

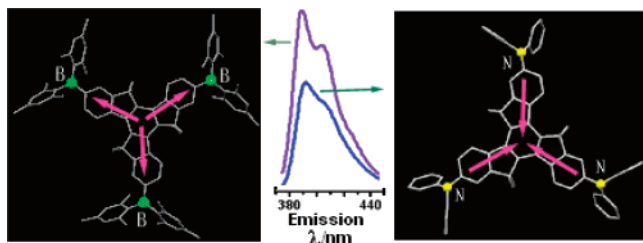
## Acceptor or Donor (Diaryl B or N) Substituted Octupolar Truxene: Synthesis, Structure, and Charge-Transfer-Enhanced Fluorescence

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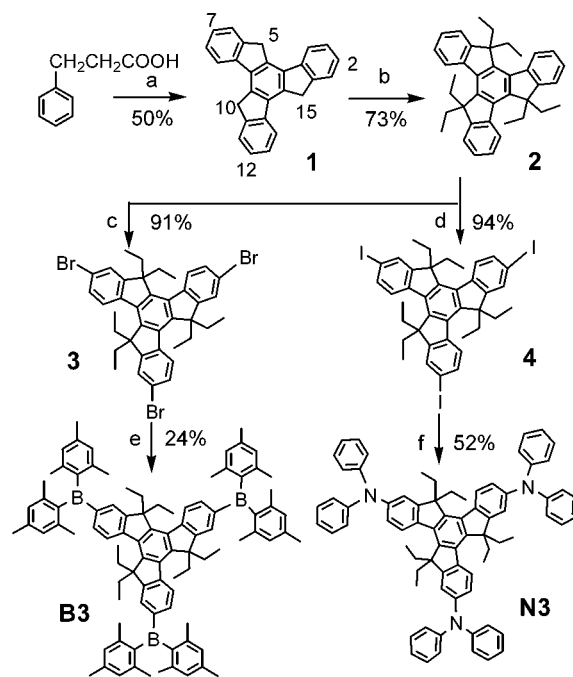
Received June 13, 2006



Two diaryl B- and N-substituted truxene charge-transfer compounds **B3** and **N3** have been synthesized. The fluorescence intensities of several nonfunctionalized truxene compounds are 1 order of magnitude weaker than that of **B3** and **N3**. To reveal the structure–property correlations, the X-ray structures of **B3** and **N3** and their precursors **3** and **4** have been determined. The extended molecular dimension, the especially shortened B–C bond, and the improved planarity of **B3** can serve as direct structural evidence for the charge transfer.

The optoelectronic properties of an organic molecule are correlated to its two structural characters: the  $\pi$ -conjugation and the charge transfer (CT) property. Besides, molecular symmetry is also a factor influencing some nonlinear optical (NLO) processes. At a glance of the rigid  $\pi$ -conjugated structure of truxene (**1**), namely 10,15-dihydro-5H-diindeno[1,2-a;1',2'-c]fluorene (Scheme 1), one can understand why this kind of heptacyclic polyarene has received considerable attention in recent years and shows some potential applications, such as in organic light-emitting diodes (OLEDs),<sup>1</sup> two-photo absorption,<sup>2</sup> and the NLO chromophore.<sup>3a</sup>

### SCHEME 1. Synthesis of **B3** and **N3**<sup>a</sup>



<sup>a</sup> Key: (a) PPA, 160 °C, 3 h; (b) Bromoethane, *n*-BuLi, THF, 0 °C, 12 h; (c) bromine, CH<sub>2</sub>Cl<sub>2</sub>, 25 °C, 12 h; (d) HIO<sub>3</sub>, I<sub>2</sub>, CH<sub>3</sub>COOH–H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O–CCl<sub>4</sub>, 80 °C, 4 h; (e) dimesitylboron fluoride, *n*-BuLi, THF, –78 °C, 2 d; (f) diphenylamine, K<sub>2</sub>CO<sub>3</sub>, Cu, 18-crown-6-ether, 1,2-dichlorobenzene, reflux, 8 h.

The chemistry of truxene at 5-, 10-, 15-positions has acquired appreciable development, and some of the resultant compounds might serve as precursors for fullerenes.<sup>4–7</sup> Recently, a variety of large  $\pi$ -delocalized dendritic truxene derivatives have been synthesized as a result of a series reactions initiated at the less crowded para position (2-, 7-, 12-positions).<sup>2,8,9</sup> However, the CT strategy in the materials chemistry of truxene seems to be considered less often.

Three-coordinate organoboron, with a vacant  $p_z$  orbit, is an excellent electronic acceptor when connecting to a  $\pi$ -delocalized system, and some B(III) compounds indeed exhibit unique optoelectronic properties.<sup>3b,10–14</sup> Similarly, three-valence nitro-

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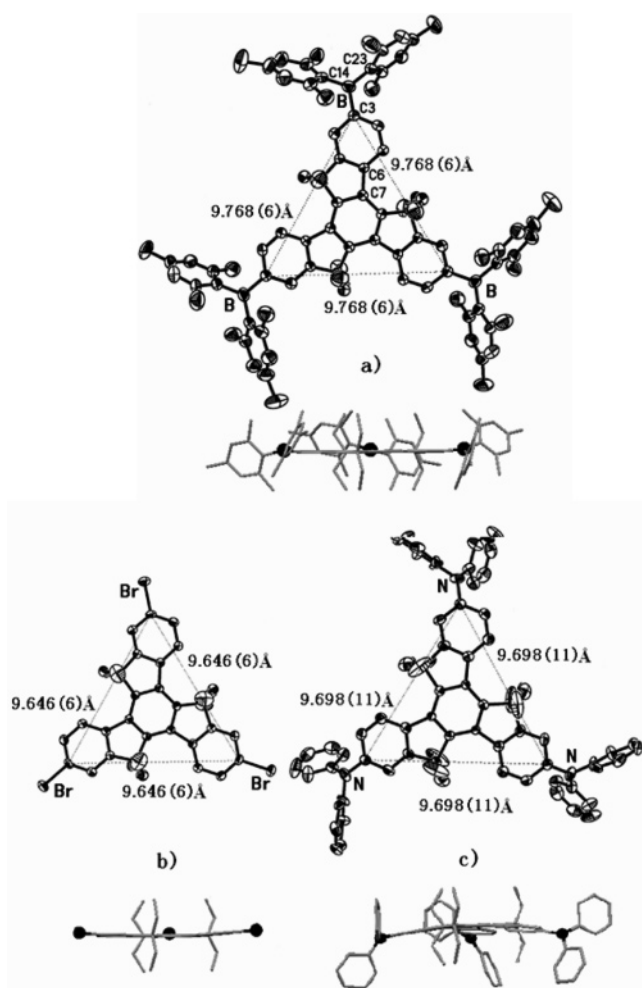
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**FIGURE 1.** ORTEP drawing of (a) **B3**, (b) **3**, and (c) **N3**. H-atoms are omitted for clarity. The structure of **4** is very similar to that of **3**.

gen is a typical donor center, and some triarylaminines have already been used as certain photofunctional materials.

In this paper, we introduce a diarylboryl acceptor or diarylamino donor to the truxene moiety and investigate the structures and optical properties of the resultant compounds.

The approach to compounds **B3** and **N3** is outlined in Scheme 1. 3-Phenylpropionic acid was converted to truxene after acylation and condensation by step-heating to 160 °C in phosphoric acid and in N<sub>2</sub> atmosphere. To remove active hydrogen atoms and to enhance the solubility, full alkylation was carried out at the 5-, 10-, and 15-positions, obtaining compound **2**. Bromoethane was used because ethyl has an appropriate size, matching the thickness of the **B3** molecule to facilitate crystallization (see Figure 1). Bromination or iodination of **2** afforded **3** or **4**, respectively. Schlenk techniques were used to obtain **B3** by reacting **3** with dimesitylboron (mesityl = 2,4,6-trimethylphenyl) fluoride in the presence of *n*-BuLi and in N<sub>2</sub>

atmosphere. Catalyzed by Cu powder, **N3** was synthesized from **4** and diphenylamine.

The crystals of **B3**, **N3**, **3**, and **4** have been determined to be with the space groups of *I43d*(**B3**), *P6<sub>3</sub>* (**N3**), and *Pa3̄*(**3** and **4**), and the molecular point groups are *C<sub>3</sub>* (for **B3**) and *C<sub>3h</sub>* (for **3**, **4**). There are two kinds of **N3** molecules in the crystal: one belongs to *C<sub>3</sub>* point group with its truxene moiety being shallow-bowl-shaped, and the other slightly deviates from *C<sub>3</sub>* symmetry.

The  $\pi$ -conjugation of all four of these structures is fairly good. The truxene moiety of **B3**, **3**, and **4** has a perfect planar octupolar *C<sub>3h</sub>* symmetry with the mean deviations from their individual least-squares plane being 0.017(4), 0.060(4), and 0.060(5) Å respectively. The significance of *C<sub>3h</sub>* point group is its pure octupolar symmetry. The idea of octupoles was introduced to NLO field in early 1990s and acquired development since then.<sup>15,16</sup>

As shown in Figure 1, three para-C atoms (2-, 7-, 12-) form an equilateral triangle with the edge length of 9.768(6) Å for **B3**, which is longer than those of **3** (9.646(6) Å) and **4** (9.644(5) Å). Considering the electron-withdrawing nature of -B(Mes)<sub>2</sub>, we believe that this two-dimensional extension is the result of CT. This kind of octupolar CT from a  $\pi$ -body to three acceptors (or conversely from three donors to a central  $\pi$ -body), such as in **B3**, may be put as  $\pi$ -A<sub>3</sub> (or  $\pi$ -D<sub>3</sub>), as an extension of the well-established A- $\pi$ -A or D- $\pi$ -D model for quadrupolar CT and D- $\pi$ -A model for dipolar CT.<sup>17</sup>

The bond length of B-C3 (1.558(7) Å) is shorter than that of B-C14 (1.565(8) Å) and B-C23 (1.588(8) Å), implying certain p- $\pi$  conjugation between the boron and the truxene moiety. The calculated HOMO orbital of a model compound of **B3** also shows a bonding nature for the B-C3 bonds (see Figure 6 in the Supporting Information). The B atom and its three-bonded C atoms are perfectly coplanar, while the N atom in **N3** is 0.15(1) Å above the plane of its three bonded C atoms.

As shown in Figure 2, the **B3** crystal has large channels along [111] direction of the cubic cell, which may allow some molecules in and off, and therefore may find some application as a chemosensor. The **N3** crystal has a 6<sub>3</sub> screw symmetry. As expected, this polar noncentrosymmetric crystal possesses 2-order NLO property with a measured powder SHG intensity (1064  $\rightarrow$  532 nm) as strong as that of the powder KDP sample.

As shown in Figure 3 and Table 1, the absorption peaks of **N3** ( $\lambda_{\text{max}} = 364$  nm) and **B3** ( $\lambda_{\text{max}} = 362$  nm) have a  $\sim 60$  nm red-shift relative to that of **2**. The extinction coefficient ( $\epsilon_{\text{max}}$ ) is increased on a scale of 0.90 (**2**):0.98 (**N3**):1.21 (**B3**). **N3** and **B3** emit strong blue-violet fluorescence at  $\lambda_{\text{max}} = 390$  and 386 nm, respectively. The fluorescence quantum yields ( $\Phi$ ) are 0.27 for **N3** and 0.34 for **B3**, which are about 4–5 times that (0.07) of **2** and rank in the largest  $\Phi$  values in the small truxene molecules. It is noteworthy that the measured fluorescence intensities (Figure 3) or the scaled intensities in terms of  $\Phi\epsilon_{\text{max}}$  (Table 1) of **N3** and **B3** are 1 order of magnitude that of **2**. The emissive rate of **N3** and **B3**, scaled by values of  $\Phi/\tau$ , are also 1 order of magnitude larger than that of **2** (Table 1). We believe

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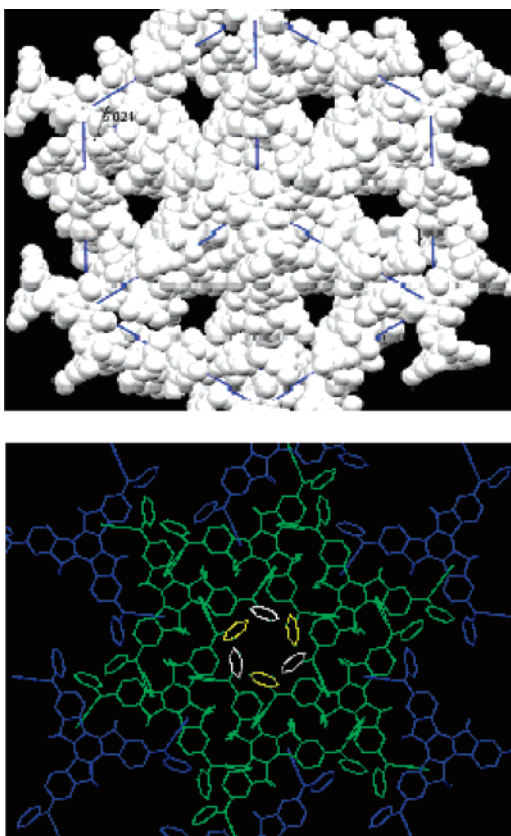
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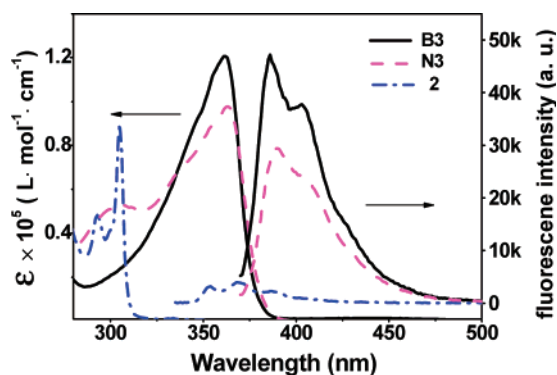
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**FIGURE 2.** Top: [111] view of the cubic **B3** crystal showing large channels with a diameter about 5 Å. That is why its density (0.692 g/cm<sup>3</sup>) is very small. Bottom: *c*-axis view of the hexagonal **N3** crystal. The blue molecules have a C<sub>3</sub> point group, and the green molecules slightly deviate from C<sub>3</sub>. The narrow phenyl channels are located at the 6<sub>3</sub> and 2<sub>1</sub> sites. The white phenyls are in one layer, and the yellow phenyls are in the neighboring layer.



**FIGURE 3.** Absorption and fluorescence spectra of **B3**, **N3**, and **2** in THF with  $c = 1.0 \times 10^{-5}$  mol/L.

that the fluorescence enhancement of **N3** and **B3** is associated with photoinduced CT. This octupolar kind of CT in exciting process does not require a dipole moment change and therefore may not followed by a large Stokes loss.

A calculation for a model compound of **B3** by using the time-dependent density functional theory (TDDFT) shows that the negative charge on any B atom in LUMO and LUMO+1 is 1 order of magnitude larger than that in HOMO (see the Supporting Information for details).

**TABLE 1.** Spectroscopic Data of **1–4**, **N3**, and **B3** in THF

	$\lambda_{\text{abs}}^a$ (nm)	$\epsilon_{\text{max}} (\times 10^4,$ $\text{M}^{-1} \text{cm}^{-1})$	$\lambda_{\text{F}}^a$ (nm)	$\Phi^b$	$\tau^c$ (ns)	$\Phi \epsilon_{\text{max}} (\times 10^3,$ $\text{M}^{-1} \text{cm}^{-1})$	$\Phi/\tau$ (ns <sup>-1</sup> )
<b>1</b>	273	7.0	361	0.07	12.5	4.9	0.006
<b>2</b>	305	9.0	368	0.07	12.6	6.3	0.006
<b>3</b>	312	9.4	376	0.01	0.3	0.94	0.03
<b>4</b>	316	9.4	368	0.01	0.5	0.94	0.02
<b>N3</b>	364	9.8	390, 405	0.27	2.1	26.5	0.13
<b>B3</b>	362	12.1	386, 403	0.34	4.4	41.1	0.08

<sup>a</sup> Linear absorption and fluorescence maxima with  $c = 1.0 \times 10^{-5}$  mol/L. <sup>b</sup> Fluorescence quantum yields determined using coumarin 307 with  $c = 1.0 \times 10^{-5}$  mol/L as standard. <sup>c</sup> Fluorescence lifetime.

In conclusion, we have carried out a detailed synthesis–structure–property study on a series of truxene derivatives. The X-ray diffraction data have revealed the structural evidence of CT of **B3** relative to its parent compounds at the ground state. The spectroscopic data and theoretical calculations suggest the photoinduced CT of **B3** and **N3** at the excited state. The acceptor- or donor-functionalized octupolar compounds **B3** and **N3** emit greatly enhanced blue fluorescence in comparison with that of the nonfunctionalized compounds. The main subject compounds in this work as well as their derivatives in future may find some application, such as the blue-light-emitting and two-photon materials, the hole-transport (**N3**) and electron-transport (**B3**) materials in OLEDs, the 2-order NLO materials (**N3**), and the chemosensors (**B3** crystal).

## Experimental Section

**2,7,12-Tri(dimesitylboryl)-5,5',10,10',15,15'-hexaethyltruxene (B3).** *n*-BuLi (2.8 M solution in *n*-hexane, 4.50 mL, 12.6 mmol) was added to a stirred solution of compound **3** (1.10 g, 1.48 mmol) in THF (30 mL) under nitrogen at  $-78^\circ\text{C}$  over 20 min, followed by natural warming to room temperature. After reacting for a further 4 h, the reactants were cooled to  $-78^\circ\text{C}$  again, and dimesitylboryl fluoride (2.20 g, 8.2 mmol) in THF (15 mL) was injected over 30 min. The temperature was allowed to naturally rise to room temperature and the mixture continuously stirred for 2 days. The reactants were then diluted with ethyl acetate, washed with water, and dried over magnesium sulfate. After solvents were removed, the crude product was obtained. After purified by column chromatography on silica gel, eluting with dichloromethane–petroleum ether (1: 20), compound **B3** was obtained (0.45 g, 24%) as a white powder. The single crystal was successfully obtained by slow evaporation of their THF solution in air: mp > 400 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm)  $\delta$  0.17 (s, 18H), 2.06 (s, 42H), 2.34 (s, 18H), 2.92 (s, 6H) 6.86 (s, 12H) 7.49–8.28 (m, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, ppm)  $\delta$  151.91, 146.71, 144.25, 144.06, 142.05, 140.95, 138.83, 138.49, 135.10, 129.84, 128.19, 124.20, 56.90, 29.17, 23.58, 21.28, 8.46; MALDI-TOF *m/z* 1254.0 [M<sup>+</sup>], 1225.1 [M – 29]<sup>+</sup>. Anal. Calcd for C<sub>93</sub>H<sub>105</sub>B<sub>3</sub>: C, 88.99; H, 8.43. Found: C, 88.63; H, 8.46. Crystal data for **B3** (C<sub>93</sub>H<sub>105</sub>B<sub>3</sub>):  $M_r = 1255.20$ , cubic, space group *I43d*,  $a = 36.383(4)$  Å,  $V = 48160(8)$  Å<sup>3</sup>,  $Z = 16$ ,  $\rho_{\text{calcd}} = 0.692$  g/cm<sup>3</sup>,  $T = 293(2)$  K, crystal dimensions 0.40 × 0.40 × 0.30 mm<sup>3</sup>,  $R_1 = 0.0693$  ( $wR_2 = 0.1625$ ) [ $I > 2\sigma(I)$ ].

**2,7,12-Tri(*N,N*-diphenylamino)-5,5',10,10',15,15'-hexaethyltruxene (N3).** A mixture of compound **4** (1.20 g, 1.35 mmol), K<sub>2</sub>CO<sub>3</sub> (2.80 g, 20.3 mmol) powder, fresh Cu (0.30 g, 4.69 mmol) powder, 18-crown-6 ether (0.20 g, 0.83 mmol), diphenylamine (1.20 g, 7.09 mmol), and 1,2-dichlorobenzene (20 mL) was heated to reflux with stirring under nitrogen atmosphere. After being reacted for a further 8 h, the mixture were cooled to room temperature and filtered off under suction. Then the filtrate was condensed and purified by column chromatography on silica gel, eluting with dichloromethane–petroleum ether (1:10), and compound **N3** was obtained (0.71 g, 52%) as a white powder. The single crystal was

successfully obtained by slow evaporation of the  $\text{CH}_2\text{Cl}_2$  solution in air: mp 310–312 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm)  $\delta$  0.17 (t, 18H,  $J = 7.03$  Hz), 1.88–1.93 (m, 6H), 2.82–2.87 (s, 6H), 6.99–7.30 (m, 36H) 8.08 (d, 3H,  $J = 8.58$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz, ppm)  $\delta$  154.19, 147.94, 146.27, 142.36, 138.33, 135.59, 129.20, 125.30, 124.13, 122.61, 121.98, 117.70, 56.51, 29.18, 8.66; MALDI-TOF  $m/z$  1011.0 [ $\text{M}^+$ ], 981.7 [ $\text{M} - 29$ ] $^+$ . Anal. Calcd for  $\text{C}_{75}\text{H}_{69}\text{N}_3$ : C, 88.98; H, 6.87; N, 4.15. Found: C, 88.68; H, 6.89; N, 4.01. Crystal data for **N3** ( $\text{C}_{75}\text{H}_{69}\text{N}_3$ ):  $M_r = 1012.33$ , hexagonal, space group  $P6_3$ ,  $a = 32.199(7)$  Å,  $c = 12.957(4)$  Å,  $V = 11634(5)$  Å $^3$ ,  $Z = 8$ ,  $\rho_{\text{calcd}} = 1.156$  g/cm $^3$ ,  $T = 298(2)$  K, crystal dimensions  $0.54 \times 0.12 \times 0.09$  mm $^3$ ,  $R_1 = 0.1069$  ( $wR_2 = 0.2709$ ) [ $I > 2\sigma(I)$ ].

**Acknowledgment.** We thank the National Natural Science Foundation of China (No. 20472044), the Ph.D. Foundation of the Ministry of Education of China, and the Foundations of the Key Laboratory of Organofluorine Chemistry of the Chinese Academy of Sciences for financial support for this work.

**Supporting Information Available:** Syntheses and characterizations of compounds **1–4**; CIF files for **3**, **4**, **B3**, and **N3**; computational work and results for **B3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO061210I