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Synthesis and Characterization of Novel Symmetrical Two-photon Chromophores Derived from Bis(triphenylaminotetrathienoacenyl) and Fused-thiophene Units

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Abstract:

Four new donor-π-donor (D-π_1–π_2–π_1-D) fused-thiophene-based chromophores, end-functionalized with electron-donating triphenyl amine (TPA) groups, were developed and characterized for a two-photon absorption study. Within this series, tetrathienoacene (thieno[2',3':4,5]thieno[3,2-b]thieno[2,3-d]thiophene; **TTA**) was employed as side-conjugated (π_1) units, and the central conjugated core (π_2) units were altered with thiophene (**T**), bithiophene (**bT**), thienothiophene (**TT**), and dithienothiophene (**DTT**) for chromophores **1-4**, respectively. The structural and photophysical relationships of the four compounds were compared, and all four chromophores showed strong fluorescence with good thermal stability. The energy gaps compression of these chromophores are verified by electrochemistry and density functional theory (DFT) calculations. The two-photon-related properties of **1-4** were examined, using femtosecond laser pulses as the probing tool. The magnitude of two-photon absorptivity is strongly dependent on the molecular conjugation length and the centered fused-thiophene unit. Within the family, the most conjugated **DTT**-centered chromophore (**4**) exhibits the strongest and the most widely dispersed two-photon absorption cross-section value of up to 3000 GM. To the best of our knowledge, this is the highest 2PA cross section values reported to date among the studied fused thiophene-based chromophores.

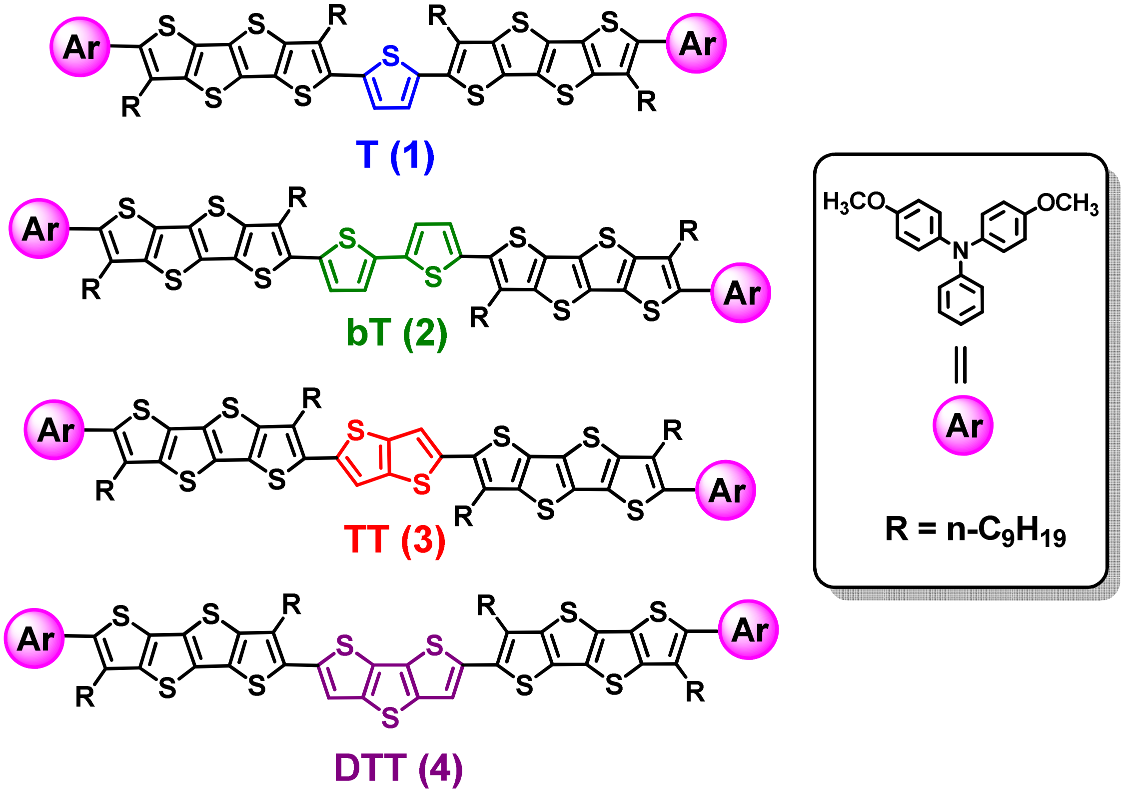
Introduction:

Two-photon absorption (2PA) involves the simultaneous absorption of two photons in the same molecules, resulting molecules promoted to the excited states from ground states.[1] Owing to the wide range potential applications of 2PA materials in the emerging field of photonics and bio-photonics,[2] such as optical power limiting,[3] frequency up-converted lasing,[4] three-dimensional data storage,[5] 3D micro fabrication,[2h, 5a, 6] non-destructive bio imaging and tracking,[2g, 7] and two-photon assisted photodynamic therapy.[8] Numerous efforts have been devoted to designing and engineering molecules with a higher 2PA cross section and different molecular structures.[9] It is noteworthy that the design of an ideal molecule for higher 2PA cross sections should include a number of key molecular features, such as an extent of conjugation with an efficient intramolecular charge transfer, and the presence of electron donor or acceptor components (or both).[10] The most extensively investigated organic compounds for two-photon absorption are the donor-bridge-donor (D-π-D),[10d] donor-bridge-acceptor (D-π-A),[11] acceptor-bridge-acceptor (A-π-A),[12] donor-bridge-acceptor-bridge-acceptor-bridge-donor (D-π-A-D-A-π-D),[13] and donor-bridge-acceptor-bridge-donor (D-π-A-π-D) architectures,[9d] with phenyl, biphenyl, fluorenyl, thiophenyl, bi-thiophenyl, anthracenyl, substituted quinoxalines and dihydrophenanthrenyl moieties as the π-electron bridge, and triphenyl amines and carbazoles as electron donors.[9a, 14] Among the π-conjugated organic building blocks, fused-thiophenes are emerging as one of the most promising moieties for organic thin film transistors (OTFTs), organic photovoltaics (OPVs) and dye-sensitized solar cells (DSSCs).[15]

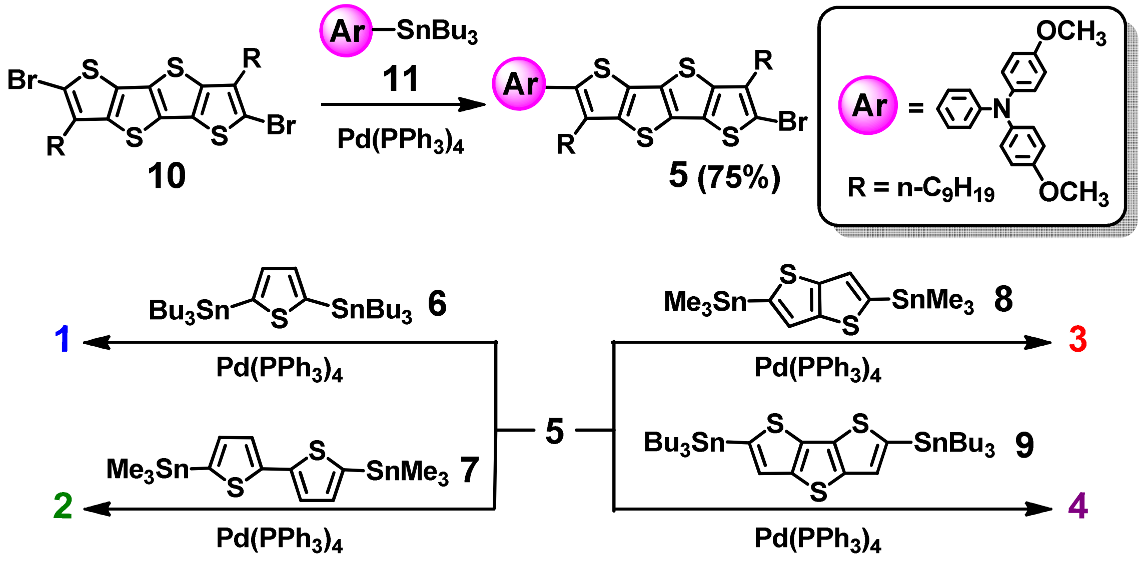
Due to their unique structural features, such as large energy gaps (higher ambient stability), high degree of conjugation, and strong intermolecular S-S interactions (leading to close molecular packing), fused-thiophenes have exhibited efficient intermolecular charge transport in OTFTs.[15a, 15b] However, for 2PA, only fused-thiophenes with two and three thiophene membered rings (i.e. thienothiophene; **TT**, and dithienothiphenes; **DTT**) as conjugated π-electron bridged chromophores have been explored, although they have poor two-photon-absorption characteristics.[16] Fused-thiophenes with more than three fused rings, such as tetrathienoacene (**TTA**),[15b] have not been explored in two-photon absorption studies due the tedious synthesis and low solubility of such compounds. Theoretical considerations suggest that centrosymmetric systems, such as D-π-A-π-D and A-π-D-π-A, will generally give stronger 2PA than that of corresponding dipolar chromophores (D-π-A).[2a] Herein, we present the synthesis and photophysical characterization of a novel series of two-photon active D-π_1-π_2-π_1-D architecture with symmetrical molecular structures, where 4,4-dimethoxytriphenyl amine is the donating unit, tetrathienoacene (**TTA**) serves as the π_1-spacer, and thiophene (**T**), bi-thiophene (**bT**), thienothiophene (**TT**), and dithienothiophene (**DTT**) units are the centered π_2-bridges. Note that the solubility of these compounds has been increased by substituting β alkyl group into tetrathienoacene.[17] By altering the conjugation connectivity at the center, the photophysical and electrochemical properties (include 2PA cross sections) of these synthesized molecules **1-4** were investigated and compared. Within this family, the **DTT**-centered chromophore (**4**) exhibits the strongest and the most widely dispersed two-photon absorption cross-section value of up to 3000 GM, rendering it the highest 2PA performing chromophore reported to date among the studied fused-thioiphene-based model compounds. This two-photon absorption cross-section value is about ten times higher than that of previously reported fused-thiophene **DTT**-based 2PA molecules.[16a]

I. Results and discussion:

The chemical structures of the four studied chromophores are shown in scheme 1, and the synthetic routes are shown in scheme 2. Compounds **1-4** were synthesized from coupling of monobrominated tetrathienoacene (**5**) with the corresponding di-stannylated derivatives of thiophene (**6**), bithiophene (**7**), thienothiophene (**8**), and dithienothiophene (**9**) via Stille coupling reactions to afford the desired products (**1-4**) in yields of 75-89%. The key intermediate compound (**5**) was synthesized by the Stille coupling reaction of dibromotetrathienoacene (**10**) with 1 equivalence of the corresponding stannylated triphenyl amine (**11**). Compound **11** was prepared by the treatment of triphenyl amine bromide with n-BuLi followed by the successive addition of tributyltin chloride.[18] To maintain adequate solubility, we have introduced a large alkyl (**R**; C_9H_{19}) substituent into both *β*–positions of the tetrathienoacene core[17a] for all chromophores; hence the targeted chromophores possess good solubility in common organic solvents, such as THF, CH_2Cl_2, $CHCl_3$ and toluene. All the newly synthesized compounds have been characterized by conventional chemical and physical methodologies.



Scheme 1. Molecular structures of the studied model chromophores (**1-4**).



Scheme 2. Synthetic route to the target chromophores **1-4** and key intermediate **5**.

II Thermal and Linear Optical Properties:

The four new fused-thiophene based chromophores are very thermally stable. The thermogravimetric analysis (TGA) plots indicate that weight loss (≈ 5%) only occurs on heating above 397 °C (see Table 1). The differential scanning calorimetry (DSC) scans show sharp endothermal peaks above 172 °C. TT-centered (**3**) and DTT-centered (**4**) chromophores exhibit higher melting points than those of T- and bT-cored chromophores (**1** and **2**). Linear absorption and fluorescence spectra of the studied chromophores **1-4** in toluene are shown in Figure 1, and the corresponding absorption data are summarized in Table 1. All four compounds exhibit an intense linear absorption in the UV-Vis region. The absorption and molar extinction coefficients (ε) are 431 (4.4×10^{4} $\mathrm{cm^{-1}M^{-1}}$), 443 (8.7×10^{4} $\mathrm{cm^{-1}M^{-1}}$), 434 (3.7×10^{4} $\mathrm{cm^{-1}M^{-1}}$), and 441 (8.1×10^{4} $\mathrm{cm^{-1}M^{-1}}$) for compounds **1-4**, respectively. Due to more extended conjugation in bithiophene- (bT), thienothiophene- (TT), and dithienothiphene- (DTT) center than thiophene- (T) core, compounds **2-4** exhibit greater red-shifted absorptions compared to compound **1**. Compound **2** is further red-shifted compared to **3** and **4**, most likely because the large stabilization energy of small fused thiophenes (in **3** and **4**) results in less favorable delocalization of electrons.[19] The optical energy gaps of compounds **1-4** are 2.40, 2.34, 2.39 and 2.37, respectively, calculated from the onset of the absorption. Compound **2** exhibits the smallest energy gap, which is verified by electrochemical study and theoretic calculation (*vide infra*).

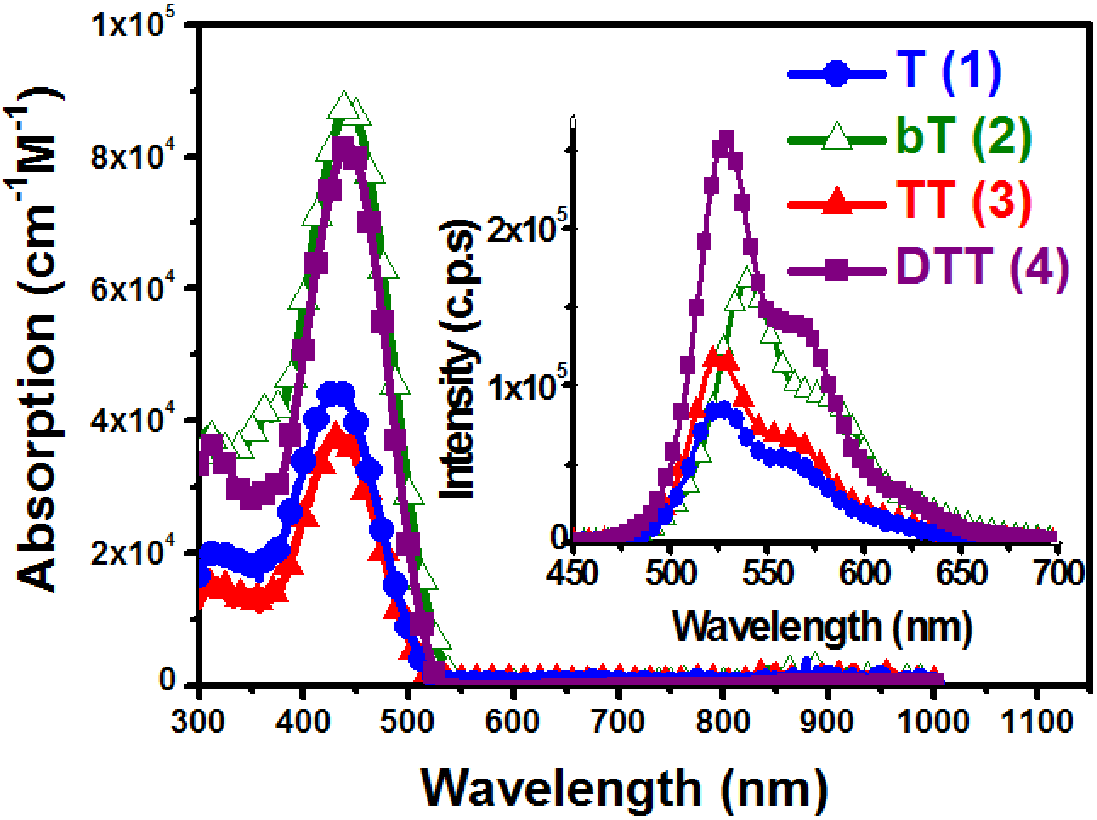


Figure 1. Linear absorption and fluorescence spectra (inset) of compounds **1-4** in toluene (10^{-6}M).

The emission spectra of all four compounds were obtained in toluene, and are listed in Table 2 and shown in Figure 1(inset). All four compounds are highly fluorescent, and the maximum emissions of these compounds increased with their extended conjugation, with the fluorescence quantum yields being 0.38, 0.43, 0.56 and 0.51 for **1-4**, respectively.

Table 1. Thermal, optical, and electrochemical properties of **1-4**.

Cpd	DSC T_m (°C)	TGA (°C; 5%)	UV-Vis λ_{max} [a] (nm)	E_{ox} (V)[b]	E_{red} (V)[b]	HOMO (eV) [c]	LUMO (eV) [c]	ΔE_{gap} (eV)	
								DPV [b]	UV[d]
1	172	405	431	0.78	-1.83	-4.98	-2.37	2.61	2.40
2	191	406	443	0.77	-1.77	-4.97	-2.43	2.54	2.34
3	234	400	434	0.77	-1.81	-4.97	-2.39	2.58	2.39
4	200	397	441	0.75	-1.80	-4.95	-2.40	2.55	2.37

[a] in toluene. [b] by DPV in o-$C_6H_4Cl_2$ at 25 °C. All potentials are reported with reference to an Fc^+/Fc internal standard (at +0.6 V). E_{red} = reductive potential; E_{ox} = oxidative potential [c] using HOMO= -(4.2+ E_{ox}); LUMO= -(4.2+ E_{red}). [d] Energy gap estimated from UV-Vis end on absorption.

III. Electrochemical Characterization:

The energy levels of the highest occupied molecular orbitals (HOMOs) and lowest-unoccupied molecular orbitals (LUMOs) are among the most important parameters to evaluate the 2PA cross section for dye molecules.[20] The electrochemical properties of the studied fused-thiophene based chromophores were examined by differential pulse voltammograms (DPVs), measured in 0.1M Bu_4NPF_6 dichlorobenzene solution at 25 ºC. The resulting oxidative and potential data are summarized in Table 1. The DPVs of **1-4** exhibited oxidation and reduction peaks at 0.78/-1.83, 0.77/-1.77, 0.77/-1.81, and 0.75/-1.80 (V), respectively. The derived HOMO/LUMOs of compounds **1-4** are -4.98/-2.37, -4.97/-2.43, -4.97/-2.39, and -4.95/-2.40 (eV), respectively. (HOMO energies were estimated using the conventional equation, E_{HOMO} = -(4.20 + E_{ox}); E_{LUMO} = -(4.20 + E_{red}), assuming ferrocene/ferrocenium oxidation at = -4.8 eV). Therefore, the corresponding HOMO-LUMO energy gaps of **1-4** are 2.61, 2.54, 2.58, and 2.55 eV, respectively (Table 1, Figure 2a). Compared to thiophene-centered molecule **1**, the HOMO energy level of analogs **2-4** were up-shifted as shown in Figure 2a, which is consistent with the known conjugation effects. The electrochemically derived HOMO-LUMO energy gaps of the four molecules are also consistent with the values obtained from the optical spectroscopy; bT-centered **2**, exhibits the smallest energy gap. Note that as the conjugation length of the spacer group increases in the same series, the HOMO energy levels are up-shifted with contracted energy gaps, verifying that the DTT- (**4**) and TT-centered (**3**) molecules have a more extended delocalization effect than T-centered (**1**).

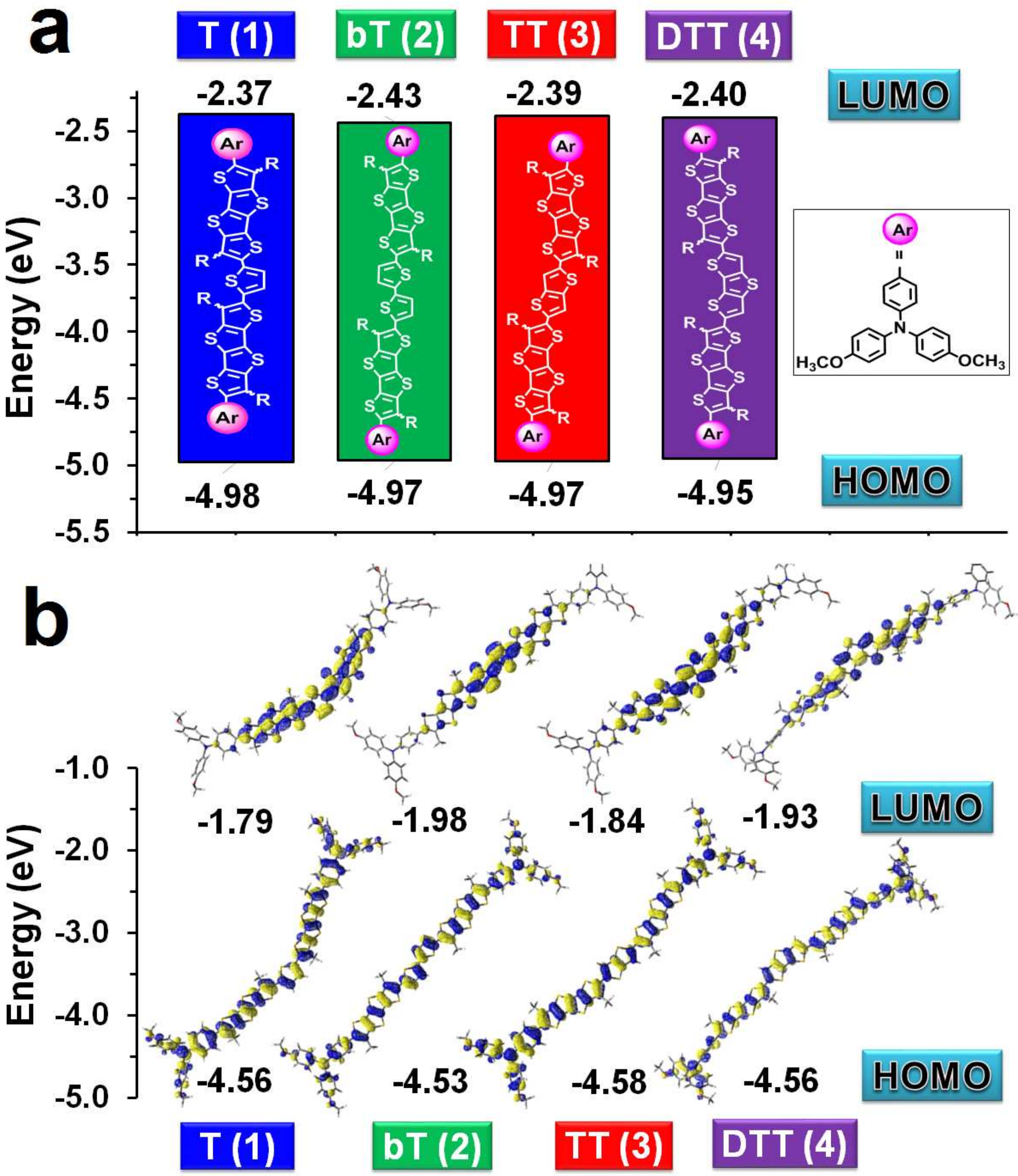


Figure 2. Energetic alignment of molecules **1-4**. a) DPV-derived HOMO and LUMO energy levels; b) DFT-derived molecular orbital contours.

IV Electronic structure analysis:

Electronic structure calculations were performed at the B3LYP/6-31G* level of density functional theory (DFT; Figure 2b). All four molecules have similar ground state geometries characterized by relatively coplanar backbones, with the HOMO level electron density clearly delocalized on the end-capped triphenylamine donors, the π_1-spacer fused-thiophenes, and the π_2-bridge thiophene moieties, whereas the LUMO level localized on the central moieties. The computed HOMO energies are -4.56, -4.53, -4.58, and -4.56 eV for **1-4**, respectively, and the excited state (LUMO) energies are -1.79, -1.98, -1.84, and -1.93 eV for **1-4**, respectively, yielding optical gaps of 2.77, 2.55, 2.74, and 2.63 eV for **1-4**, respectively. With the most centralized electron density of LUMO level, molecule **2** has the lowest computed LUMO energy and thus results the most compressed HOMO-LUMO energy gap, which is well consistent with the values obtained from optical spectroscopy and electrochemically-derived DPV data. Time-dependent DFT (TD-DFT) computations also show that the principal optical transitions of **2** and **4** exhibit similar large oscillator strengths, (3.161 and 3.163, respectively), which in good agreement with the high experimental extinction coefficients for **2** and **4** (87,000 and 81,000 $M^{-1}cm^{-1}$, respectively).

Table 2. Photophysical properties of **1-4** in solution.[a]

Compound	$\lambda_{\mathbf{max}}^{abs}$/nm^{b}	ε^{c} [10^4 $cm^{-1}M^{-1}$]	λ_{max}^{em} [nm]^{d}	Φ_F^{e}	τ_{1PA-FL} [ns]^{f}	δ_2^{max} [GM]^{g}
T (**1**)	431	4.4	525	0.38	0.9	1900
bT (**2**)	443	8.7	540	0.43	0.96	2100
TT (**3**)	434	3.7	528	0.56	0.96	2400
DTT(4)	441	8.1	531	0.51	1.02	3000

The concentration was 1×10^{-6} M and 1×10^{-4} M for 1PA-related and 2PA-related measurements, respectively; [b] One-photon absorption maxima; [c] Molar absorption coefficient; [d] 1PA-induced fluorescence emission maximum; [e] Fluorescence quantum efficiency; [f] 1PA-induced fluorescence lifetimes; [g] Maximum 2PA cross-section values (with experimental error ~ ±15%); 1 GM = 1×10^{-50} cm^4s/photon-molecule.

V. Two photon absorption:

The measured two photon absorption (2PA) spectra for these compounds in toluene are shown in Figure 3, and the data is summarized in Table 2. All four compounds show strong 2PA activity, and the 2PA cross section values for compounds **1-4** are 1900, 2100, 2500 and 3000 GM, respectively. The 2PA cross section values increased in order from compounds **1** to **4**. The chromophores with fused-thiophenes as bridging connectors (**3** and **4**) exhibit significantly amplified 2PA cross section values compared to **2** (bithiophene as the bridging center) with similar conjugations. This not only clearly indicates that the incorporation of fused-thiophenes as bridging and centered core units can significantly enhance the 2PA strength but also demonstrates that fused-thiophenes are suitable candidates for two-photon absorption based applications. It is noted that the peak positions of the 2PA bands of the studied chromophores in Fig. 3 are hypsochromically shifted compared to the wavelength positions of twice of their linear absorption maxima ($i.e.\, 2\lambda_{\max}^{1PA} > \lambda_{\max}^{2PA}$). This implies that the most accessible two-photon state for each model dye molecule is higher in energy than that of the one-photon state of this compound. Similar trend has been observed and reported previously for other symmetrically substituted fluorophores.[21] The 2PA-induced fluorescence emissions of these compounds can be seen in Figure 4(a), which were recorded from the surface of the sample. The power-squared dependence of the 2PA-induced fluorescence intensity on the excitation intensity of these fluorophores was also examined. Figures 4 (b-e) shows the logarithmic plots of the experimental data, and the results from the linear fitting (i.e slope ~ 2) confirm that the 2PA process is responsible for the up-converted fluorescence emissions that were observed in all cases.

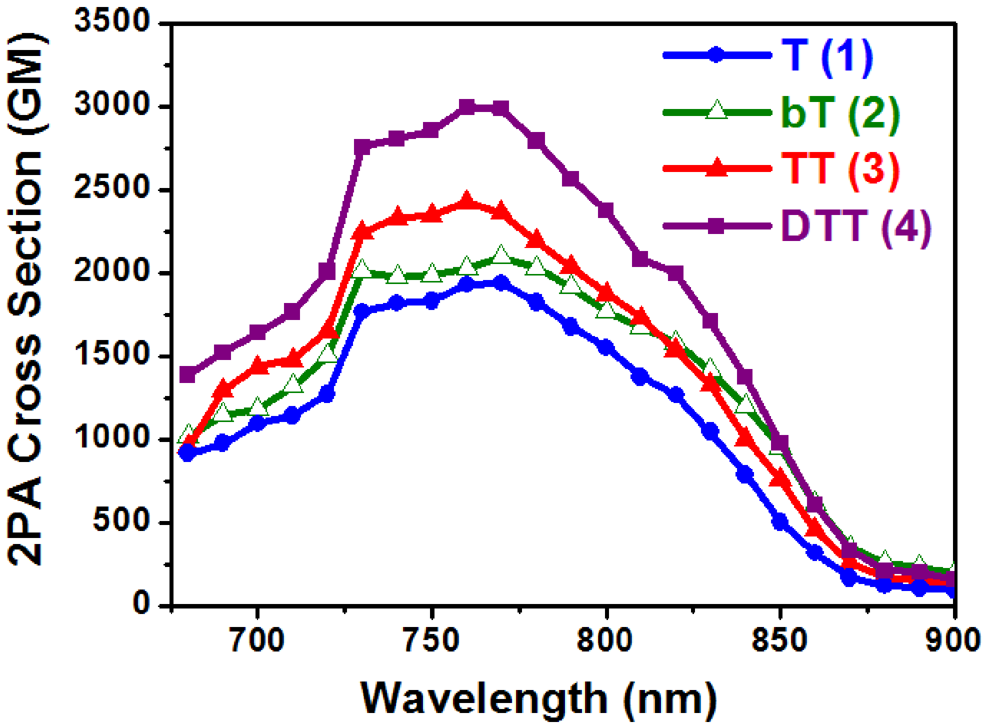


Figure 3. Degenerate two-photon absorption spectra of **1-4.** (1×10^{-4} M) in toluene measured by the 2PEF method (experimental error ca. ±15 %).

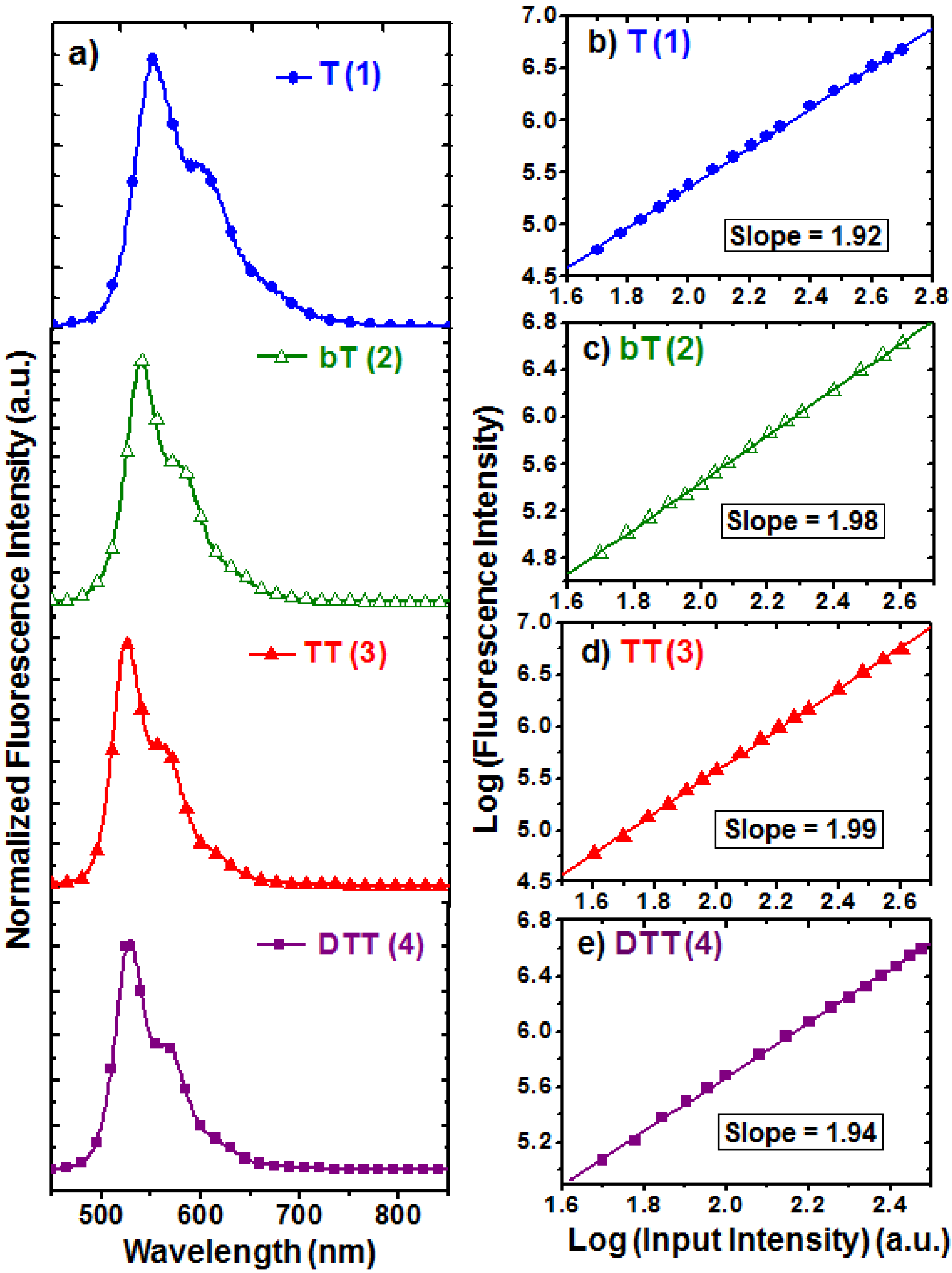


Figure 4. a) Normalized two-photon excited up-conversion spectra of fluorophores **1-4** in toluene at 1x10^{-6} M; b-e) are the logarithmic plots of power-squared dependence of the 2PA-induced fluorescence intensities on the input intensities of these compounds in toluene.

Conclusion:

In conclusion, a series of D-π_1-π_2-π_1-D type conjugated model chromophores were synthesized using tetrathienoacene (TTA) as the bridging π_1-unit and thiophene (T), bithiophene (bT), thienothiophene (TT), and dithienothiophene (DTT) as the central π_2-units and triphenylamine as the electron-donating end-groups. The related thermal, electrochemical, and optical properties of these model dye molecules were investigated through corresponding methods. The DTT-cored congener (**4**) exhibits the strongest 2PA of up to 3000 GM in the near-IR region, and this could be attributed to the extension of the π-length of the central rigid core, rendering the later the highest 2PA performing chromophore reported to date among the fused-thioiphene-based model compounds. This study suggests that incorporation of oligo- to fused-thiophenes as bridging or central π-units can significantly enhance the 2PA cross section values and β-alkyl substituted tetrathienoacenes acts as highly efficient bridging units for 2PA chromophores. The experimentally derived structure property relationships are in good agreement with the DFT electronic structure calculations. We believe that the structural motif of our chromophores may serve as a benchmark for the future development of fused-thiophene-based chromophores for two-photon-related applications.

Experimental section

Materials and Methods: All chemicals and solvents were of reagent grade and were obtained from Aldrich, Alfa and TCI Chemical Co. Solvents for reactions (toluene and THF) were distilled under nitrogen from sodium/benzophenone ketyl, and halogenated solvents were distilled from CaH_2. NMR spectra were measured using a Bruker 300 or 500 MHz spectrometer with chloroform-*d* as solvents. UV–Vis spectra were recorded using a Shimadzu UV3600 UV–Vis–NIR spectrophotometer. Mass spectrometric data were obtained with a JMS-700 HRMS instrument. Dibromotetrathienoacene (**10**),[17a] 4-tributylstannyl-N,N-bis(4-

methoxyphenyl)aniline (**11**)[18], 2,5-bis(tributylstannyl)thiophene (**6**)[22], 5,5'-bis(trimethylstanny-l)-2,2'-bithiophene (**7**),[23] 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene (**8**)[24] and 2,6-bis(tributylstannyl)dithieno[3,2-b:2',3'-d]thiophene (**9**)[25] were prepared according to the procedures described in the literature.

Compound (5): $Pd(PPh_3)_4$ (0.03 mmol) was added to a solution of dibromotetrathienoacene (**10**) (2.05 g, 3.10 mmol) and 4-tributylstannyl-N,N-bis(4-methoxyphenyl) aniline (**11**) (1.89 g, 3.10 mmol) in toluene. The mixture was stirred and refluxed under nitrogen overnight. After completion of the reaction, the solvent was evaporated under a vacuum and the residue was purified by column chromatography on silica gel with dichloromethane:hexane (1:9) as the eluent to produce a pale yellow solid (75 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.7, 2H), 7.13 (d, *J* = 8.7 4H), 6.96 (m, 2H), 6.87 (m, 4H), 3.82 (s, 6H), 2.82 – 2.71 (m, 4H), 1.76 – 1.71 (m, 4H), 1.35 – 1.27 (m, 24H), 0.91 – 0.86 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 156.32, 148.56, 142.24, 140.57, 139.33, 138.78, 135.45, 131.94, 131.25, 131.13, 130.05, 129.89, 128.53, 127.14, 126.16, 119.64, 114.92, 108.24, 55.56, 32.02, 29.72, 29.65, 29.45, 29.21, 29.14, 28.38, 28.24, 22.81, 14.26. HRMS (*m/z*, FAB+) calcd for $C_{48}H_{56}BrNO_2S_4$ 885.2377, found 885.2379 and 887.2360.

General Procedure for Stille Cross-Coupling Reactions of final targets: $Pd(PPh_3)_4$ (0.01 equiv) was added to a solution of compound **5** (2.1 equiv) and stannyl derivatives **6-9** (1.0 equiv) in toluene. The resulting mixture was refluxed overnight under nitrogen. After removal of solvent, the obtained residue was purified by column chromatography on silica gel with dichloromethane and hexane as the eluent. Further purification was done by trituration with acetone to give the target molecules.

Compound 1 (Bis(4T)-T):

The title compound was obtained as an orange-red solid (yield = 89 %). Mp: 172 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.28 (d, *J* = 8.7 Hz, 4H), 7.17-7.11 (m, 10H), 6.96 (d, *J* = 8.7 Hz, 4H), 6.87 (d, *J* = 9.0 Hz, 8H), 3.81 (s, 12H), 2.98 (t, *J* = 7.8 Hz, 4H), 2.81 (t, *J* = 7.8 Hz, 4H), 1.83-1.78 (m, 8H), 1.46 – 1.27 (m, 48H), 0.87-0.85 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.20, 148.42, 142.44, 142.27, 140.49, 139.11, 136.55, 132.84, 132.42, 131.21, 131.10, 130.39, 129.78, 129.24, 128.66, 127.04, 126.18, 126.12, 119.55, 114.81, 55.50, 31.92, 29.83, 29.72, 29.63, 29.60, 29.54, 29.49, 29.37, 29.35, 29.18, 29.11, 29.02, 28.30, 22.70, 14.14. HRMS (*m/z*, FAB+) calcd for $C_{100}H_{114}N_2O_4S_9$ 1694.6265, found 1694.6260.

Compound 2 (Bis(4T)-bT):

The title compound was obtained as a red solid (yield = 79 %). Mp: 191 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 4H), 7.17 – 7.14 (m, 10H), 7.10 (m, 2H), 6.99 (m, 4H), 6.90 (m, 8H), 3.85 (s, 12H), 2.97 (m, 4H), 2.83 (m, 4H), 1.85 – 1.80 (m, 8H), 1.52 – 1.32 (m, 48H), 0.94 – 0.92 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.34, 148.51, 142.93, 142.58, 142.17, 140.61, 139.51, 139.32, 138.17, 133.32, 132.62, 131.20, 131.14, 130.77, 129.78, 129.76, 128.72, 126.99, 126.26, 119.68, 117.92, 114.91, 55.48, 31.94, 29.74, 29.58, 29.49, 29.39, 29.32, 29.27, 29.14, 29.05, 28.94, 28.30, 22.62, 14.01. HRMS (*m/z*, FAB+) calcd for $C_{104}H_{116}N_2O_4S_{10}$ 1776.6142, found 1776.6161.

Compound 3 (Bis(4T)-TT):

The title compound was obtained as orange-red solid (yield = 85 %). Mp: 234 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (m, 6H), 7.15 – 7.14 (m, 8H), 6.98 (d, *J* = 8.5 Hz, 4H), 6.90 (d, *J* = 8.9 Hz, 8H), 3.85 (s, 12H), 2.99 (t, *J* = 7.5 Hz, 4H), 2.83 (t, *J* = 7.5 Hz, 4H), 1.89 – 1.78 (m, 8H), 1.52 – 1.32 (m, 48H), 0.94 – 0.92 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.34, 148.51, 142.58, 142.17, 140.61, 139.51, 139.32, 138.17, 133.32, 132.62, 131.20, 131.13, 130.77, 129.78, 128.72, 126.99, 126.26, 119.68 , 117.92, 114.91, 55.48, 31.86, 29.73, 29.58, 29.49, 29.39, 29.32, 29.26, 29.13, 29.05, 28.94, 28.30 , 22.62, 14.01 . HRMS (*m/z*, FAB+) calcd for $C_{102}H_{114}N_2O_4S_{10}$ 1750.5986, found 1750.5974.

Compound 4 (Bis(4T)-DTT):

The title compound was obtained as an orange-red solid (yield = 75 %). Mp: 200 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.28 (m, 6H), 7.14 (d, *J* = 8.8 Hz, 8H), 6.98 (d, *J* = 8.5 Hz, 4H), 6.89 (d, *J* = 8.8 Hz, 8H), 3.84 (s, 12H), 2.98 (t, *J* = 7.5 Hz, 4H), 2.81 (t, *J* = 7.5 Hz, 4H), 1.90 – 1.74 (m, 8H), 1.46 – 1.25 (m, 48H), 0.94 – 0.92 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.33, 148.49, 142.60, 142.18, 141.38, 140.61, 139.33, 137.26, 133.31, 132.66, 131.17, 131.11, 130.75, 130.59, 129.76, 129.70, 128.70, 126.99, 126.26, 119.67, 119.09, 114.90, 55.48, 31.86, 29.72, 29.59, 29.49, 29.39, 29.32, 29.27, 29.10, 29.05, 28.94, 28.30, 22.62, 14.00. HRMS (*m/z*, FAB+) calcd for $C_{104}H_{114}N_2O_4S_{11}$ 1806.5701, found 1806.5713.

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Keywords: tetrathienoacene • dithienothiophene • thienothiophene • chromophores • non-linear optics • two-photon absorption

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Graphical Abstract:

Synthesis and Characterization of Novel Symmetrical Two-photon Chromophores Derived from Bis(triphenylaminotetrathienoacenyl) and Fused-thiophene Units

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