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Triarylborane-terminalized branched π -conjugative dyes: Synthesis, structure and optoelectronic properties



^a College of Science, Northwest A&F University, Yangling 712100, PR China
^b State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, PR China

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ABSTRACT

Organic optoelectronic materials with high fluorescence quantum yield, both in solution and in the solid state, have attracted considerable interest in recent years. In this work, we designed and synthesized three triarylborane-terminalized branched π -conjugative compounds, including two C₃-symmetric π -3A(acceptor) triarylboron dyes: 2,7,12-tri(5-(dimesitylboryl)thiophen-2-yl)-5,5',10,10',15,15'-hexaethyl-truxene and 2,7,12-tri((5-(dimesitylboryl)thiophen-2-yl)ethynyl)-5,5',10,10',15,15'-hexaethyltruxene, and a 2D(donor)- π -A asymmetric dye: 2,7-di(*N*,*N*-diphenylamino)-12-(5-(dimesitylboryl)thiophen-2-yl)-5,5',10,10',15,15'-hexaethyltruxene. The three compounds displayed prominent optical properties. The ethynyl spaced thiophene analogue emitted intense fluorescence both in the THF solution and in the solid state with excellent quantum yields. Interestingly, their solid powders showed a very different fluorescence colour from their respective THF solution. The results of theoretical calculations were in good agreement with the experimental absorption and CV spectra. The high reversibility of the three boron-containing dyes in their redox process indicates substantial stability of the produced species, which make them promising light-emitting materials.

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1. Introduction

Three-coordinate organoboron, with a vacant p_z orbital, is an excellent π -electronic acceptor when connected to a π -conjugated system. In recent years, three-coordinate organoboron compounds have attracted a great deal of attention because of their excellent photophysical and electronic properties [1]. Meanwhile, the availability of the empty p_z orbital makes three-coordinate organoboron compounds highly susceptible to the addition by Lewis bases, resulting in their relatively poor stability. An effective method of improving the stability is to utilize the aromatic substituents, which arise from bulky aryl groups to provide protection for the central boron atom by blocking the approach of nucleophiles [1a,2]. In the last decade, stable triarylboron compounds (triarylboranes) have been exploited extensively in a wide range of applications as optoelectronic materials, such as nonlinear optical materials [3],

transporting and emissive materials in organic light-emitting devices (OLEDs) [4], two-photon absorption and emission materials [5] as well as selective chemosensors for fluoride and cyanide anions [6] and heat-sensitive materials [7]. For practical application, having enough high solid-state fluorescence efficiency is a fundamental issue for luminescent materials. However, most triarylboranes are highly emissive only in dilute solution and tend to show a decrease of fluorescence efficiency in the solid state due to the aggregation-caused quenching (ACQ) effect. The successful examples of stable and highly emissive triarylboranes in both solution and the solid state with a fluorescence quantum yield close to unity are still quite limited [8].

An effective strategy of molecular design to achieve an intense emissive organic compound in both solution and the solid-state is the construction of a multibranched π -conjugated framework with large building blocks [9]. The branched steric bulkiness will inherently reduce the intermolecular dipole–dipole interaction and $\pi \cdots \pi$ stacking, which will generally result in drastic fluorescence self-quenching in the aggregation state. In addition, in comparison to the linear molecules and polymers, branched π conjugated molecules have a number of advantages for applications in optoelectronic devices, for example, the two- or three-





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^{*} Corresponding author. Tel./fax: +86 29 87082520.

E-mail addresses: jywang@nwsuaf.edu.cn, jinyiwangpharm@gmail.com (J. Wang).

¹ These two authors contributed equally to this work.

dimensional architectures, the well-defined molecular structure and good film-forming processing [10]. In this context, it is of particular interest to develop triarylborane-containing branched π conjugated organic emissive materials exhibiting high fluorescence efficiency in both solution and the solid state.

As far as this issue is concerned, truxene (10.15-dihydro-5Hdiindeno[1.2-*a*:1'.2'-*c*]fluorene), a heptacyclic polyarene, was chosen to construct the branched framework. Due to its C₃-symmetric skeleton and three-dimensional topology, the truxene unit has been intensively developed as a π -conjugated central core to fabricate star-shaped optoelectronic molecules, such as OLEDs [11], organic field-effect transistors (OFETs) [12], liquid crystals [13] and two-photon absorption materials [14]. Considering the good thermal and chemical stability, 2-thienyl and 2-thienyl-ethynyl were respectively used as the π -bridge to connect the 2, 7, 12-positions of truxene [15]. As for the termini of the branches, to continue our effort in the development of highly emissive materials utilizing the boron element, dimesitylboron (mesityl = 2,4,6-trimethylphenyl) group is a favourable choice for our proposed design principle: this bulky unit can suppress the $\pi \cdots \pi$ stacking and the strong electronwithdrawing ability can facilitate intramolecular/intermolecular charge transfer. Herein, we report three boron-containing branched π -conjugative compounds, including two C₃-symmetric π -3A(acceptor) triarylboron dyes: 2,7,12-tri(5-(dimesitylboryl)thiophen-2-yl)-5,5',10,10',15,15'-hexaethyltruxene (S3B3) and 2,7,12tri((5-(dimesitylboryl)thiophen-2-yl)ethynyl)-5,5',10,10',15,15'-hex aethyltruxene (**C3B3**), and a 2D(donor)- π -A asymmetric dye: 2,7di(*N*.*N*-diphenvlamino)-12-(5-(dimesitylboryl)thiophen-2-yl)-5.5' ,10,10',15,15'-hexaethyltruxene (N2SB). Their photophysical properties in both solution and the solid state, theoretical calculations, electrochemical properties, as well as the X-ray single-crystal structures of their precursors, have been comprehensively studied.

2. Experimental section

2.1. 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. ¹H NMR spectra were recorded at 25 °C on Bruker Avance 500 MHz spectrometer using CDCl₃ as solvent. ¹³C NMR spectra were recorded at 25 °C on Bruker Avance 125 MHz spectrometer using CDCl₃ 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 **1–5** were synthesized according to literature methods [6h] and compounds **S3** and **C3** were synthesized following the literature [6i,14c].

2.1.1. Synthesis of compound N2S

A mixture of compound **5** (0.50 g, 0.54 mmol), 2-thiopheneboronic acid (0.10 g, 0.78 mmol), Pd(PPh₃)₄ (20 mg, 0.02 mmol), toluene (30 mL), ethanol (8 mL) and 2 M aqueous K₂CO₃ 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 Na₂SO₄. 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. ¹H NMR (CDCl₃, 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). ¹³C NMR (CDCl₃, 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 C₆₇H₆₂N₂S: C, 86.78; H, 6.74; S, 3.46. Found: C, 86.71; H, 6.84; S, 3.35.

2.1.2. Synthesis of compound S3B3

n-BuLi (2.4 M solution in n-hexane, 0.20 mL, 0.48 mmol) was added to a stirred solution of compound S3 (100 mg, 0.13 mmol) in THF (10 mL) under nitrogen at -78 °C over 5 min, and followed by warming to room temperature naturally. After reacting for further 4 h, the reactants were cooled to -78 °C again, and dimesitylboron fluoride (0.20 g, 0.74 mmol) in THF (5 mL) was injected over 5 min. The temperature was allowed to naturally rise to room temperature and the mixture continuously stirred for two days. Then the reactants were diluted with ethyl acetate, washed with water and dried over magnesium sulfate. After removal of the solvents, the crude product was obtained. After purification by column chromatography on silica gel, eluting with dichloromethane-petroleum ether (1:5), compound S3B3 was obtained (58 mg, 29%). S3B3: a yellowish-green powder, m.p. 201–203 °C. ¹H NMR (CDCl₃, 500 MHz, ppm): δ 0.19–0.22 (t, I = 7.5 Hz, 18H), 1.52–2.06 (m, 42H), 2.32 (s, 18H), 2.94-2.98 (m, 18H), 6.85 (s, 12H), 7.38-7.41 (m, 6H), 7.51–7.53 (d, J = 10 Hz, 3H), 7.58 (s, 3H), 8.29–8.31 (d, J = 10 Hz, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 157.4, 153.6, 144.8, 144.3, 141.9, 140.9, 140.0, 138.5, 132.8, 132.4, 128.2, 125.4, 124.7, 124.3, 123.0, 119.5, 56.9, 29.7, 23.5, 21.3, 8.6. MALDI-TOF: *m*/*z* 1501.4 [*M*⁺], 1472.8 [*M*-29]⁺. Elemental Anal. Calcd. for C₁₀₅H₁₁₁B₃S₃: C, 83.98; H, 7.45; S, 6.41. Found: C, 83.91; H, 7.12; S, 6.42.

2.1.3. Synthesis of compound C3B3

A similar synthetic and purification procedure as for **C3B3** was followed for **S3B3** using compound **C3** as the precursor. Then compound **C3B3** (41.5%) was obtained. **C3B3:** a light green powder, m.p. 222–224 °C. ¹H NMR (CDCl₃, 500 MHz, ppm): δ 0.22–0.25 (t, J = 7.5 Hz, 18H), 2.10–2.32 (m, 42H), 2.35 (s, 18H), 2.97–3.02 (m, 6H), 6.88 (s, 12H), 7.41–7.43 (d, J = 10 Hz, 6H), 7.54–7.56 (d, J = 10 Hz, 3H), 7.61 (s, 3H), 8.32–8.34 (d, J = 10 Hz, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 152.9, 145.3, 141.1, 140.9, 140.1, 138.8, 138.5, 135.3, 133.6, 129.8, 128.2, 125.3, 124.6, 120.7, 97.6, 83.6, 57.0, 29.5, 23.5, 21.3, 8.5. MALDI-TOF: m/z 1572.7 [M⁺], 1543.6 [M-29]⁺. Elemental Anal. Calcd. for C₁₁₁H₁₁₁B₃S₃: C, 84.72; H, 7.11; S, 6.11. Found: C, 84.91; H, 7.02; S, 6.12.

2.1.4. Synthesis of compound N2SB

A similar synthetic and purification procedure as for **N2SB** was followed for **S3B3** using compound **N2S** as the precursor. Then compound **N2SB** (30.9%) was obtained. **N2SB**: a light green powder, m.p. 188–190 °C. ¹H NMR (CDCl₃, 500 MHz, ppm): δ 0.23–0.27 (m, 18H), 1.89–2.18 (m, 18H), 2.33 (s, 6H), 2.87–2.97 (m, 6H), 6.86 (s, 6H), 7.00–7.05 (m, 6H), 7.18–7.19 (m, 6H), 7.27–7.30 (m, 6H), 7.46–7.47 (m, 1H), 7.56–7.57 (m, 1H), 7.69–7.71 (d, *J* = 10 Hz, 6H), 8.08–8.10 (d, *J* = 10 Hz, 1H), 8.14–8.16 (d, *J* = 10 Hz, 1H), 8.24–8.26 (d, *J* = 10 Hz, 1H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 157.6, 154.2, 153.8, 147.9, 146.5, 143.2, 141.9, 141.4, 140.9, 138.6, 138.5, 135.3, 129.3, 128.2, 125.2, 124.9, 124.3, 122.8, 120.0, 119.7, 117.6, 56.8, 56.7, 29.5, 29.4, 29.2, 23.5, 21.3, 8.7, 8.6. MALDI-TOF: *m/z* 1173.9 [M⁺], 1144.8 [M-29]⁺. Elemental Anal. Calcd. for C₈₅H₈₃BN₂S: C, 86.85; H, 7.12; N, 2.38; S, 2.73. Found: C, 86.67; H, 7.02; N, 2.37; S, 2.65.

2.2. Single crystal X-ray diffraction

The single crystals of compounds **S3** and **N2S** were firstly obtained by the slow diffusion of their respective CHCl₃: cyclohexane (2:1, v/v) solutions for several days at room temperature. Since the two crystals are stable under ambient condition, the data collection was done without any insert gas protection at room temperature on a Bruker SMART APEX-II CCD area detector using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Data reduction and integration, together with global unit cell refinements were done by the INTEGRATE program of the APEX2 software. Semi-empirical absorption corrections were applied using the SCALE program for area detector. The structures were solved by direct methods and refined by the full matrix least-squares methods on F^2 using SHELX. The single-crystal structure of compound **C3** has been reported by our group [14c].

2.3. Photophysical properties measurement

UV–vis absorption spectra for the solutions and the films were recorded with a Shimadzu UV-2550 spectrophotometer. Photoluminescence (PL) spectra were recorded using a Shimadzu RF-5301PC spectrofluorimeter. The fluorescence quantum yield (Φ) in solution was determined using rhodamine B in ethanol as a reference according to a previously reported method [16]. Quantum yields of the films and the solid-state powder were determined with a PTI C-701 calibrated integrating sphere system [17]. Steadystate fluorescence spectra and 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 solid films were prepared through solution process (THF, 1.0×10^{-4} mol/L, 1500– 2000 rpm) with 50–100 nm thickness.

2.4. Theoretical calculation

In order to understand the spectral behaviour and elucidate the influence of the different symmetric pattern on the electronic structures, the orbital energy of compounds **S3B3**, **C3B3** and **N2SB** 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.

2.5. Electrochemical properties measurement

Cyclic voltammetry (CV) was performed on CHI660D workstation and measurements were carried out in THF containing 0.1 M n-Bu₄NClO₄ as the supporting electrolyte, platinum disc as the working electrodes, platinum wire as the counter electrode and Ag/ AgNO₃ as the reference electrode under N₂ atmosphere. The scan rate was maintained at 100 mV s⁻¹.

3. Results and discussion

3.1. Synthesis

The synthetic approach to the title compounds is outlined in Scheme 1. Compound 1 was used as the starting material. After quantitative bromination and/or iodination, compound 1 was respectively converted to compounds 2, 3 and 4, which has been reported in our previous work [6h]. Compounds S3 and C3 were synthesized via conventional Suzuki reaction and Sonogashira cross-coupling reaction from compounds 2 and 3. The synthesis of



Scheme 1. Synthesis of title compounds. (a) Bromine, CH₂Cl₂, 25 °C, 12 h; (b) and (j) 2-Thiopheneboronic acid, Pd(PPh₃)₄, K₂CO₃, THF, reflux, 8 h; (c), (f) and (k) Dimesitylboron fluoride, *n*-BuLi, THF, -78 °C, 2 d; (d) and (h) HIO₃, I₂, CH₃COOH-H₂SO₄-H₂O-CCl₄, 80 °C, 4 h; (e) 2-ethynylthiophene, Pd(PPh₃)₄, *n*-Bu₄NF, Et₃N, THF, reflux, 3 h; (g) Propylene carbonate, NBS, 60 °C, 2 h; (i) Diphenylamine, K₂CO₃, Cu (powder), 18-crown-6-ether, 1,2-dichlorobenzene, reflux, 8 h.

compound **N2S** was firstly processed through selective Ullmann condensation between diphenylamine and compound **4**, which stems from the different reactivities between aryl bromide and aryl iodide, then a conventional Suzuki reaction. After respective boronation of compounds **S3**, **C3** and **N2S** using dimesitylboron fluoride, the title compounds **S3B3**, **C3B3** and **N2SB** were obtained. All the new compounds were characterized with ¹H NMR, ¹³C NMR, elemental analysis and MALDI/TOF mass spectroscopy. The intermediates **S3**, **C3** and **N2S** have been verified by their X-ray single-crystal structures.

3.2. X-ray crystallography

Determination of X-ray single-crystal structure is the most effective tool for acquiring the ground-state molecular structure to reveal the molecular structure—property correlations. The greatest effort has been exerted to get the single crystals of all the intermediates and title compounds. But it failed to achieve the single crystals of the three boron-containing compounds because of their huge branched fabrications. Fortunately, the single crystals of their respective precursors **S3**, **C3** and **N2S** have been obtained by the slow diffusion of their CHCl₃: cyclohexane (2:1, v/v) solution for several days at room temperature [18]. As shown in Fig. 1(a), (d) and (g), all the truxene moieties of **S3**, **C3**, and **N2S** exhibit highly planar geometry with the mean deviations from their individual least-squares plane being 0.018(5), 0.016(8) and 0.037(6) Å,

respectively. For the S3 single molecule, the distances between the three thiophene rings and the truxene are respectively 1.482(5), 1.466(5) and 1.479(5) Å, which are shorter than typical $C(sp^3)$ - $C(sp^3)$ single bonds and longer than typical $C(sp^2)=C(sp^2)$ double bonds, implying a certain extent of conjugation between truxene and thiophene. Another structural feature of **S3** is that the three thiophene rings are almost coplanar with the truxene unit. The average dihedral angle between the thiophene ring and the nearest benzene is only 11.2(5)°, which will facilitate the intramolecular charge transfer. The **S3** molecules are packed in the $P2_1/n$ space group. Though the molecular skeleton is highly planar, there is no $\pi \cdots \pi$ stacking found in the crystal packing. The blue molecules are almost perpendicular to the grey molecules in Fig. 1(b). In addition, the intermolecular C–H $\cdots\pi$ interactions between the blue molecules and the grey molecules possibly play an important role for the stabilization of the crystal packing.

Unlike **S3**, the thiophene rings of the **C3** molecule are perpendicular to the central truxene. The average dihedral angle between thiophene rings and truxene is $89.6(9)^{\circ}$ (Fig. 1(d)), which is very unusual in common aromatic conjugative systems. This special structure is mainly attributed to two factors. One is the intermolecular C–H··· π interactions. The **C3** molecules are packed in the *P*-1 space group with layer-by-layer packing character (Fig. 1(e)). There are notable intermolecular C–H··· π interactions existing between the two neighbouring layers (Fig. 1(f)). The 3-position



Fig. 1. X-ray single-crystal structures of compounds **S3** (a, b, c), **C3** (d, e, f) and **N25** (g, h, i): **ORTEP** of **S3** (a), **C3** (d) and **N25** (g, h, i): **orter** of **S3** (a), **C3** (d) and **N25** (g, h, i): **orter** of **S3** (a), **C3** (d) and **N25** (g, h, i): **orter** of **S3** (a), **C3** (d) and **N25** (g, h, i): **orter** of **S3** (a), **C3** (d) and **N25** (g, h, i): **orter** of **S3** (a), **C3** (d) and **N25** (g); (b) side view of **S3** packing; (c) illustration of the C– H… π stacking in **S3**; (e) side view of **C3** packing, the molecules in the same packing layer were marked in the same colour and the distance between the green layer and yellow layer is about 4.50 Å; (f) top view of **C3** and illustration of the C–H… π stacking; (h) side view of **N25** packing; (i) illustration of the C–H… π stacking in **N25**. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

hydrogen atoms of the thiophene units point toward the plane of the benzene portion of the truxene rings in the neighbouring layer, which leads to the thiophene plane being perpendicular to the plane of truxene. The other is the intramolecular $\pi - \pi$ conjugation. This formed perpendicular configuration will facilitate the overlap of the parallel π_5^6 -bonding orbital of thiophene and the π (p_y-p_y)-bonding orbital of the bonded acetylene group, and result in good $\pi - \pi$ conjugation between thiophene unit and acetylene group.

In the single crystal of asymmetric molecule **N2S**, the dihedral angle and the distance between thiophene and truxene are 15.3(3)° and 1.482(5) Å respectively. The three benzene rings around nitrogen atom are arranged in a propeller-like fashion, with the dihedral angles being 83.1(3), 75.5(3) and 64.2(3)° respectively (Fig. 1(g)). The **N2S** molecules are packed in the $P2_1/c$ space group. Similar to **S3**, the blue molecules are perpendicular to the grey molecules (Fig. 1(h)), and intermolecular C-H··· π interactions link blue molecules and grey molecules into dimers (Fig. 1(i)).

3.3. Photophysical properties

The UV–vis absorption and PL spectra of compounds **S3B3**, **C3B3** and **N2SB** in THF solution, films and the solid-state powder were measured (Figs. 2 and 3). The corresponding data are summarized in Table 1, together with those of their precursors **S3**, **C3** and **N2S** for comparison.

As shown in Fig. 2, the UV–vis absorptions of the three boroncontaining compounds exhibit obvious spectral features of their respective precursor. For example, the absorption maxima (λ_{abs}) of compound **S3B3** peaked at 340 nm is identical with that of compound **S3**, and the spectral shape of **S3B3** is also very similar to that of **S3** (Fig. 2(a)). Likewise, **C3B3** exhibits an identical absorption band (377 nm) with that of **C3** (375 nm). The identical absorption bands indicate the same $\pi - \pi^*$ charge transfer (CT) processes. In accordance with expectation, compounds **S3B3**, **C3B3** and **N2SB** feature their respective weak shoulder band at the longer



Fig. 2. The normalized UV–vis absorption (a, c and e) and photoluminescence (b, d and f) spectra of compounds S3B3, C3B3 and N2SB with their respective precursors S3, C3 and N2S in THF with $c = 1.0 \times 10^{-5}$ mol/L.



Fig. 3. The normalized UV–vis absorption (a) and photoluminescence (b) spectra of compounds **S3B3, C3B3** and **N2SB** in THF with $c = 1.0 \times 10^{-5}$ mol/L (a, b) and in films (c, d). And their UV–vis absorption (e) and photoluminescence (f) in solid powder. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

wavelength (~406 nm), which is presumably assigned to the intramolecular π – p_{π} CT from the highest occupied molecular orbitals (HOMOs) to the lowest unoccupied molecular orbitals (LUMOs). In the PL spectra, the emission peaks of the three boron-containing compounds respectively show remarkable red shifts in comparison with those of their precursor in the same solvent (THF). The spectral phenomena indicate that the introduction of the π -electronic acceptor (three-coordinate organoboron) into the π -conjugative system can effectively facilitate intramolecular CT and improve molecular photophysical properties.

When considering the difference of the three boron-containing compounds, it was discovered that the absorption maxima of compound **C3B3** (377 nm) in THF solution are obviously red-shifted in comparison with that of compounds **S3B3** (340 nm) and **N2SB** (363 nm) because of the expanded π conjugation (Fig. 3(a)). However, whatever the positions of absorption maxima, all of the

three compounds showed similar longest-wavelength absorption at ~406 nm. For their emission spectra (Fig. 3(b)), it is surprising that **C3B3** demonstrates the almost same maximum emission peak as **S3B3** at 429 nm irrespective of the difference in the conjugation length of their branches. Comparing **S3B3** with **N2SB**, we can draw the conclusion that the substitution of two branches of **S3B3** by two diphenylamino donors results in an 87-nm red-shift of the fluorescence in THF, but a reduced fluorescence quantum yield (0.75 \rightarrow 0.22).

For light-emitting materials, most of their applications are required to be used in the solid state, e.g. thin films, powder or crystal. In this case, having sufficiently high solid-state fluorescence efficiency is a fundamental issue. The photophysical properties of compounds **S3B3**, **C3B3** and **N2SB** both in films and in the solid powder were measured (Fig. 3(c)-(f)). As expected, the three boron-containing compounds exhibit intriguing solid-state

c	\mathbf{c}
n	n
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	Solution in THF						Film			Solid powder		
	$\lambda_{abs}(nm)^a \ \epsilon_{max}(10^4 \ M^{-1} \ cm^{-1})$	$\epsilon_{\rm max}(10^4,{ m M}^{-1}~{ m cm}^{-1})$	$\lambda_{em}(nm)^a$	$\Delta \tilde{v}^{b}$	Φ^{c}	$\tau(ns)^d$	$\lambda_{abs}(nm)$	$\lambda_{em}(nm)$	Φ^{e}	$\lambda_{em}(nm)$	Φ^{e}	τ(ns
S 3	340	16.3	385, 400	3.59	0.59	2.1	_	_	_	_	_	_
C3	354,375	10.8,	390,406	3.64	0.58	1.5	_	_	_	_	-	_
N2S	358	7.1	410	3.62	0.68	2.3	_	_	_	_	_	_
S3B3	340,352,404	10.0, 8.1, 1.4	383,400,429	5.15	0.75	2.7	340,409	420,440	0.67	455,519	0.15	11.4
C3B3	377,405	12.1, 10.2	429	3.27	0.63	2.9	379,408	447	0.60	495	0.79	15.2
N2SB	363,388,407	8.4, 5.7, 4.4	516	8.14	0.22	6.3	365,408	499	0.43	462	0.57	17.6

 Table 1

 The photophysical data of the subject compounds.

^a With $c = 1.0 \times 10^{-5}$ mol/L.

^b Stokes-shift.

^c Fluorescence quantum yield determined using rhodamine B in ethanol as standard.

^d Fluorescence lifetime.

^e Fluorescence quantum yield in the solid state is obtained in a calibrated integrating sphere.

luminescence (Fig. 3(d) and (f), Table 1). Especially compounds C3B3 and N2SB, their solid-state fluorescence efficiency reached 0.79 (for C3B3) and 0.57 (for N2SB) in powder form, indicating their potential applications as excellent non-doped luminescent materials, e.g. OLEDs.

However, it is noteworthy that the powdered compounds C3B3 and N2SB show very different fluorescence from their respective THF solutions. As shown in Figs. 3f and 4, the THF solution of C3B3 emits blue fluorescence peaked at 429 nm. Unexpectedly, its solid powder exhibits bright-green fluorescence peaked at 495 nm. In contrast, the THF solution of C3B3 emits green fluorescence, but its solid powder form emits blue. We noted that the fluorescence lifetime of solid-state powders of the three compounds were significantly longer than those of their THF solution (Table 1), which may imply that their solid-state fluorescence is mainly from an aggregation-induced excimer, not the single molecule [19]. Because of the molecular multibranch configuration and steric bulk of dimesitylboron, it is impossible that these molecules were packed in the form of H-aggregation (intermolecular $\pi \cdots \pi$ stacking interactions) in the solid state. We speculate that these molecules organized into the aggregative state in a staggered staircase-like J-aggregation or infilled arrangements through weak intermolecular interactions. Moreover, their starshaped molecular geometry provides the possibility of the staggered staircase or infilled arrangements, e.g., the terminal of one branch embeds into the vacancy between the two branches of another molecule.

S3B3 C3B3 N2SB

Fig. 4. Photo of the THF solutions ($c = 1.0 \times 10^{-5}$ mol/L) and as-prepared solid powders of compounds **S3B3**, **C3B3** and **N2SB** under 365-nm UV light. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.4. Theoretical studies

In order to understand the spectral behaviour and intramolecular charge transfer modes, we conducted theoretical calculations of the three boron-containing compounds. The optimizations of the molecular geometry and total energy calculations were carried out using time-dependent density-functional theory (TD-DFT) calculations at the B3LYP/6-31G* level. As shown in Fig. 5, the calculation results showed that the HOMO and HOMO-1 (or LUMO and LUMO+1) of the C_3 -symmetric compounds S3B3 and C3B3 have very similar energy. Their HOMO and HOMO-1 mainly delocalized over the truxene-thiophene framework, and the LUMO and LUMO+1 mainly delocalized over the triarylboron framework. Notably, the charge transfer of the 2D $-\pi$ -A compound N2SB was more prominent than those of S3B3 and C3B3. After being excited, the charge was entirely shifted from triarylamine (HOMO) to triarylboron (LUMO). Meanwhile, the results show that the introduction of the electron-donating diphenylamino groups led to a remarkable increase in the HOMO energy level by 0.65 eV and consequently a decrease of the energy gap between HOMO and LUMO compared with that of S3B3, which corresponds to the relatively strong absorption of N2SB in the right-hand tails (415-440 nm) of the absorption profiles.

3.5. Electrochemical properties

To further evaluate the potential applicability in electronic devices, the electrochemical properties of the three title compounds were studied by cyclic voltammetry, and their CV diagrams can be found in Fig. 6. **S3B3** and **C3B3** show only reversible reduction waves. Their half-wave reduction potentials $(E_{1/2}^{red})$ are almost identical regardless of the difference in the conjugation length, being -2.35 and -2.30 eV vs. Ag/Ag⁺. **N2SB** shows not only a reversible reduction wave, but also a reversible oxidation wave due to the diphenylamino groups. The $E_{1/2}^{red}$ of **N2SB** is higher than those of **S3B3** and **C3B3**, being -1.95 eV vs. Ag/Ag⁺ and the half-wave oxidation potentials $(E_{1/2}^{rxd})$ were -0.51 eV vs. Ag/Ag⁺. The high reversibility of all the three compounds in the redox process demonstrates the substantial stability of the produced species.

Under such experimental conditions, the redox potential of Fc/ Fc⁺, which possesses an absolute energy level of -4.8 eV relative to the vacuum level for calibration, is located at 0.39 eV [14b]. So, we can draw the evaluation of the HOMO energy levels by the equation: HOMO = $-E_{1/2}^{vd}$ - 4.41. As a result, the HUMO energy level of **N2SB** is -4.92 eV, and the LUMO energy level can be calculated by the equation: LUMO = HOMO- E_g , where E_g is the energy bandgap determined from the longest wavelength absorption onset (430 nm), being -1.97 eV, which is highly consistent with the results of the theoretical calculation (Fig. 5).



Fig. 5. Molecular orbital diagrams of the frontier molecular orbits of S3B3 (left), C3B3 (middle) and N2SB (right). Due to the large molecular size, the ethyl and methyl groups have been replaced by H atoms.

4. Conclusion

In summary, we have designed and synthesized three truxenecored branched π -conjugative compounds **S3B3**, **C3B3** and **N2SB**, in which triarylboron units were used as the termini of the branches. The X-ray single-crystal structures of their precursors S3, C3 and N2S were studied. The results show that the intermolecular $C-H\cdots\pi$ interactions play an important role for the stabilization of the three crystal packings. Interestingly there was no $\pi \cdots \pi$ stacking found in any one crystal packing. The photophysical and electrochemical properties of compounds S3B3, C3B3 and N2SB have been carefully examined. Because of the electron-withdrawing nature of the three-coordinate organoboron, molecular multibranched configuration and dimesitylboron's steric bulkiness, the three compounds display prominent optical properties. Especially, π -expanded C₃-symmetric compound **C3B3** which emits intense fluorescence in both the THF solution and the solid state with excellent quantum yields. In addition, the high reversibility of the three compounds in their redox process demonstrates the substantial stability of the produced species, which make them promising light-emitting materials.



Fig. 6. Cyclic voltammogram of compounds S3B3, C3B3 and N2SB in THF; electrolyte 0.1 M n-Bu₄NClO₄, scan rate 100 mV s⁻¹.

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