86, 29.53, 26.01, 22.65, 14.08; Anal. calcd. for C₄₉H₄₇N₃OS₂: C, 77.64; H, 6.25; N, 5.54; S, 8.46; found: C, 77.82; H, 6.46; N, 5.32; S, 8.79.

The details of characterization of the synthesized materials are given in ESI.

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Scheme 1. Synthetic pathways of TPyT, TPyP and P2TPy. Reagents and reaction conditions: (a) ammonium acetate, microwave, 400 W, 120°C, 0.5 h; (b)1-bromodecane, K₂CO₃, DMF, 85–90°C, 8 h; (c) POCl₃, DMF, 90–95°C, 48 h; (d) C₂H₅ONa, CHCl₃, C₂H₅OH, RT, 4–12 h.



Fig. 1. Chemical structures of TPyT, TPyP and P2TPy.

3. Results and discussion

3.1 Synthesis

The synthetic steps of organic compounds **TPyT**, **TPyP** and **P2TPy** are depicted in scheme 1 and their structures are shown in Fig. 1. In the first step, one pot solvent free green synthesis of intermediate **3** was carried out under microwave condition, which was alkylated to improve the solubility in different organic solvents using 1-bromodecane, to yield intermediate **4**. Then, the intermediate **4** was formylated via Vilsmeier Haack reaction to attain intermediate **5**. Finally, the intermediate **5** was subjected to well–known Knoevenagel condensation reactions with active methylene compounds *viz.*, thiophene–2–acetonitrile, phenylacetonitrile and 1,4-phenylenediacetonitrile to obtain the target compounds **TPyT**, **TPyP** and **P2TPy**, respectively.

3.2 Optical properties

The plot of absorption and photoluminescence (PL) emission spectra of **TPyT**, **TPyP** and **P2TPy** are shown in Fig. 2. The corresponding numeral data are summarized in Table 1. As shown in Fig. 2 (a), there exist strong peaks of absorption maxima (λ_{max}) at wavelengths 395, 377 and 419 nm corresponding to **TPyT**, **TPyP** and **P2TPy**, respectively. These observed absorption maxima are the results of π - π * transition within the conjugated backbone. The molecules **TPyT** and **TPyP** exhibit similar absorption profiles from 300 to near 500 nm region. The effective donor-acceptor interaction between the thiophene and the cyanovinylene groups in **TPyT** compared to that between phenyl and cyanovinylene groups in **TPyP** shift the absorption maxima of **P2TPy** is bathochromically shifted compared to that of **TPyT** and **TPyP** due to the extension of conjugation in **P2TPy**. Further, by exciting all the three compounds at their respective λ_{max} , the emission profiles were recorded, which exhibit similar trend as those

of absorption profiles with the emission wavelengths at 537, 500 and 562 nm for \mathbf{TPyT}_{A059} $\mathbf{TPyT}_{P00047G}$ and **P2TPy**, respectively (Fig. 2(b)). The optical band gaps (E_g) were calculated considering the intersection point of absorption and emission spectra to be 2.66, 2.74 and 2.55 eV for **TPyT**, **TPyP** and **P2TPy**, respectively. The higher degree of conjugation in **P2TPy** resulted in a considerable reduction of E_g in **P2TPy** when compared to that of **TPyT** and **TPyP**.



Fig. 2. (a) absorption and (b) PL spectra of TPyT, TPyP and P2TPy in chloroform $(1 \times 10^{-5} M)$.

Table 1 List of optical	electrochemical and theoretical	al data of TPvT , TPvP and P2	ΓPv.
1			•

Compounds	$\lambda^{abs}{}_{max}$	3	λ^{pl}_{max}	$\mathrm{E}_{\mathrm{g}}^{\mathrm{opt}}$	Eoxonset	НОМО	LUMO	E_{g}^{th}
	(nm)	(10^3 M^{-1})	(nm)	(eV)	(V)	(eV)	(eV)	
		$cm^{-1})$						
ТРуТ	399	79.49	537	2.66	0.82	-5.35ª	-2.69 ^b	2.93
ТРуР	377	89.48	500	2.74	0.99	-5.52ª	-2.78 ^b	3.14
P2TPy	419	78.67	562	2.55	0.91	-5.44 ^a	-2.89 ^b	2.73

 E_g^{opt} Optical band gap calculated from the intersection of normalized absorption and emission spectra.

E^{ox}onset Onset oxidation potential vs SCE.

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

^b Experimental results using equation (2).

 $E_{g}{}^{th}$ theoretically estimated HOMO LUMO band gap.

3.3 Electrochemical properties

To investigate the redox behavior of the synthesized compounds, the cyclic voltammetry (CV) measurements were carried out. The cyclic voltammograms of **TPyT**, **TPyP** and **P2TPy** are shown in Fig. 3a–c, respectively. The highest occupied molecular orbital (HOMO) energies were determined using equation (1) from first oxidation potential whereas lowest unoccupied molecular orbital (LUMO) energies were calculated using equation (2).

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

where, E^{ox}_{onset} and E_{FOC} are the onset oxidation potentials of the molecules and ferrocene (E_{FOC} = 0.27 V vs SCE, respectively, -4.8 eV is the HOMO energy level of ferrocene against vacuum. $E_{LUMO} = E_{HOMO} + E_g^{opt}$(2)

where, E_g^{opt} is the optical band gap.

The onsets of oxidation potentials are at 0.82, 0.99 and 0.91 V for **TPyT**, **TPyP** and **P2TPy**, respectively. And the HOMO levels are determined to be -5.35, -5.52 and -5.44 eV for **TPyT**, **TPyP** and **P2TPy**, respectively. Similarly, the LUMO levels are at -2.69, -2.78 and -2.89 eV for **TPyT**, **TPyP** and **P2TPy**, respectively. Due to the higher electron donating ability of thiophene than phenyl moiety, the molecule **TPyT** possesses higher HOMO level compared to that of **TPyP** and **P2TPy**. The electrochemical data are listed in Table 1.



Fig. 3. Cyclic voltammograms of (a) **TPyT**, (b) **TPyP** and (c) **P2TPy**. The inset shows enlarged image of the oxidation peak in the anodic region.

Thermo gravimetric analysis (TGA) was performed to determine the thermal stability of the processing compounds **TPyT**, **TPyP** and **P2TPy**. As shown in the Fig. 4, no significant weight loss is observed up to a temperature of ~350°C for **TPyT** and **TPyP**, after which, an abrupt weight loss is observed for both the molecules, indicating the complete decomposition of the molecules. The onset of decomposition temperatures (T_d) corresponding to **TPyT** and **TPyP** are 347 and 369°C, respectively. The higher T_d of **TPyP** is due to the presence of 2-phenylacrylonitrile unit in **TPyP** which is more stable than 2-thiopheneacrylonitrile present in **TPyT**. However, the polymer **P2TPy** exhibits the thermal stability up to 384°C and a sharp weight loss above 384°C, indicating the complete decomposition of polymer backbone. It is seen from the TGA plots of **TPyT**, **TPyP** and **P2TPy** that they exhibit considerably higher T_d. This is attributed to the presence of cyanovinylene moiety in **TPyT**, **TPyP** and **P2TPy** which makes them thermally stable²⁵. From the TGA results it can be concluded that the stability of the materials is good enough to be used in photovoltaics/ optoelectronics.



Fig. 4. TGA curves of (a) TPyT and TPyP, (b) P2TPy.

3.5 Theoretical studies

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Density functional theory (DFT) calculations were performed to acquire better understanding of the electronic structure and distribution of electrons in the synthesized compounds. The electronic structure of **TPyT**, **TPyP** and a dimer simulating the structure of the polymer **P2TPy** were determined using tools of DFT as implemented in Gaussian 09 package²⁶. The optimization of the ground state geometry was carried out including solvent effects (chloroform) through the Polarizable Continuum Model (PCM) using the B3LYP hybrid functional with 6-31G(d,p) basis set. Vibrational frequencies were computed at the same level of theory to confirm that these structures were minima on the energy surfaces. For computing the vertical transition energies, the TD-DFT tools as implemented in G09 were used. The

performance of several functionals (B3LYP, M06, CAM-B3LYP, X3LYP, LC-WPBC PRODUCTION COMPACTION AND A COMPACT AND wB97XD, HSEh1PBE, and BMK) was tested by comparison of the calculated spectra to the experimental ones. It was observed that the best results were obtained using the wB97XD hybrid functional. Therefore, TD-DFT calculations were carried out at the wB97XD/6-31G(d,p)/PCM (chloroform) level of theory to produce a number of 15 singlet-to-singlet transitions. The calculated absorption spectra were obtained from the outputs of G09 using the Gaussum free software. The ground state optimized geometry, HOMO and LUMO energy levels are shown in Fig. 5. The decyloxy unit was considered as methoxy group for the easy calculation. As shown in Fig. 5, except the decyloxy substituted phenyl group, which is twisted by an angle of $\sim 30^{\circ}$ from the thiophene-pyridine plane, the HOMO and LUMO orbitals are uniformly distributed over central pyridine, spacer thiophene, cyanovinylene and on the peripheral groups as a result of structural planarity in the case of **TPyT** and **TPyP**. This type of spatial distribution on entire molecular backbone suggests the $\pi - \pi^*$ type transition in **TPvT** and TPvP, whereas, in the case of P2TPv the HOMO is majorly distributed on thiophene and 1,4-phenyleneacrylonitrile group present in the right wing and partially distributed on central pyridine and thiophene present in the left wing. There is a twisting of 1,4phenyleneacrylonitrile group in the left wing, as a result of which the HOMO distribution is restricted to thiophene unit. The LUMO in **P2TPy** is majorly localized on central pyridine, thiophene and 1,4-phenyleneacrylonitrile group present in the right wing. Further, to study the excited state electronic transitions, the TD-DFT calculations were carried out. Structural optimizations were performed on P2TPya (dimer) and one simple structure (monomer, **P2TPyb**) (Fig. 7). Simulated absorption spectra were taken for all the conformers along with TPyT and TPyP. The simulated spectra of P2TPya and P2TPyb showed good results in terms of comparison with experimental data and it seems that extending the number of units shifts the spectrum to longer wavelength region. Fig. 6 shows the predicted spectra for TPyT, TPyP and for the most stable conformations (dimer) and monomer of P2TPy compared to the experimental solution spectrum. Theoretically determined HOMO LUMO band gap for TPyT, **TPyP** and **P2TPy** is given in Table 1.



Fig. 5. Optimized ground state geometry and HOMO/LUMO distribution of **TPyT**, **TPyP** and **P2TPy**.



Fig. 6. Predicted spectra for **TPyT**, **TPyP** and most stable conformations (dimer) and monomer of **P2TPy** compared to the experimental solution spectrum.



Fig. 7. (a) optimized geometry of P2TPy dimer (b) optimized geometry of P2TPy monomer.
3.6 Third order NLO properties

3.6.1 NLA properties

(a)

The open-aperture (OA) Z-scan measurements were carried out to study the NLA behavior of TPyT, TPyP and P2TPy. A 50 µJ laser beam with a pulse width of 7 ns, corresponding to the peak on-axis intensity of 1.386 GWcm⁻² was used to examine the NLA behavior of the compounds. The linear transmittance was set at 60-65% (experimental details are given in ESI). The OA Z-scan curves obtained from TPyT, TPyP and P2TPy, by dissolving them in CHCl₃ are shown in the Fig. 8a-c, respectively. On analyzing the figures, it is observed that at the focus (z=0), the curves are symmetric and there is a decrease in the transmittance which becomes minimum at the focus, revealing the reverse saturable absorption (RSA) of the compounds. At high laser energies, the RSA is associated with two-photon absorption (2PA), which is assisted with excited state absorption (ESA). Therefore, the net effect is termed as "effective 2PA" process²⁷. In order to determine the nonlinear absorption coefficient (β_{eff}) of **TPyT**, **TPyP** and **P2TPy**, the experimental data were theoretically fitted to an ESA assisted 2PA using equation S1. Further, on solving the nonlinear propagation (dI/dz) using equation S2, (fourth-order Runge-Kutta method), the output laser intensity was numerically calculated for a given input intensity. The obtained experimental results were fitted with less error with the normalized transmittance (T(z)) (equation S3), which was derived from equations S1 and S2. The imaginary part of the third order nonlinear susceptibility (im $\chi^{(3)}$) for OA configuration was determined using the equation S4. The calculated β_{eff} and im $\chi^{(3)}$ are given in Table 2. The calculated β_{eff} values for **TPyT**, **TPyP** and **P2TPy** are 1.48×10⁻¹⁰, 2.08×10⁻¹⁰ and 7.02×10⁻¹⁰ m W⁻¹, respectively. The obtained β_{eff} values of **TPyT**, **TPyP** and **P2TPy** are comparable with β_{eff} values of some of the well-known materials (Table 2).



Fig. 8. Z-scan curves of (a) TPyT, (b) TPyP and (c) P2TPy under OA configuration.

3.6.2 Optical limiting studies

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A good optical limiter is the one which shows maximum transmittance at low input intensity regime and decreased transmittance on increasing the on-axis intensity. Here, the optical limiting data is extracted from NLA behavior of the compounds and the optical limiting data of **TPyT**, **TPyP** and **P2TPy** were obtained by plotting a graph of normalized transmittance versus input intensity (Fig. 9a–c), obtained from the OA Z–scan analysis. From the graph, it is seen that the onset of optical limiting values of the compounds **TPyT**, **TPyP** and **P2TPy** are at 1.11, 0.83 and 0.16 J cm⁻², 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 8.34, 4.16 and 1.42 J cm⁻² for **TPyT**, **TPyP** and **P2TPy**, respectively. The polymer **P2TPy** has shown significantly low onset and LT values compared to that of molecules **TPyT** and **TPyP** and moreover, the obtained relatively low optical limiting data are comparable and are even better than the similar materials reported (Table 2).

For an instance, Gopi *et al.*²⁸ synthesized a new solution processable quinoxaline based pushpull molecule with 3-ethyl rhodanine as acceptor unit and investigated the NLO properties of the molecule, which showed an effective TPA with β_{eff} value as high as 10.0×10^{-10} m W⁻¹ with the LT of 2.46 J cm⁻². Vintu *et al.*²⁹ synthesized a novel anthracene supported 5,11dihydroindolo [3,2-*b*] carbazole- based polymer for nonlinear optical application, which

showed a very high β_{eff} of 11.6×10⁻¹⁰ m W⁻¹ with the LT of 1.03 J cm⁻². Zawadzka ef_3 bore online synthesized two 5,10-A₂B₂ porphyrin series with different metals in the core and investigated the NLO properties, and with tin (IV) complex, SnCl₂ CCTMS, porphyrin showed RSA with the β_{eff} of 6.4×10⁻¹⁰ m W⁻¹. K.P *et al.*³¹ observed the enhancement in the NLO property of 7CB nematic liquid crystal upon doping it with CdSe quantum dot (QD) in different concentrations. The pure 7CB nematic liquid crystal showed β_{eff} of 2.0×10⁻¹⁰ m W⁻¹ while after doping with 0.75 and 1% of CdSe QD, the β_{eff} raised to 5.5×10⁻¹⁰ m W⁻¹ with the LT of 3.02 J cm⁻² and 7.8×10^{-10} m W⁻¹ with the LT of 2.1 J cm⁻², respectively. The available reports indicate that in most of the cases the optical nonlinearity is increased by doping with some inorganic materials, whereas, few of the pure organic materials have also shown increase in the β_{eff} as a result of conjugation. However, the synthesized compounds TPyT, TPyP and P2TPy exhibited higher NLA, improved β_{eff} and significantly low onset and LT values, establishing their efficient optical power limiting behavior in their pristine state compared to some of the reported molecules. The results revealed that these synthesized compounds could serve the potentials as optical limiters for human eye and other sensitive sensors in laser photonics. Unfortunately, we could not perform nonlinear refraction (NLR) studies as the NLA is much stronger than refraction of the compounds.



Fig. 9. Optical limiting curves of (a) TPyT, (b) TPyP and (c) P2TPy at an input intensity of 1.386 GW cm⁻².

Table 2 NLO parameters of **TPyT**, **TPyP** and **P2TPy** and few comparisons with work reported under similar experimental conditions.

Sample	$\beta_{\rm eff}(10^{-10})$	Limiting	Im $\chi^{(3)}$ (10 ⁻¹²)	References Doppoor	
	(mW ⁻¹)	(mW ⁻¹) threshold			
		(Jcm ⁻²)			
ТРуТ	1.48	8.34	4.67596	This work	
TPyP	2.08	4.16	6.56524	This work	
P2TPy	7.02	1.42	22.1203	This work	
	10	2.46	-	28	
+ } } }	11.6	1.03	32.331	29	
5,10-A ₂ B ₂ porphyrin– SnCl ₂ _CCTMS complex	6.4	-	-	30	
7CB	2.0	-	7.42	31	
7CB + 0.75% CdSe QD	5.5	3.02	20.4	31	
7CB + 1.0% CdSe QD	7.8	2.1	28.9	31	

As already mentioned in the introduction part, the optical nonlinearity of organic materials is solely resulting from the conjugation, the extended conjugation in **TPyT**, **TPyP** and **P2TPy** enhance the NLO properties of the materials. Moreover, the predominant increment in the β_{eff} and substantial reduction in optical limiting values of polymer **P2TPy** compared to that of molecules **TPyT** and **TPyP** is due to the higher extension of conjugation, improved interaction between the electron donor and acceptor units, increased ICT and the polarizability in **P2TPy**. Between the **TPyT** and **TPyP**, the **TPyP** shows higher NLO property due to the presence of phenyl acrylonitrile moiety which extends the conjugation in **TPyP** compared to that of thiophene acrylonitrile in **TPyT**.

4. Conclusion

In conclusion, novel D–A–D type trigonal-shaped nonlinear materials: two small molecules of the product (**TPyT** and **TPyP**) and one structurally similar conjugated polymer (**P2TPy**), were designed and synthesized. The opto-electronic properties of the polymer were compared with small molecules. The extended conjugation in **P2TPy** compared to that of **TPyT** and **TPyP** red shifted the absorption maximum and reduced the energy gap. The presence of phenylacrylonitrile unit resulted in the enhanced nonlinear absorption in **TPyP** and **P2TPy** compared to **TPyT**. The higher degree of conjugation in **P2TPy** improved the interaction between the electron donor and acceptor units, the ICT and the polarizability of the polymer, resulting in the predominant increment in the β_{eff} (7.02×10⁻¹⁰ m W⁻¹) and substantial reduction in optical limiting value (1.42 J cm⁻²) compared to that of **TPyT** and **TPyP**. The results obtained here for **P2TPy** is better than some of the NLO materials reported. Therefore, the material synthesized here could be of promising candidates for all-optical limiting devices in laser photonics.

Associated content

Supporting Information

Includes characterization details, spectral characterizations of the intermediates and final compounds, experimental set up of Z–scan measurements and the equations used for the theoretical fitting of Z–scan experimental data.

Conflicts of interest

None.

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References

1 D. Day, M. Gu and A. Smallridge, Rewritable 3D Bit Optical Data Storage in a PMMA-Based Photorefractive Polymer, *Adv. Mater.*, 2001, **13**, 1005–1007.

- Page 18 of 21
- 2 S. Tao, T. Miyagoe, A. Maeda, H. Matsuzaki, H. Ohtsu, M. Hasegawa, S. Takaishys/Depp00047G Yamashita and H. Okamoto, Ultrafast Optical Switching by using Nanocrystals of a Halogen-Bridged Nickel-Chain Compound Dispersed in an Optical Polymer, *Adv. Mater.*, 2007, **19**, 2707–2710.
- 3 P. N. Prasad and D. J. Williams, *Introduction to nonlinear optical effects in molecules and polymers*, Wiley New York etc., 1991, vol. 1.
- 4 J. L. Bredas, C. Adant, P. Tackx, A. Persoons and B. M. Pierce, Third-Order Nonlinear Optical Response in Organic Materials: Theoretical and Experimental Aspects, *Chem. Rev.*, 1994, 94, 243–278.
- 5 M. G. Papadopoulos, A. J. Sadlej and J. Leszczynski, *Non-linear optical properties of matter*, Springer, 2006.
- 6 H. S. Nalwa, Organic materials for third-order nonlinear optics, *Adv. Mater.*, 1993, 5, 341–358.
- 7 P. Gu, X. Xu, F. Zhou, T. Zhao, G. Ye, G. Liu, Q. Xu, J. Ge, Q. Xu and J. Lu, Study of Linear and Nonlinear Optical Properties of Four Derivatives of Substituted Aryl Hydrazones of 1,8-Naphthalimide, *Chin. J. Chem.*, 2014, **32**, 205–211.

- 8 B. Luther-Davies and M. Samoc, Third-order nonlinear optical organic materials for photonic switching, *Curr. Opin. Solid State Mater. Sci.*, 1997, **2**, 213–219.
- 9 H. Ma, A. K.-Y. Jen and L. R. Dalton, Polymer-Based Optical Waveguides: Materials, Processing, and Devices, *Adv. Mater.*, 2002, **14**, 1339–1365.
- 10C. W. Spangler, Recent development in the design of organic materials for optical power limiting, J. Mater. Chem., 1999, 9, 2013–2020.
- 11 D. Dini, M. J. F. Calvete and M. Hanack, Nonlinear Optical Materials for the Smart Filtering of Optical Radiation, *Chem. Rev.*, 2016, **116**, 13043–13233.
- 12P. Zhao, D. Wang, H. Gao, J. Zhang, Y. Xing, Z. Yang, H. Cao and W. He, Third-order nonlinear optical properties of the "clicked" closed-ring spiropyrans, *Dyes Pigments*, 2019, 162, 451–458.
- 13L. Xu, D. Zhang, Y. Zhou, Y. Zheng, L. Cao, X.-F. Jiang and F. Lu, 4-N, N-bis(4methoxylphenyl) aniline substituted anthraquinone: X-ray crystal structures, theoretical calculations and third-order nonlinear optical properties, *Opt. Mater.*, 2017, 70, 131–137.
- 14W.-P. To, K. T. Chan, G. S. M. Tong, C. Ma, W.-M. Kwok, X. Guan, K.-H. Low and C.-M. Che, Strongly Luminescent Gold(III) Complexes with Long-Lived Excited States: High Emission Quantum Yields, Energy Up-Conversion, and Nonlinear Optical Properties, *Angew. Chem. Int. Ed.*, 2013, **52**, 6648–6652.

- 15H. Zhou, F. Zhou, S. Tang, P. Wu, Y. Chen, Y. Tu, J. Wu and Y. Tian, T_{WQ} -physical properties and absorption dyes with thiophene as π electron bridge: Synthesis, photophysical properties and optical data storage, *Dyes Pigments*, 2012, **92**, 633–641.
- 16B. H. Cumpston, S. P. Ananthavel, S. Barlow, D. L. Dyer, J. E. Ehrlich, L. L. Erskine, A. A. Heikal, S. M. Kuebler, I.-Y. S. Lee, D. McCord-Maughon, J. Qin, H. Röckel, M. Rumi, X.-L. Wu, S. R. Marder and J. W. Perry, Two-photon polymerization initiators for three-dimensional optical data storage and microfabrication, *Nature*, 1999, **398**, 51–54.
- 17 S. Brown, Photodynamic Therapy: Two photons are better than one, *Nat. Photonics*, 2008, 2, 394–395.
- 18P. Hanczyc, A. Justyniarski, D. A. Gedefaw, M. R. Andersson, M. Samoc and C. Müller, Two-photon absorption of polyfluorene aggregates stabilized by insulin amyloid fibrils, *RSC Adv.*, 2015, **5**, 49363–49368.
- 19B. A. Reinhardt, L. L. Brott, S. J. Clarson, A. G. Dillard, J. C. Bhatt, R. Kannan, L. Yuan, G. S. He and P. N. Prasad, Highly Active Two-Photon Dyes: Design, Synthesis, and Characterization toward Application, *Chem. Mater.*, 1998, **10**, 1863–1874.
- 20M. Albota, D. Beljonne, J.-L. Brédas, J. E. Ehrlich, J.-Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Röckel, M. Rumi, G. Subramaniam, W. W. Webb, X.-L. Wu and C. Xu, Design of Organic Molecules with Large Two-Photon Absorption Cross Sections, *Science*, 1998, 281, 1653–1656.
- 21 J. Jia, T. Li, Y. Cui, Y. Li, W. Wang, L. Han, Y. Li and J. Gao, Study on the synthesis and third-order nonlinear optical properties of D-A poly-quinacridone optical materials, *Dyes Pigments*, 2019, 162, 26–35.
- 22 G. Barbarella, M. Melucci and G. Sotgiu, The Versatile Thiophene: An Overview of Recent Research on Thiophene-Based Materials, *Adv. Mater.*, 2005, **17**, 1581–1593.
- 23K. R. Justin Thomas, Y.-C. Hsu, J. T. Lin, K.-M. Lee, K.-C. Ho, C.-H. Lai, Y.-M. Cheng and P.-T. Chou, 2,3-Disubstituted Thiophene-Based Organic Dyes for Solar Cells, *Chem. Mater.*, 2008, 20, 1830–1840.
- 24P. D. Vellis, S. Ye, J. A. Mikroyannidis and Y. Liu, New divinylene trimers with triphenylpyridine segments: Synthesis, photophysics, electrochemical and electroluminescent properties, *Synth. Met.*, 2008, **158**, 854–860.
- 25 J.-M. Park, S. K. Park, W. S. Yoon, J. H. Kim, D. W. Kim, T.-L. Choi and S. Y. Park, Designing Thermally Stable Conjugated Polymers with Balanced Ambipolar Field-Effect Mobilities by Incorporating Cyanovinylene Linker Unit, *Macromolecules*, 2016, **49**, 2985– 2992.

- 26 R. A. Gaussian09, 1, mj frisch, gw trucks, hb schlegel, ge scuseria, ma robb, jr_Dcheeseyjantricle Online
 g. Scalmani, v. Barone, b. Mennucci, ga petersson et al., gaussian, *Inc Wallingford CT*, 2009,
 121, 150–166.
- 27K. A. Vishnumurthy, A. V. Adhikari, M. S. Sunitha, K. A. A. Mary and R. Philip, Design and synthesis of a new thiophene based donor–acceptor type conjugated polymer with large third order nonlinear optical activity, *Synth. Met.*, 2011, **161**, 1699–1706.
- 28V. Gopi, S. Subbiahraj, K. Chemmanghattu and P. C. Ramamurthy, 2,3-di(2-furyl) quinoxaline bearing 3 -ethyl rhodanine and 1,3 indandione based heteroaromatic conjugated T-shaped push -pull chromophores: Design, synthesis, photophysical and non-linear optical investigations, *Dyes Pigments*, 2020, **173**, 107887.
- 29M. Vintu, G. Unnikrishnan, E. Shiju and K. Chandrasekharan, Indolo[3,2-b]carbazole-based poly(arylene ethynylene)s through Sonogashira coupling for optoelectronic and sensing applications, *J. Appl. Polym. Sci.*, 2019, **136**, 46940.
- 30M. Zawadzka, J. Wang, W. J. Blau and M. O. Senge, Nonlinear absorption properties of 5,10-A2B2 porphyrins – correlation of molecular structure with the nonlinear responses, *Photochem. Photobiol. Sci.*, 2013, **12**, 996–1007.

31 P. K.p., D. M.c., N. John V., C. K. and S. Varghese, Enhanced optical nonlinearity in nematic liquid crystal on doping with CdSe quantum dot, *J. Mol. Liq.*, 2019, **273**, 497–503.

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Diagrammatic representation of excited state assisted two-photon absorption (2PA) behavior of donor–acceptor type conjugated polymer (**P2TPy**), exhibiting extremely low optical limiting threshold.

