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Butterfly-Shaped Thiophene-Pyridine Hybrids: Green Electroluminescence and Large Third-Order Optical Nonlinearities

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Abstract

A set of four symmetric, butterfly-shaped 4-(4-(decyloxy)phenyl)-2,6-di(thiophen-2yl)pyridine (TPY) derivatives *viz.*, **2TPA-TPY** containing TPY moiety at the center and triphenylamine units as end groups, **2CBZ-TPY** possessing TPY moiety at the center and Nethyl carbazole units as end groups, **2TPy-TPA** comprising triphenylamine unit at the center with TPY moiety at the periphery and **2TPY-CBZ** consisting of N-ethyl carbazole at the center with TPY moiety at the periphery was synthesized. The synthesized molecules show reverse saturable absorption (RSA) which is consistent with two-photon absorption (2PA) associated with excited state absorption (ESA) when excited using a 532 nm laser beam. The molecules **2TPA-TPY** and **2TPY-TPA** possess extremely low limiting thresholds of 1.73 and 2.68 J cm⁻², respectively. The organic light emitting diode (OLED) fabricated as a proof of concept using selected molecule **2TPA-TPY** as emitter exhibits green emission with a maximum luminance of 207 cd m⁻², a current efficiency (η_{CE}) of 1.51 cd A⁻¹, a maximum power efficiency (η_{Pmax}) of 0.46 lm W⁻¹ and an external quantum efficiency (η_{EQE}) of 0.48 % at 100 cd m⁻².

1. Introduction

Designing and developing new families of organic molecules with the specific features is at the heart of optoelectronics. Indeed, a number of organic molecules have drawn immense attention due to their prime applications in the fields like OLEDs, nonlinear optics (NLO), organic solar cells (OSCs) and field effect transistors (FETs). In particular, ample interest has ChemPlusChem

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been developed towards OLEDs owing to their advantages such as light weight, low cost, thinness, flexibility, high brightness and wide viewing angles. In addition, they are also considered as one of the most anticipated device architectures for solid state lighting sources as well as a key technology for flat-panel displays^[1-4]. The prerequisite of monochromatic redgreen-blue (RGB) primaries with narrow bandwidth to the BT.2020 standard demands great challenge for the development of RGB luminescent materials^[5]. However, the ultrapure green emission strictly needs narrower half width spectrum and defined emission peak wavelength as compared to the other colors^[6,7]. Although it is difficult to develop high color purity emitters and to achieve excellent devices, from the point of chemical approach one way of improving the major factors such as low thermal stability, chemical purity and poor efficiency that restrict the device performance is designing of rigid either star/butterfly-shaped or dendrite-shaped molecules^[8–10]. Moreover, due to the advantages like excellent thermal stability, high purity, good thin film formation and solution processability of star/butterfly-shaped molecules over the linear molecules, they have gained enormous attention in the recent past^[11–14].

To date, there has been a rapid technological development in NLO which demands the rational design and synthesis of organic materials to achieve enhanced nonlinear optical properties^[15]. Among the organic materials studied, the high molecular weight π -conjugated molecules with donor-acceptor-donor (D–A–D) arrangement have been the attracting candidates due to their extensive π -delocalization which enables intramolecular charge transfer (ICT) between D and A units, providing high polarizability to the system, which results in superior nonlinear optical properties in addition to their fast-optical responses, ease of fabrication, light weight and flexibility^[16,17]. In addition, materials with 2PA or RSA property are remarkably used in many photonic industry such as optical limiters for protecting human eye and sensitive devices from high energy lasers^[18], 3D optical data storage^[19], microfabrication^[20], energy up-conversion^[21] and two-photon photodynamic therapy^[22]. However, there is still room for developing novel molecules which can exhibit TPA/RSA.

Among a wide varieties of electron donors exploited in the optoelectronic field, thiophene is found to be one of the most explored heterocyclic compounds due to its unique optical and electronic properties^[23]. The degree of π -conjugation of thiophene-based materials affects the FMO energies, which in turn affect the energy gap, photophysical and electrochemical properties. Moreover, the extent of π -conjugation also governs the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) energy levels and electrical conductivity, making the thiophene based materials as an inimitable part in synthetic chemistry and optoelectronics^[24–26]. Another excellent electron donor is, propeller shaped triphenylamine

moiety possessing a continuous conjugation between the central nitrogen atom and peripheral phenyl groups^[27]. In addition, it has a high triplet energy of 3.04 eV and possesses good hole transporting property^[28–30]. Similarly, carbazole, another electron donating group, which when incorporated into a conjugated backbone, provides good charge-transport function, high thermal stability, solubility, moderately high oxidation potential and extended glassy state^[31,32] and hence, carbazole containing molecules also have attracted much attention in the optoelectronic industry. On the other hand, the simplest electron accepting unit in the category of small band gap material containing D–A units is pyridine ring, possessing an electron deficient imine nitrogen^[33]. The high thermal stability, chemical stability and effective electron-transporting abilities of pyridine make pyridine to have significant role in optoelectronic industry^[31].

On the basis of foregoing points, herein, two sets of four symmetric, novel butterfly-shaped molecules (**2TPA-TPY**, **2CBZ-TPY**, **2TPY-TPA** and **2TPY-CBZ**) were designed and synthesized. In one set (**2TPA-TPY** and **2CBZ-TPY**) the central pyridine core (served as electron acceptor) was connected to terminal triphenylamine (**2TPA-TPY**)/carbazole (**2CBZ-TPY**) moiety (served as electron donor) through thiophene (served as π -linker), which provided a D– π –A– π –D structural configuration to the system, whereas, in another set (**2TPY-TPA** and **2TPY-CBZ**), the central triphenylamine (**2TPy-TPA**)/carbazole (**2TPY-TPA** and **2TPY-CBZ**), the central triphenylamine (**2TPy-TPA**)/carbazole (**2TPY-TPA** and **2TPY-CBZ**), the central triphenylamine (**2TPy-TPA**)/carbazole (**2TPY-CBZ**) moiety was connected to the peripheral thiophene–pyridine–thiophene unit (D–A– π) to provide D–A– π –D– π –A–D configuration. Their thermal, photophysical and electrochemical properties were discussed in detail along with the theoretical evidence. In addition, the third-order NLO properties of all the four molecules were discussed and the electroluminescent property of the selected molecule **2TPA-TPY** was also investigated by fabricating OLED.



Figure 1. Molecular structures of 2TPA-TPY, 2CBZ-TPY, 2TPY-TPA and 2TPY-CBZ.





Scheme 1. Synthetic pathways of 2TPA-TPY, 2CBZ-TPY, 2TPY-TPA and 2TPY-CBZ. Reagents and reaction conditions: (a) ammonium acetate, microwave, 400 W, 120–180°C, 0.5 h, yield: 68%; (b)1-bromodecane, K₂CO₃, DMF, 85–90°C, 8 h, yield: 90%; (c) POCl₃, DMF, 90–95°C, 48 h, yield: 26–49%; (d) sodium borohydride, CH₃OH, RT, 12 h, yield: 90–92%; (e) PPh₃HBr, CHCl₃, 60°C, 3 h, yield: 93–94%; (f) NaH, C₂H₅Br, DMF, RT, 12 h, yield: 82%; (g) POCl₃, DMF, 60–65°C, 24 h, yield: 38–49%; (h) C₂H₅ONa, CHCl₃, C₂H₅OH, RT, 12 h, yield: 56–63%.

2. Results and discussion

2.1 Synthesis

Scheme 1 depicts the synthesis of 2TPA-TPY, 2CBZ-TPY, 2TPY-TPA and 2TPY-CBZ, and their chemical structures are shown in Figure 1. The molecules were synthesized using multistep synthetic protocol. The green synthesis of core moiety 3 involves one-pot multicomponent reaction under solvent-free (neat) condition via microwave irradiation. The intermediate 3 was alkylated to improve the solubility to achieve intermediate 4 which was formylated to obtain intermediates 5 and 6. The reduction of intermediates 5 and 6 yielded the intermediates 7 and 8, respectively, which were later converted into their corresponding Wittig salts 9 and 10. Finally, Wittig reaction of intermediate 9 with bis(4-formylphenyl)phenylamine and intermediate 14 produced 2TPY-TPA and 2TPY-CBZ, respectively, while, Wittig reaction of intermediate 13 produced 2TPA-

TPY and **2CBZ-TPY**, respectively. The characterization details of all the intermediates and final molecules are given in the ESI.

2.2 Photophysical studies

The UV-vis absorption spectra of 2TPA-TPY, 2CBZ-TPY, 2TPY-TPA and 2TPY-CBZ exhibit two absorption bands (Figure 2a–d). One absorption band is located at higher energy UV region (280–330 nm) and the other is located at lower energy visible region (350–460 nm). The band at higher energy region is attributed to π - π * transition and that at lower energy region ascribes to ICT transition from the electron donating triphenylamine/carbazole moiety to the electron accepting pyridine group. The absorption maxima (λ_{max}) of **2TPA-TPY**, **2CBZ-TPY**, 2TPY-TPA and 2TPY-CBZ are observed at 409, 394, 419 and 404 nm, respectively. The absorption spectra clearly display the effect of variation of peripheral groups on the conjugation and hence, the absorption of the molecules. As it is seen in Figure 2a–d, there is a considerable red shift in the absorption of 2TPA-TPY and 2TPY-TPA compared to that of 2CBZ-TPY and **2TPY-CBZ**. This bathochromic shift is attributed to the higher electron donating ability of triphenylamine group in 2TPA-TPY and 2TPY-TPA compared to that of carbazole in 2CBZ-**TPY** and **2TPY-CBZ**. Moreover, the higher λ_{max} of **2TPY-TPA** is resulted from the higher degree of conjugation in 2TPY-TPA compared to that of 2TPA-TPY, 2CBZ-TPY and 2TPY-**CBZ**. The optical band gap (E_g) determined from the point of intersection of absorption and emission spectra is 2.64, 2.71, 2.62 and 2.76 eV for 2TPA-TPY, 2CBZ-TPY, 2TPY-TPA and 2TPY-CBZ, respectively.

The fluorescence spectra at RT show an emission peak at 503, 450, 488 and 461 nm for **2TPA-TPY**, **2CBZ-TPY**, **2TPY-TPA** and **2TPY-CBZ**, respectively (**Figure 2a–d**), by exciting at their corresponding λ_{max} . In addition, there is a considerable red shift in the absorption (**Figure 3a**) and emission spectra (**Figure 3b**) of all the four molecules in the solid state compared to that of solution state. This is due to the increased intermolecular interactions in the solid state. For an ideal fluorophore, fluorescence quantum yield (Φ_F) is one of the deciding factors. In view of this, their absolute solid-state fluorescence quantum yields were obtained, and they are 0.153, 0.021, 0.041 and 0.038 for **2TPA-TPY**, **2CBZ-TPY**, **2TPY-TPA** and **2TPY-CBZ**, respectively. The emission profiles of the four molecules were also measured at 77 K in degassed toluene to ensure the emission from the triplet state. It is observed that the low temperature emission profiles are overlapping with the RT emission profiles (**Figure 2a–d**), which suggests the nonexistence of phosphorescence and validates the pure fluorescence emission (with the enhanced vibronic bands). Further, the time-resolved photoluminescence decay dynamics were studied at RT to measure the lifetime of the molecules. The time-resolved photoluminescence

decay profiles for the molecules in the degassed toluene are given in **Figure S31**. The molecules **2TPA-TPY**, **2CBZ-TPY**, **2TPY-TPA** and **2TPY-CBZ** possess a short lifetime (τ_F) of 2.93, 2.42, 1.17 and 1.18 ns, respectively, which is attributing to the relaxation from S₁ to S₀. And there is no any delayed component observed, indicating the pure fluorescence emission. The data of absorption and emission studies are summarized in **Table 1**.



Figure 2. UV-Vis absorption spectra at RT (measured in CHCl₃, 10^{-5} M) and fluorescence emission spectra at RT and 77K (measured in toluene, 10^{-5} M) of a) **2TPA-TPY**, b) **2CBZ-TPY**, c) **2TPY-TPA** and d) **2TPY-CBZ**.



Figure 3. a) Absorption in thin film and b) emission profiles in the solid state of 2TPA-TPY, 2CBZ-TPY, 2TPY-TPA and 2TPY-CBZ.

Molecules	λ _{max} ^{abs} [solution/ thin film] (nm)	λ _{max} ^{pl} [solution/ solid state] (nm)	Eg [optical ^[a] / calculated] (eV)	Φ _F ^[b] (±0.02)	$ au_{F}^{[c]}$ (ns)
2TPA-TPY	409/420	503/543	2.64/3.05	0.153	2.93 ± 0.03
2CBZ-TPY	394/408	450/569	2.71/3.26	0.021	2.42 ± 0.01
2TPY-TPA	419/430	488/538	2.62/2.98	0.041	$1.17\pm 0.05^{[*]}$
2TPY-CBZ	404/417	461/542	2.76/3.19	0.038	1.19 ± 0.005

Table 1. Optical absorption and emission data of **2TPA-TPY**, **2CBZ-TPY**, **2TPY-TPA** and**2TPY-CBZ**.

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

[b] Absolute fluorescence quantum yield determined using an integrated sphere in solid state at RT.

[c] Amplitude weighted average lifetime, biexponential, [*] triexponential.

2.3 Electrochemical properties

Figure 4a–d depict the cyclic voltammograms of **2TPA-TPY**, **2CBZ-TPY**, **2TPY-TPA** and **2TPY-CBZ**, respectively, that were obtained by cyclic voltammetry (CV) measurements. The observed onset oxidation peaks of first oxidation peak (E^{ox}_{onset}) are 0.77, 0.80, 0.71 and 0.82 V vs SCE for **2TPA-TPY**, **2CBZ-TPY**, **2TPY-TPA** and **2TPY-CBZ**, respectively. As observed, the molecules undergo multistep oxidation process. The oxidation peaks other than the first oxidation peak could be due to the oxidation of different units present in the molecule. The small oxidation peaks observed at ~1.67–1.7 V in all the four molecules could be associated with vinylene bond oxidation^[34]. The oxidation peak observed at ~1.2 V may be due to the oxidation of N-substituted carbazole in **2CBA-TPY** and **2TPY-CBZ**^[34] whereas, the potential range between 0.8–1.5 V in **2TPA-TPY** and **2TPY-TPA** could be related to the oxidation of triphenylamine unit which depends on the substituents attached to the phenyl ring of triphenylamine unit^[35]. The energy of the HOMO (E_{HOMO}) calculated from the equation (1) is -5.31, -5.34, -5.25 and -5.36 eV for **2TPA-TPY**, **2CBZ-TPY**, **2TPY-TPA** and **2TPY-CBZ**, respectively.

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

where, E^{ox}_{onset} and E_{FOC} are the onset oxidation potentials of the molecules and ferrocene, respectively, and -4.8 eV is the HOMO energy level of ferrocene against vacuum. The energy of the LUMO (E_{LUMO}) determined from the equation (2) is -2.67, -2.63, -2.63 and -2.60 eV for **2TPA-TPY**, **2CBZ-TPY**, **2TPY-TPA** and **2TPY-CBZ**, respectively. $E_{LUMO} = E_{HOMO} + E_g....(2)$

The presence of stronger electron donating triphenylamine group contributes to a lower oxidation potential and higher HOMO energy level in **2TPA-TPY** and **2TPY-TPA** compared to carbazole containing **2CBZ-TPY** and **2TPY-CBZ**. The electrochemical data are listed in **Table 2**.



Figure 4. Cyclic voltammograms of a) 2TPA-TPY, b) 2CBZ-TPY, c) 2TPY-TPA and d) 2TPY-CBZ.

Table 2. Electrochemical, theoretical and thermal results of **2TPA-TPY**, **2CBZ-TPY**, **2TPY-TPA** and **2TPY-CBZ**.

Molecules	E ^{ox} onset (V)	HOMO [optical/calculated] (eV)	LUMO [optical/calculated] (eV)	Tg/Td (°C)
2TPA-TPY	0.77	-5.31/-4.73	-2.67/-1.68	72.32/426
2CBZ-TPY	0.80	-5.34/-4.76	-2.63/-1.50	66.12/432
2TPY-TPA	0.71	-5.25/-4.70	-2.63/-1.72	27.63/417
2TPY-CBZ	0.82	-5.36/-4.77	-2.60/-1.58	36.33/428

2.4 Theoretical calculations

Figure 5 represents the ground state optimized geometry and the HOMO/LUMO distribution of **2TPA-TPY**, **2CBZ-TPY**, **2TPY-TPA** and **2TPY-CBZ**. The long decyloxy chain is replaced by methoxy group to reduce the calculation time. As seen in **Figure 5**, in the case of

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2TPA-TPY and **2CBZ-TPY**, except the decyloxy substituted phenyl group which is twisted by an angle of ~41° from the thiophene-pyridine plane, the HOMO is distributed majorly on spacer thiophene and vinylic linkage. The HOMO distribution is also extended on nitrogen atom and on one of the phenyl group (which is attached to the vinylic bond) of peripheral triphenylamine in 2TPA-TPY and of ethyl carbazole in 2CBZ-TPY. Further, a partial distribution of HOMO over central pyridine ring is also seen. Since the free phenyl groups in terminal triphenylamine are twisted by an angle of $\sim 42^{\circ}$ from the thiophene-pyridine plane, HOMO is distributed to a lesser extent on triphenylamine group in 2TPA-TPY. Similarly, due to the small twisting from its co-planarity of unsubstituted phenyl group of terminal ethyl carbazole, HOMO is spread to a lesser extent on ethyl carbazole in 2CBZ-TPY. On the other hand, the LUMO is localized mainly on central pyridine and spacer thiophene units; and partially distributed over vinylic linkage both in 2TPA-TPY and 2CBZ-TPY. In addition, there is a minor distribution of LUMO on substituted phenyl group of triphenylamine and ethyl carbazole in 2TPA-TPY and 2CBZ-TPY, respectively. Correspondingly, in the case of 2TPY-**TPA** and **2TPY-CBZ**, the HOMO is majorly localized on spacer thiophene, vinylic linkage, central triphenylamine in 2TPY-TPA and on central carbazole in 2TPY-CBZ, while the LUMO is localized primarily on electron acceptor pyridine ring, spacer thiophene and vinylic linkage. Also, there is a partial distribution of LUMO over substituted phenyl rings of donor triphenylamine and carbazole unit in 2TPY-TPA and 2TPY-CBZ, respectively. It is observed that, the HOMO of all the four molecules is mainly situated on electron donors, while LUMO is mainly localized on electron withdrawing pyridine unit, which indicates the D-A type charge transfer character of the molecules. And, a significant overlap of orbitals is observed from the electron density distribution of HOMO and LUMO levels, suggesting the ambipolar property, which may support for the proper transport of holes/electrons and to maintain the active electronic communication between the acceptor and the donor^[36,37]. The calculated HOMO and LUMO values are given in Table 2.



Figure 5. The optimized molecular structures and HOMO/LUMO distributions of 2TPA-TPY, 2CBZ-TPY, 2TPY-TPA and 2TPY-CBZ.

2.5 Thermal properties

Thermal properties of the molecules were analyzed by differential scanning colorimetry (DSC) and thermogravimetric analysis (TGA). The DSC and the TGA plots of **2TPA-TPY**, **2CBZ-TPY**, **2TPY-TPA** and **2TPY-CBZ** are depicted in **Figure 6** and **Figure 7**, respectively and the results are summarized in **Table 2**. The DSC analysis shows that the molecules are amorphous in nature, as there are no exothermic melting peaks observed during the two heating cycles (**Figure 6**). And, all the four molecules exhibit a clear glass transition temperature (Tg) during the second heating cycle. In fact, molecules **2TPY-TPA** and **2TPY-CBZ** show Tg of 27.63 and 36.33°C, respectively, whereas, molecules **2TPA-TPY** and **2CBZ-TPY** exhibit comparatively better Tg of 72.32 and 66.12°C, respectively. The higher Tg of **2TPA-TPY** and **2CBZ-TPY** compared to that of **2TPY-TPA** and **2TPY-CBZ** is attributed to the presence of bulky side groups in **2TPA-TPY** and **2CBZ-TPY**, which hinders the rotational flexibility, thereby increases the Tg^[38].

The TGA results reveal that the molecules possess extremely good thermal stabilities with the high degradation temperatures. The decomposition temperature (T_d) of **2TPA-TPY** and **2CBZ-TPY** (corresponding to 5% weight loss) is observed at 426 and 432°C, respectively, whereas, the T_d of **2TPY-TPA** and **2TPY-CBZ** is observed at 417 (corresponding to 20% weight loss) and 428°C (corresponding to 10% weight loss), respectively. In addition, a slight degradation

is observed at 218 and 240°C (corresponding to 2% weight loss), in **2TPY-TPA** and **2TPY-CBZ**, respectively, which is due to the decomposition of peripheral, low molecular weight component (4-(4-(decyloxy)phenyl)-2,6-di(thiophen-2-yl)pyridine), present in them. The relatively higher T_d of **2CBZ-TPY** and **2TPY-CBZ** compared to that of triphenylamine containing **2TPA-TPY** and **2TPY-TPA** is due to the presence of carbazole (structurally more rigid compared to triphenylamine) unit in them, which improves the structural rigidity of **2CBZ-TPY** and **2TPY-CBZ**. Apparently, the excellent thermal stability with high T_d of all the four molecules is attributed to the bulky $D-\pi-A-\pi-D/D-A-\pi-D-\pi-A-D$ structural arrangement^[39] with relatively large molecular weights, which leads to a homogeneous and amorphous film and thus, improves the quality of the film at high temperatures, which is a criterion for their practical use in OLEDs.



Figure 6. DSC plots of a) 2TPA-TPY, b) 2CBZ-TPY, c) 2TPY-TPA and d) 2TPY-CBZ.



Figure 7. TGA plots of 2TPA-TPY, 2CBZ-TPY, 2TPY-TPA and 2TPY-CBZ.

2.6 Third–order NLO studies

2.6.1 Nonlinear absorption (NLA) studies

Under ultra-short 50 μ J laser excitation (532 nm, 7 ns pulse width), corresponding to on–axis intensity of 1.386 GW cm⁻², the open aperture (OA) Z–scan analysis was carried out, wherein the transmitted beam was measured without the aperture in front of the detector, to determine the NLA of the molecules^[40]. The linear transmittance was maintained at 70–72% (the details of the experiment are given in ESI). **Figure 8a–d** show the OA Z–scan signatures of **2TPA-TPY**, **2CBZ-TPY**, **2TPY-TPA** and **2TPY-CBZ** in CHCl₃ solution, respectively. The interaction of laser beam with the molecules produces a valley pattern i.e., the transmittance of the molecules decreases gradually towards the focal point and reaches a minimum with the deep transmittance trough at the focus where the curves are symmetric at z=0, which signifies the RSA behavior of the molecules with the positive NLA of the incident light. On the nanosecond time scale the RSA is combined with TPA and ESA, which is collectively called as "the effective TPA" process^[41,42]. The experimental data are matching well with the theoretical model for ESA assisted TPA process in all the four molecules.

Following the intensity dependent absorption coefficient ($\alpha(I)$) for ESA assisted TPA (associated with saturable absorption (SA)), OA Z–scan recordings were theoretically fitted using equation (3) to determine the nonlinear absorption coefficient (β_{eff}) and is given by,

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

where, α_0 is the linear absorption coefficient, *I* is the incident laser intensity, I_s is the saturation intensity, β_{eff} is the nonlinear absorption coefficient associated to the RSA response^[43]. Pulse propagation equation to calculate β_{eff} is given by,

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

where, z is the propagation distance within the sample. The first term in equation (4) expresses the SA and the next term indicates effective TPA part.

The normalized transmittance is given by,

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

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

 L_{eff} is the effective sample length, L is the sample length, α_0 is the unsaturated linear absorption coefficient, z is the position of the sample, $z_o = \pi \omega_o^2 / \lambda$ is the Raleigh range, ω_0 is the beam waist radius at the focal point and λ is the wavelength of laser beam.

The imaginary part of the third-order nonlinear susceptibility $(\chi^{(3)})$ is given by,

$$\operatorname{Im} \chi^{(3)} = \frac{n_o^2 \varepsilon_o c \lambda \beta_{eff}}{2\pi}(6)$$

where, n_0 is the linear refractive index, c is the speed of light and ε_0 is the permittivity of free space.

Using the equations (3) and (5), the experimental data were fitted to the theoretical model to obtain NLA parameters (**Table 3**).

The numerically fitted OA Z–scan results disclose enhanced NLO responses of the synthesized molecules. The obtained β_{eff} values for **2TPA-TPY**, **2CBZ-TPY**, **2TPY-TPA** and **2TPY-CBZ** are 4.45, 3.65, 3.91 and 2.58×10⁻¹⁰ m W⁻¹, respectively, which are very much closer and predominantly better than those reported in the literature (**Table 3**).



Figure 8. Z–scan curves of a) **2TPA-TPY**, b) **2CBZ-TPY**, c) **2TPY-TPA**and d) **2TPY-CBZ** under OA configuration.

2.6.2 Optical limiting (OL) studies

The OL data of 2TPA-TPY, 2CBZ-TPY, 2TPY-TPA and 2TPY-CBZ were extracted from the graphs of normalized transmittance obtained from OA Z-scan analysis against input fluence (Figure 9a–d). From the graph, the onsets of limiting action (the value of input fluence at which the intensity of output transmittance starts decreasing) are observed at 0.18, 0.49, 0.38 and 0.65 J cm^{-2} and the limiting threshold (LT) values (the value of input fluence at which the intensity of output pulse becomes 50% of the initial value) are 1.73, 2.72, 2.68 and 4.68 J cm⁻² for 2TPA-TPY, 2CBZ-TPY, 2TPY-TPA and 2TPY-CBZ, respectively. From the results it is evidenced that the molecules in the present study exhibit exceptional OL action with very low onset and LT values. These significantly reduced values are analogous and better than those of many reported values (Table 3). For an instance, under similar conditions, in our previous communication, one of the thiophene-pyridine based small molecule exhibited excellent NLO properties with β_{eff} and LT of 2.08×10⁻¹⁰ m W⁻¹ and 4.16 J cm⁻², respectively^[44]. Shiju *et al.*^[45] investigated the NLO response of phenothiazine (PTZ)-silver (Ag) organometallic hybrid system, which showed β_{eff} of 3.60×10⁻¹⁰ m W⁻¹ and LT of 3.43 J cm⁻², which is two orders of magnitude higher than that of pristine PTZ. Zhang *et al.*^[46] 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 with the LT of 2.82 J cm⁻², whereas new quinoxaline based push-pull molecule with 1,3-indandione as acceptor was synthesized and its third-order NLO properties were studied by Gopi *et al.*^[47], which showed an effective TPA with very high β_{eff} of 2.0×10⁻¹⁰ m W⁻¹ and low LT of 1.15 J cm⁻². Further, Mi *et al.*^[48] synthesized Zn-complexed D– π –A type porphyrin derivative, Por-Zn-N, through [2+2] click reactions and studied the NLO response of the material, which showed RSA with β_{eff} of 4.8×10^{-10} m W⁻¹. Specifically, **2TPA-TPY** and **2CBZ-TPY** of the present study having similar structural arrangement as that of our previously reported molecules wherein the same core structure (i.e., TPY) was connected to small end groups such as thiophene/phenyl acrylonitriles^[44], show enhanced NLO properties compared to the previous molecules. This is mainly attributed to the improved ICT, increased polarity and extended conjugation existed due to the presence of bulkier end groups (triphenylamine/carbazole) in the present molecules compared to thiophene/phenyl acrylonitriles. Moreover, the LT value of **2TPA-TPY** (1.73 J cm⁻²) is similar to that of our previously reported polymer, P2TPy (1.42 J cm⁻²)^[44] which suggests that the proper selection of bulkier end group and structural modifications in small molecules could lead to comparable NLO properties as that of polymers and could replace the polymeric materials in optical limiting devices.

From the literature reports it is noticed that the enhancement in the nonlinearity is mainly due to the doping of organic compounds with some inorganic materials with the exception of some of the pure organic materials, which showed improved nonlinearity without any doping. However, the materials in the present study have shown remarkable nonlinear response with substantial increment in the β_{eff} of the order 10^{-10} m W⁻¹ and exceptionally well optical limiting behavior with very low LT in their pristine form, which is comparable and better than some of the well-known reported materials, making them capable materials for optical power limiting devices in photonics.



Figure 9. Optical limiting curves of a) **2TPA-TPY**, b) **2CBZ-TPY**, c) **2TPY-TPA** and d) **2TPY-CBZ** at an input intensity of 1.386 GW cm⁻².

2.6.3 Nonlinear refraction (NLR) studies

The pure NLR components were evaluated by dividing closed aperture (CA) data by the corresponding normalized OA Z–scan data to eliminate the NLA part present in CA Z–scan data. The closed by open signatures of **2TPA-TPY**, **2CBZ-TPY**, **2TPY-TPA** and **2TPY-CBZ** are depicted in **Figure 10a–d**, respectively. As it is seen from the figure, there is a prefocal peak followed by null and postfocal valley, which indicates the negative sign of refractive index, representing a self-defocusing nature and thus, negative nonlinearity of **2TPA-TPY**, **2CBZ-TPY**, **2TPY-TPA** and **2TPY-CBZ**. As a result, molecules act like diverging lens. By fitting experimental data to the equation (7), the normalized transmittance (T) at CA condition was determined, and is given by,

$$T(z,\Delta\Phi_o) = 1 + \frac{4\left(\frac{z}{z_o}\right)}{\left(\left(\frac{z}{z_o}\right)^2 + 1\right)\left(\left(\frac{z}{z_o}\right)^2 + 9\right)}\Delta\Phi_o....(7)$$

where, *T* is the normalized transmittance, $\Delta \Phi_o$ is the on–axis nonlinear phase shift at the focus. Therefore, the nonlinear refractive index (η_2) (the NLR coefficient) is calculated by,

$$n_2(esu) = \frac{cn_0\lambda\Delta\Phi_o}{80\pi^2 I_o L_{eff}}.$$
(8)

The real $\chi^{(3)}$ is related to η_2 by the relation (in electrostatic unit),

$$\operatorname{Real}\chi^{(3)} = 2n_o^2 \varepsilon_o c n_2....(9)$$

The NLR parameters of **2TPA-TPY**, **2CBZ-TPY**, **2TPY-TPA** and **2TPY-CBZ** are listed in **Table 3**.



Figure 10. Z–scan curves of a) **2TPA-TPY**, b) **2CBZ-TPY**, c) **2TPY-TPA** and d) **2TPY-CBZ** under CA configuration.

Sample	βeff	Limiting	η²	χ^3	References
	$(\times 10^{-10} \mathrm{mW}^{-1})$	threshold	(esu)	(esu)	
		(J cm ⁻²)		(10^{-12})	
			11		
2ТРА-ТРҮ	4.45	1.73	7.06357×10 ⁻¹¹	14.0157	This work
2CBZ-TPY	3.65	2.72	6.21902×10 ⁻¹¹	11.5239	This work
2TPY-TPA	3.91	2.68	7.63576×10 ⁻¹¹	12.3421	This work
2TPY-CBZ	2.58	4.68	4.78997×10 ⁻¹¹	8.1398	This work
TPyP	2.08	4.16	-	6.56524	[44]
Phenothiazine	3.60	3.43	8.0	-	[45]
(PTZ)–silver (Ag) organometallic hybrid system					
Graphene oxide-	2.6	2.82	-	-	[46]
Fe ₃ O ₄					
	2.0	1.15	-	-	[47]
Zn-complexed D– π–A type porphyrin derivative, (Por–Zn–N)	4.8	-	-	-	[48]

Table 3. Comparison of NLA and NLR parameters of **2TPA-TPY**, **2CBZ-TPY**, **2TPY-TPA**and **2TPY-CBZ** with similar results reported.

The butterfly-shaped molecules in the present study possess highly delocalized π -electronic cloud, resulting from the structural planarity, which provides a prolonged π -conjugation between the electron donor and acceptor groups via excellent ICT interactions, inducing the

19

polarization in the molecules, which leads to a remarkably high β_{eff} value and extremely low LT values of the pristine molecules.

Further, the higher extent of electron donating ability of triphenylamine moiety than the carbazole unit brings about a notable increment in the β_{eff} value and exceptional reduction in the LT value in the case of **2TPA-TPY** and **2TPY-TPA** compared to that of **2CBZ-TPY** and **2TPY-CBZ**. Thus, it is worth to note that these materials would be efficient limiters which would provide safety for damages caused by high intensity sources.

2.7 Electroluminescence properties

Out of four molecules synthesized, 2TPA-TPY exhibits comparatively good film formation and higher solid-state fluorescence quantum yield. As a result, a multilayer non-doped OLED was fabricated employing **2TPA-TPY** as the emissive material and the electroluminescence properties were investigated. The device configuration is as follows: ITO (150 nm)/PEDOT:PSS (30 nm)/NPB (20 nm)/2TPA-TPY (40 nm)/TPBi (35 nm)/LiF (1 nm)/Al (100 nm). In the device, patterned ITO (indium tin oxide)-coated glass substrate was used as a transparent anode, PEDOT:PSS (Poly(3,4-ethylene dioxythiophene)-poly(styrenesulfonate)) as hole injecting material, NPB (N,N'-Di(1-naphthyl)-N,N'-diphenyl-(1,1'biphenyl)-4,4'diamine) as hole transporting layer (HTL), **2TPA-TPY** as emissive material, TPBi (2,2',2"-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) as electron transporting layer (ETL) and hole blocking layer, LiF (lithium fluoride) served as electron injecting layer (EIL) and Al (aluminium) as cathode (Figure 11a), and the energy level diagram is shown in Figure 11b. The current density-voltage-luminance (J-V-L) characteristic, current density-luminance, current density-current efficiency and electroluminescence (EL) spectra of the fabricated device are presented in Figure 12a-d, respectively. As sown in Figure 12a, the device exhibits good diode characteristic with a turn-on voltage of 7.74 V (at 1 cd m⁻²), a maximum luminance of 207 cd m^{-2} , η_{CE} of 1.51cd A^{-1} , η_{Pmax} of 0.46 lm W^{-1} and η_{EOE} of 0.48 % at 100 cd m^{-2} (Table 4). The device emits bright green light having maximum emission (λ_{max}^{em}) at 512 nm with a narrow full width half maximum (FWHM) of 68 nm and commission internationale de leclairage (CIE) coordinates of (0.290, 0.606) at 12 V (Figure 12e). It is seen that the presence of triphenylamine unit as end groups with $D-\pi-A-\pi-D$ configuration effectively reduced the aggregation and crystallinity, and thus, facilitated the formation of homogeneous film by solution processing. Also, there is no any change in the EL peak shape, that reveals the excellent spectral stability of the device. The fabricated device is unoptimized and there is a large scope for the optimization of various parameters which can further improve the device performance.



Figure 11. a) Device configuration and b) the energy level diagram showing the HOMO and LUMO energies of different component materials.



Figure 12. Device characteristics (a) J–V–L characteristic, (b) J–L curve, (b) J– η_{CE} curve, (d) EL spectrum of solution processed un-doped OLED fabricated using **2TPA-TPY** as emissive material, (e) CIE 1931 chromaticity coordinates (x,y) of OLED based on **2TPA-TPY**, (f) photograph of the device in dark and (g) photograph of the device in light .

Molecule	Vonset	λ^{em}_{max}	L _{max}	ηc	ηρ	EQE
	(V)	(nm)	(cdm ⁻²)	$(cd A^{-1})$	(lm W ⁻¹)	(%)
2TPA-TPY	7.74	512	207	1.51	0.46	0.48

 Table 4. Electroluminescence data of 2TPA-TPY in OLED device.

3. Conclusion

In conclusion, four butterfly-shaped molecules possessing D– π –A– π –D/ D–A– π –D– π –A–D configuration, comprising of 2,4,6-trisubstituted pyridine, thiophene, triphenylamine and carbazole moieties were synthesized, characterized and their optoelectronic properties were investigated. The molecules **2TPA-TPY** and **2TPY-TPA** possess red shifted absorption and emission maxima, and also possess higher HOMO energy level compared to **2CBZ-TPY** and **2TPY-CBZ**. Localization of HOMO on electron donor and LUMO on acceptor group renders D–A type charge transfer and the overlapping of orbitals provides ambipolar property for all the four molecules. All the four molecules exhibit excited state assisted TPA with the β_{eff} as high as 10^{-10} m W⁻¹. The molecules **2TPA-TPY** and **2TPY-TPA** show remarkably high β_{eff} of 4.45 and 3.91×10^{-10} m W⁻¹, and extremely low limiting threshold of 1.73 and 2.68 J cm⁻², respectively. The un-doped solution processed OLED using **2TPA-TPY** as emitter exhibits bright green electroluminescence at 512 nm with narrow FWHM of 68 nm, turn-on voltage of 7.74 V (at 1 cd m⁻²), a maximum luminance of 207 cd m⁻², η_{CE} of 1.51cd A⁻¹, η_{Pmax} of 0.46 lm W⁻¹ and η_{EQE} of 0.48 % at 100 cd m⁻². The striking results of **2TPA-TPY** demonstrate its potential use as optical limiter in photonics and emissive material in OLEDs.

4. Experimental Section

4.1 Materials and methods

The chemicals were purchased from commercial suppliers 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%), 1-bromodecane (Sigma Aldrich, 98%), K₂CO₃ (Loba Chemie, 99%), sodium borohydride (Spectrochem Pvt. Ltd., 96%), triphenylphosphine hydrobromide (Sigma Aldrich, 97%), 9H-carbazole (Loba Chemie, 95%), 1-bromoethane (Sigma Aldrich, 98%), sodium hydride (NaH) (Sigma Aldrich, 60% dispersion in mineral oil), 4-formyltriphenylamine (Sigma Aldrich, 97%) and bis(4-formylphenyl)phenylamine (Sigma Aldrich, 95%). Organic solvents were purified according to the standard procedures prior to the usage. All the reactions were carried out under argon atmosphere in round bottomed (RB) flask. The progress of the reaction

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was monitored by thin layer chromatography (TLC) performed on aluminum plates pre-coated with 60 F254 silica gel (Merck KGaA). The developed TLCs were observed under a short/long wavelength ultra-violet-visible (UV-Vis) lamp. The intermediates and final compounds were purified by silica gel column chromatography (60–120 mesh size) using suitable solvent mixtures.

4.2 Synthesis

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

The intermediate $\mathbf{3}$ was synthesized following the procedure mentioned in the literature^[44].

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

The intermediate **4** was synthesized according to the procedure mentioned in the literature^[44].

Synthesis of 5-(4-(4-(decyloxy)phenyl)-6-(thiophen-2-yl)pyridin-2-yl)thiophene-2carbaldehyde (5) and 5,5'-(4-(4-(decyloxy)phenyl)pyridine-2,6-diyl)bis(thiophene-2carbaldehyde) (6)

The intermediate 6 was synthesized following the procedure mentioned in the literature^[44].

The intermediate **5** was separated from the crude product of intermediate **6** by column chromatography using a mixture of pet ether/ethyl acetate (9:1, 8:2, v/v) (1.1 g, yield: 26%) as yellow solid. ESI–MS (*m/z*) calcd. for C₃₀H₃₃NO₂S₂: 503.20 found: 504.37 [M+H]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.96 (s, 1H, –CHO), 7.79–7.71 (m, 5H, Ar–H), 7.66 (d, *J* = 8.0 Hz, 2H, Ar–H), 7.46 (d, *J* = 4.0 Hz, 1H, Ar–H), 7.17–7.15 (m, 1H, Ar–H), 7.05 (d, *J* = 8.0 Hz, 2H, Ar–H), 4.04 (t, *J* = 6.8 Hz, 2H, –OCH₂), 1.87–1.83 (m, 2H, –CH₂–), 1.53–1.49 (m, 2H, –CH₂–), 1.31–1.28 (m, 12H, –CH₂–), 0.91 (t, *J* = 6.4 Hz, 3H, –CH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 183.2, 160.4, 154.2, 152.9, 151.0, 149.9, 144.3, 144.1, 136.7, 129.8, 128.1, 128.0, 125.1, 126.0, 115.9, 115.2, 115.1, 68.2, 31.8, 29.5, 29.3, 30.0, 29.2, 26.0, 22.6, 14.0; Anal. calcd. for C₃₀H₃₃NO₂S₂: C, 71.53; H, 6.60; N, 2.78; S, 12.73; found: C, 70.99; H, 6.87; N, 2.03; S, 12.27.

Synthesisof(5-(4-(4-(decyloxy)phenyl)-6-(thiophen-2-yl)pyridin-2-yl)thiophen-2-
yl)methanol(7)and((4-(4-(decyloxy)phenyl)pyridine-2,6-diyl)bis(thiophene-5,2-
diyl))dimethanol(8)

In a clean and dry RB flask, a solution of intermediate **5** (1.00 g, 1.98 mmol) in methanol (10 mL) was prepared. To this solution, sodium borohydride (0.15 g, 3.97 mmol) was added and the mixture was stirred at room temperature (RT) for 4 h. After the completion of the reaction, the solution was quenched using ice-cold water, the obtained solid was filtered, washed with excess of distilled water, dried and purified by column chromatography using a mixture of pet ether/ethyl acetate (8:2, v/v) as eluent to obtain intermediate **7** as white solid (0.92 g, yield:

92%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.75 (d, J = 2.8 Hz, 1H, Ar–H), 7.67–7.58 (m, 5H, Ar–H), 7.52 (d, J = 4.0 Hz, 1H, Ar–H), 7.39 (d, J = 4.0 Hz, 1H, Ar–H), 7.12–7.10 (m, 1H, Ar–H), 7.01–6.99 (m, 2H, Ar–H), 4.84 (s, 2H, –CH₂OH), 3.99 (t, J = 6.8 Hz, 2H, –OCH₂), 1.99 (s, 1H, –CH₂OH), 1.82–1.79 (m, 2H, –CH₂–), 1.47–1.45 (m, 2H, –CH₂–), 1.28 (m, 12H, –CH₂–), 0.87 (t, J = 6.4 Hz, 3H, –CH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 160.3, 152.5, 152.2, 149.4, 144.8, 144.5, 130.3, 127.7, 127.5, 126.2, 124.7, 124.4, 115.1, 114.3, 114.2, 68.2, 60.3, 31.8, 29.5, 29.3, 26.0, 22.5, 14.0; Anal. calcd. for C₃₀H₃₅NO₂S₂: C, 71.25; H, 6.98; N, 2.77; S, 12.68; found: C, 71.98; H, 6.32; N, 2.89; S, 12.41.

The above-mentioned procedure was followed to get intermediate **8** wherein, intermediate **6** (2.00 g, 3.76 mmol) was made to react with NaBH₄ (0.56 g, 15.04 mmol) (1.82 g, yield: 90%). ESI–MS (*m*/*z*) calcd. for C₃₁H₃₇NO₃S₂: 535.22 found: 536.44 [M+H]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.58 (d, *J* = 8.8 Hz, 2H, Ar–H), 7.54 (s, 2H, Ar–H), 7.50 (d, *J* = 4.0 Hz, 2H, Ar–H), 7.00–6.97 (m, 4H, Ar–H), 4.83 (s, 4H, –CH₂OH), 4.01 (t, *J* = 6.8 Hz, 2H, –OCH₂), 2.50 (s, 2H, –CH₂OH), 1.86–1.79 (m, 2H, –CH₂–), 1.51–1.46 (m, 2H, –CH₂–), 1.36–1.31 (m, 12H, –CH₂–), 0.91 (t, *J* = 7.2 Hz, 3H, –CH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 160.1, 152.2, 149.3, 146.3, 144.7, 130.2, 128.0, 126.0, 124.4, 115.0, 114.1, 68.2, 60.3, 31.8, 29.5, 29.4, 29.3, 29.2, 26.0, 22.6, 14.1; Anal. calcd. for C₃₁H₃₇NO₃S₂: C, 69.50; H, 6.96; N, 2.61; S, 11.97; found: C, 69.08; H, 6.50; N, 2.93; S, 12.08.

Synthesis of 2-(5-((bromotriphenyl- λ^5 -phosphanyl)methyl)thiophen-2-yl)-4-(4-(decyloxy)phenyl)-6-(thiophen-2-yl)pyridine (9) and 2,6-bis(5-((bromotriphenyl- λ^5 phosphanyl)methyl)thiophen-2-yl)-4-(4-(decyloxy)phenyl)pyridine (10)

A mixture of intermediate **7** (0.7 g, 1.38 mmol) and triphenylphosphine hydrobromide (0.57 g, 1.66 mmol) was taken in chloroform (CHCl₃) (10 mL) and refluxed at 60°C for 3 h. Then, the solvent was removed under reduced pressure and diethyl ether (5 mL) was added to solidify the product. The intermediate **9** was obtained as yellow solid and used as such for the next step (1.08 g, yield: 94%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.86–7.77 (m, 10H, Ar–H), 7.69 (m, 6H, Ar–H), 7.61–7.56 (m, 3H, Ar–H), 7.50 (s, 2H, Ar–H), 7.43 (d, *J* = 4.8 Hz, 1H, Ar–H), 7.22 (s, 1H, Ar–H), 7.14–7.12 (m, 1H, Ar–H), 7.00 (d, *J* = 8.4 Hz, 2H, Ar–H), 5.83 (d, *J* = 13.6 Hz, 2H, –CH₂–P), 4.02 (t, *J* = 6.8 Hz, 2H, –OCH₂), 1.84–1.81 (m, 2H, –CH₂–), 1.49–1.47 (m, 2H, –CH₂–), 1.29 (m, 12H, –CH₂–), 0.89 (t, *J* = 6.8 Hz, 3H, –CH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 160.6, 151.5, 151.3, 150.8, 136.6, 135.2, 134.5, 134.4, 133.5, 130.5, 130.4, 130.2, 129.1, 128.4, 128.3, 126.4, 125.6, 118.1, 117.1, 116.8, 115.1, 68.3, 59.4, 31.8, 29.6, 29.3, 29.2, 28.3, 27.5, 25.9, 22.7, 14.0; Anal. calcd. for C4₈H₄₉BrNOPS₂: C, 69.38; H, 5.94; N, 1.69; S, 7.72; found: C, 69.14; H, 5.56; N, 1.91; S, 7.85.

Intermediate **10** was synthesized according to the above-mentioned procedure wherein, intermediate **8** (1.0 g, 1.86 mmol) was made to react with triphenylphosphine hydrobromide (0.76 g, 2.23 mmol) (2.05 g, yield: 93%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.87–7.77 (m, 17H, Ar–H), 7.72–7.64 (m, 12H, Ar–H), 7.45–7.40 (m, 4H, Ar–H), 7.20–7.18 (m, 2H, Ar–H), 7.07 (s, 2H, Ar–H), 6.88 (d, *J* = 8.0 Hz, 2H, Ar–H), 5.94 (d, *J* = 14.0 Hz, 4H, –CH₂–P), 3.96 (t, *J* = 6.8 Hz, 2H, –OCH₂), 1.84–1.79 (m, 2H, –CH₂–), 1.47–1.29 (m, 14H, –CH₂), 0.88 (t, *J* = 6.4 Hz, 3H, –CH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 160.6, 150.2, 149.9, 143.1, 135.0, 134.6, 134.5, 133.0, 131.0, 130.2, 130.1, 128.3, 126.9, 118.0, 114.9, 68.2, 59.3, 31.8, 29.5, 29.4, 29.2, 27.1, 26.7, 26.0, 22.6, 14.0; Anal. calcd. for C₆₇H₆₅Br₂NOP₂S₂: C, 67.85; H, 5.52; N, 1.18; S, 5.41; found: C, 67.67; H, 5.32; N, 1.58; S, 5.97.

Synthesis of 9-ethyl-9H-carbazole (12)

To a solution of 9H-carbazole (2.0 g, 11.96 mmol) in DMF (15 mL), sodium hydride (0.86 g, 35.88 mmol) was added portion wise under argon at 0°C and the reaction mixture was stirred at RT for 30 min. Later, 1-bromoethane (1.07 mL, 14.35 mmol) was added drop wise and the reaction mixture was stirred at RT for 6 h. After the completion of the reaction, the resulted solution was quenched using ice cold water, then the solid product obtained was filtered and the crude product was purified using column chromatography with pet ether as eluent to get intermediate **12** as white solid (2.93 g, yield: 82%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.17 (d, *J* = 6.8 Hz, 2H, Ar–H), 7.52 (t, *J* = 6.8 Hz, 2H, Ar–H), 7.45 (d, *J* = 8.0 Hz, 2H, Ar–H), 7.30 (t, *J* = 7.2 Hz, 2H, Ar–H), 4.38 (q, *J* = 7.2 Hz, 2H, -NCH₂), 1.46 (t, *J* = 7.2 Hz, 3H, –CH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 139.9, 125.6, 122.9, 120.4, 118.7, 108.4, 37.4, 13.7; Anal. calcd. for C₁₄H₁₃N: C, 86.12; H, 6.71; N, 7.17; found: C, 86.28; H, 6.36; N, 7.27.

Synthesis of 9-ethyl-9H-carbazole-3-carbaldehyde (13) and 9-ethyl-9H-carbazole-3,6dicarbaldehyde (14)

Intermediates **13** (1.12 g, yield: 49%) and **14** (0.98 g, yield: 38%) were synthesized according to the procedure mentioned for intermediate **5** in which precursors used were POCl₃ (3.81 mL, 40.96 mmol), DMF (3.15 mL, 40.96 mmol) and intermediate **12** (2.0 g, 10.24 mmol) and the reaction was carried out at 65°C for 24 h. **13**: ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.05 (s, 1H, –CHO), 8.55 (s, 1H, Ar–H), 8.11 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.97 (d, *J* = 8.4 Hz, 1H, Ar–H), 7.51 (t, *J* = 7.2 Hz, 1H, Ar–H), 7.42–7.39 (m, 2H, Ar–H), 7.30 (t, *J* = 7.2 Hz, 1H, Ar–H), 4.32 (q, *J* = 7.2 Hz, 2H, –NCH₂), 1.42 (t, *J* = 7.2 Hz, 3H, –CH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 191.7, 143.5, 140.6, 128.5, 127.1, 126.7, 123.9, 123.1, 123.0, 120.7, 120.2, 109.1, 108.6, 37.8, 13.7; Anal. calcd. for C₁₅H₁₃NO: C, 80.69; H, 5.87; N, 6.27; found: C, 80.31; H, 5.76; N, 6.38.

14: ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.16 (s, 2H, –CHO), 8.69 (s, 2H, Ar–H), 8.11 (d, J = 8.0 Hz, 2H, Ar–H), 7.58 (d, J = 8.0 Hz, 2H, Ar–H), 4.48 (q, J = 7.2 Hz, 2H, –NCH₂), 1.53 (t, J = 7.2 Hz, 3H, –CH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 191.6, 144.2, 129.5, 127.8, 127.0, 124.0, 123.1, 120.7, 109.4, 109.1, 108.6, 37.9, 13.8; Anal. calcd. for C₁₆H₁₃NO₂: C, 76.48; H, 5.21; N, 5.57; found: C, 76.62; H, 5.33; N, 5.21.

Synthesis of 4,4'-((1E,1'E)-((4-(4-(decyloxy)phenyl)pyridine-2,6-diyl)bis(thiophene-5,2-diyl))bis(ethene-2,1-diyl))bis(N,N-diphenylaniline) (2TPA-TPY)

In a two necked RB flask, 4-formyltriphenylamine (0.14 g, 0.50 mmol) and intermediate 10 (0.30 g, 0.25 mmol) were dissolved in a solvent mixture of ethanol and chloroform (1:1) (6 mL) under argon atmosphere. Then, sodium ethoxide (0.023 g, 1.01 mmol, 1 mL) was added in portion wise and the reaction mixture was stirred at RT for 12 h. The excess of solvent was removed under reduced pressure and the crude product was purified by column chromatography using pet ether/dichloromethane (DCM) (8:2, v/v) as mobile solvent to get 2TPA-TPY as a yellow solid (0.163 g, yield: 63%). MALDI-TOF-MS (m/z) calcd. for $C_{69}H_{63}N_3OS_2$: 1013.44 found: 1013.849 [M+H]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.65 (d, J = 8.0 Hz, 2H, Ar–H), 7.61 (s, 2H, Ar–H), 7.58 (d, J = 4.0 Hz, 2H, Ar–H), 7.38 (d, J = 8.0 Hz, 4H, Ar-H), 7.29-7.25 (m, 10H, Ar-H), 7.15-7.11 (m, 9H, Ar-H), 7.06-7.02 (m, 13H, Ar-H), 4.02 (t, J = 6.8 Hz, 2H, $-OCH_2$), 1.86–1.81 (m, 2H, $-CH_2$ –), 1.51–1.47 (m, 2H, $-CH_2$ –), 1.28–1.25 (m, 12H, –CH₂–), 0.88 (t, J = 6.4 Hz, 3H, –CH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 160.2, 152.4, 149.3, 147.5, 145.4, 143.0, 131.0, 130.5, 129.3, 128.7, 128.1, 127.3, 126.6, 125.3, 124.6, 123.4, 123.1, 120.3, 115.1, 114.2, 68.2, 31.9, 29.7, 29.6, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1; Anal. calcd. for C₆₉H₆₃N₃OS₂: C, 81.70; H, 6.26; N, 4.14; S, 6.32; found: C, 81.65; H, 6.17; N, 4.23; S, 6.44.

Synthesis of 3,3'-((1E,1'E)-((4-(4-(decyloxy)phenyl)pyridine-2,6-diyl)bis(thiophene-5,2-diyl))bis(ethene-2,1-diyl))bis(9-ethyl-9H-carbazole) (2CBZ-TPY)

The molecule **2CBZ-TPY** was synthesized following the procedure for **2TPA-TPY**, using the precursors intermediate **13** (0.113 g, 0.50 mmol) and intermediate **10** (0.30 g, 0.25 mmol) (0.137 g, yield: 59%). MALDI–TOF–MS (m/z) calcd. for C₆₁H₅₉N₃OS₂: 913.41 found: 913.652 [M+H]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.26 (s, 2H, Ar–H), 8.15 (d, J = 8.0 Hz, 2H, Ar–H), 7.70–7.66 (m, 4H, Ar–H), 7.63–7.62 (m, 4H, Ar–H), 7.51–7.47 (m, 2H, Ar–H), 7.43–7.39 (m, 4H, Ar–H), 7.37–7.31 (m, 4H, Ar–H), 7.28–7.25 (m, 2H, Ar–H), 7.10 (d, J = 4.0 Hz, 2H, Ar–H), 7.04 (d, J = 8.0 Hz, 2H, Ar–H), 4.38 (q, J = 7.2 Hz, 4H, –NCH₂), 4.03 (t, J = 6.4 Hz, 2H, –OCH₂), 1.85–1.81 (m, 2H, –CH₂–), 1.50–1.48 (m, 2H, –CH₂–), 1.46 (t, J = 7.0 Hz, 3H, –CH₃), 1.29–1.25 (m, 12H, –CH₂–), 0.89 (t, J = 6.8 Hz, 3H, –CH₃); ¹³C NMR (100 MHz,

CDCl₃) δ (ppm): 160.1, 152.5, 149.2, 145.9, 142.7, 140.4, 139.8, 130.6, 130.3, 128.2, 126.2, 125.8, 125.3, 124.4, 123.4, 123.0, 120.5, 119.4, 119.1, 118.8, 115.0, 114.1, 108.7, 108.6, 68.2, 37.7, 31.9, 29.7, 29.6, 29.3, 29.2, 26.0, 22.7, 14.1, 13.9; Anal. calcd. for C₆₁H₅₉N₃OS₂: C, 80.14; H, 6.50; N, 4.60; S, 7.01; found: C, 80.31; H, 6.37; N, 4.77; S, 7.22.

Synthesis of 4-((E)-2-(5-(4-(4-(decyloxy)phenyl)-6-(thiophen-2-yl)pyridin-2-yl)thiophen-2-yl)vinyl)-N-(4-((E)-2-(5-(4-(4-(decyloxy)phenyl)-6-(thiophen-2-yl)pyridin-2-

yl)thiophen-2-yl)vinyl)phenyl)-N-phenylaniline (2TPY-TPA)

The molecule **2TPY-TPA** was synthesized following the procedure for **2TPA-TPY**, using the precursors bis(4-formylphenyl)phenylamine (0.054 g, 0.18 mmol) and intermediate **9** (0.30 g, 0.36 mmol) (0.136 g, yield: 61%). MALDI–TOF–MS (*m/z*) calcd. for C₈₀H₈₁N₃O₂S₄: 1243.52 found: 1243.866 [M+H]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.71–7.69 (m, 3H, Ar–H), 7.67–7.64 (m, 7H, Ar–H), 7.60–7.59 (m, 2H, Ar–H), 7.44–7.30 (m, 8H, Ar–H), 7.21–7.13 (m, 8H, Ar–H), 7.10–7.00 (m, 11H, Ar–H), 4.03 (t, *J* = 6.8 Hz, 4H, –OCH₂), 1.86–1.89 (m, 4H, – CH₂–), 1.52–1.45 (m, 4H, –CH₂–), 1.29–1.25 (m, 24H, –CH₂–), 0.88 (t, *J* = 6.4 Hz, 6H, –CH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 160.2, 153.0, 152.5, 149.5, 147.0, 145.4, 145.0, 143.1, 131.5, 131.3, 130.5, 129.8, 128.2, 127.9, 127.6, 127.3, 125.3, 124.7, 123.9, 115.1, 114.4, 68.2, 31.9, 29.7, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1; Anal. calcd. for C₈₀H₈₁N₃O₂S₄: C, 77.19; H, 6.56; N, 3.38; S, 10.30; found: C, 77.38; H, 6.67; N, 3.44; S, 10.09.

Synthesisof3,6-bis((E)-2-(5-(4-(4-(decyloxy)phenyl)-6-(thiophen-2-yl)pyridin-2-yl)thiophen-2-yl)vinyl)-9-ethyl-9H-carbazole (2TPY-CBZ)

The molecule **2TPY-CBZ** was synthesized following the procedure for **2TPA-TPY**, using the precursors intermediate **14** (0.046 g, 0.18 mmol) and intermediate **9** (0.30 g, 0.36 mmol) (0.121 g, yield: 56%). MALDI–TOF–MS (*m/z*) calcd. for C₇₆H₇₉N₃O₂S₄: 1193.51 found: 1193.815 [M+H]⁺; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.73–7.62 (m, 12H, Ar–H), 7.57–7.41 (m, 8H, Ar–H), 7.30–7.29 (m, 3H, Ar–H), 7.17–7.15 (m, 2H, Ar–H), 7.12–7.10 (m, 2H, Ar–H), 7.05–7.03 (m, 4H, Ar–H), 6.98–6.96 (m, 1H, Ar–H), 4.39 (q, *J* = 7.2 Hz, –NCH₂), 4.03 (t, *J* = 6.8 Hz, –OCH₂), 1.85–1.80 (m, 4H, –CH₂–), 1.50–1.48 (m, 4H, –CH₂–), 1.45 (t, *J* = 7.0 Hz, 3H, –CH₃), 1.28–1.25 (m, 24H, –CH₂–), 0.88 (t, *J* = 6.4 Hz, 6H, –CH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 160.2, 152.4, 149.4, 145.8, 145.1, 142.6, 140.2, 130.5, 128.2, 128.1, 127.9, 127.6, 125.4, 124.7, 123.4, 115.0, 114.3, 108.9, 68.2, 31.9, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1; Anal. calcd. for C₇₆H₇₉N₃O₂S₄: C, 76.41; H, 6.67; N, 3.52; S, 10.73; found: C, 76.62; H, 6.51; N, 3.32; S, 10.90.

Associated content

Supplementary data

Characterization details, spectral characterizations of the intermediates and final compounds, time-resolved photoluminescence decay curves, experimental set up of Z–scan measurements and OLED device fabrication procedure.

Conflicts of interest

None.

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Keywords: electroluminescence • light-emitting diodes • nonlinear optics • photo physics • thiophenes.

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TOC/ Graphical abstract

Ambipolar butterfly-shaped 4-(4-(decyloxy)phenyl)-2,6-di(thiophen-2-yl)pyridine derivative (**2TPA-TPY**) as green emitter for non-doped OLED exhibiting an external quantum efficiency (η_{EQE}) of 0.48 % at 100 cd m⁻², and possessing enhanced two-photon absorption property and extremely low optical limiting property with a limiting threshold of 1.73 J cm⁻².

