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Synthesis and characterization of two-photon active chromophores based on asymmetrically substituted tetrathienoacene scaffolds

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Four new asymmetric donor-π-acceptor (D-π-A) fused-thiophene based chromophores were developed and characterized for a two-photon absorption study. In the chromophores the alkylated tetrathienoacene served as a π spacer, *p*-methoxytriphenylamine was used as an electron donor, and a cyanoalkyl acetate unit was employed as the acceptor. To investigate the effect of elongated conjugation on this system, thiophene units were systematically incorporated between the central core and each capped ends. The thermal, optical, and electrochemical properties of these compounds were investigated. The photo-physical, electrochemical and electronic properties of these molecules were compared, and all four chromophores exhibit strong fluorescence and high thermal stability. The elucidated structure-property correlations are in agreement with the theoretical calculations based on the density functional theory. The compound containing a thiophene unit between the donor and spacer exhibits a maximal two-photon absorption cross-section value of 1130 GM.

1. Introduction

The development of organic materials with higher two-photon absorption (2PA) cross-sections has attracted much interest due to their valuable applications in photonics and bio-photonics, such as two-photon dynamic therapy [1,2], two photon optical power limiting [3,4], frequency up-converted lasing [5], 3D microfabrication [6], three-dimensional data storage [7], non-destructive bioimaging and tracking [8], and the localized release of bioactive species. Although the 2PA cross-section values can be enhanced by choosing appropriate π conjugated building blocks with enforced coplanarity, it is also important that a π conjugated chromophore should possess good chemical and optical properties, such as easy processability, durability, photostability and good fluorescence quantum yields [9]. The most extensively studied π-conjugated chromophores for two-photon properties are alkenyl, alkynyl, phenyl, biphenyl, fluorenyl, thiophenyl, bi-thiophenyl, anthracenyl, substituted quinoxalinyl and dihydrophenanthrenyl compounds [3,10–22]. Recent work has shown that tetrathienoacenes (TTA) are one of the best candidates for 2PA chromophores [23,24]. Tetrathienoacenes are promising materials with applications in organic thin film transistors (OTFT) [25], organic photovoltaics (OPV) [26], and dye-sensitized solar cells (DSSC) [27] due to their unique features of extensive conjugation, and strong intra- and intermolecular S–S interactions, which make the core highly coplanar and thus have excellent charge transport properties [28]. In addition, TTAs exhibit high stabilities and the solubility of the derived TTAs can be tuned by altering the core attached alkyl substituents [29,30]

Recently we have reported the first tetrathienoacenes to serve as a π conjugated spacer with D-π-D architecture chromophores in order to achieve two-photon properties [23,24], and the results showed stronger and more widely dispersed two-photon absorption for these new TTA-based molecules. In the current study we further explore a new series of two-photon active molecules with a Donor-π-Acceptor (D-π-A) framework, where *p*-methoxy triphenylamine (TPA) served as an electron donor, thieno[2′,3′:4,5]thieno

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[3,2-*b*]thieno[2,3-*d*]thiophene (**TTA**) was employed as the π-spacer, and cyanoalkyl acetate (**CA**) was utilized as the acceptor unit. The photo-physical and electrochemical properties of this series were systematically investigated by strategically inserting the thiophene units between the donor and spacer or among the spacer and acceptor. In addition, the electronic properties of these newly developed TTAs were investigated using density functional theory (DFT). Among this new series, a significant enhancement in two-photon cross section values was observed when thiophene was inserted between the donor and spacer, with compound **T4T** (**2**) exhibiting the highest 2PA cross sections of up to 1130 GM.

2. Experimental section

2.1. Materials and methods

All chemicals and solvents were of reagent grade and were obtained from Aldrich, Arco, or TCI Chemical Co. Solvents for reactions (toluene, benzene, ether, 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 the solvent. UV–Vis spectra were recorded using a Shimadzu UV3600 UV–Vis–NIR spectrophotometer. Electrospray ionization mass spectrometry was performed using a JMS-700 HRMS spectrometer. 3,7-dinonylthieno[2′,3′:4,5]thieno[3,2-*b*]thieno[2,3-*d*]thiophene (**10**), 3,7-dinonylthieno[2′,3′:4,5]thieno[3,2-*b*]thieno[2,3-*d*]thiophene-2-carbaldehyde (**8**), 2,6-dibromo-3,7-dinonylthieno[2′,3′:4,5]thieno[3,2-*b*]thieno[2,3-*d*]thiophene (**9**), 4-tributylstannyl-*N*,*N*-bis(4- methoxyphenyl)aniline (**11a**) [31], 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(5-(tributylstannyl)thiophen-2-yl)phenyl)aniline (**11b**) [27] were prepared according to the procedures described in the literature.

2.1.1. *6-bromo-3,7-dinonylthieno[2′,3′:4,5]thieno[3,2-b]thieno[2,3-d]thiophene-2-carbaldehyde [27]* ***7***

Compound **8** (0.4 g, 0.57 mmol) and NBS (0.122 g, 0.68 mmol) were dissolved in THF (25 mL). After stirring at 50 °C for 6 h, the mixture was poured into water (50 mL). The obtained precipitate was filtered and recrystallized from dichloromethane to obtain compound **7** as a yellow solid (0.39 g). Yield 88%. ^1H NMR ($CDCl_3$, 300 MHz): δ 10.08 (s, 1H), 3.12 (t, $J = 7.61$ Hz, 2H), 2.77 (t, $J = 7.61$ Hz, 2H), 1.70–1.86 (m, 4H), 1.26–1.41 (m, 24H), 0.84–0.90 (m, 6H).

2.1.2. *5-(6-bromo-3,7-dinonylthieno[2′,3′:4,5]thieno[3,2-b]thieno[2,3-d]thiophen-2-yl)thiophene-2-carbaldehyde [27]* ***6***

Compound **9** (0.4 g, 0.57 mmol) and NBS (0.122 g, 0.68 mmol) were dissolved in THF (25 mL). After stirring at 50 °C for 6 h, the mixture was poured into water (50 mL). The obtained precipitate was filtered and further recrystallized from dichloromethane to obtain compound **6** as a yellow solid (0.39 g). Yield 88%. ^1H NMR ($CDCl_3$, 300 MHz): δ 9.84 (s, 1H), 7.62 (d, $J = 3.96$ Hz, 1H), 7.13 (d, $J = 3.96$ Hz, 1H), 2.82–2.95 (m, 2H), 2.67 (t, $J = 7.63$ Hz, 2H), 1.64–1.79 (m, 4H), 1.19–1.47 (m, 24H), 0.82–0.99 (m, 6H).

2.2. General procedure for ***5a-d***

A mixture of the stannyl compound **11a-d** (1.2 equiv), **6–7** (1.0 equiv) and $Pd(PPh_3)_4$ (0.05 equiv) in degassed toluene (30 mL) was heated at reflux for 20 h. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel (hexane/dichloromethane 5:1) to obtain the desired carbaldehyde **5a-d**.

2.2.1. *6-(4-(bis(4-methoxyphenyl)amino)phenyl)-3,7-dinonylthieno[2′,3′:4,5]thieno[3,2-b]thieno[2,3-d]thiophene-2-carbaldehyde* ***5a***

^1H NMR ($CDCl_3$, 300 MHz): δ 10.0 (s, 1H), 7.30 (d, $J = 8.6$ Hz, 2H), 7.16 (d, $J = 7.4$, 4H), 6.99 (d, $J = 7.4$ Hz, 2H), 6.90 (d, $J = 7.4$ Hz, 2H), 3.81 (s, 6H), 3.02 (t, $J = 6.8$ Hz, 2H), 2.78 (t, $J = 7.2$ Hz, 2H), 1.83–1.74 (m, 4H), 1.42–1.32 (m, 24H), 0.97–0.90 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 181.66, 158.34, 148.79, 146.30, 145.01, 141.61, 141.33, 140.31, 138.08, 137.17, 137.13, 131.19, 131.02, 129.77, 128.36, 127.16, 125.51, 119.31, 114.85, 55.51, 31.90, 31.85, 30.17, 29.59, 29.56, 29.53, 29.50, 29.45, 29.34, 29.28, 29.04, 28.26, 28.20, 22.69, 22.67, 14.14. HRMS (*m/z*, FAB+) calcd for $C_{49}H_{57}NO_3S_4$: 835.3221, found 835.3221.

2.2.2. *6-(5-(4-(bis(4-methoxyphenyl)amino)phenyl)thiophen-2-yl)-3,7-dinonylthieno[2′,3′:4,5]thieno[3,2-b]thieno[2,3-d]thiophene-2-carbaldehyde* ***5b***

^1H NMR ($CDCl_3$, 300 MHz): δ 10.0 (s, 1H), 7.42 (d, $J = 8.4$ Hz, 2H), 7.10–7.26 (m, 6H), 6.93 (d, $J = 8.4$ Hz, 2H), 6.85 (d, $J = 8.7$ Hz, 4H), 3.80 (s, 6H), 3.09–3.14 (m, 2H), 2.93–2.98 (m, 2H), 1.79–1.84 (m, 4H), 1.26–1.37 (m, 24H), 0.86–0.95 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 181.66, 156.15, 148.63, 148.21, 145.62, 145.33, 141.64, 140.49, 137.89, 137.40, 136.83, 134.05, 133.55, 132.27, 131.60, 128.37, 127.44, 126.80, 126.37, 125.68, 122.07, 120.27, 114.79, 55.51, 31.90, 31.85, 30.15, 29.71, 29.54, 29.49, 29.45, 29.39, 29.34, 29.28, 29.00, 28.87, 28.18, 22.69, 22.67, 14.12. HRMS (*m/z*, FAB+) calcd for $C_{53}H_{59}NO_3S_5$: 917.3098, found 917.0032.

2.2.3. *5-(6-(4-(bis(4-methoxyphenyl)amino)phenyl)-3,7-dinonylthieno[2′,3′:4,5]thieno[3,2-b]thieno[2,3-d]thiophen-2-yl)thiophene-2-carbaldehyde* ***5c***

^1H NMR ($CDCl_3$, 300 MHz): δ 9.90 (s, 1H), 7.74 (d, $J = 3.52$ Hz, 2H), 7.47–7.20 (m, 3H), 7.13 (d, $J = 8.80$ Hz, 4H), 6.95 (d, $J = 8.80$ Hz, 2H), 6.87 (d, $J = 8.80$ Hz, 4H), 3.81 (s, 6H), 3.00 (t, $J = 7.63$ Hz, 2H), 2.81 (m, 1H), 1.83–1.72 (m, 4H), 1.48–1.18 (m, 24H), 0.88–0.85 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): 182.47, 156.27, 148.69, 146.52, 143.16, 142.63, 142.30, 140.41, 139.97, 136.85, 135.27, 133.59, 131.09, 130.86, 130.67, 129.77, 129.35, 128.54, 127.10, 125.90, 119.44, 114.83, 55.51, 31.93, 31.90, 29.80, 29.62, 29.55, 29.52, 29.43, 29.37, 29.36, 29.32, 29.27, 29.10, 29.00, 28.29, 22.71, 14.16. δ HRMS (*m/z*, FAB+) calcd for $C_{53}H_{59}NO_3S_5$: 917.3098, found 917.3107.

2.2.4. *5-(6-(5-(4-(bis(4-methoxyphenyl)amino)phenyl)thiophen-2-yl)-3,7-dinonylthieno[2′,3′:4,5]thieno[3,2-b]thieno[2,3-d]thiophen-2-yl)thiophene-2-carbaldehyde* ***5d***

^1H NMR ($CDCl_3$, 300 MHz): δ 9.90 (s, 1H), 7.73 (d, $J = 3.96$ Hz, 1H), 7.42 (d, $J = 8.7$ Hz, 2H), 7.28–7.26 (m, 1H), 7.17–7.06 (m, 6H), 6.93 (d, $J = 8.7$ Hz, 2H), 6.95 (d, $J = 9.0$ Hz, 4H), 3.81 (s, 6H), 3.02–2.93 (m, 4H), 1.80–1.75 (m, 4H), 1.44–1.26 (m, 24H), 0.90–0.84 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 182.44, 156.12, 148.51, 146.37, 145.17, 143.51, 142.97, 142.34, 140.53, 136.80, 135.19, 133.90, 133.29, 132.50, 132.21, 131.45, 130.54, 129.71, 128.57, 127.09, 126.77, 126.61, 126.33, 125.90, 125.83, 122.02, 120.33, 114.79, 55.51, 31.91, 29.81, 29.74, 29.58, 29.53, 29.43, 29.38, 29.34, 29.27, 29.06, 28.97, 28.88, 22.71, 14.16. HRMS (*m/z*, FAB+) calcd for $C_{57}H_{61}NO_3S_6$: 999.2976, found 999.2973.

2.3. General procedure for final target compounds

Aldehyde **5a-d** (1.0 equiv.), cyanoalkyl acetate (3.0 equiv.) and a few drops of triethylamine were dissolved in chloroform (30 mL) under a nitrogen atmosphere and heated to reflux overnight. After the completion of the reaction, water was added and the product was extracted with dichloromethane, washed with brine and dried over anhydrous $MgSO_4$. The crude product was purified by column