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Asymmetric multibranched conjugated molecules: Synthesis, structure and photophysical properties

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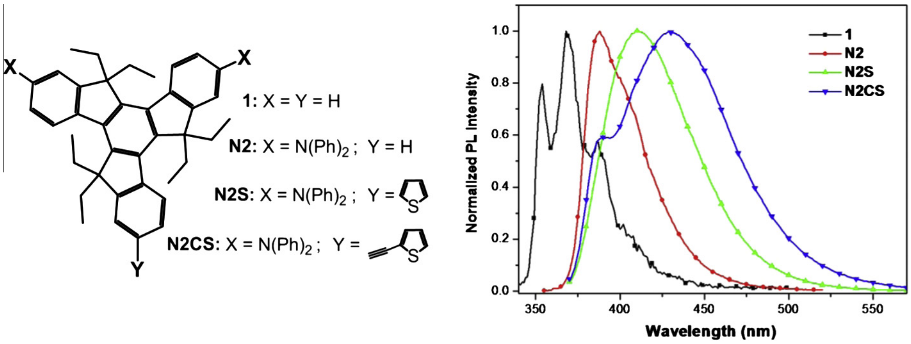
HIGHLIGHTS

- Two truxene-cored asymmetric multibranched π-conjugated molecules were synthesized.
- The two compounds exhibit almost same absorption maxima, but different emission.
- The theoretical results reveal the HOMO → LUMO transition is not their main transition.

GRAPHICAL ABSTRACT



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ABSTRACT

The symmetric multibranched π-conjugated compounds with C_3 or C_6 configuration have been intensively studied. The reports on asymmetric multibranched compounds are very limited. In this work, we designed and synthesized two asymmetric multibranched π-conjugated molecules using truxene as the central core, diphenylamino and thiophenyl (or thiophenylethynyl) groups as the different branches respectively: 2,7-di(*N,N*-diphenylamino)-12-(2-thiophenyl)-5,5′,10,10′,15,15′-hexaethyltruxene and 2,7-di(*N,N*-diphenylamino)-12-(2-thiophenylethynyl)-5,5′,10,10′,15,15′-hexaethyltruxene. Their photophysical properties have been explored combining with their theoretical calculation and X-ray single-crystal structure of a key intermediate. Though their different π-conjugation length of branches, the two title compounds exhibit almost same absorption maxima. However, their emission peaks behave a gradual red-shift with the increase of the conjugation length. The theoretical calculation results indicate that the two asymmetric compounds behave a main transition from the HOMO − 1 to the LUMO or from the HOMO to the LUMO + 1 upon excited.

Introduction

Multibranched organic π-conjugated molecules, due to their fascinating molecular architecture and unique properties, have attracted great interest in this decade [1–7]. In comparison to the linear molecules and polymers, branched π-conjugated molecules have some advantages for applications in optoelectronic devices, for example, the three-dimensional architectures, well-defined molecular structure and good film-forming processing. In recent years, a large number of multibranched π-conjugated molecules have been exploited extensively in a wide range of applications as optoelectronic materials [8–14]. However, more research

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mainly focused on the symmetric molecular system. In other words, most of these multibranched molecules exhibit C_n symmetric configurations (mostly C_3 and C_6), and every branch of the same molecule behaves the same chemical structure. Studies that focus on the properties and structure–function relationship investigation of asymmetric multibranched molecules are very limited [15,16], which may be on account of the difficulty in synthesis.

Generally, multibranched optoelectronic molecules are constructed from an interior functional core with several photo- and electro-active branching units. Truxene (10,15-dihydro-5*H*-diindeno[1,2-a;1′,2′-c]fluorene), due to its C_3-symmetric skeleton and planar π-conjugated polyarene structure, has been intensively studied as a π-conjugated central core to fabricate branched optoelectronic molecules [17–29]. Herein, we are of particular interest to develop the asymmetric multibranched compounds using truxene as central unit. In order to endow the designed molecules with good optoelectronic properties as well as thermal and chemical stability, we availably functioned truxene at its 2,7,12-positions with diphenylamino, thiophenyl and thiophenylethynyl respectively to get two asymmetric π-conjugated molecules: 2,7-di(*N*,*N*-diphenylamino)-12-(2-thiophenyl)-5,5′,10,10′,15,15′-hexaethyltruxene (**N2S**) and 2,7-di(*N*,*N*-diphenylamino)-12-(2-thiophenylethynyl)-5,5′,10,10′,15,15′-hexaethyltruxene (**N2CS**). In this work, we present a photophysical and theoretical calculation studies combining with the X-ray single-crystal structure of an intermediate.

Experimental section

Synthesis and characterizations of the subject compounds

Solvents for reactions and spectral measurements were dried and distilled before use. The reagents used for reactions were purchased from J&K Scientific Ltd. ^{1}H NMR spectra were recorded at 25 °C on Bruker Avance 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, 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.

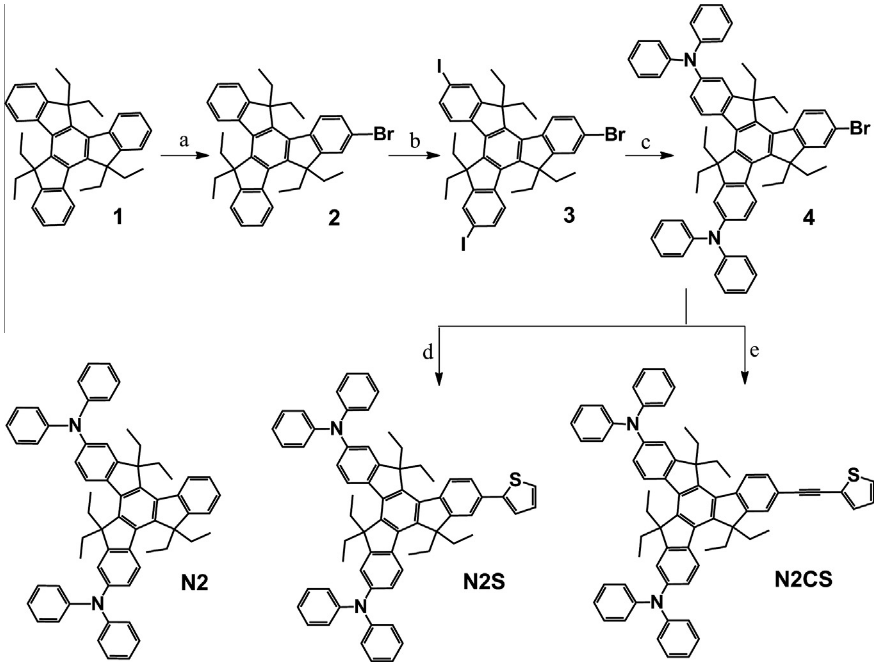
Compounds **1**–**4** and **N2** were synthesized according to literature methods reported by us [16].

Synthesis of compound N2S

A mixture of compound **4** (0.50 g, 0.54 mmol), 2-thiopheneboronic acid (0.10 g, 0.78 mmol), $Pd(PPh_3)_4$ (20 mg, 0.02 mmol), toluene (30 mL), ethanol (8 mL) and 2 M aqueous K_2CO_3 solution (2 mL) was heated and stirred at 80 °C under a nitrogen atmosphere for 24 h. The mixture were 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 (1:20) as the eluent to get compound **N2S** (0.16 g, 31.9%). **N2S**: a yellow powder, m.p. 156–158 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 0.21–0.28 (m, 18H), 1.89–2.15 (m, 6H), 2.84–2.99 (m, 6H), 7.02–7.12 (m, 6H), 7.32–7.33 (m, 3H), 7.46–7.49 (m, 2H), 7.55–7.58 (m, 16H), 7.57–7.67 (m, 2H), 8.09–8.27 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 154.22, 153.67, 152.67, 147.96, 129.24, 129.05, 128.24, 128.09, 126.35, 126.04, 125.31, 124.92, 124.59, 124.21, 122.95, 122.88, 122.69, 122.27, 121.98, 119.47, 117.66, 67.98, 56.65, 29.40, 29.19, 25.63, 21.46, 8.69, 8.65, 8.61. MALDI-TOF: *m*/*z* 927.3 [M$^+$], 898.9 [M-29]$^+$. Elemental Anal. Calcd. for $C_{67}H_{62}N_2S$: C, 86.78; H, 6.74; N, 3.02; S, 3.46. Found: C, 86.71; H, 6.84; S, 3.35.

Synthesis of compound N2CS

A mixture of compound **4** (0.50 g, 0.54 mmol), 2-ethynylthiophene (0.10 g, 0.84 mmol), $Pd(PPh_3)_4$ (20 mg, 0.02 mmol), *n*-Bu_4NF (50 mg), THF (20 mL) and triethylamine (10 mL) was heated to reflux with stirring after flushed with nitrogen for half an hour. After reacting for 10 h under nitrogen, the mixture were cooled to room temperature and poured into water (100 mL). After extraction with $CHCl_3$ 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 (1:10) as eluent to get compound **N2CS** (0.32 g, 62%). **N2CS**: a



Scheme 1. Synthesis of title compounds **N2S** and **N2CS**. For comparison, compound **N2**, a known compound reported in our previous study, is also shown. (a) Propylene carbonate, NBS, 60 °C, 2 h; (b) HIO_3, I_2, $CH_3COOH–H_2SO_4–H_2O–CCl_4$, 80 °C, 4 h; (c) Diphenylamine, K_2CO_3, Cu (powder), 18-crown-6-ether, 1,2-dichlorobenzene, reflux, 8 h; (d) 2-Thiopheneboronic acid, $Pd(PPh_3)_4$, K_2CO_3, Toluene/ethanol/H_2O, under N_2, 80 °C, 24 h; (e) 2-ethynylthiophene, $Pd(PPh_3)_4$, *n*-Bu_4NF, Et_3N, THF, under N_2, reflux, 10 h.

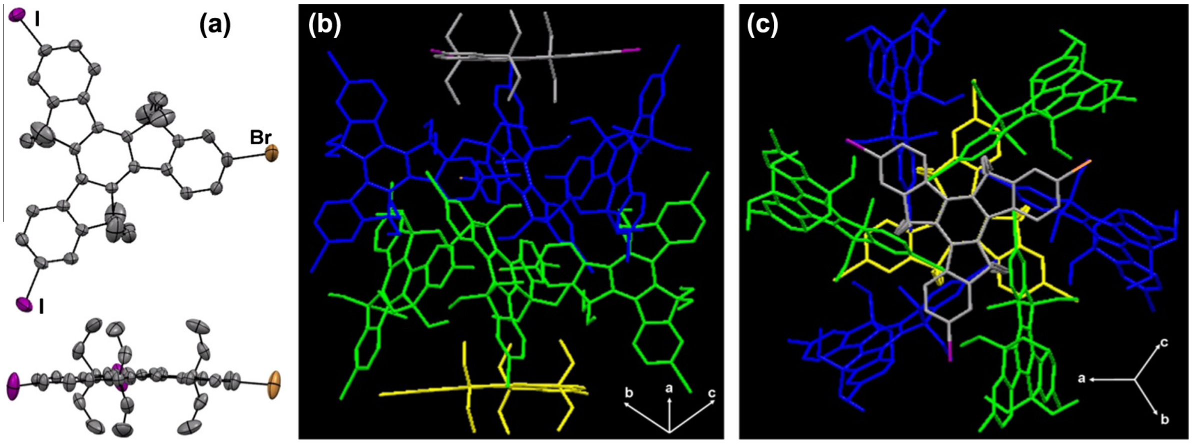


Fig. 1. X-ray single-crystal structures of compound 3: (a) **ORTEP** of compound **3**; (b) side and (c) top view of compound **3** packing. H-atoms are omitted for clarity.

Table 1
The photophysical data of compounds **1**, **N2**, **N2S** and **N2CS**.

	λ_{abs}[a] (nm)	ε_{max} (10^4, M^{-1} cm^{-1})	λ_F[a] (nm)	Φ [b]	τ [c] (ns)	$\Delta\tilde{\nu}$[d](10^3, cm^{-1})	$\Delta\tilde{\nu}/\Delta f$[e] ($10^3$, cm^{-1})
1	305	9.0	368	0.07	12.6	5.61	–
N2	360	5.6	390	0.36	1.9	2.14	5.0
N2S	357	7.13	410	0.68	2.0	3.62	7.9
N2CS	362	9.57	429	0.65	2.1	4.31	8.3

[a] Linear absorption and fluorescence maxima with $c = 1.0 \times 10^{-5}$ mol/L.
[b] Fluorescence quantum yields determined using coumarin 307 with $c = 1.0 \times 10^{-5}$ mol/L as standard.
[c] Fluorescence lifetime.
[d] Stokes-shift.
[e] The slope of plot of $\Delta\tilde{\nu}$ versus Δf in aprotic solvents based on the Lippert–Mataga equation, where $\Delta f = [(\varepsilon - 1)/(2\varepsilon + 1)] - [(n^2 - 1)/(2n^2 + 1)]$.

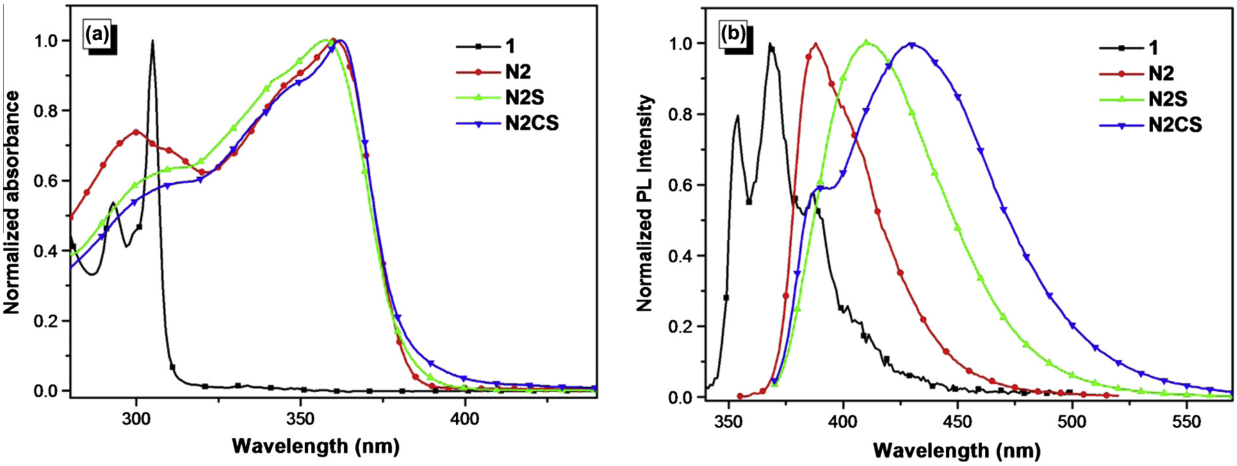


Fig. 2. Normalized absorption (a) and emission (b) spectra of compounds **1**, **N2**, **N2S** and **N2CS** with $c = 1.0 \times 10^{-5}$ mol/L in THF.

yellow powder, m.p. 162–164 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 0.24–0.29 (m, 18H), 1.89–2.11 (m, 6H), 2.84–2.95 (m, 6H), 6.99–7.31 (m, 9H), 7.42–7.47 (m, 2H), 7.49–7.55 (m, 18H), 8.07–8.25 (m, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz, ppm): δ 154.17, 152.99, 147.97, 147.92, 146.52, 146.29, 143.68, 143.40, 142.66, 141.27, 138.64, 135.24, 131.77, 129.59, 129.25, 127.15, 125.31, 125.15, 124.47, 124.25, 124.16, 123.63, 122.74, 122.63, 121.97, 120.42, 117.73, 117.60, 94.21, 82.82, 56.70, 56.65, 56.54, 29.46, 29.28, 29.16, 8.68, 8.63, 8.61. MALDI-TOF: *m*/*z* 950.5 [*M*$^+$], 921.3 [*M*-29]$^+$. Elemental Anal. Calcd. for $C_{69}H_{62}N_2S$: C, 87.12; H, 6.57; N, 2.94; S, 3.37. Found: C, 87.33; H, 6.41; S, 3.31.

Single crystal X-ray diffraction

The single crystal of compound **3** was firstly obtained by the slow diffusion of its THF: cyclohexane (2:1, v/v) solution for several days at room temperature. The data collection was done on a Bruker SMART APEX-II CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. Semi-empirical absorption corrections were applied using the SCALE program for area detector. The structure was solved by direct methods and refined by the full matrix least-squares methods on F^2 using SHELX.

Photophysical properties measurement

UV–vis absorption spectra for the solutions were recorded with a Shimadzu UV-2550 spectrophotometer. Photoluminescence (PL) spectra were recorded using a Shimadzu RF-5301PC spectrofluorimeter. Fluorescent decay curves were obtained using an Edinburgh FLS920 fluorescence spectrometer equipped with a time-correlated single photon counting (TCSPC) card. Reconvolution fits of the decay profiles were performed with F900 analysis software to obtain the lifetime values. The fluorescence quantum yield (Φ) in solution was determined using coumarin 307 in ethanol as a reference.

Theoretical calculation

The orbital energy of compounds **N2S** and **N2CS** were respectively calculated by using the Gaussian 09 program at the B3LYP Time-Dependent Density Functional Theory (TD-DFT). The 6-31G$*$ was used to optimize their single-molecular ground-state geometries. All ethyl substituents were replaced with H atoms for simplicity.

Results and discussion

Synthesis

The key procedure of synthesizing the asymmetric compounds **N2S** and **N2CS** is the synthesis of the asymmetric halogenide of truxene, which needs quantitative bromination and iodination of compound **1**. As shown in Scheme 1, we firstly used 1 equivalent *N*-bromosuccinimide (NBS) to get the monobromo substitution **2**. Then, compound **2** was fully iodinated by iodine and iodic acid at the active 7- and 12-positions to obtain **3**. The synthesis of compound **4** was processed through a selective Ullmann condensation

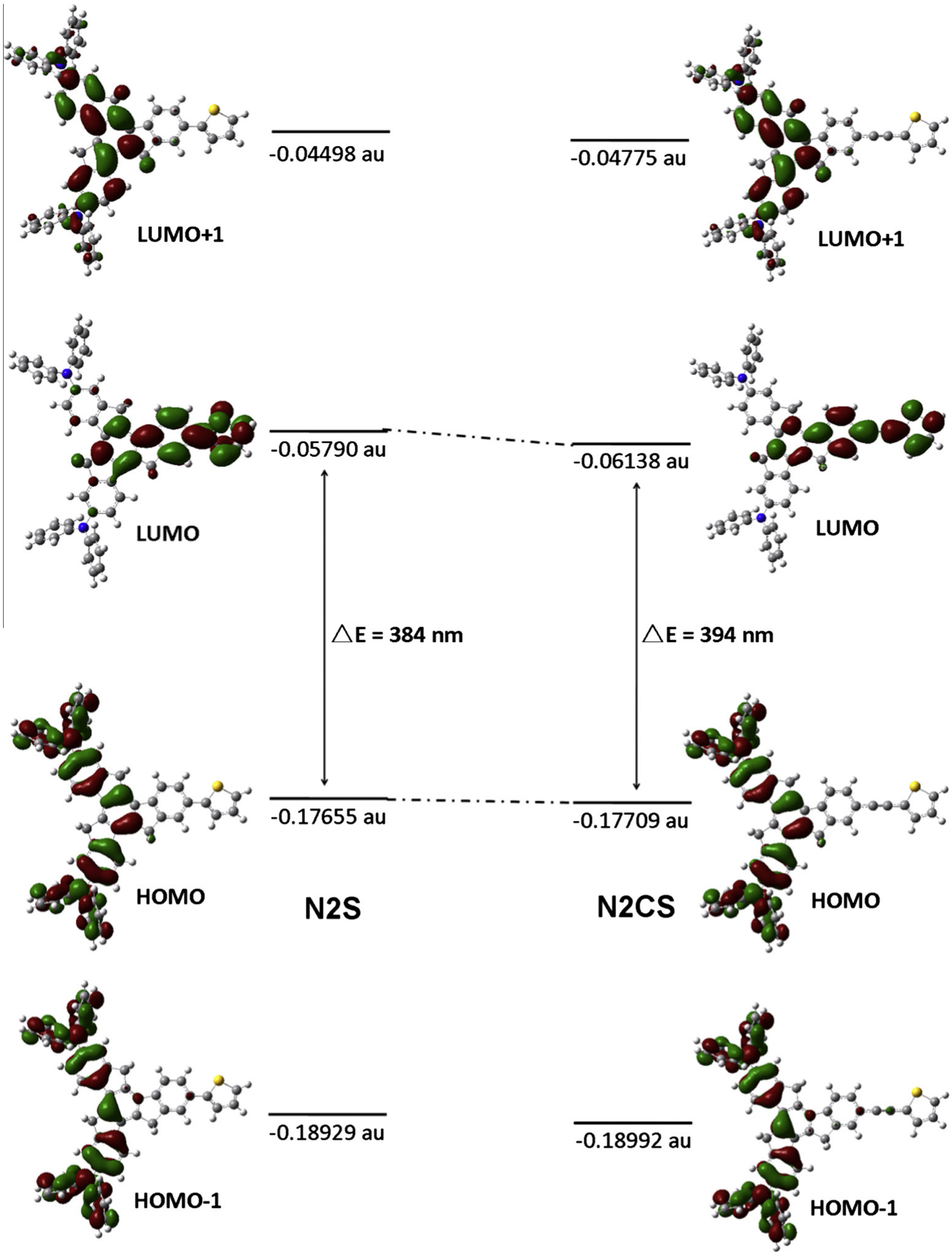


Fig. 3. Molecular orbital diagrams of the frontier molecular orbits of **N2S** (left) and **N2CS** (right). All of the ethyl substituents were replaced with H atoms for simplicity.

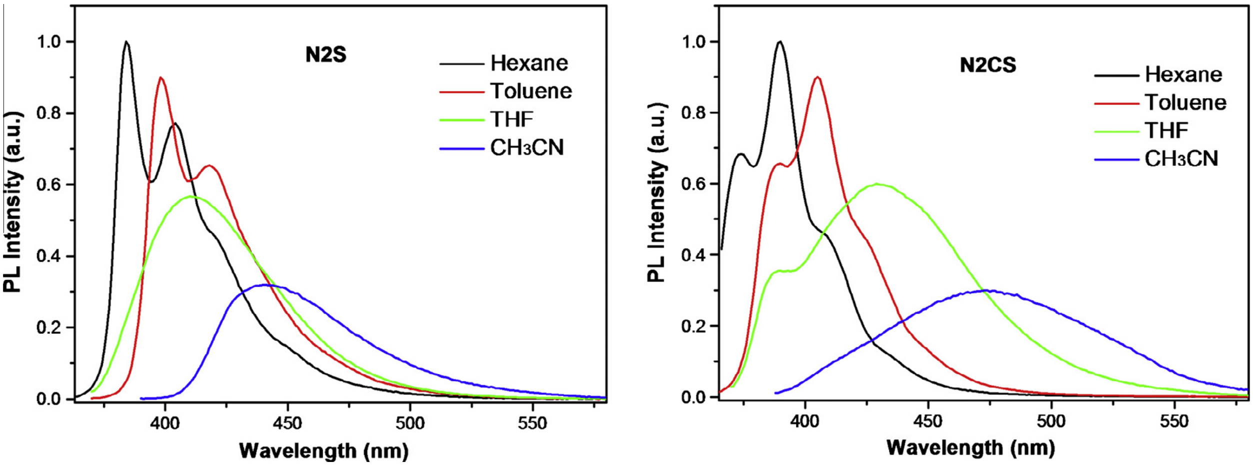


Fig. 4. Photoluminescence spectra of compounds **N2S** (left) and **N2CS** (right) in different solvents with $c = 1.0 \times 10^{-5}$ mol/L.

between diphenylamine and compound **3**, which stems from the different reactivities between aryl bromide and aryl iodide. Finally, the conventional Suzuki and Sonogashira cross-coupling of **4** with 2-thiophene-boronic acid and 2-ethynylthiophene gave the target molecules **N2S** and **N2CS** respectively. Details of the synthesis and characterizations are given in the experimental section.

X-ray crystallography

The single crystal of the key intermediate **3** has been obtained by the slow diffusion of its THF/cyclohexane solution for several days at room temperature and the X-ray single-crystal structure has been determined to be with the space group of *Pa* $\bar{3}$ [30]. As shown in Fig. 1a, the truxene unit of **3** lies approximately in a plane and the maximum displacement from the least-square plane by all the 27 carbon atoms of the truxene framework is 0.119(2) Å. The average interplanar angle between the three terminal benzene rings and the central benzene ring is only 3.91(3)°, which indicates that the planar configuration will facilitate the intramolecular charge transfer and π-electronic delocalization.

Though the molecular skeleton is highly planar, there is no $\pi \cdots \pi$ stacking found in the crystal packing, which probably arises from the six splaying ethyl groups. As shown in Fig. 1b and c, compound **3** exhibits interesting crystal packing. There are eight molecules in per crystal unit cell and they are marked in different color for clarity. The truxene plane of the grey molecule is almost parallel with that of the yellow molecule. The interplanar angle between blue (or green) molecule and grey (or yellow) molecule is 70.53(3)°. From the top view ([1 1 1] direction), we can see that the blue and green molecules exhibit a 6_3 screw symmetry.

Photophysical properties

The UV–vis absorption and PL spectra of compounds **N2S** and **N2CS** in THF solution have been measured. The corresponding photophysical data were summarized in Table 1, together with those of two known compounds **1** and **N2** for comparison [16].

As shown in Fig. 2a and Table 1, the non-functionalized compound **1** exhibits obvious vibronic feature, which is attributed to its rigid planar framework. After connecting two diphenylamino groups to compound **1**, the absorption maxima (λ_{abs}) of compound **N2** locates at 360 nm, which is red-shifted 55 nm in comparison with that of compound **1** (305 nm). This strong absorption band is presumably assigned to the intramolecular π–p_π charge transfer. However, after π-conjugative extension of **N2**, compounds **N2S** and **N2CS** unexpectedly demonstrate the almost same maximum absorption peaks as **N2**.

In order to understand the spectral behavior and charge transfer mode, we conducted theoretical calculations of compounds **N2S** and **N2CS**. The optimizations of the molecular geometry were carried out using Time-Dependent Density-Functional Theory (TD-DFT) calculations at the B3LYP/6-31G$*$ level. As shown in Fig. 3, upon excited, the charge of **N2S** and **N2CS** shift from triarylamine to thiophene-containing branching. The two compounds exhibit different energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The results combing with the spectral experiment (their almost same absorption maxima) indicate that the main transitions of both **N2S** and **N2CS** are not the direct transition from the HOMO to the LUMO. The transition oscillator strength of the two compounds from the HOMO to the LUMO are very small ($f = 0.0986$ for **N2S** and $f = 0.0462$ for **N2CS**), which may correspond to the weak absorption of **N2S** and **N2CS** in the right hand tails (380–400 nm) of the absorption profiles (Fig. 2a). They carry on the energy-level transitions from the HOMO − 1 to the LUMO or from the HOMO to the LUMO + 1.

Unlike the absorption spectra, their emission spectra demonstrate different maximum emission peak (Fig. 2b). With the increase of the conjugation length, their emission behaves a gradual red-shift in THF. Though the strong electron-donating nature of diphenylamino group, compounds **N2S** and **N2CS** exhibit moderate emission solvatochromism (Fig. 4), which results from the weak electron-withdrawing property of thiophene. In addition, the highest value of $\Delta\bar{\nu}/\Delta f$ of compound **N2CS** reveals its highest excited-state polar, which indicates compound **N2CS** carries on more prominent intramolecular charge transfer than **N2** and **N2S** upon excited. On the other hand, we also noted that the non-functionalized compound **1** exhibits a longer fluorescence lifetime than the functionalized compounds **N2**, **N2S** and **N2CS** (Table 1), which indicates compound 1 has the higher stability of the photoexcited state.

Conclusion

In conclusion, we designed and synthesized two asymmetric multibranched π-conjugated molecules using truxene as the central core, diphenylamino and thiophenyl (or thiophenylethynyl) groups as the different branches respectively. Their photophysical properties have been studied with that of one known compound which has been reported by us. The three compounds exhibit almost same absorption maxima irrespective of the difference in the conjugation length of their branches in THF, but a gradual emission red-shift with the increase of the conjugation length. Their results of the theoretical calculation combing with the spectral experiments indicate that the main energy-level transitions of the two asymmetric multibranched compounds are not the direct transition from the HOMO to the LUMO upon excited, but from the HOMO − 1 to the LUMO or from the HOMO to the LUMO + 1.

Acknowledgments

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