Dyes and Pigments 95 (2012) 236–243

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Symmetrical and asymmetrical (multi)branched truxene compounds: Structure and photophysical properties☆

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ARTICLE INFO

Article history:
Received 7 March 2012
Received in revised form
16 April 2012
Accepted 18 April 2012
Available online 9 May 2012

Keywords:
Truxene
Thiophene
Structure
Photophysical properties
Charge-shift
Synthesis

ABSTRACT

A series of symmetrical and asymmetrical (multi)branched truxene derivatives have been synthesized by incorporating different π-conjugated functional groups to truxene. Linear absorption and single- and two-photon excited fluorescence properties of the obtained compounds were examined. The spectral data combining the results of theoretical calculation and the X-ray crystal structures demonstrate that the intramolecular charge transfer of the C_3-symmetric truxene-core compounds keep independence of every branch and shifts site-to-site upon excitation. The asymmetric molecule **SN** behaves the intramolecular excitation transfer between more than two energy levels, which maybe different from the symmetric ones. Meanwhile, the C_3-symmetric octupolar conformation and the $C(sp^2) = C(sp^2)$ π-linker are effective structural pattern for two-photon absorption compounds.

1. Introduction

C_3-symmetric organic molecules, due to their fascinating structures and unique optical properties, have been extensively studied in this decade for their potential applications in optoelectronics [1]. Designing new families of π-conjugated star-shaped C_3-symmetric molecules and investigating the structure–property have attracted increasing interest. Owing to the pioneering work of Pei, Skabara and Echavarren and co-workers [1c,2], truxene (10,15-dihydro-5H-diindeno[1,2-*a*;1′,2′-*c*]fluorene), a heptacyclic polyarene, due to its C_3-symmetric octupolar skeleton and three-dimensional topology, has been intensively developed as an ideal π-conjugated central core to fabricate star-shaped optoelectronic molecules (organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), liquid crystals, two-photon absorption, etc.) via readily available functionalization at its 2, 7, 12- or 5, 10, 15-positions [3–15]. Among the present truxene-cored compounds, most present C_3-symmetrical hype-conjugated system has three long peripheral emanating rigid chains. Optoelectronic properties of these compounds have been studied thoroughly as well. However, reports that focused on the structure–function relationship investigation with respect to different conjugated branches, moreover, the truxene-cored asymmetrical architectures are limited.

As far as this issue is concerned and considering the good thermal and chemical stability of thiophene-based optoelectronic materials [16–19], we chose different π-conjugated groups, 2-thiophenyl, 2-thiophenyl-vinyl and 2-thiophenyl-ethynyl, respectively, as the branches and connected them to the truxene core via Suzuki reaction, Heck and Sonogashira cross-coupling reaction, respectively, to synthesize three symmetrical short chain truxene compounds (**S3**, **TS3** and **SC**). These reactions are recognized as the most facile access to produce optoelectronic materials in recent years. Furthermore, we designed and synthesized an asymmetrical compound (**SN**), using diphenylamino and thiophene moiety as two different extremes. In this study, the UV–vis absorption and single- and two-photon excited fluorescence of all these compounds have been tested. As for the asymmetrical compound **SN**, the electrochemical determination and the theoretic calculation have been carried out as well. These intrinsic features give a deep insight into the effects of chemical structures on the photophysical properties and the charge transfer states.

☆ The CCDC No. of compounds **S1** and **SC**: 857287 & 857288.

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doi:10.1016/j.dyepig.2012.04.008

2. Experimental section

2.1. Synthesis and characterizations of the subject compounds

Solvents for reactions were dried and distilled before use. Solvents used for absorption and fluorescence measurements were HPLC grade. ^{1}H NMR spectra were recorded at 25 °C on Bruker Avance 400 or 500 MHz spectrometer using $CDCl_3$ as solvent. ^{13}C NMR spectra were recorded at 25 °C on Bruker Avance 125 MHz spectrometer using $CDCl_3$ as solvent. Element analyses (C, H, N, S) were performed using a PE 2400 autoanalyser. Mass spectrometry analyses were performed by a Bruker Biflex III matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometer.

5,5′,10,10′,15,15′-Hexaethyltruxene (**1**), 2,7,12-tribromo-5,5′,10,10′,15,15′-hexaethyltruxene (**2**), 2,7,12-triiodo-5,5′,10,10′,15,15′-hexaethyltruxene (**3**) and 2-bromo-5,5′,10,10′,15,15′-hexaethyltruxene (**4**) were synthesized following Ref. [15b].

2.1.1. *2,7-dibromo-12-(2-thiophenyl)-5,5′,10,10′,15,15′-hexaethyltruxene (**S1**), 2-dibromo-7,12-di(2-thiophenyl)-5,5′,10,10′,15,15′-hexaethyltruxene (**S2**) and 2,7,12-tri(2-thiophenyl)-5,5′,10,10′,15,15′-hexaethyltruxene (**S3**)*

A mixture of 2,7,12-tribromo-5,5′,10,10′,15,15′-hexaethyltruxene (**2**) (0.70 g, 0.94 mmol), 2-thiophene-boronic acid (0.60 g, 4.70 mmol), $Pd(PPh_3)_4$ (30 mg, 0.03 mmol), THF (20 mL) and 2 M aqueous K_2CO_3 solution (5 mL) was heated to reflux with stirring under a nitrogen atmosphere for 8 h. The mixture was cooled to room temperature and poured into water (100 mL). After extraction with dichloromethane (DCM), the organic phase was dried over Na_2SO_4. The solvent was removed and the residue was purified by column chromatography on silica gel using DCM-hexane (1:10) as the eluent to get compounds **S1** (0.35 g, 49.2%), **S2** (0.15 g, 21.7%) and **S3** (0.14 g, 19.2%).

*2.1.1.1. **S1**.* A yellow green powder, m.p. 187–189 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 0.21–0.25 (m, 18H), 2.09–2.19 (m, 6H), 2.90–3.02 (m, 6H), 7.13–7.13 (m, 1H), 7.32–7.33 (m, 1H), 7.44–7.45 (m, 1H), 7.51–7.54 (m, 2H), 7.57–7.59 (m, 2H), 7.67–7.69 (m, 2H), 8.16–8.21 (m, 2H), 8.30–8.31 (d, J = 8.0, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 155.2, 155.1, 153.5, 153.3, 144.6, 143.9, 143.6, 139.6, 139.4, 138.7, 138.1, 133.0, 129.5, 128.1, 126.0, 125.9, 125.7, 125.6, 125.0, 124.8, 124.4, 123.1, 121.1, 119.5, 57.2, 57.1, 57.0, 29.5, 29.4, 8.6, 8.5. MALDI-TOF: m/z 750.6 [M^+], 721.5 [$M - 29]^+$. Elemental Anal. Calcd. for $C_{43}H_{42}Br_2S$: C, 68.80; H, 5.64; S, 4.27. Found: C, 68.71; H, 5.81; S, 4.29.

*2.1.1.2. **S2**.* A yellow green powder, m.p. 180–182 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 0.21–0.28 (m, 18H), 2.15–2.23 (m, 6H), 2.98–3.07 (m, 6H), 7.13–7.15 (t, J = 4.0, 2H), 7.32–7.33 (d, J = 5.0, 2H), 7.39–7.47 (m, 4H), 7.68 (s, 4H), 8.34–8.36 (d, J = 8.5, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 153.7, 152.8, 144.8, 144.1, 140.2, 138.5, 132.7, 128.1, 126.7, 126.2, 125.0, 124.6, 124.3, 123.0, 122.4, 119.5, 56.9, 56.8, 29.6, 29.5, 8.6, 8.5. MALDI-TOF: m/z 753.5 [M^+], 724.6 [$M - 29]^+$. Elemental Anal. Calcd. for $C_{47}H_{45}BrS_2$: C, 74.88; H, 6.02; S, 8.51. Found: C, 74.36; H, 6.43; S, 8.61.

*2.1.1.3. **S3**.* A yellow green powder, m.p. 159–162 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 0.26–0.29 (t, J = 7.5, 18H), 2.18–2.24 (m, 6H), 3.01–3.05 (m, 6H), 7.14–7.15 (m, 3H), 7.32–7.33 (d, J = 5.0, 3H), 7.45 (s, 3H), 7.68–7.70 (d, J = 7.0, 6H), 8.35–8.36 (d, J = 9.0, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 153.7, 144.8, 144.2, 140.1, 138.5, 132.7, 128.1, 125.0, 124.7, 124.3, 123.0, 119.5, 56.9, 29.6, 8.6. MALDI-TOF: m/z 757.4 [M^+], 728.2 [$M - 29]^+$. Elemental Anal. Calcd. for $C_{51}H_{48}S_3$: C, 80.90; H, 6.39; S, 12.71. Found: C, 81.14; H, 6.87; S, 12.35.

2.1.2. *2,7,12-tri(2-thiophenevinyl)-5,5′,10,10′,15,15′-hexaethyltruxene (**TS3**)*

A mixture of 2,7,12-triiodo-5,5′,10,10′,15,15′-hexaethyltruxene (**3**) (0.50 g, 0.56 mmol), 2-vinylthiophene (0.40 g, 3.64 mmol), $Pd(PPh_3)_4$ (20 mg, 0.02 mmol), n-Bu_4NF (50 mg), DMF (20 mL) and triethylamine (5 mL) was heated to 100 °C with stirring under a nitrogen atmosphere for 8 h. The mixture was cooled to room temperature and poured into water (100 mL). After extraction with DCM (100 mL), the organic phase was dried over $MgSO_4$. The solvent was removed and the residue was purified by column chromatography on silica gel using DCM-hexane (1:5) as the eluent to get compound **TS3** (0.35 g, 74.1%). **TS3**: a yellow green powder, m.p. 247–251 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.24–0.27 (t, J = 6.9, 18H), 2.17–2.22 (m, 6H), 3.00–3.05 (m, 6H), 6.88–7.13 (m, 12H), 7.22–7.54 (m, 9H), 8.31–8.33 (d, J = 8.0, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 153.3, 144.5, 140.3, 137.1, 134.1, 132.2, 128.7, 128.6, 126.5, 126.1, 126.0, 124.1, 123.3, 120.2, 56.9, 29.7, 8.5. MALDI-TOF: m/z 835.4 [M^+], 806.5 [$M - 29]^+$, 513.3 [$M - 322]^+$. Elemental Anal. Calcd. for $C_{57}H_{54}S_3$: C, 81.97; H, 6.52; S, 11.52. Found: C, 81.54; H, 6.90; S, 11.17.

2.1.3. *2,7,12-tri(2-thiophenyl-ethynyl)-5,5′,10,10′,15,15′-hexaethyltruxene (**SC**)*

A mixture of 2,7,12-triiodo-5,5′,10,10′,15,15′-hexaethyltruxene (**3**) (0.50 g, 0.56 mmol), 2-ethynylthiophene (0.40 g, 3.70 mmol), $Pd(PPh_3)_4$ (20 mg, 0.02 mmol), n-Bu_4NF (50 mg), THF (15 mL) and triethylamine (15 mL) was heated to reflux with stirring after flushed with nitrogen for half an hour. After reacting for 3 h under nitrogen, the mixture was cooled to room temperature and poured into water (100 mL). After extraction with DCM (100 mL) several times, the organic phase was dried over $MgSO_4$. The solvent was removed and the residue was purified by column chromatography on silica gel using DCM-hexane (1:5) as the eluent to get compound **SC** (0.36 g, 78.2%). **SC**: a yellow powder, m.p. 286–288 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 0.22–0.25 (t, J = 7.3, 18H), 2.16–2.20 (m, 6H), 2.96–3.00 (m, 6H), 7.04–7.06 (m, 3H), 7.32–7.35 (m, 6H), 7.55–7.57 (d, J = 8.0, 3H), 7.62 (s, 3H), 8.31–8.32 (d, J = 8.5, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 152.9, 145.1, 140.7, 138.5, 131.9, 129.8, 127.3, 127.2, 125.2, 124.5, 123.5, 121.0, 57.0, 29.5, 8.6. MALDI-TOF: m/z 829.2 [M^+]. Elemental Anal. Calcd. for $C_{57}H_{48}S_3$: C, 82.56; H, 5.83; S, 11.60. Found: C, 82.64; H, 6.13; S, 11.32.

2.1.4. *2-(N,N-diphenylamino)-7-(2-thiophenyl)-5,5′,10,10′,15,15′-hexaethyltruxene (**SN**)*

A similar synthetic and purification procedure as for **S3** was followed for **SN** using 2-bromo-7-(N,N-diphenylamino)-5,5′,10,10′,15,15′-hexaethyltruxene (**6**) as the precursor. Then compound **SN** (72.3%) was obtained. **SN**: a yellow green powder, m.p. 122–124 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 0.21–0.27 (m, 18H), 1.94–1.99 (m, 2H), 2.08–2.21 (m, 4H), 2.90–3.05 (m, 6H), 7.05 (s, 3H), 7.13 (s, 1H), 7.19–7.21 (d, J = 7.5, 5H), 7.28–7.31 (t, J = 6.8, 5H), 7.37 (s, 2H), 7.43–7.44 (m, 2H), 7.64–7.66 (m, 2H), 7.32–7.33 (m, 1H), 8.16–8.18 (d, J = 8.5, 1H), 8.27–8.28 (d, J = 8.0, 1H), 8.33–8.34 (d, J = 7.5, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 153.7, 152.8, 148.0, 144.9, 143.4, 140.7, 140.4, 140.3, 138.8, 132.5, 129.3, 128.1, 126.5, 126.1, 125.3, 124.9, 124.6, 124.2, 122.9, 122.7, 122.3, 122.0, 119.5, 117.6, 56.8, 56.7, 29.7, 29.4, 29.3, 8.7, 8.6. MALDI-TOF: m/z 760.1 [M^+], 731.4 [$M - 29]^+$. Elemental Anal. Calcd. for $C_{55}H_{53}NS$: C, 86.91; H, 7.03; N, 1.84; S, 4.22. Found: C, 86.73; H, 7.52; N, 1.69; S, 4.22.

2.2. Photophysical properties measurement

All absorption spectra were recorded on a UV1800 spectrometer. Steady state fluorescence spectra and decay curves were obtained on an Edinburgh FLS920 fluorescence spectrometer. Reconvolution fit of the decay profiles were made with F900 analysis software to get the lifetime value. The solid films were prepared through solution process (THF, 1.0 × 10^{-4} mol/L, 1500–2000 rpm) with 50–100 nm thickness.

TPA cross section σ was measured by the two-photon excited fluorescence (TPEF) method using coumarin 307 as reference solution, which is based on the supposition that the TPEF intensity is proportional to the product of σ and fluorescent quantum yield Φ [20]. TPEF spectra were obtained using a Tsunami 3941-M3-BB femtosecond Ti:sapphire laser with a 532 nm Millennia Pro 5 semiconductor laser instrument as an excited source. An Ocean USB2000 fluorescence spectrometer was used to record the TPEF spectra. To reduce the re-absorption to TPEF, the exciting laser beam was focused as closely as possible to the sample cell wall by a lens, which faced the slit of fluorescence spectrometer.

2.3. *Electrochemical properties measurement*

Cyclic voltammetry (CV) was performed on CHI660D workstation and measurements were carried out in THF containing 0.1 M *n*-Bu_4NClO_4 as the supporting electrolyte, platinum disc as the working electrodes, platinum wire as the counter electrode and Ag/$AgNO_3$ as the reference electrode under N_2 atmosphere. The scan rate was maintained at 20 mV s^{-1}.

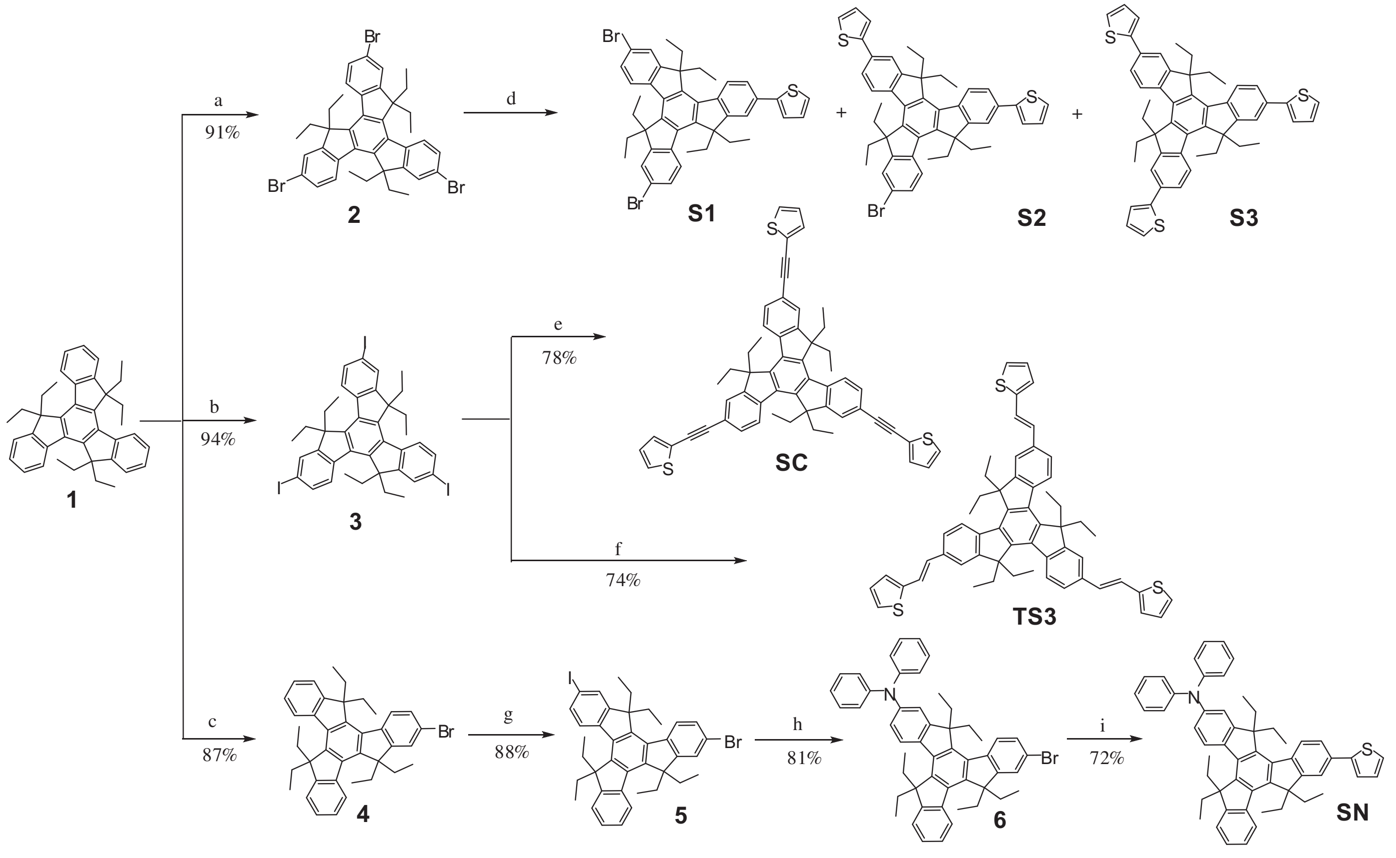
3. Results and discussion

3.1. *Synthesis*

The synthetic approach to the title compounds is outlined in Scheme 1. Tribromo-hexaethyltruxene (**2**) was initially selected as the precursor to synthesis the title compound **S3** using $Pd(PPh_3)_4$ as the catalyst under conventional condition. However, the main product was found to be the mono-substituted compound **S1** with a yield of 49%, and the tri-substituted compound **S3** was obtained in a yield of 19% merely under this condition because of the poor cross-coupling efficiency of bromide in Suzuki reaction. After that, we used more active triiodo-hexaethyltruxene to perform the Sonogashira and Heck cross-coupling reactions and achieved the three-fold transformations to afford the C_3-symmetric molecules **SC** and **TS3** in desired yields (78% and 74%, respectively). The synthesis of the asymmetrical compound **SN** was processed mainly through selective Cu-mediated Ullmann condensation between diphenylamine and 2- bromo-7-iodo-hexaethyltruxene, which stems from the different reactivities between aryl bromide and aryl iodide. It is pretty clear that, the quantitative bromination and iodination also are two key procedures. The halogenated truxene derivatives **2**, **3** or **4** can be prepared via tri-brominated, tri-iodinated or mono-brominated of hexaethyltruxene **1**, which has been reported by our group previously [15]. All the intermediates and the target molecules were purified by column chromatography. The new compounds were characterized with ^1H NMR, ^{13}C NMR, elemental analysis and MALDI/TOF mass spectroscopy. All the target compounds displayed excellent solubility in the common solvents, such as toluene, THF and chloroform, and so on.

3.2. *X-ray crystallography*

Two single crystal structures of compounds **S1** and **SC** were firstly determined from crystals prepared by the slow diffusion of $CHCl_3$: cyclohexane (2:1, v/v) mixture solution of the title



Scheme 1. Synthesis of the title compounds. (a) Bromine, CH_2Cl_2, 25 °C, 12 h; (b) and (g) HIO_3, I_2, $CH_3COOH–H_2SO_4–H_2O–CCl_4$, 80 °C, 4 h; (c) 1,2-Propanediol carbonate, NBS, 60 °C, 2 h; (d) and (i) thiophen-2-yl-2-boronic acid, $Pd(PPh_3)_4$, K_2CO_3, THF, reflux, 8 h; (e) 2-ethynylthiophene, $Pd(PPh_3)_4$, *n*-Bu_4NF, Et_3N, THF, reflux, 3 h; (f) 2-vinylthiophene, $Pd(PPh_3)_4$, *n*-Bu_4NF, Et_3N, DMF, 100 °C, 8 h; (h) Diphenylamine, K_2CO_3, Cu (powder), 18-crown-6-ether, 1,2-dichlorobenzene, reflux, 8 h.

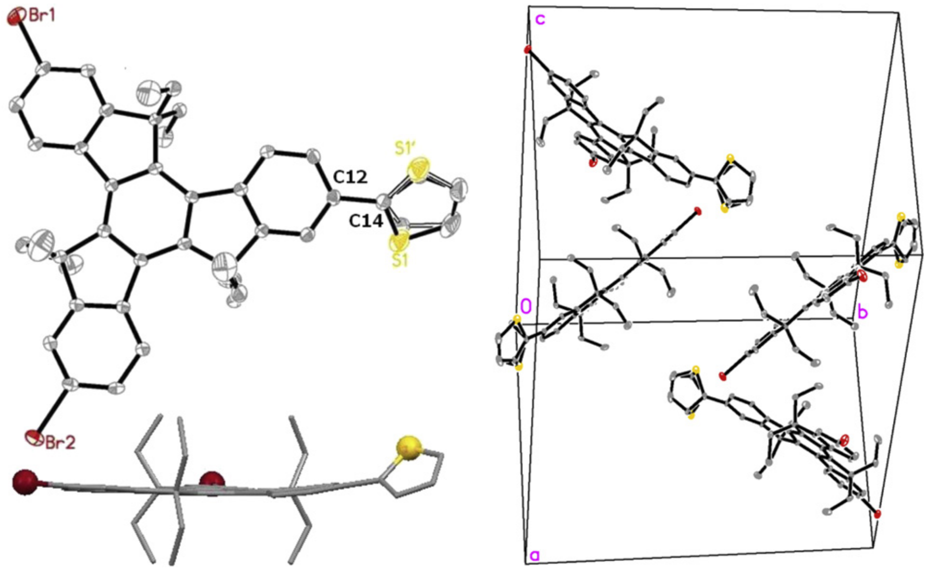


Fig. 1. ORTEP and packing drawing of compound **S1**. H-atoms are omitted for clarity.

molecules for several days at room temperature (Figs. 1 and 2). The truxene moiety of the two molecules exhibits a highly planar geometry with the mean deviation from its least-square plane being 0.023(7) and 0.016(8) Å, respectively. For **S1**, the thiophene group bounded to the truxene is disordered and does not lie within the plane of the truxene unit. The dihedral angle between the thiophene ring and the nearest benzene is 39.1(8)°. The molecules are packed in $P2_1/c$ space group. Though molecular skeleton is planar, there is no π–π stacking found in the crystal packing.

For **SC**, as shown in Fig. 2, the thiophene rings are almost vertical to the truxene plane and the average dihedral angle between thiophene ring and the nearest benzene to thiophene is 89.6(9)°. The average distance between the thiophene and the acetylene group is 1.417(9) Å, implying good conjugation. The layered crystal packing of **SC** is obviously different from that of **S1**, and the distance between the neighboring layer (e.g. the green layer and yellow layer) is only 4.495(8) Å. On the other hand, the **SC** crystal has a 6_3 screw symmetry. The nature of the layered packing and the polar noncentrosymmetry indicate that compound **SC** has the potential application in OFETs and 2-order nonlinear optical (NLO) materials.

3.3. *Linear absorption and single-photon excited fluorescence (SPEF)*

As shown in Fig. 3 and Table 1, both the linear absorption and SPEF spectra for compounds **S3**, **SC**, **SN** and **TS3** exhibit obvious vibronic features either in solution or in films, which are attributed to their rigid planar frameworks. Their absorption spectra both in solution and in the solid films show strong π–π* electron absorption bands. In accordance with expectation, the absorption maxima (λ_{abs}) of compounds **SC** and **TS3** (362 and 386 nm in THF) are obviously red-shifted in comparison with that of compound **S3** (340 nm in THF) because of the enhanced conjugation. It should be noted that, the π–π* electron absorption (λ_{abs}) of 2-thiophenyl-ethynyl substituted truxene **TS3** has a 24 nm red shift relative to that of 2-thiophenyl-vinyl substituted truxene **SC** in THF. These results indicate that **TS3** exhibits more effective conjugation and more facilitate charge transfer during the excitation than compound **SC**. For the emission spectra, to our surprise, the compound **SC** demonstrates a similar fluorescence behavior to the compound **S3** with a slight red shift (~5 nm) of emission peaks, which is obviously different from that of compound **TS3**.

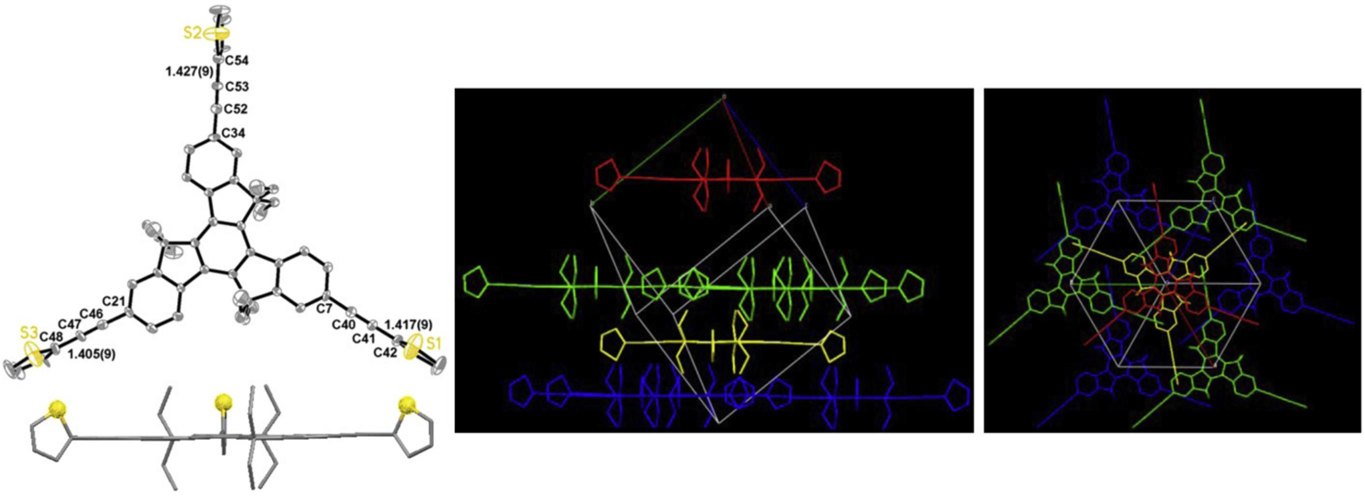


Fig. 2. ORTEP and packing drawing of compound **SC**. H-atoms are omitted for clarity. The molecules in the same packing layer were marked in the same color.

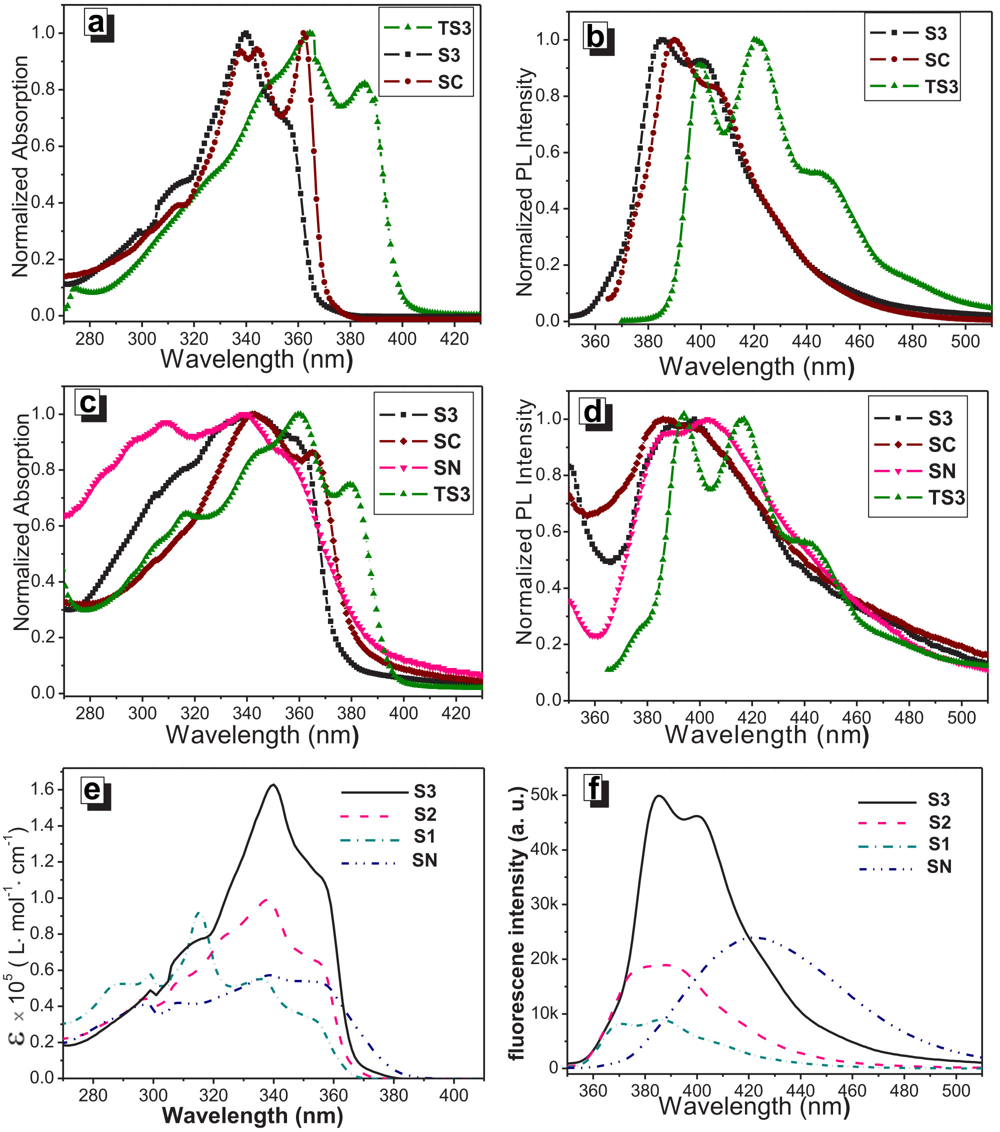


Fig. 3. The normalized linear absorption and single-photon excited fluorescence spectra of compounds **S3**, **SC**, **SN** and **TS3** in THF (a, b) and in films (c, d). And the linear absorption (e) and single-photon excited fluorescence spectra (f) of compounds **S1**, **S2**, **S3** and **SN** in THF.

As to the influence of branched number on the photophysical properties, we found that the spectra shapes and absorption maxima (λ_{abs}) of π–π^* electron absorption bands of compounds **S1**, **S2** and **S3** are almost independent of the number of substituent groups, as shown as in Fig. 3(e and f). However, the molar extinction coefficients (ε_{max}) of the three analogs are found to increase nearly linear with the number of branches (1.0(**S1**): 1.8(**S2**): 3.0(**S3**)). From these photophysical characteristics, it seems that the

Table 1
The photophysical data of the subject compounds.

	λ_{abs}[a] (solution, nm)	ε_{max} (10^4 M^{-1} cm^{-1})	λ_{abs} (film, nm)	λ_{SF}[a] (solution, nm)	λ_{SF} (film, nm)	λ_{TF}[b] (nm)	$\Delta\tilde{\nu}$[c] (10^3 cm^{-1})	$\Delta\tilde{\nu}/\Delta f$[d] ($10^3$ cm^{-1})	Φ[e]	τ[f] (ns)	σ[g] (GM)
S1	315, 336	9.2, 5.5	–	371, 386	–	–	3.63	5.3	0.32	0.92	–
S2	338	9.9	–	388	–	–	3.61	4.8	0.38	0.92	–
S3	340	16.3	342	385, 400	398	409	3.59	4.3	0.59	2.1	64
SC	338, 344, 362	10.8, 11.0, 11.6	342, 365	390, 406	386, 396	418	3.64	5.8	0.58	1.5	184
TS3	364, 386	10.1, 8.3	360, 380	400, 421	394, 416	436	3.72	5.4	0.56	1.6	235
SN	339, 355	5.5, 5.3	309, 339	422	386, 403	431	5.71	7.8	0.80	1.7	43

[a] Linear absorption and SPEF maxima with $c = 1.0 \times 10^{-5}$ mol/L in THF.
[b] TPEF maxima with $c = 1.0 \times 10^{-3}$ mol/L in THF.
[c] Stokes-shift.
[d] The slope of plot $\Delta\tilde{\nu}$ of versus Δf based on the Lippert-Mataga equation, where $\Delta f = [(\varepsilon - 1)/(2\varepsilon + 1)] - [(n^2 - 1)/(2n^2 + 1)]$.
[e] Fluorescence quantum yields determined using diphenylanthracene as standard in THF.
[f] Fluorescence lifetime in THF.
[g] The TPA cross section calculated with TPEF-based method using coumarin 307 as standard in THF; 1 GM = 10^{-50} cm^4 s $photon^{-1}$.

intramolecular charge transfer during the excitation keeps independence of every branch and shift site-to-site from the rich electrical thiophenes to the truxene core. Hence, the C_3-symmetric molecules **S3**, **SC** and **TS3** will present the identical C_3-symmetric configuration in the excited states as well, which can also be derived from the smaller values of $\Delta\tilde{\nu}/\Delta f$ in Table 1. We also noticed that the fluorescence quantum yields (Φ) of compounds **S1** and **S2** are relatively low, this might be due to the heavy halogen atoms which could enhance intersystem crossing or other non-radiative processes to quench the fluorescence.

When it comes to the asymmetrical compound **SN**, we found that two characteristic $\pi-\pi^*$ electron absorption bands (peaked at 339 and 355 nm), which are attributed to the charge transfer from the thiophene and diphenylamine to the truxene moiety, respectively. The conclusions drawn from the absorption spectra of compound **S1** and **N1** (2-(*N*,*N*-diphenylamino)-5,5′,10,10′,15,15′-hexaethyltruxene) was reported by our research group [15b]. Differently, the emission peak of the asymmetrical molecule **SN** shows a remarkable red shift (~30 nm) compared with that of **S1** and **N1** in the same solvent THF, and locates at 422 nm. In order to understand the spectral behavior, we carried out a TD-DFT (time-dependent density functional theory) calculation at the B3LYP/6-31G* level. Based on the experimental results, we found that the most allowable transition is located at 358 nm (with the oscillator strength $f = 0.71$), which is consistent with the absorption spectrum of **SN**. The lowest-lying allowable transition appears at 381 nm between HOMO and LUMO, but the oscillator strength f is only 0.04. On the other hand, the higher value of $\Delta\tilde{\nu}/\Delta f$ reveals that higher polar emitting excited state which is different from that of the symmetrical compounds (e.g. **S3** and **SC**). According to these calculated results, we assume that intramolecular excitation transfer of the asymmetrical compound **SN** occurs between three or more energetically degenerate excited states, for instance from HOMO to LUMO+1, and then the exciton will be trapped in the most stable site from where emission mainly occur (LUMO → HOMO), as shown in Fig. 4.

3.4. Electrochemical properties

The electrochemical properties of the all the title compounds have been studies by cyclic voltammetry (CV). However, the compound **SN** only exhibited redox property. The CV diagram of compound **SN** in THF with tetra-*n*-butylammonium perchlorate (n-Bu_4NClO_4) as the supporting electrolyte, platinum disc as the working electrodes, a platinum wire as the counter electrode and $Ag/AgNO_3$ as the reference electrode under N_2 atmosphere is shown in Fig. 5. Under these conditions, the onset oxidation potential ($E_{1/2\ \mathrm{oxd}}$) of ferrocene was 0.49 eV versus Ag/Ag^+. On the basis of the evaluated $E_{1/2\ \mathrm{oxd}}$ (0.68 V) of **SN**, the energy of HOMO level can be estimated as −4.99 eV ($\mathrm{HOMO} = -E_{1/2\ \mathrm{oxd}} - 4.31$) [12,21]. The energy of LUMO level of **SN** is −1.48 eV, calculated from the energy of HOMO level and energy bandgap (E_g) determined from the longest wavelength absorption onset ($\mathrm{LUMO} = \mathrm{HOMO} - E_g$). These produced values are roughly according with the theoretical calculated results, which afford the energies of HOMO level and LUMO level of **SN** are −4.85 and −1.24 eV, respectively.

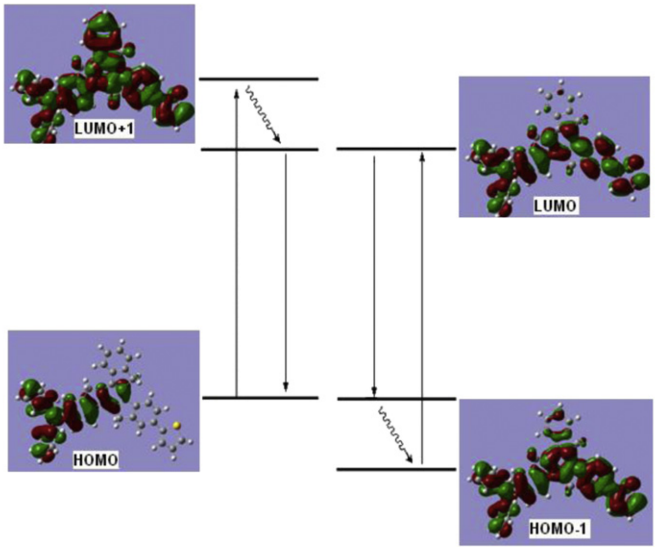


Fig. 4. Schematic of the frontier molecular orbitals, and two feasible transitions of **SN** based on DFT calculation (six ethyl groups were replaced by H-atoms).

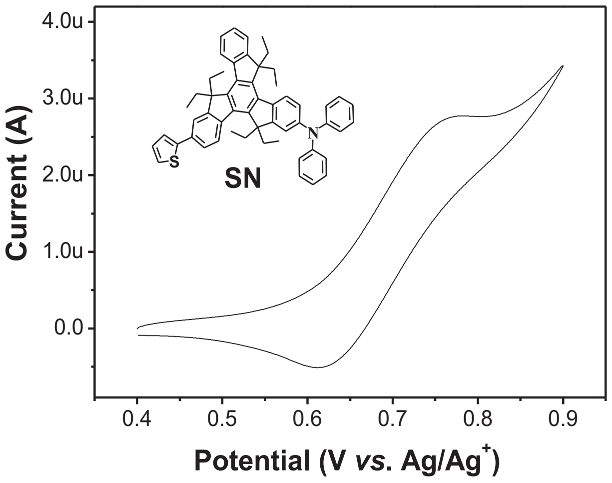


Fig. 5. Cyclic voltammogram of compound **SN**; electrolyte 0.1 M n-Bu_4NClO_4, scan rate 20 mV s^{-1}.

3.5. Two-photon excited fluorescence (TPEF)

Because of highly relying on the experimental conditions, such as the laser, concentration and the references for TPEF method, the

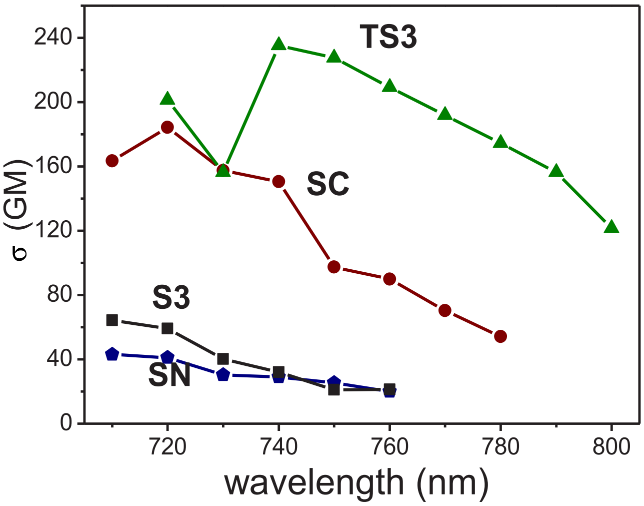


Fig. 6. Two-photon excitation spectra of compounds **SN**, **S3**, **SC** and **TS3** in THF with $c = 1.0 \times 10^{-3}$ mol/L.

accuracy of the measurement of two-photon absorption (TPA) cross-sections (σ) is still difficult up to now. But the comparison of the values measured under the same conditions should be reliable. As shown in Fig. 6, the σ values of the title compounds noticeably increase with the extending π-conjugation. Beyond that, compound **TS3** with C(sp^2) = C(sp^2) double bond as the π-linker displays the highest σ value among these compounds, with 51 GM higher than that of the compound **SC** with C(sp) ≡ C(sp) triple bond as the π-linker. This implies that more effective intramolecular charge transfer is carried through in the compound **TS3** upon two-photon excitation. We also noted that, though higher quantum yield Φ, the compound **SN** has smaller σ value in comparison with that of **S3**. The results demonstrate that octupolar conformation is a veritably excellent pattern for TPA molecules [3,22].

4. Conclusion

In summary, a series of symmetrical and asymmetrical (multi) branched truxene derivatives with 2-thiophenyl, 2-thiophenyl-vinyl, 2-thiophenyl-ethynyl and diphenylamino respectively as the peripheral functional groups have been synthesized. The single- and two-photon photophysical properties and the theoretical calculation revealed that C(sp^2) = C(sp^2) double bond as the π-conjugated bridge facilitate the charge transfer more available than C(sp) ≡ C(sp) triple bond, regardless of the mode of excitation (single- or two-photon). The C_3-symmetric molecules **S3**, **SC** and **TS3** present the identical C_3-symmetric configuration in the excited states. C_3-symmetric octupolar conformation displays an excellent pattern for TPA. In addition, the asymmetric molecule **SN** behaves the intramolecular excitation transfer between more than two energy levels, which is obviously different from the symmetric molecules.

Acknowledgment

Financial support from the Ph.D. Programs Foundation of Ministry of Education of China (No. 20090204120033) and the Fundamental Research Funds for the Central Universities (No. Z109021106) is gratefully acknowledged.

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