# Mesitylboron-Substituted Ladder-Type Pentaphenylenes: Charge-Transfer, Electronic Communication, and Sensing Properties

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***Abstract:*** A series of dimesitylboron (**B**)- or ditolylamino (**N**)-substituted ladder-type pentaphenylenes (**PP**) has been designed and synthesized. The UV–vis absorption spectra of compounds **BPPN**, **BPPB**, and **NPPN** reveal an identical maximum wavelength at 432 nm, which indicates that the **B** and **N** centers have very similar contributions to the extended conjugation. A rather weak solvatochromism in the UV–vis absorption spectra is observed for compound **BPPN**, while a remarkable solvatochromic emission is achieved even though the distance between the **B** and the **N** centers is as huge as 22 Å. The photoluminescence of **BPPN** shows a bathochromic shift of 108 nm when the solvent polarity is increased from cyclohexane (453 nm) to acetone (561 nm). Compound **BPPN** acts as a colorimetric and fluorescent chemosensor with high sensitivity ($10^{-5}$ M) and selectivity for $F^-$ over other halogen ions. By inhibiting the charge transfer (CT) from the **N** center to the **B** center, the intense green CT emission of compound **BPPN** rapidly switches into the sky-blue emission of **PP** when $F^-$ is bound to the **B** center. Furthermore, a CT emission can be switched "on" and "off" when compound **BPPB** is used as $F^-$ sensory material. Such an intramolecular CT emission between the two **B** centers has so far never been reported. Corresponding studies by cyclic voltammetry and differential pulse voltammetry reveal a two-step reduction of the two bridged **B** centers in compound **BPPB**, which might suggest that the charge delocalizes through the whole molecule and that the terminal redox centers communicate through the pentaphenylene bridge.

## Introduction

Boron-containing π-conjugated systems have attracted attention due to their intriguing electronic and photophysical properties.[1–11] The conjugation 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 charge transfer from an electron donor to the boron center, unique absorption and emission, and a low reduction potential rendering the compound susceptible to n-doping. These have enabled applications as nonlinear optical[12–21] and charge-transport materials,[22] as well as emitters in organic light-emitting devices (OLEDs).[23–28] It has also been demonstrated that three-coordinated boron compounds can be used as selective and sensitive chemosensors[29–34] for the detection of fluoride ions,

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which are the smallest anions and play an important role in the prevention of dental caries, osteoporosis, and fluorosis.[35] Although fluoride sensors containing boron centers have been exploited extensively, a surprisingly small amount of work has focused on utilizing donor−acceptor charge-transfer (CT) properties.[28,36] All previously reported three-coordinated boron sensors which produce intense CT fluorescence have very short spacers bridging the boron and donor centers.[37,38] Wang et al.[39,40] developed U-shaped and V-shaped sensor molecules with donor and acceptor moieties; however, the geometric distances between the amino and the boron centers were only ~10 Å. This was to ensure efficient charge transfer since the CT interaction decreases remarkably with increasing spacer distance.

As we have recently reported, in bisarylamine-substituted ladder-type pentaphenylene (**NPPN**) cation (Chart 1), the charge delocalizes in the mixed-valence form **NPPN$^{+\bullet}$**, and both redox centers can communicate through the pentaphenylene bridge.[41] Herein, ladder-type pentaphenylene (**PP**), a planar and well-conjugated spacer, was used to bridge the ditolylamino (**N**) and dimesitylboron (**B**) centers or the two **B** centers, as shown in Chart 1. Compared to other bridged boron−nitrogen or boron−boron systems known so far, the new compounds show several advantages: (i) Although the distance between the amino and the boron centers is calculated to be as huge as 22 Å, intense CT fluorescence was still observed. (ii) After binding to fluoride ion, the fluorescence in most previously reported CT systems containing boron centers changed from the CT emission to the spacer emission. Since most of the reported spacers are short and simple systems, the emissions are rather weak or occur in the ultraviolet region and thus cannot be observed with the naked eye. To facilitate the sensing process, therefore, blue fluorescent ladder-type pentaphenylene with high fluorescence quantum yield (QY)[41] is selected as the spacer. Thus, the binding of F$^-$ to the **B** center in compound **BPPN** can inhibit the CT transition (green emission) and simultaneously activate the blue emission of pentaphenylene, which can be easily detected even with the naked eye. (iii) Redox systems based on conjugated triarylamine units are well-established in studies of intervalence charge transfer (IVCT) since they provide the simplest models for the investigation of basic CT processes.[42−47] However, bridged

**Chart 1**
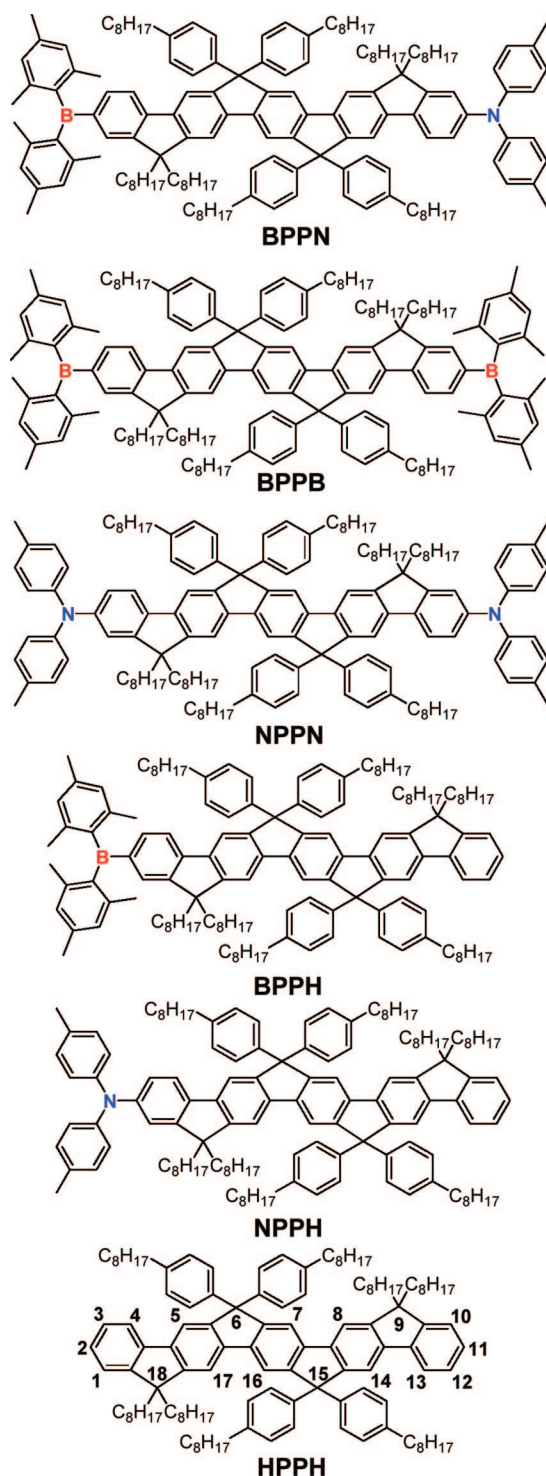


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diboronic compounds have rarely been used for studying CT phenomena.[48,49] In this work, bis(dimesitylboron)-substituted pentaphenylene (**BPPB**) (Scheme 1) was also designed and

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**Scheme 1.** Synthetic Route to Compounds **BPPN**, **BPPB**, and **BPPH**
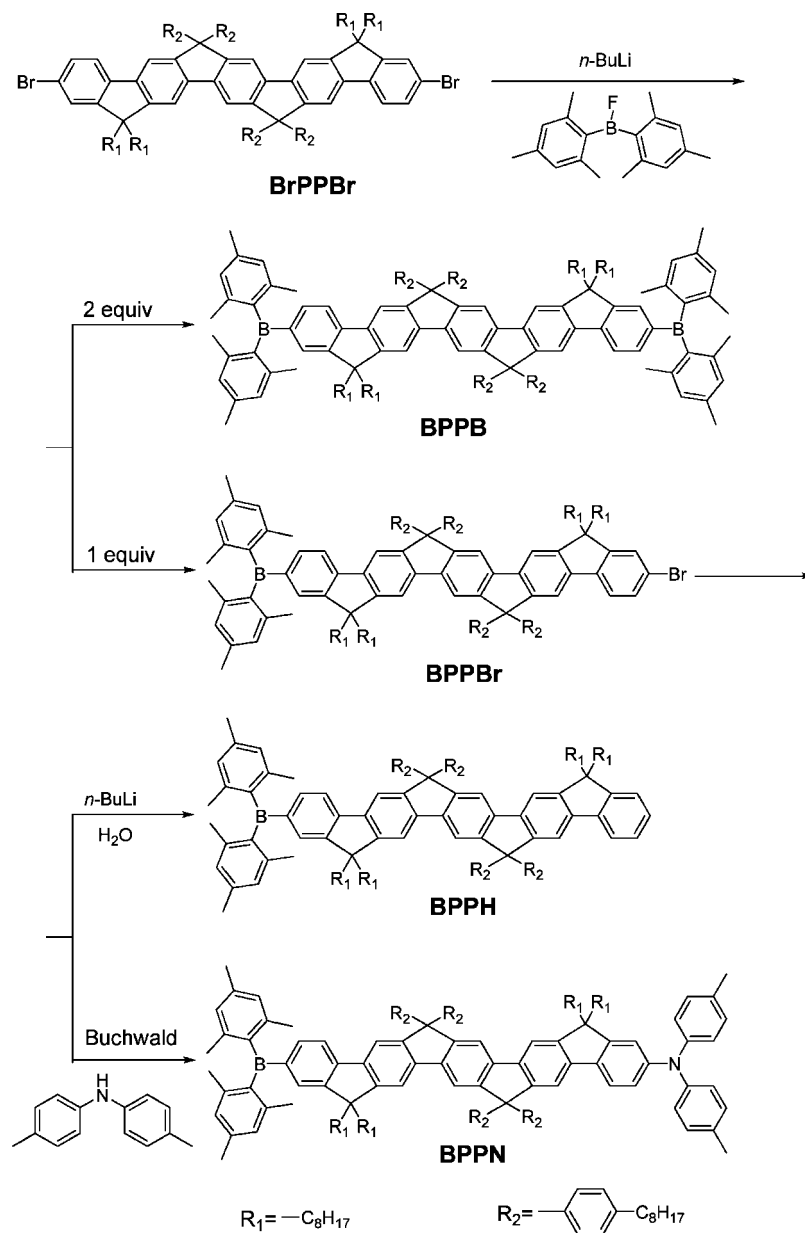


synthesized. Its IVCT behavior due to the intramolecular interaction between the two **B** centers was investigated by means of fluorescence titration, cyclic voltammetry (CV), and differential pulse voltammetry (DPV).

## Results and Discussion

**Synthesis and Structure Characterization.** The synthesis of the target compounds **BPPN** and **BPPB** begins with alkyl- and aryl-substituted ladder-type dibromopentaphenylene (**BrPPBr**), which has previously been developed in our laboratory.[50,51] The synthetic approach to the target compounds is depicted in Scheme 1, in which the pentaphenylene (**PP**) derivatives are named according to their different end groups, i.e., **B** for dimesitylboron, **N** for ditolylamino groups, and **H** for no

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substituent. The addition of 2.2 equiv of *n*-butyllithium to the solution of compound **BrPPBr** in tetrahydrofuran, followed by the addition of 2.4 equiv of dimesitylboron fluoride, produced compound **BPPB** in 80% yield. When compound **BrPPBr** was treated with 1.1 equiv of *n*-butyllithium, followed by 1.2 equiv of dimesitylboron fluoride, the asymmetrically substituted intermediate compound **BPPBr** was obtained with a yield of 36%. Compound **BPPN** was then synthesized by Buchwald coupling[52] of **BPPBr** and ditolylamine with palladium acetate as catalyst and purified by chromatography on silica gel in 74% yield. For control experiments, model compound **BPPH** was synthesized by lithiation of **BPPBr** with *n*-butyllithium and quenching with water in 93% yield.

The structures of the resulting compounds **NPPB**, **BPPB**, and **BPPH** were proven by ^{1}H NMR and ^{13}C NMR spectroscopy and elemental analysis. Additionally, the MALDI-TOF mass spectra exhibited single intense signals corresponding to the

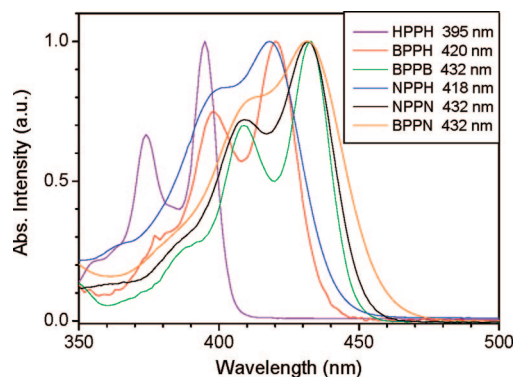(52) Guram, A. S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 7901.

**Figure 1.** UV−vis absorption spectra of **PP** derivatives.



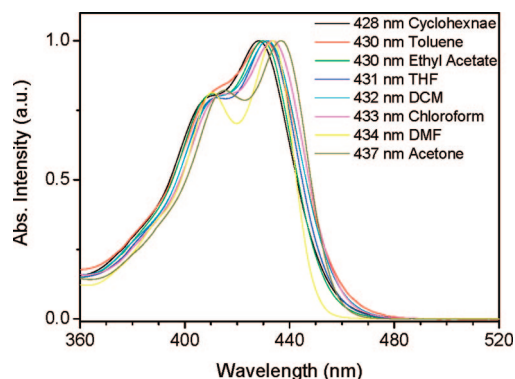**Figure 2.** UV−vis absorption spectra of compound **BPPN** in different solvents.



**Figure 3.** PL spectra of compound **BPPN** in different solvents.



**Figure 4.** HOMO and LUMO diagrams of compounds **BPPN** and **BPPB**.

calculated masses of compounds **BPPB**, **BPPB**, and **BPPH**, as illustrated in Figure S1 (Supporting Information).

**Optical Properties.** The UV−vis absorption spectra of a series of dimesitylboron and ditolylamino end-capped pentaphenylenes were measured in dichloromethane (DCM) solutions (ca. $10^{-5}$ M) (Figure 1). Stepwise incorporation of pentaphenylene with dimesitylboron from **HPPH** to **BPPH** and from **BPPH** to **BPPB** induces a bathochromic shift of 25 and 12 nm, respectively, in the absorption spectra, which suggests that the electron-deficient boron center contributes to extend the conjugation. As shown in Figure 1, the absorption spectra of **BPPN**, **BPPB**, and **NPPN** demonstrate identical maxima ($\lambda_{max} = 432$ nm), indicating that the boron and amino groups have similar effects on the extent of conjugation. The absorption onset of compound **BPPN** shows a weak bathochromic shift compared to those for compounds **BPPB** and **NPPN**, which could be ascribed to a contribution from an overlapping CT band from the **N** to the **B** centers.[36] Moreover, the absorption spectra of compound **BPPN** were slightly solvent-dependent. As illustrated in Figure 2, with the solvent polarity increasing from cyclohexane (428 nm) to acetone (437 nm), a bathochromic shift of 9 nm could be observed. In contrast to the weak solvatochromism in absorption spectra, the differences in the corresponding photoluminescence (PL) spectra are quite remarkable. Compound **BPPN** displayed significant solvent-dependent PL (Figure 3), and a bathochromic shift of 108 nm of the PL spectra for **BPPN** was observed when the solvent polarity increased from cyclohexane (453 nm) to acetone (561 nm). Such a bathochromic shift of more than 100 nm has already been reported[53,54] and is characteristic for an efficient charge transfer from the **N** center to the **B** center through the extended bridge.[39] Such a distinct solvatochromism found in PL spectra is ascribed to the more polarized excited
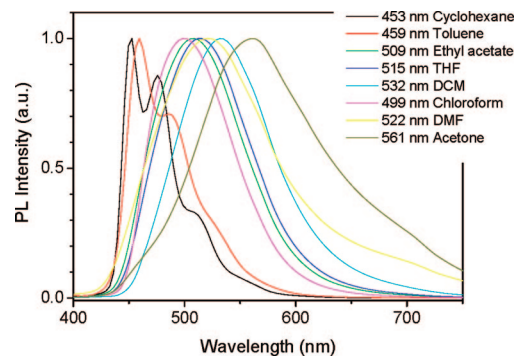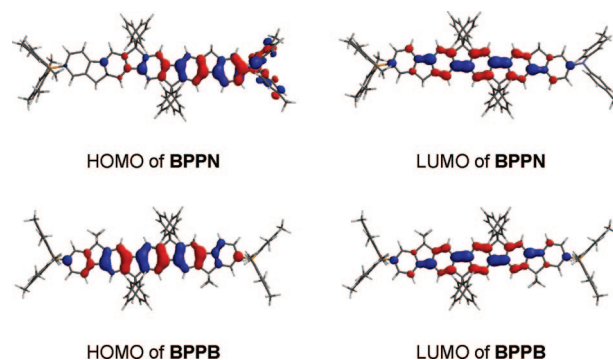
state.[55] Upon excitation the electron transfer from the highest occupied molecular orbital (HOMO), localized primarily on the arylamino moiety, to the lowest unoccupied molecular orbital (LUMO), localized on the dimesitylboron and pentaphenylene moieties, the dipole is enhanced in the excited $S_1$ state. Therefore, a more polar solvent is able to stabilize such a polarized excited state by the reorientation of the solvent molecules to accommodate the increased dipole, lowering the energy of the system and thereby leading to the bathochromic shift in the PL spectra of compound **BPPN**.[55] For comparison, this remarkable CT emission could not be observed in compound **BPPB** due to the absence of the amino center. However, **BPPB** also demonstrates a slightly solvent-dependent PL. Molecular orbital calculations (DFT, B3LYP, 6-31G*)[56] revealed that the HOMO of **BPPB** is dominated by the **PP** spacer, whereas the LUMO includes the two boron centers and the **PP** spacer (Figure 4). Thus, the lowest electronic transition is consistent with the charge transfer between the **PP** spacer and the two **B** centers.[39]

**Sensing Properties.** The sensing properties of compound **BPPN** with regard to different tetrabutylammonium anion salts were characterized in 10 $\mu$M DCM solutions. Figure 5a shows a photograph of **BPPN** in DCM solutions containing excess amounts (ca. 1 mM) of various anions (F⁻, Cl⁻, Br⁻, I⁻, BF₄⁻, PF₆⁻, and CN⁻). The solutions remained yellowish upon addition of all the above anions, except for F⁻ and CN⁻, where the solution turned almost colorless (Figure S2). Upon addition

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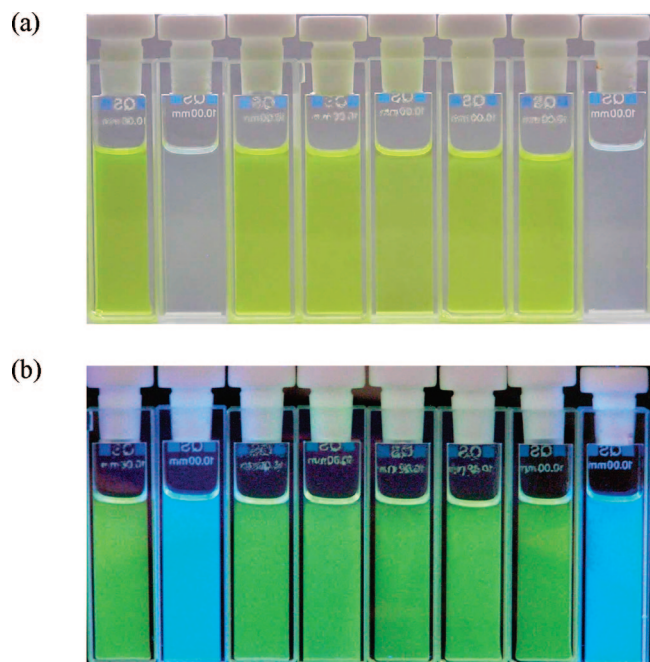(56) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

**Figure 5.** (a) Photograph showing the interactions of anions with sensor **BPPN** in DCM solutions. (b) Fluorescence of **BPPN** with anions in DCM solutions. The cells are illuminated with a hand-held UV lamp. From left to right: none, $F^-$, $Cl^-$, $Br^-$, $I^-$, $BF_4^-$, $PF_6^-$, $CN^-$.
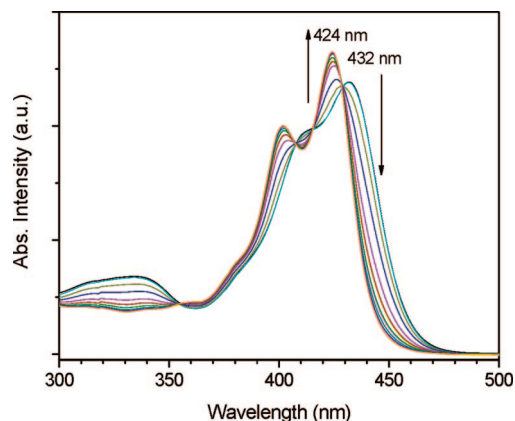


**Figure 6.** UV−vis absorption spectra of **BPPN** in DCM solutions upon addition of $F^-$.

of $F^-$ to the DCM solution of **BPPN**, a new absorption band at 424 nm appeared along with the disappearance of the main absorption band at 432 nm (Figure 6). These absorption changes indicate the appearance of the B−F complex and originate from the occupation of the empty orbital and the interruption of the extended conjugation including the **B** atom.[57] This can be identified by the titration of model compound **BPPH** with $F^-$ (Figure S3). Similarly, upon adding $F^-$ to the DCM solution of **BPPH**, the absorption band at 415 nm decreased while a new band appeared at 409 nm due to the formation of a charged boron center.

In addition to serving as a colorimetric chemosensor, compound **BPPN** could also be used as a fluorescent chemosensor for $F^-$.[58−60] The corresponding images of **BPPN** illuminated with a hand-held UV lamp in DCM solutions (ca. 10 $\mu$M) upon
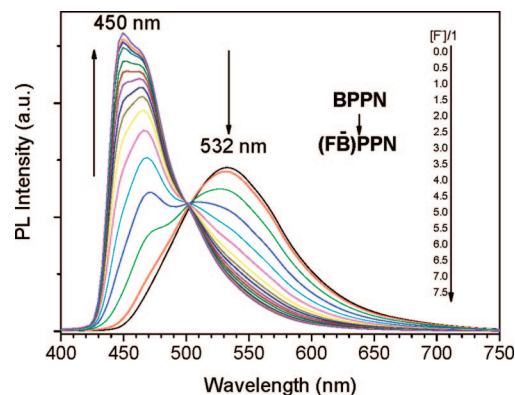


**Figure 7.** PL spectra of compound **BPPN** upon addition of $F^-$.

addition of excess amounts of anions (ca. 1 mM) are presented in Figure 5b. The yellowish-green fluorescence of compound **BPPN** in DCM solutions does not change upon the addition of anions, except for $F^-$ and $CN^-$. With the stepwise addition of $F^-$, the CT emission band at 532 nm is "turned off" and a new blue emission band at 450 nm "turned on" (Figure 7), which is characteristic of the **PPN** emission due to the inhibition of the charge transfer from the **N** center to the **B** center (Figure 8). Corresponding Stern−Volmer plots are shown in Figure S4. The detection limit for $F^-$ was measured to be around $10^{-5}$ M under the experimental conditions, which suggests that compound **BPPN** is a highly sensitive sensory material for $F^-$.

Interestingly, the sensing behavior of bis(dimesitylboron)-substituted pentaphenylene (**BPPB**) is much more complicated than that of **BPPN** and provides detailed information on the intramolecular interaction. The fluorescence titration could be divided into two subprocesses, as shown in Figure 9. With the stepwise addition of $F^-$, the intensity of the emission band at 450 nm decreased, while another very broad shoulder appeared at 520 nm with a clear isosbestic point at 505 nm. This can only originate from the boron monoanion **BPPB$^-$F** and is thus assigned to the intramolecular charge transfer from the negatively charged **B** center to the other neutral one (Figure 8). Moreover, this long-wavelength emission band is solvent-dependent. When the sensing behavior was investigated in acetone solution, a similar broad CT emission shoulder also appeared around 550 nm (Figure S5) with a bathochromically shifted isosbestic point at 540 nm. However, when cyclohexane was used as solvent, no long-wavelength CT emission band could be observed (Figure S6). Although charge transfer from anionic four-coordinate boronate species to cationic centers at the other end of a conjugated spacer has been investigated,[61,62] such an intramolecular CT emission band between two reducible boron centers has never been reported. In most previously described cases with multiple **B** centers, only fluorescence quenching could be observed when sensing $F^-$. Upon further titration with $F^-$, the green emission at 520 nm completely disappeared, while an intense shoulder at 430 nm, with a clear isosbestic point shifted from 505 to 487 nm, increased continu-

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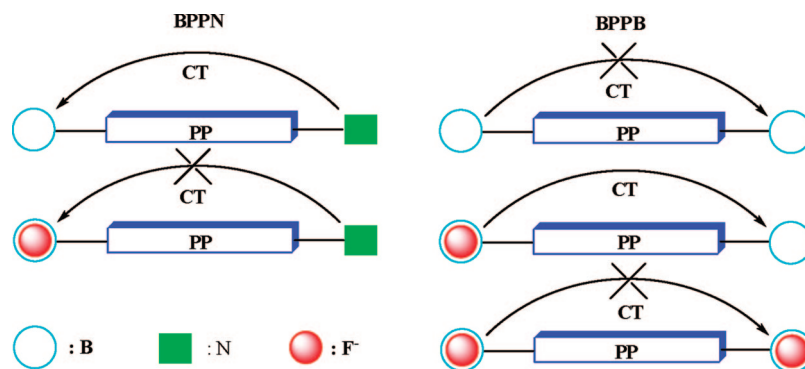
**Figure 8.** Schematic representation of the different emission processes occurring in **BPPN** and **BPPB** upon coordination of F⁻.
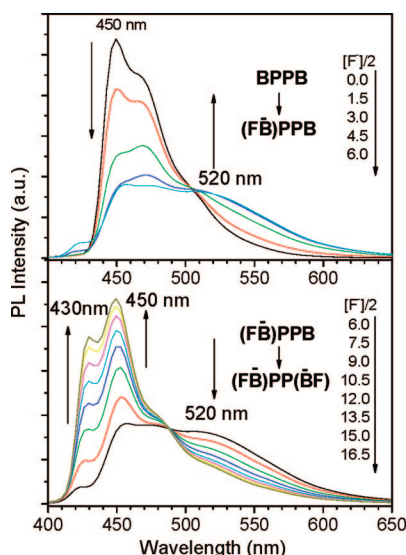


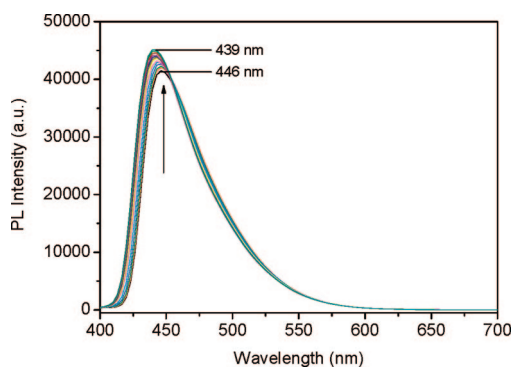**Figure 9.** PL spectra of compound **BPPB** in DCM solutions upon addition of F⁻.



**Figure 10.** PL spectra of **BPPH** in DCM solutions upon addition of F⁻.



**Figure 11.** Differential pulse voltammograms of **BPPN**, **BPPB**, and **BPPH**, measured in DCM (for oxidation) and THF (for reductions).

ously. This hypsochromic shift of the PL spectrum is obviously due to the formation of dianion **FB⁻PPB⁻F**. When a similar experiment was performed for model compound **BPPH**, as shown in Figure 10, only a hypsochromic shift of 7 nm (446→439 nm) was observed upon addition of F⁻ into the DCM solution of **BPPH** due to the absence of another **B** center, which also excludes a CT interaction between the **PP** skeleton and the **B** center.

**Electrochemical Properties.** To investigate the electronic communication between the two **B** centers, the electrochemical behavior of **BPPB** was studied by CV and DPV. As shown in
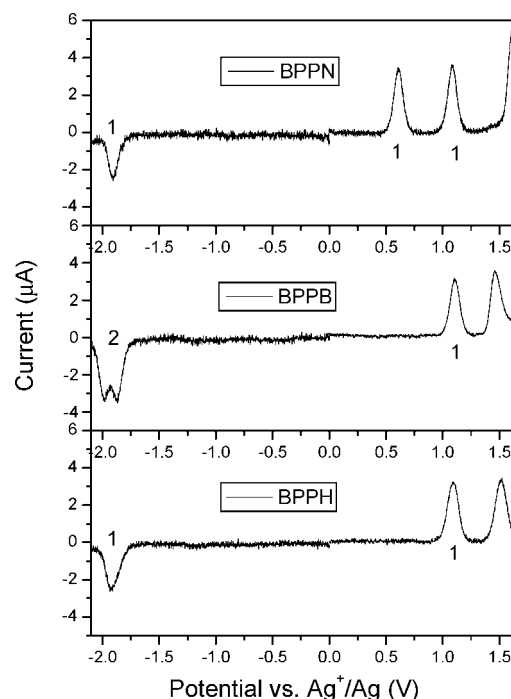
Figure S7, compound **BPPB** displays two reversible one-electron cathodic redox steps, corresponding to the sequential acceptance of electrons at **B** centers to form the stable radical anion and dianion. Compared with the CV of monodimesityl-boron **BPPH**, the first low-potential redox wave ($E = -1.94$ V) fits well with that of **BPPB**, indicating that the first electron is accepted at one of the **B** centers. However, unlike the one reversible redox couple found for **BPPH**, **BPPB** shows two reversible reduction processes in the low-potential region at $E = -1.88$ and $-1.99$ V, respectively. This implies that the two electrons are accepted successively from the two dimesitylboron moieties and that a higher potential is needed to transform **BPPB⁻•** into **BPPB²⁻**. The separation of 0.11 V suggests a low electron coupling energy and a weak communication between the two **B** centers through the long **PP** spacer.[63,64] Correspondingly, according to the peak integrals, the DPV of **BPPB** (Figure 11) also displays two one-electron reductions at $-1.87$ and $-1.98$ V. The splitting of the reductions of two dimesitylboron

(63) Kaim, K.; Schultz, A. *Angew. Chem., Int. Ed.* **1984**, *23*, 615.
(64) Sundararaman, A.; Venkatasubbaiah, K.; Victor, M.; Zakharov, L. N.; Rheingold, A. L.; Jakle, F. *J. Am. Chem. Soc.* **2006**, *128*, 16554.

units into two steps suggests charge delocalization through the conjugated ladder-type pentaphenylene in its mixed-valence radical monoanion **BPPB⁻·** and long-distance electron communication between the two dimesitylboron branches. Compared with the two oxidation couples at 1.1 and 1.5 V in the DPV spectra of both **BPPB** and **BPPH**, compound **BPPN** displays one more redox couple at 0.6 V, which is attributed to the oxidation of the ditolylamino group.

## Conclusions

In summary, boron-containing pentaphenylenes **BPPN** and **BPPB** have been synthesized from **BrPPBr**. The charge-transfer absorption band of compound **BPPN** exhibits slight solvatochromism, while the emission shows remarkable solvatochromic effect even though the distance between the **B** and **N** centers is as huge as 22 Å. With the solvent polarity increase from cyclohexane to acetone, the PL spectrum of compound **BPPN** in solutions shows a bathochromic shift of 108 nm. When F⁻ is bound to the **B** center of compound **BPPN**, the intense green CT emission is "switched off", while the strong blue emission of the **PP** spacer is recovered, which can be easily observed with the naked eye. Therefore, by suppressing this CT interaction, compound **BPPN** acts as a highly selective and sensitive colorimetric and fluorescent chemosensor for fluoride ions over other halogen ions. Most importantly, we also report on the first solvent-dependent intramolecular CT emission from one, negatively charged **B** center to the other, neutral one in compound **BPPB** when sensing fluoride ions. This intramolecular CT emission in the long-wavelength region is "switched on" when only one **B** center is charged by F⁻ and "switched off" when both are charged. Further CV and DPV investigations indicate that the charges delocalize on the **PP** bridge and IVCT are achieved in this reducible system. This unique study may offer an effective way to improve the understanding of charge transfer and charge-carrier transport in boron-containing conjugated oligomers or polymers and facilitate their ongoing exploration in optoelectronic applications. Our ongoing work is focused on further in depth studies of OLED devices and two-photon absorption measurements.

## Experimental Section

**Measurement and Characterization.** ${}^1$H and ${}^{13}$C NMR spectra were recorded on a Bruker AMX 300 NMR instrument (300 and 75 MHz, respectively) with dichloromethane-$d_2$ as solvent and tetramethylsilane as internal standard. Chemical shifts are reported in parts per million. FD mass spectra were performed with a VG-Instruments ZAB 2-SE-FDP spectrometer. The elemental analyses were carried out by the Microanalytical Laboratory of Johannes Gutenberg University. The UV−vis−NIR absorption measurements were performed on a Perkin-Elmer Lambda 15 spectrophotometer and the PL measurements on a SPEX Fluorolog 2 type F212 steady-state fluorometer. Cyclic voltammetry and differential pulse voltammetry were performed on an EG&G Princeton Applied Research potentiostat, model 273, in a solution of Bu$_4$NPF$_6$ (0.1 M) in dry dichloromethane with a scan rate of 50 mV/s at room temperature under argon. A platinum electrode was used as the working electrode, an Ag wire as the reference electrode, and a platinum wire as the counter electrode.

**Material Synthesis.** All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified or freshly distilled prior to use according to standard procedures. All chemical reactions were carried out under an inert atmosphere. Intermediate dibromopentaphenylene **BrPPBr** was synthesized according to previous work in our group.

**Synthesis of 2,11-Dimesitylboron-6,6,15,15-tetra(p-octylphenyl)-9,9,18,18-tetraoctyl(ladder-type pentaphenylene) (BPPB).** Under nitrogen atmosphere and at −78 °C, n-BuLi (1.35 mL, 1.6 M in hexane) was added dropwise to a dry tetrahydrofuran (40 mL) solution containing dibromopentaphenylene (1.79 g, 1 mmol). After 30 min stirring, 0.6 g of dimesitylboron fluoride in 20 mL of THF was added slowly to the reaction solution. The temperature of the solution was raised back to room temperature, and after another 12 h stirring, the reaction was quenched with brine. The solution was extracted with ethyl acetate and subjected to flash column chromatography (silica gel, DCM/hexane = 1:10). A light yellow solid was obtained in 80% yield (1.7 g). ${}^1$H NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ (ppm): 7.74 (s, 2H), 7.62−7.49 (m, 6H), 7.36−7.29 (m, 4H), 7.14 (d, 8H, $J$ = 8.4 Hz), 7.03 (d, 8H, $J$ = 8.4 Hz), 6.74 (s, 8H), 2.47 (t, 8H, $J$ = 7.8 Hz), 2.22 (s, 12H), 2.00−1.72 (m, 32H), 1.51−1.41 (m, 8H), 1.21−1.17 (m, 40 H), 1.12−0.93 (m, 40H), 0.79−0.70 (m, 24H), 0.60−0.47 (b, 8H). ${}^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) $\delta$ (ppm): 151.6, 151.3, 151.2, 150.6, 149.8, 149.7, 146.7, 144.8, 144.4, 144.2, 142.8, 142.7, 141.3, 140.7, 140.3, 140.0, 139.8, 139.7, 138.8, 137.7, 137.6, 134.7, 134.6, 131.3, 129.5, 128.9, 127.5, 127.4, 127.3, 123.2, 121.5, 119.3, 118.3, 117.4, 116.9, 116.7, 116.4, 115.5, 113.7, 63.5, 54.0, 39.7, 34.7, 31.1, 31.0, 30.7, 29.2, 29.1, 28.7, 28.6, 28.5, 28.4, 28.3, 23.1, 23.0, 22.3, 21.8, 20.1, 19.7, 13.1. Elemental analysis for C$_{158}$H$_{208}$B$_2$. Calcd: (%) C, 89.14; H, 9.85. Found: (%) C, 88.61; H, 9.51. MALDI-TOF: $m/z$ 2128.

**Synthesis of 2-Bromo-6,6,15,15-tetra(p-octylphenyl)-9,9,18,18-tetraoctyl-mesitylboron(ladder-type pentaphenylene) (BPPBr).** Under nitrogen atmosphere and at −78 °C, n-BuLi (0.65 mL, 1.6 M in hexane) was added dropwise to a dry tetrahydrofuran (40 mL) solution containing **BrBBBr** (1.79 g, 1 mmol). After 30 min stirring, 0.3 g of dimesitylboron fluoride in 20 mL of THF was added slowly to the reaction solution. The temperature of the solution was brought back to room temperature, and after another 12 h of stirring, the reaction was quenched with brine. The solution was extracted with ethyl acetate and subjected to flash column chromatography (silica gel, DCM/hexane = 1:15). A light yellow solid was obtained in 36% yield (710 mg). ${}^1$H NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ (ppm): 7.73 (s, 2H), 7.61−7.49 (m, 6H), 7.36−7.22 (m, 3H), 7.14 (d, 9H, $J$ = 8.1 Hz), 7.03 (d, 8H, $J$ = 8.1 Hz), 6.74 (s, 4H), 2.47 (t, 8H, 7.8 Hz), 2.22 (s, 6H), 1.90 (m, 20H), 1.50−1.40 (m, 8H), 1.21−1.17 (m, 40H), 1.09−0.95 (m, 40H), 0.79−0.67 (m, 24H), 0.55 (b, 8H). ${}^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) $\delta$ (ppm): 152.5, 152.4, 152.3, 151.8, 151.7, 151.5, 151.1, 150.8, 145.6, 145.3, 143.9, 143.8, 142.4, 141.9, 141.5, 141.4, 141.2, 141.0, 140.7, 140.3, 139.8, 138.8, 135.8, 130.6, 128.7, 128.5, 128.4, 127.2, 127.0, 123.2, 119.9, 119.5, 118.1, 117.9, 117.8, 117.4, 115.0, 64.7, 55.2, 40.9, 40.8, 35.8, 32.2, 32.1, 31.9, 30.4, 30.3, 30.0, 29.9, 29.8, 29.6, 29.5, 24.2, 23.5, 23.0, 22.9, 21.3, 14.2. MALDI-TOF: $m/z$ 1960.

**Synthesis of 2-Mesitylboron-6,6,15,15-tetra(p-octylphenyl)-9,9,18,18-tetraoctyl-p-tolyl(ladder-type pentaphenylene) (BPPN).** Under nitrogen atmosphere, a mixture of compound **BPPBr** (100 mg, 0.06 mmol), bis(p-tolyl)amine (50 mg, 0.25 mmol), Pd(OAc)$_2$ (1 mg, 0.005 mmol), P(t-Bu)$_3$ (2 mg, 0.01 mmol), and Cs$_2$CO$_3$ (44 mg, 0.14 mmol) in toluene (10 mL) was stirred and heated at 80 °C for 8 h. After the reaction solution cooled to room temperature, brine was added. The solution was extracted with ethyl acetate and subjected to flash column chromatography (silica gel, DCM/hexane = 1:15). A yellow solid was obtained in 74% yield (80 mg). ${}^1$H NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ (ppm): 7.70 (d, 2H, $J$ = 6.9 Hz), 7.60 (d, 2H, $J$ = 6.0 Hz), 7.54−7.46 (m, 3H), 7.36−7.29 (m, 3H), 7.14 (d, 8H, $J$ = 7.2 Hz), 7.03 (d, 8H, $J$ = 8.1 Hz), 6.98−6.95 (m, 5H), 6.89 (d, 4H, $J$ = 8.4 Hz), 6.80−6.74 (m, 5H), 2.47 (t, 8H, $J$ = 7.5 Hz), 2.21 (s, 6 H), 2.15 (s, 6H), 1.90 (m, 20H), 1.49 (m, 8H), 1.20−1.16 (m, 40H), 1.11−0.92 (m, 40H), 0.76−0.69 (m, 24H), 0.52 (b, 8H). ${}^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) $\delta$ (ppm): 152.6, 152.3, 151.8, 150.8, 145.6, 145.3, 143.8, 142.4, 141.9, 141.3, 141.1, 140.8, 140.7, 140.6, 140.5, 139.0, 138.9, 136.9, 136.8, 136.7, 135.9, 130.6, 128.7, 128.5, 128.3, 119.5, 118.1, 117.9, 115.0, 64.7, 55.2, 40.8, 35.8, 32.2, 31.9, 30.3, 29.8, 29.6, 29.5, 24.2, 23.5, 23.0, 22.9, 22.4,

21.3, 14.2. Elemental analysis for $C_{154}H_{200}BN$. Calcd: (%) C, 89.09; H, 9.71; N, 0.67. Found: (%) C, 88.82; H, 10.08; N, 0.39. MALDI-TOF: *m/z* 2076.

**Synthesis of 2-Mesitylboron-6,6,15,15-tetra(*p*-octylphenyl)-9,9,18,18-tetraoctyl(ladder-type pentaphenylene) (BPPH).** Under nitrogen atmosphere and at −78 °C, *n*-BuLi (0.1 mL, 1.6 M in hexane) was added dropwise to a dry tetrahydrofuran (40 mL) solution containing compound **BPPBr** (0.2 g, 0.1 mmol). After 30 min of stirring, the reaction was quenched with brine. The solution was extracted with ethyl acetate and subjected to flash column chromatography (silica gel, DCM/hexane = 1:15). A light yellow solid was obtained in 93% yield (90 mg). [^1]H NMR (300 MHz, CD$_2$Cl$_2$) δ (ppm): 7.73(s, 2H), 7.61−7.49 (m, 6H), 7.36 (s, 1H), 7.32 (d, 1H, *J* = 7.5 Hz), 7.26 (m, 1H), 7.14 (d, 10H, *J* = 8.4 Hz), 7.03 (d, 8H, *J* = 7.8 Hz), 6.74 (s, 4H), 2.47 (t, 8H, *J* = 7.8 Hz), 2.21 (s, 6H), 1.90 (m, 20H), 1.50−1.39 (m, 8H), 1.21−1.17 (m, 40H), 1.12−0.95 (m, 40H), 0.79−0.67 (m, 24H), 0.57 (b, 8H). [^13]C NMR (75 MHz, CD$_2$Cl$_2$) δ (ppm): 152.5, 152.4, 152.3, 151.8, 151.6,

151.4, 151.1, 150.8, 145.6, 145.3, 143.9, 143.8, 142.4, 141.9, 141.5, 141.4, 141.2, 141.1, 141.0, 140.7, 140.3, 139.7, 138.8, 135.8, 130.6, 128.7, 128.5, 128.4, 127.2, 126.9, 123.2, 119.9, 119.5, 118.1, 117.9, 117.8, 117.4, 115.0, 55.2, 40.9, 40.8, 35.8, 32.2, 32.1, 31.9, 30.4, 30.3, 29.8, 29.6, 29.5, 24.2, 23.5, 23.0, 22.9, 21.3, 14.2. Elemental analysis for $C_{140}H_{187}B$. Calcd: (%) C, 89.40; H, 10.02. Found: (%) C, 89.30; H, 9.99. MALDI-TOF: *m/z* 1880.

**Supporting Information Available:** Detailed UV−vis absorption and PL spectra upon titration. This material is available free of charge via the Internet at http://pubs.acs.org.

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