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Tridurylboranes Extended by Three Arylethynyl Groups as a New Family of Boron-Based π-Electron Systems

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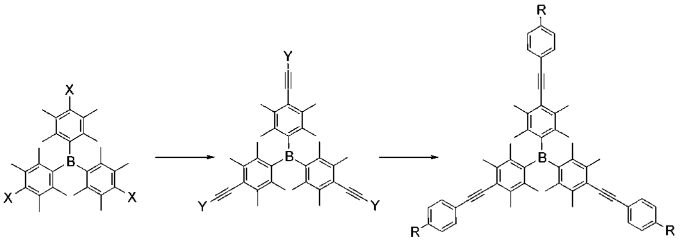
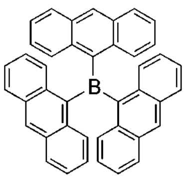
ABSTRACT

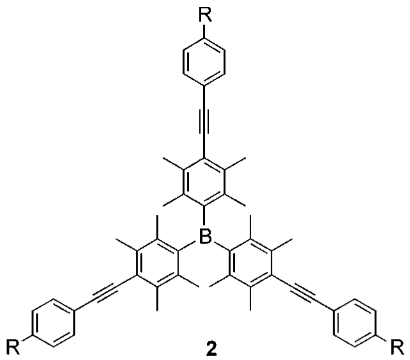


A series of tris(phenylethynylduryl)boranes ($R-C_6H_4-C{\equiv}C$-duryl)$_3$B with various substituents R have been prepared as air-stable solids owing to the steric protection of the boron atom by the three bulky duryl groups. These compounds show unique photophysical properties due to the $p_\pi-\pi^*$ conjugation through the p-orbital on the boron atom. In particular, a push–pull type derivative with R = NMe_2 exhibits a significant solvatochromism of fluorescence from blue to orange colors.

Boron-containing π-conjugated systems have recently attracted increasing attention as a new class of π-electron materials for optoelectonics.[1−6] The $p_\pi-\pi^*$ conjugation[7] of the vacant p-orbital on boron with the π^* orbital of the attached carbon π-conjugated moieties is responsible for some outstanding properties such as unique absorption and emission,[1,2,4,5] a low reduction potential susceptible to n-doping,[1−3,8] and high electron-transporting properties.[3] The photophysics of triphenylboranes has been well documented to include (1) the substituent effects on the phenyl rings[9] and, recently, (2) the fact that the push−pull types of π-electron systems having both amino and dimesitylboryl groups have been disclosed as potent nonlinear optical materials.[4] We have recently reported trianthrylborane **1** and its derivatives based on the concept that the introduction of three identical π-conjugated moieties (i.e., three anthryl groups) onto a boron atom allows divergently extended π-conjugation through the vacant p-orbital of the boron in the LUMO.[2] Consequently, the highly delocalized low-lying LUMO significantly influences their intramolecular charge-transfer transitions,[9] causing their long-wavelength absorptions. In line with this concept, we have now designed new boron-based π-electron systems: the tridurylborane deriva-



1
λ_{max} 470 nm



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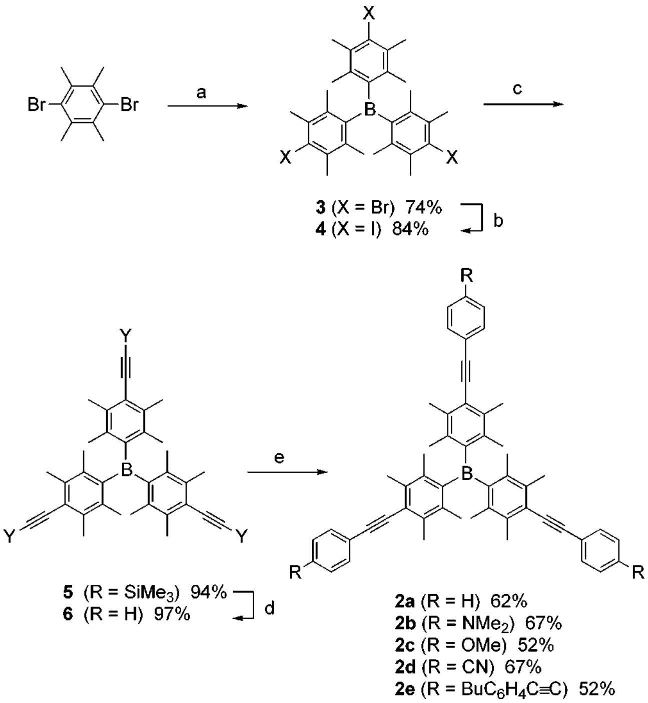
tives **2** extended by three arylethynyl groups. The present design relies on the introduction of three bulky duryl groups onto a boron atom to obtain sufficient chemical stability[10] and the employment of the ethynylene spacer to effectively extend the π-conjugation. Reported herein are their syntheses, structures, and photophysical properties including solvatochromism.

A series of tridurylborane derivatives **2** has been synthesized using tris(ethynylduryl)borane **6** as the key precursor, as shown in Scheme 1. Thus, the mono-lithiation of dibromodurene followed by reaction with $BF_3 \cdot OEt_2$ gave tris(bromoduryl)borane **3**. The successive treatments of **3** with *t*-BuLi in THF and iodine produced tris(iododuryl)borane **4**. The Pd/Cu-catalyzed cross-coupling[11] of **4** with trimethylsilylacetylene gave **5**, which was desilylated under alkaline conditions to give the tris(ethynylduryl)borane **6**. Finally, the Pd/Cu-catalyzed cross-coupling[11] of **6** with aryl halides successfully afforded a series of **2** bearing various terminal aryl groups. In this synthesis, the transformation from tribromide **3** to triiodide **4** is crucial, because of the low reactivity of the tribromide toward the Pd/Cu-catalyzed coupling reaction. All tridurylborane derivatives **2** are significantly stable toward air and water due to the steric protection of the central boron atom by three bulky duryl groups.[12]

Scheme 1[a]



[a] (a) i, *n*-BuLi (1.0 molar amount), Et_2O, −78 °C; ii, $BF_3 \cdot OEt_2$ (0.3 molar amount), −78 °C to rt.; (b) i, *t*-BuLi (6.0 molar amount), THF, −78 °C to rt; ii, I_2 (4.5 molar amount), rt; (c) $Me_3SiC{\equiv}CH$ (4.5 molar amount), $PdCl_2(PPh_3)_2$ (0.15 molar amount), CuI (0.30 molar amount), Et_2NH, rt; (d) KOH, MeOH/THF, rt; (e), ArX (3.0 molar amount), $PdCl_2(PPh_3)_2$ (0.05−0.15 molar amount), CuI (0.10−0.30 molar amount), piperidine at rt for **2a**−**2d** and Et_2NH in reflux for **2e**. As the ArX, appropriate ArI was used for **2a**−**2c** and ArBr for **2d**−**2e**.

Among the obtained tridurylboranes, the structure of **2a** has been determined by X-ray crystallography.[13] The ORTEP drawing is shown in Figure 1. The molecule has a crystallographic C_2 axis along with the B1−C19 bond. The central boron is completely trigonal planar. Three duryl groups are arranged in a propeller-like fashion, and the dihedral angles between the boron plane and the duryl planes are 53−55°.[14] The outer benzene rings maintain a high coplanarity with the duryl groups with 17−18° dihedral angles, suggesting that the ethynylene spacer is effective for extending the π-conjugation.

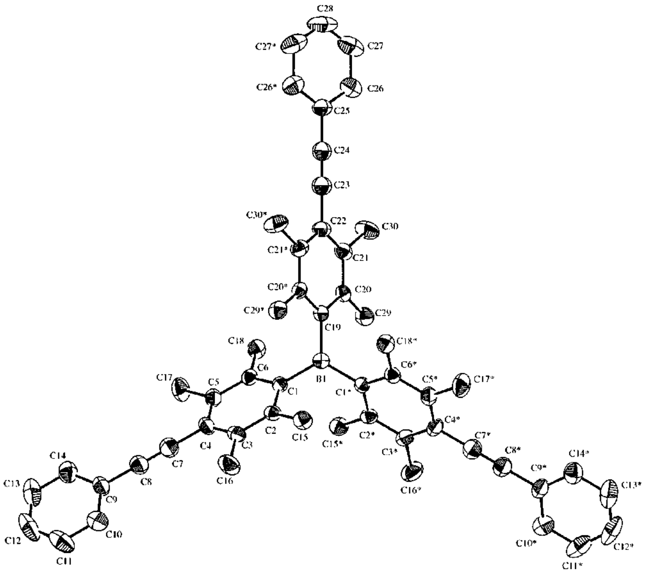


Figure 1. ORTEP drawing of **2a** (50% probability for thermal ellipsoids). Selected bond lengths [Å] and bond angles [deg]: B1−C1 1.589(3), C1−C2 1.420(3), C2−C3 1.397(4), C3−C4 1.409(4), C4−C7 1.448(4), C7−C8 1.161(4), C1−B1−C1* 119.6(3), C1−B1−C19 120.2(1), C4−C7−C8 179.7(3), C7−C8−C9 179.4(3).

The photophysical properties of the tridurylborane derivatives **2** in THF solutions are summarized in Table 1, together with those of some related compounds including diarylacetylenes **7** and the mono-arylethynyl group-substituted dimesitylboranes **8**,[15] for comparison.

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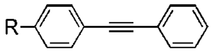
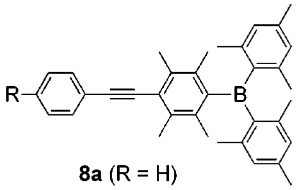
Table 1. Photophysical Properties of Tridurylborane Derivatives and Related Compounds

compound	UV−vis,[a] λ_{max}/nm[b]	log ϵ	FL,[a] λ_{max}/nm[c]	Φ_F [d]
2a (R = H)	364	4.77	415	0.35
2b (R = NMe_2)	393	4.83	512	0.16
2c (R = OMe)	371	4.75	432	0.45
2d (R = CN)	369	4.91	412	0.48
2e (R = Ar-CC)[e]	379	5.08	415	0.54
7a (R = H)	299	4.35	337	n.d.
7b (R = NMe_2)	329	4.47	380	n.d.
8a (R = H)	345	4.34	391	0.45
8b (R = NMe_2)	376	4.37	496	0.27

[a] In THF. [b] Only the longest absorption maxima are shown. [c] Emission maximum wavelength excited at the absorption maximum. [d] Determined using anthracene as a standard. [e] Ar = 4-*n*-BuC_6H_4.



7a (R = H)
7b (R = NMe_2)



8a (R = H)
8b (R = NMe_2)

In the UV−visible absorption spectra, all compounds **2** show unique and intense bands with their maxima around 360−400 nm. Some notable features are summarized as follows. (1) The λ_{max} of **2a** is about 60 nm longer than that of diphenylacetylene **7a** and, more importantly, about 20 nm longer than that of **8a**. This result represents one of the notable effects of the incorporation of the three arylethynyl π-systems. The absorption of **2** can be interpreted as the intramolecular charge-transfer transition from the diarylacetylene moiety to the triarylborane moiety[9] and, therefore, the extent of the π-conjugation through the vacant p-orbital of boron in the LUMO is relevant for the charge-transfer transition energy.[2] Thus, the red shift from **8a** to **2a** is conceivably due to the difference in the extent of the π-conjugation in the LUMO. (2) From **2a** to **2e**, the λ_{max} shifts to longer wavelengths by only 15 nm, despite the introduction of three additional arylethynyl moieties as the R groups in **2e**. This suggests that the extension of the π-conjugation in the LUMO of the triarylboranes has a certain limitation and that the additional arylethynyl moieties in **2e** are not significantly effective in extending the π-conjugation. (3) Among **2a**−**2d** with various substituents (R = H, NMe_2, OMe, and CN), compound **2b** bearing the electron-donating NMe_2 group has the longest absorption maximum. This should be rationalized in terms of the strongest π-donor ability of the amino-substituted diarylacetylene moiety to the boron center.[4]

In the fluorescence spectra in THF, all compounds **2** show strong emissions around 415−430 nm with 50−60 nm Stokes shifts except for **2b**, which has about a 80−100 nm longer emission maximum than those of the others. These unique properties of **2b** are due to its highly solvent-dependent emission. The data for the solvent effect for **2b** are summarized in Table 2 together with those for the parent **2a** and the mono-arylethynyl-substituted analogue **8b**. A bathochromic shift of about 80 nm is observed for the emission of **2b** from 457 nm in benzene to 534 nm (with a shoulder at 570 nm) in DMF (Figure 2a), whereas **2a** shows only a 20 nm red shift. This spectral change for **2b** corresponds to the change in the emission color from blue

Table 2. Solvent Effect on the Emission Wavelengths of Tridurylborane Derivatives **2a** and **2b** and a Related Compound, **8b**

compound	FL, λ_{max}/nm[a] benzene	THF	DMF
2a (R = H)	409	415	432
2b (R = NMe_2)	457	512	534
8b (R = NMe_2)	443	496	530

[a] Excited at 366 nm.

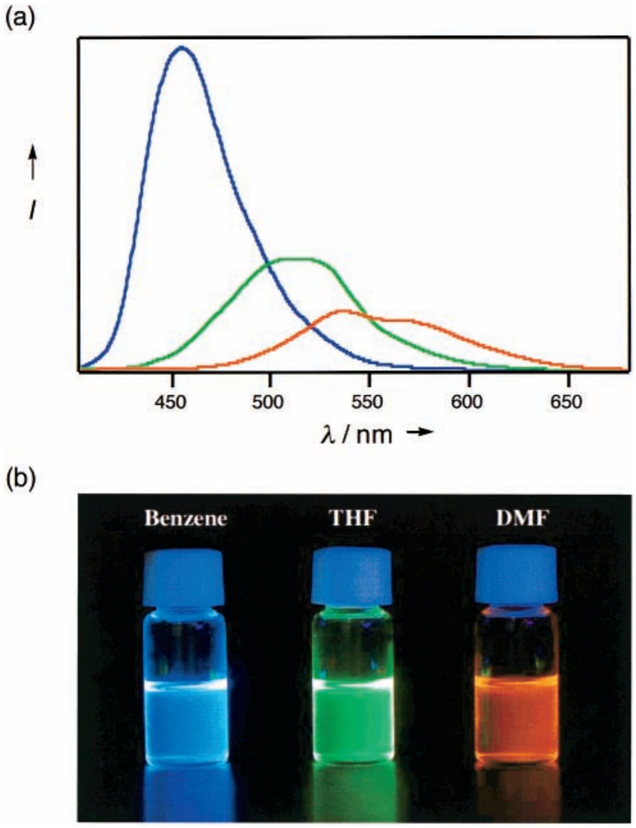


Figure 2. Fluorescence of **2b**: (a) the emission spectra in various solvents (benzene, blue line; THF, green line; DMF, orange line) and (b) a picture of the solutions under irradiation of light at 365 nm. The spectrum in DMF is magnified 10× in intensity.

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to orange, as visualized in Figure 2b. As observed in the UV−visible absorption spectra, the emission maximum of **2b** in each solvent is slightly longer than that of the monosubstituted analogue **8b**. It should also be noted that no significant solvatochromism is observed in the UV−visible absorption spectra of **2b**: λ_{max} 394 nm in benzene, 393 nm in THF, and 393 nm in DMF. This suggests the highly polarized excited state produced by the intramolecular charge-transfer transition in **2b**.

In summary, we have disclosed a series of tridurylborane derivatives which may be useful as a new core unit for boron-based π-electron systems with substantial chemical stability. The unique absorption and emission properties of the present π-electron systems are of interest for applications to opto-electronics such as nonlinear optical materials and organic electroluminescent devices. Further study in this line is now in progress in our laboratory.

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Supporting Information Available: Experimental procedures and data for all new compounds and crystal structural data for **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) π-Conjugation through vacant p-orbital of boron, for examples, see: (a) Zweifel, G.; Clark, G. M.; Leung, T.; Whitney, C. C. *J. Organomet. Chem.* **1976**, *117*, 303. (a) Eisch, J. J.; Galle, J. E.; Kozima, S. *J. Am. Chem. Soc.* **1986**, *108*, 379. (b) Budzelaar, P. H. M.; van der Kerk, S. M.; Krogh-Jespersen, K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 3960. (c) Eisch, J. J.; Shafii, B.; Odom, J. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 1847. (d) Byun, Y.-G.; Saebo. S.; Pittman, C. U., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 3689. (e) Sugihara, Y.; Yagi, T.; Murata, I.; Imamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 1479. (f) Salzner, U.; Lagowski, J. B.; Pickup, P. G.; Poirier, R. A. *Synth. Met.* **1998**, *96*, 177.

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(12) All tridurylboranes were isolated through usual aqueous workup followed by silica gel column chromatography without any decomposition.

(13) Crystal data of **2a** (instrument; Rigaku RAXIS-IV): $C_{54}H_{51}B_1$, FW = 710.81, crystal size 0.30 × 0.30 × 0.20 mm, monoclinic, $C2/c$ (No. 15), $a = 16.212(1)$ Å, $b = 22.153(1)$ Å, $c = 14.9162(9)$ Å, $\beta = 127.956(2)°$, $V = 4224.0(4)$ Å^3, $Z = 4$, $D_c = 1.118$ g cm^{-3}, μ(Mo Kα) = 0.62 cm^{-1}, number of unique reflections = 4461, temperature −110 °C, $R = 0.068$, $R_w = 0.089$, and GOF = 1.20.

(14) These values are comparable to those observed for the crystal structure of trianthrylborane **1**, see ref 2.

(15) Compounds **8** were prepared essentially in a manner similar to the synthesis of **2** using (bromoduryl)dimesitylborane instead of tris(bromoduryl)borane **3**.