

Boron as a key component for new π -electron materials*

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Abstract: For the molecular design of new π -electron materials, the incorporation of main group elements into the π -conjugated frameworks is a powerful approach to modifying the nature of the parent π -conjugated systems. In particular, the group 13 boron is of interest, since the boron element has several characteristic features, such as an effective orbital interaction with the π -conjugated frameworks through the vacant p-orbital (i.e., p_{π} - π^* conjugation), high Lewis acidity, and trigonal planar geometry. By exploiting these features of the boron atom, we have designed and synthesized several types of new π -electron materials, including trianthrylborane- or dibenzoborole-based π -conjugated systems as a new fluoride ion sensor, boryl-substituted thienylthiazole as a new building unit for electron-transporting materials, and B, B', B'' -trianthrylborazine (B_3N_3)-based materials as a model of the bundled system of π -conjugated frameworks.

Keywords: boron; p - π^* conjugation; fluoride ion sensors; electron-transporting materials; borazine.

INTRODUCTION

One important direction in the current main group chemistry is the exploration of the potentials of the main group compounds as the new functional materials [1]. In view of the optical and electronic applications, π -conjugated systems containing main group elements are a promising class of compounds. In the design of new π -conjugated molecules, two key issues should be noted. One is how to create molecules that have desirable electronic structures. The other is how to control their solid-state structures. In these regards, an incorporation of main group elements into the π -conjugated framework has decisive advantages. The utilization of the characteristic features of the main group compounds, such as the special orbital interaction, diversity in coordination numbers, and unique structural features around the element atoms, enables access to new π -conjugated systems with intriguing photophysical and electronic properties. Among the main group elements, the group 13 boron is of particular interest in this context [2]. Since the pioneering studies by Williams [3] and Kaim [4], boryl groups are widely utilized as a π -electron accepting group [5,6]. A number of fascinating boryl-substituted π -conjugated systems have been synthesized to date [7–9], some of which have been applied in various fields, such as nonlinear optics [10,11], two-photon absorption and emission materials [12], and organic light-emitting diodes [13–15].

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With this background, our contribution to this field is to provide a new direction to the molecular design for the boron-based functional materials. Figure 1 shows three characteristic features of the boron element that we use as a basis of our molecular designs. The first one is the fact that boron has a vacant p-orbital. By connecting the boron with π -conjugated systems, p_{π} - π^* conjugation effectively takes place, leading to the appearance of unique electronic and photophysical properties. The second one is the Lewis acidity of boron. Boron compounds readily form unique complexes with Lewis bases or nucleophilic species. This complexation may be important for tuning the electronic structure or for constraining the three-dimensional molecular structure. The third one is its structural feature. Boron takes a trigonal planar geometry, which may be a good building block for constructing complex molecules. By exploiting these features, we have designed several types of new functional materials. In this paper, we report these results with the emphasis on their molecular designs.

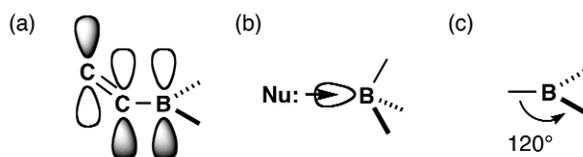


Fig. 1 Three fundamental features of boron for the molecular designs of new π -electron materials: (a) p - π^* conjugation; (b) Lewis acidity; and (c) trigonal planar geometry.

USE p_{π} - π^* CONJUGATION: BORON-CONTAINING STARBURST π -ELECTRON SYSTEMS

Our first target molecule was the starburst-type π -conjugated system with boron atoms at the branching points [16]. As a model compound, we designed trianthrylborane **1**, as shown in Fig. 2. There are two important points in the design. One is the introduction of three identical π -frameworks onto the boron atom, which makes it possible to extend the lowest unoccupied molecular orbital (LUMO) over the entire molecule through the p_{π} - π^* conjugation and significantly decreases its LUMO level. The other point is the steric protection of the boron atom by the bulky substituents. In general, the boron compounds are highly Lewis acidic. In order to handle them without special care, it is necessary to protect the boron atom with bulky substituents. From these points of view, we chose anthracene as the bulky π -conjugated framework.

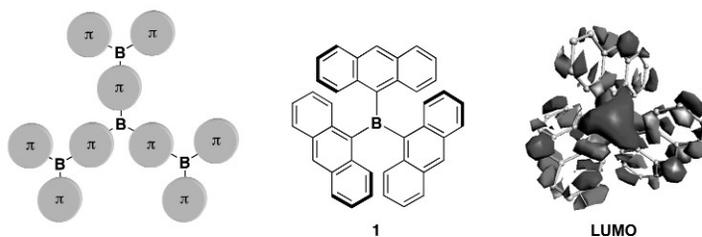


Fig. 2 Schematic drawing of boron-containing starburst π -electron system, its model system, trianthrylborane **1** and the LUMO of **1** calculated at the HF/6-31G(d) level of theory.

Compound **1** was easily prepared by the reaction of 9-anthryllithium with $\text{BF}_3 \cdot \text{OEt}_2$. The obtained compound is quite stable toward oxygen and water. The three anthryl groups are arranged in a propeller-like fashion with a dihedral angle between the central boron plane and anthracene plane of about 53° , suggesting that the π -conjugation through the boron atom is not very effective. Nevertheless,

this compound is red as crystals and orange in solution [17]. In the UV–vis absorption spectra, this compound shows a new characteristic band at 470 nm together with the band assignable to the anthracene π - π^* transition. Notably, this new band can be assigned to the transition from the highest occupied molecular orbital (HOMO) localized on one anthryl moiety to the LUMO delocalized over the molecules (Fig. 2) [16,18].

We prepared more extended boron compounds **2** and **3**, which are extended by three dimesitylboryl groups or dianthrylboryl groups, respectively (Table 1). As expected, the extension by these additional boron moieties causes a substantial red shift in the absorption maxima. Thus, an about 65-nm red-shift was observed from **1** to **3**. In addition, the reduction potential also decreased from **1** to **3** by about 0.3 V. These findings suggest that the p_{π} - π^* conjugation in the LUMO is effectively extended to the external boron atoms.

Table 1 UV–vis absorption^a and cyclic voltammetry^b data for the extended trianthrylborane derivatives.

	1	2	3
UV–vis absorption	470	524	535
λ_{\max}/nm			
$E_{\text{pc}}/\text{V}^{\text{c}}$	-1.87	-1.77 ^d	-1.56

^aIn THF.

^bMeasured under the following condition; sample conc. 1 mM in 0.1 M Bu_4NClO_4 $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ 1/1 solution, scan rate 100 mV/s, unless otherwise stated.

^cCathodic peak potential vs. ferrocene/ferrocenium couple.

^d CH_2Cl_2 was used as a solvent due to the low solubility.

An interesting direction of this chemistry is to apply these molecules to chemosensors [19,20]. Since the boron compound is a Lewis acid, it can bind an anionic species, resulting in the change in the π -conjugation mode, as shown in Fig. 3. Thus, while, in the tri-coordinated triarylboryl, the p_{π} - π^* conjugation is turned on, after the boron compound binding the anion to form the borate species, the conjugation would be turned off. On the basis of this idea, we examined the titration of fluoride ion using trianthrylborane **1**, as shown in Fig. 4. When tetrabutylammonium fluoride was added to a tetrahydrofuran (THF) solution of **1**, in the UV–vis spectra, the characteristic band at 470 nm completely disappeared and new bands appeared around the anthracene region. Importantly, this spectral change was associated with a color change from orange to colorless. That is, the trianthrylborane acts as a colorimetric sensor for the fluoride ion. We also examined other ions to investigate the selectivity. While the binding constant for the fluoride ion is significantly high at about 10^5 M^{-1} , for other anions, only low binding constants were observed for the acetate or hydroxy ions ($\sim 10^3 \text{ M}^{-1}$) and no response was detected for other halogenide ions such as Cl^- and Br^- . The high selectivity of the present system toward the fluoride ion may be partly due to the strong bonding energy between the boron and fluorine or to the small size of the fluoride ion that allows it to coordinate to the sterically congested boron center.

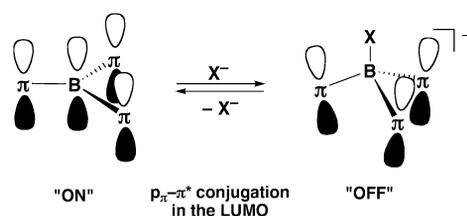


Fig. 3 Anion sensing using boron-containing π -electron systems based on on/off change in the $p_{\pi}-\pi^*$ conjugation.

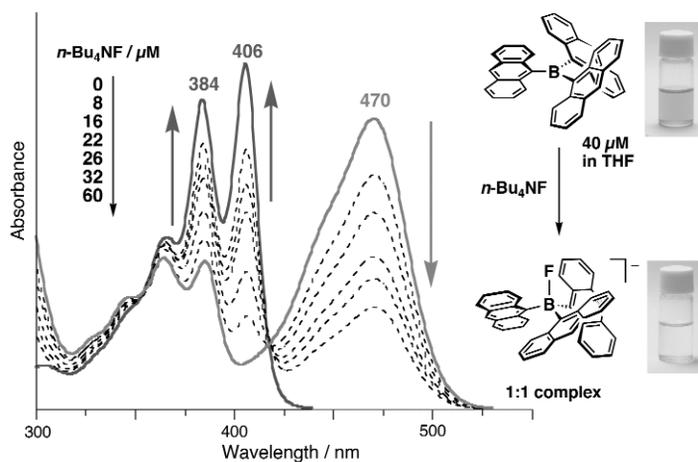


Fig. 4 Change in the UV-vis absorption spectra of **1** in THF, upon addition of tetrabutylammonium fluoride.

DIBENZOBOROLE-BASED π -ELECTRON SYSTEMS: NEW "TURN-ON" TYPE FLUORIDE SENSOR

Anion sensing can also be achieved using other types of boron compounds. As another example, we employed the dibenzoborole-containing π -conjugated systems [21]. As shown in Fig. 5, its LUMO is delocalized through a vacant p-orbital of the boron atom. Upon the addition of an external anion to form a tetra-coordinated borate complex, the $p_{\pi}-\pi^*$ conjugation in the LUMO would be turned off, since the vacant p-orbital of the boron is no longer available.

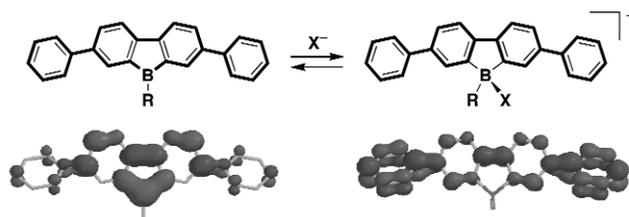


Fig. 5 Change in the LUMO of the dibenzoborole-based π -electron systems, upon the formation of the borate complex.

However, in this case, the resultant LUMO is still delocalized over the entire π -conjugated framework. Therefore, this on/off change in the p_{π} - π^* conjugation would result in a different type of sensing output compared to that of trianlylborane. On the basis of this idea, we synthesized several extended dibenzoborole derivatives **4–6**, as shown in Chart 1.

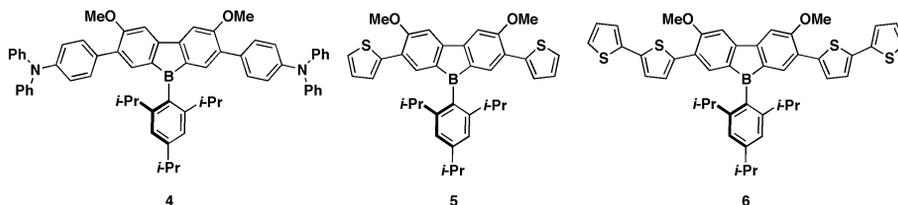


Chart 1 Dibenzoborole-containing π -electron systems.

Interestingly, these molecules showed an unusual solvent effect in the fluorescence [21,22]. In THF solution, these molecules show an orange to red fluorescence. In sharp contrast, all these molecules show an intense blue emission in dimethylformamide (DMF). This can be rationalized by considering the coordination of DMF solvent to the boron center. These results encouraged us to apply these molecules as the sensors.

In fact, when we examined the titration of fluoride ion using the triphenylamine derivative **4**, a significant change in the fluorescence spectra was observed. Thus, while compound **4** has a weak emission at a rather long wavelength (λ_{em} 561 nm), upon the addition of the fluoride ion, this emission band completely disappeared and a new intense band appeared at 419 nm, as shown in Fig. 6. Thus, an approximate 140-nm blue shift in the maximum wavelength and about a 30-fold increase in the quantum yield were observed by the formation of the borate complex. This “turn-on” and “color-change” dual output is noteworthy as a chemosensor. In addition, the produced borate could be changed back to the starting borane by the treatment with a stronger Lewis acid such as $\text{BF}_3 \cdot \text{OEt}_2$.

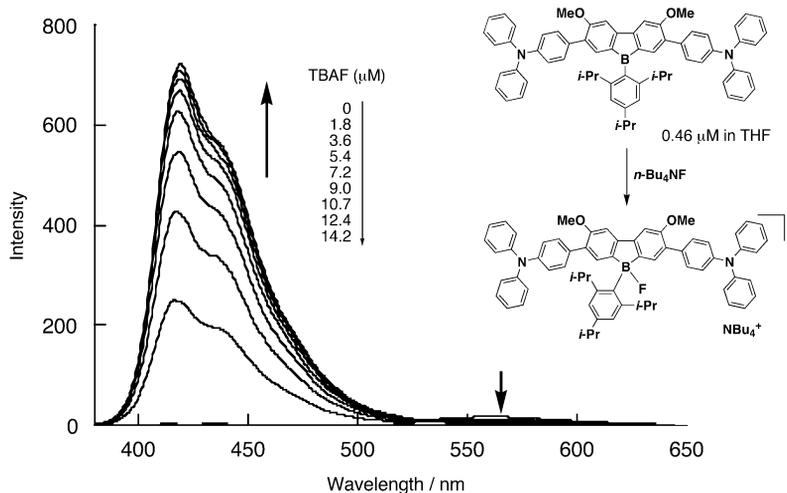


Fig. 6 Change in the fluorescence spectra of **4** in THF, upon the addition of tetrabutylammonium fluoride.

Besides the sensing application, the dibenzoborole skeleton itself is also of importance as a building unit for new π -electron materials [23]. The dibenzoborole is a boron analog of fluorene and carbazole, which are currently important building units for fluorescent and hole-transporting materials, respectively. In this context, the dibenzoborole should have a great potential as a building unit for electron-transporting materials, considering its high electron affinity due to the p_{π} - π^* conjugation. To utilize the dibenzoborole skeleton for this purpose, however, there is one problem, that is, how to kinetically stabilize the molecule. The aforementioned results demonstrated that the tri(isopropyl)phenyl group on the boron atom in **4–6** is not bulky enough to protect, since, in these compounds, even a weak donor molecule such as DMF can coordinate to the boron center. Therefore, the introduction of a bulkier substituent on the boron atom is essential. We have quite recently succeeded in the synthesis of supermesityl (2,4,6-tri(*t*-butyl)phenyl)-substituted dibenzoborole derivatives, that show identical fluorescence spectra both in THF and DMF, indicative of the effective steric protection by the bulky supermesityl group [24].

USE LEWIS ACIDITY OF BORON: NEW MOLECULAR DESIGN FOR ELECTRON-TRANSPORTING MATERIALS

The development of excellent n-type organic semiconducting materials has long been an important subject in the field of organic electronics. In this section, a new molecular design for them that exploits the Lewis acidity of the boron atom is described. In general, the widely accepted molecular design for them is to employ C=N-containing *N*-heteroaromatic rings as the building unit, because of their intrinsic high electron affinity. So far, a number of fascinating π -electron systems have been synthesized along this line [25]. We now intend to modify the electronic nature of these π -systems by introducing the boryl groups through the formation of the intramolecular B–N coordination, as shown in Fig. 7 [26]. We expected that this sort of Lewis acid–Lewis base interaction would not only constrain the π -conjugated framework in a coplanar fashion, but also perturb the electronic structure by decreasing the LUMO level.

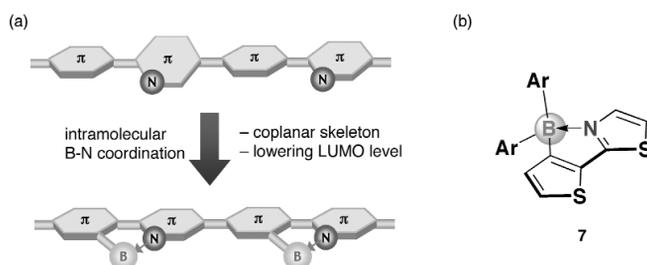


Fig. 7 New design of electron-transporting materials (a) structural and electronic modification based on the intramolecular B–N coordination and (b) a boryl-substituted thienylthiazole **7** as a key building unit.

On the basis of this concept, we designed a boryl-substituted thienylthiazole **7** as a key building unit (Fig. 7). We envisioned that the intramolecular B–N coordination would not only fix the thienylthiazole skeleton in an *s-cis* conformation, but also enhance its electron affinity. In addition, the use of the thienylthiazole skeleton would allow us to achieve a stepwise regioselective functionalization, because while the 5,5'-positions of the thienylthiazole skeleton are reactive toward metalation, the reactivity of these positions is somewhat different from each other. This possible regioselective functionalization would lead to the synthesis of a wide range of derivatives.

Compound **7** was synthesized by the lithiation of 3-bromo-2-thienyl-2-thiazole, followed by the reaction with dimesitylfluoroborane. The obtained compound is very stable and purified by silica gel

column chromatography. As expected, we found that the lithiation of **7** with *n*-BuLi selectively took place at the 5-position of the thiazole ring. On the basis of this reaction, we synthesized a series of functionalized derivatives and with these derivatives in hand, a series of dimers including the head-to-tail dimer **8**, tail-to-tail dimer **9**, and head-to-head dimer **10** have been synthesized, in which the thiophene ring is denoted as the head and thiazole as the tail. Figure 8 shows cyclic voltammograms for the series of compounds. A comparison between compound **7** and its parent 2-thienyl-2-thiazole clearly demonstrates that the B–N coordination significantly decreases the reduction potential by about 0.5 V. In addition, **7** shows a reversible redox process, suggesting that the reduced state is somewhat stabilized by this structure. The extension of the π -conjugation length from the monomer to the dimers further decreases the reduction potential by about 0.3–0.4 V, while the difference in the regiochemistry among these dimers does not have a significant effect.

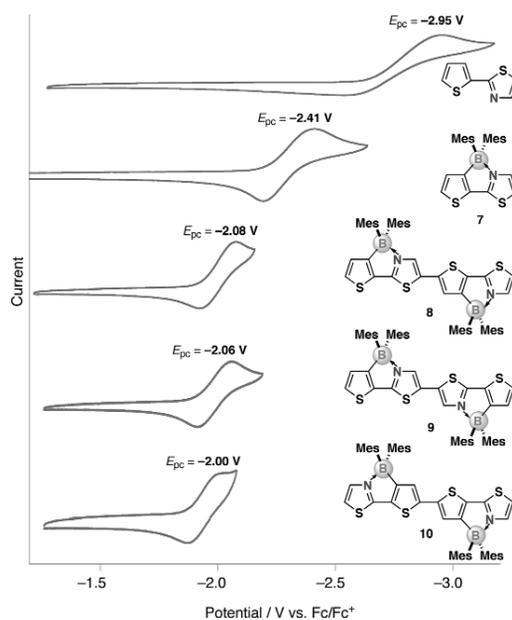


Fig. 8 Cyclic voltammograms for a series of thienylthiazole derivatives: Measured in THF with *n*-Bu₄NPF₆ (0.1 M); scan rate 0.10 V s⁻¹.

X-ray crystallography revealed that all the dimers have completely coplanar π -conjugated frameworks. Among the series of dimers, interestingly, the head-to-head dimer **10** forms a face-to-face π -stacking structure, in which the electron-accepting thiazole ring and the electron-donating thiophene ring are facing to each other. As a consequence, this molecule forms a one-dimensional array, as shown in Fig. 9. Related to this solid-state structure, it is noteworthy that the compound indeed has a relatively high electron mobility of 10⁻⁴ cm² V⁻¹ s⁻¹, while this compound did not show any hole-transporting ability at all, according to a preliminary time-of-flight (TOF) measurement using its vacuum-deposited film. We plan to further continue the study on this structure–property relationship.

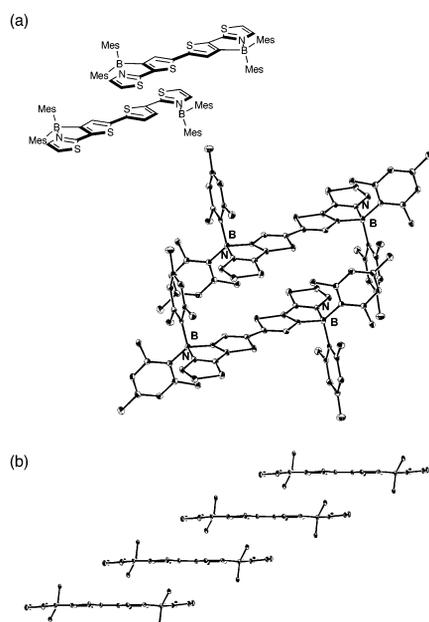
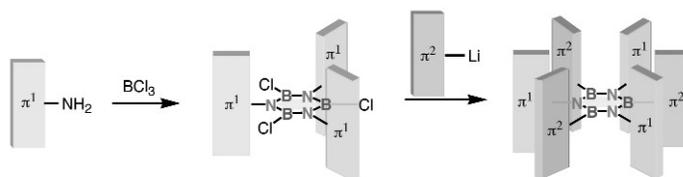


Fig. 9 Crystal packing structure of the head-to-head dimer **10**: (a) a perspective view and (b) a side view. Mesityl groups are omitted for clarity.

USE A STRUCTURAL FEATURE: π -CONJUGATED MOLECULE BUNDLE WITH A BORAZINE CORE

The third direction of our molecular design is to exploit the trigonal planar geometry of the boron atom. The properties of the π -electron materials are highly dependent on the solid-state structure. In this regard, controlling the arrangement of the π -conjugated systems in the solid state is crucial for the control of their properties. Our approach to this issue is to make a bundle of π -conjugated frameworks with a certain core unit using the covalent bonds [27]. As the core unit, we now choose the borazine (B_3N_3) six-membered ring. One advantage of using this skeleton is the facile and general synthesis. Thus, we can readily incorporate two different, in total, six π -conjugated frameworks onto the borazine core unit using the one-pot procedure shown in Scheme 1. Although benzene might be the primary conceivable candidate for the core skeleton [28], difficulty is often encountered in the synthesis of such sterically congested trigonally symmetric benzenes in terms of efficiency and regioselectivity. The borazine skeleton has a definite advantage over the benzene regarding this point.



Scheme 1 Synthesis of borazine-based π -conjugated molecule bundle.

As a prototype of the borazine-based bundle, we synthesized a series of B,B',B'' -trianthryl- N,N',N'' -triarylborazines (Fig. 10). Thus, the reaction of BCl_3 with appropriate aniline derivatives produced the corresponding B,B',B'' -trichlorotriarylborazines, which were subsequently treated with 9-anthryllithium to afford a series of trianthrylborazines bearing various p -substituted phenyl groups as the aryl groups on the nitrogen atoms. Although the overall yields using this procedure were only moderate to good, the procedure is essentially facile and allows us to synthesize the bundled systems on a gram scale.

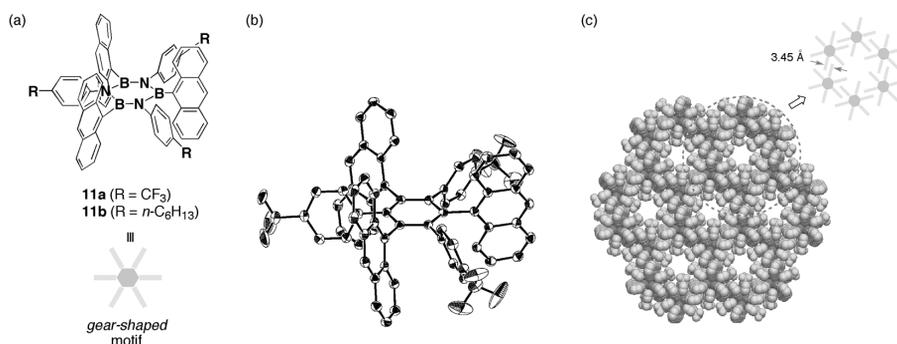
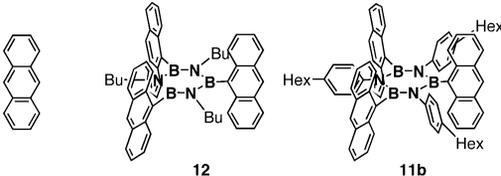


Fig. 10 Structure of B,B',B'' -trianthryl- N,N',N'' -triarylborazines **11**: (a) Schematic drawing of **11**; (b) ORTEP drawing of **11a** (50 % thermal probability); (c) Crystal packing structure of **11a**.

Figure 10 shows the crystal structure of the CF_3 -substituted derivative **11a**. This compound has a three-fold symmetry axis. The anthryl and phenyl groups are nearly arranged orthogonally to the borazine plane. This structure can be schematically represented as the gear-shaped motif shown in Fig. 10a. As a consequence, it forms a unique honeycomb-like packing, as shown in Fig. 10c. Notably, this packing structure consists of an offset face-to-face intermolecular π -stacking between the anthryl moieties with a cofacial π - π distance of about 3.45 Å.

To investigate the effect of the bundled structure on the properties, three compounds are compared to one another, which include anthracene, the alkyl-substituted trianthrylborazine **12**, and the aryl-substituted trianthrylborazine **11b** (Table 2). Notably, two kinds of bundled effects were observed. First, in the fluorescence spectra, the fluorescence intensity significantly increased. In terms of the quantum yield, an about two-fold enhancement was observed from anthracene to **11b**. Second, regarding the electrochemical property, the oxidation potential of the anthracene moiety steadily decreased in the order of anthracene > **12** > **11b**. This is rationalized by considering the through-space or through-bond orbital interaction in the borazine framework. These results suggest the effectiveness of the present design for the properties tuning of π -electron materials.

Table 2 Fluorescence^a and electrochemical^b data for anthracene and *B,B',B''*-trianthrylborazine derivatives.


	Anthracene	12	11b
Fluorescence			
λ_{em} (nm)	380	390	397
Φ_f	0.27	0.38	0.62
Oxidation			
$(E_{pa}/V \text{ vs. } Fc/Fc^+)$	+0.92	+0.91	+0.79

^aIn THF. The quantum yields are determined with anthracene as a standard.

^bDetermined by cyclic voltammetry in CH_2Cl_2 containing $Bu_4N^+ClO_4^-$ (0.1 M) with scan rate of 100 mV s⁻¹.

CONCLUSION

In summary, the designs and synthesis of three kinds of new boron-containing materials have been described. It should be noted that these systems were designed based on the three fundamental features of the boron element, i.e., the existence of a vacant p-orbital, the Lewis acidity of boron, and the geometric feature of boron. We believe that these features are the keys that lead organoboron chemistry to materials science, and on the basis of these molecular designs, fascinating functional π -electron materials will be developed.

ACKNOWLEDGMENTS

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