

Phenylene Bridged Boron–Nitrogen Containing Dendrimers

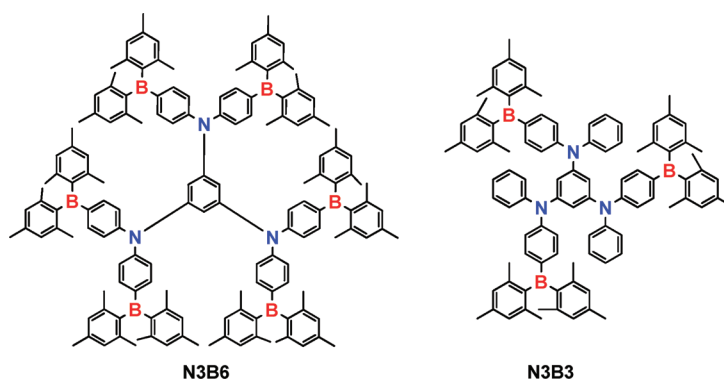
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ABSTRACT



The synthesis and characterization of novel phenylene bridged boron–nitrogen containing π -conjugated dendrimers N3B6 and N3B3, with peripheral boron atoms and 1,3,5-triaminobenzene moiety as a core, are presented. UV–vis absorption and emission measurements reveal that the optical properties of the resulting compounds can be controlled by changing the donor/acceptor ratio: a 1:1 ratio results in a more efficient charge transfer than the 1:2 ratio. This was proven by the red shift of the emission maxima and the stronger solvatochromic effect in N3B3 compared to N3B6.

The synthesis of π -conjugated molecules with well-organized chromophores¹ has received attention due to their applications in organic electronics such as photovoltaics or organic light-emitting diodes (OLED). Among them, π -conjugated dendrimers² are of interest in view of (i) the extension of the conjugation into more than one dimension, (ii) the rigid structure, (iii) the high chromophore to surface ratio, as well as (iv) the monodispersity and purity. π -Conjugated dendrimers containing electron-donating groups, for example, amine³ or thiophene⁴ units, are widely studied in electronic devices. In contrast, dendritic structures with electron-

acceptor units⁵ or both donor and acceptor moieties⁶ are uncommon. Incorporation of boron moieties into conjugated

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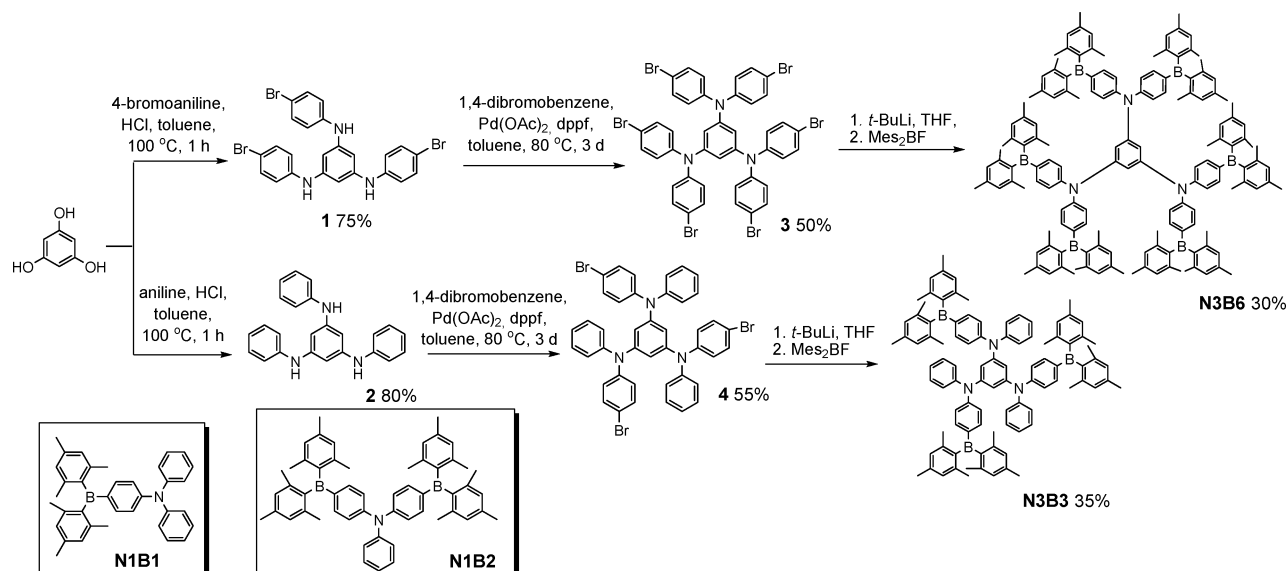
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Scheme 1. Synthetic Pathway for Compounds **N3B6** and **N3B3**



systems⁷ is one approach toward improving and tuning properties for use in organic electronics through lowering the LUMO levels. A boron center possesses a vacant p-orbital and can thus serve as an acceptor unit. Efficient overlap between its empty orbital and the π -conjugated framework then gives rise to a bathochromic shift of the UV–vis absorption and emission signals. Boron acceptor units in conjugation with appropriate electron donors show intense intramolecular charge transfer.⁸

Although there are many papers on donor–acceptor systems with boron units,^{9,10} these are mostly restricted to systems with just one or two boron centers. Examples of dendritic structures bearing boron moieties are very rare.^{5b,11} Kawashima et al.¹¹ recently reported dendrimers based on dibenzoazaborines in the periphery and a benzothiadiazole (BTZ) unit as the core. Optical investigation of these dendrimers indicated intramolecular charge transfer in the excited state from the azaborine units to the BTZ unit. To the best of our knowledge, there is no report concerning π -conjugated dendrimers with boron atoms in the periphery and nitrogen atoms as a core (and *vice versa*). Therefore, we became interested in dendrimers bearing amine moieties

as donors and boryl groups as acceptors, bridged by phenylenes. This allowed us to study the effect of the donor/acceptor (D–A) ratio on the optical properties of the resulting compounds.

1,3,5-Tris(di(4-dimesitylboryl-phenyl)amino)benzene (**N3B6**) and 1,3,5-tris((4-dimesitylboryl-phenyl)phenylamino)benzene (**N3B3**) were synthesized in three steps as shown in Scheme 1. The first step involved acid-catalyzed condensation of commercially available phloroglucinol with 4-bromoaniline or aniline to achieve 1,3,5-tris(4-bromophenylamino)benzene (**1**) and 1,3,5-tris(phenylamino)benzene (**2**),¹² respectively, in 75–80% yield. Compounds **1** and **2** were subjected to Buchwald–Hartwig amination¹³ with 1,4-dibromobenzene in the presence of palladium(II) acetate and bis(diphenylphosphino)ferrocene (dppf) as a catalytic system to furnish compounds **3** and **4** in 50% yield. The final products **N3B6** and **N3B3** were obtained in about 30% yield by treatment of **3** and **4**, respectively, with *t*-BuLi followed by addition of dimesitylboron fluoride. Model compounds **N1B1**¹⁴ and **N1B2** were synthesized via halogen–metal exchange from commercially available bromo- or dibromo-triphenylamine, respectively (Supporting Information). Pure samples were obtained after purification by size exclusion chromatography. The synthesized compounds are yellowish solids soluble in common organic solvents. The bulky mesityl groups stabilize them against air and moisture.

The optical properties of **N3B6** and **N3B3** were studied by UV–vis absorption and emission spectroscopy (Figure 1 and Table 1). Both of them exhibit two absorption bands in the range from 300 to 400 nm. The weaker one (~310

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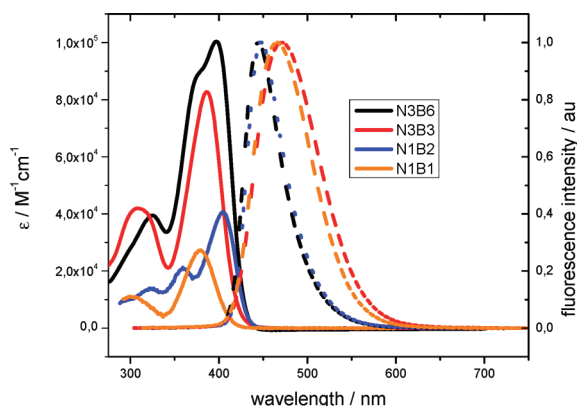


Figure 1. UV–vis absorption (solid lines) and emission spectra (dashed lines) of **N3B6**, **N3B3**, **N1B2**, and **N1B1** in DCM (1.3×10^{-5} M). Excited at 375 nm.

nm) can be identified as originating from the aromatic backbone and the stronger one (~ 385 nm) as a charge transfer transition from the amino group to the boron center. This was further confirmed by fluoride titration experiments as discussed below. The charge transfer band of **N3B6** consists of a shoulder at 385 nm and a maximum at 395 nm, while **N3B3** shows a band at 385 nm. As documented in Figures S1 and S2 in Supporting Information, absorption spectra do not change upon increasing the solvent polarity.

Interestingly, the difference in the emission spectra of both compounds is significant. In the case of **N3B6**, with a D-A ratio 1:2, blue emission at 445 nm is observed. Changing the D-A ratio to 1:1 (**N3B3**) causes a bathochromic shift of 26 nm. Obviously, in the case of **N3B3** every amine moiety interacts with just one boron atom, whereas in **N3B6** the donating strength of amine group is “distributed” over two boron atoms thus weakening D-A interactions. Comparing the emission maxima of dendrimers with those of model compounds **N1B1** and **N1B2** (Figure 1), no red shift was observed, indicating lack of conjugation between dendrons due to the dihedral angle between these moieties and their 1,3,5-benzene core. Because of the strong blue emission (quantum yield = 0.6) compound **N3B6** is of potential interest as an emitter in OLEDs.

In view of the lack of solvatochromism in the absorption spectra, the solvent dependence in the emission spectra is remarkable. As shown in Figures S5 and S6 in Supporting

Information, bathochromic shifts of 27 and 61 nm for **N3B6** and **N3B3**, respectively, were observed when the polarity of the solvent increased from hexane to acetone. This can be attributed to the charge transfer transition from the nitrogen donor to the boron acceptor.¹⁵ As proven by solvent-dependent emission measurements, the strength of these interactions is influenced by the D-A ratio. In the case of **N3B3**, in which each amine moiety interacts with only one boron center, more efficient charge transfer occurs and the red shift of the emission band is stronger than that of **N3B6**.

In general, three-coordinated organoboron compounds can be used as fluoride sensors.^{5b,16} A fluoride anion occupies the empty orbital of the boron atom and thus inhibits the charge transfer from the nitrogen center. The character of the boron center is thereby changed from an acceptor to a donor. As shown in Figure 2, upon stepwise addition of TBAF to the solution of **N3B6** the emission band was red-shifted¹⁷ by 100 nm. When more than 3 equiv of F^- was added, the band at 540 nm disappeared and a new band at 410 nm could be seen. This phenomenon can be explained by switching the character of one of the boron atoms attached to an amine moiety from an acceptor to a donor. This gives rise to new D-D-A chromophore that shows stronger D-A interactions in the excited state than the parent **N3B6** molecule. Further addition of F^- switches off all acceptor centers, inhibiting any charge transfer and making the entire molecule a donor with a new band at 410 nm. Treatment of compound **N3B3** (Figure 2) with TBAF results in a blue shift of the emission spectra. This can be attributed to the fact that addition of each eq of F^- turns off D-A properties of one B-N charge transfer moiety. In contrast to **N3B6**, no new D–A interactions appear. A similar tendency was observed for the model compounds **N1B2** and **N1B1** (Figure S14 in Supporting Information). The charge transfer band in the UV–vis absorption spectra gradually decreased upon addition of F^- anions (Figures S9–S12 in Supporting Information). No stepwise changes were observed, and thus it was impossible to determine binding constants for the intermediates.

The electrochemical properties of **N3B6** and **N3B3** were studied by cyclic voltammetry (CV) as shown in Table 1, which revealed similar values of HOMO and LUMO levels for **N3B6** and **N3B3**. The energy gaps of these compounds were calculated to be 2.64 and 3.63, respectively, which is in good agreement with the optical band gap.

Table 1. UV–vis Absorption, Emission, and CV Data of Compounds **N3B6** and **N3B3**

compound	$\lambda_{\max}^a$ [nm], $\log \epsilon^a$	$E_{\max}^a$ [nm]	QY ^{a,b}	optical band gap ^c [eV]	HOMO ^d [eV]	LUMO ^e [eV]	ΔE [eV]	HOMO ^f [eV]	LUMO ^f [eV]
N3B6	395, 5.00	445	0.6	2.89	−5.51	−2.87	2.64	−5.19	−1.82
N3B3	385, 4.92	471	0.5	2.95	−5.53	−2.90	2.63	−5.10	−1.63

^a Measured in DCM. ^b Calculated using DPA as standard. ^c Calculated using onset of the absorption spectra; HOMO and LUMO levels calculated from cyclic voltammetry measurements vs Ag/AgCl using ferrocene as standard. ^d Measured in DCM. ^e Measured in THF. ^f Calculated using B3LYP/6-31G*.

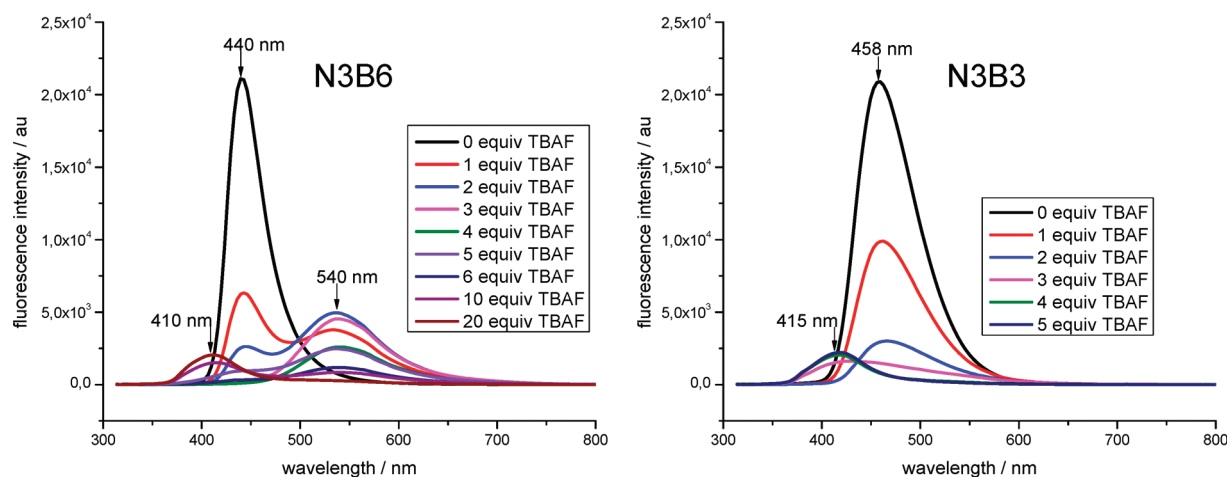


Figure 2. Changes in the emission spectra of compounds **N3B6** (1.3×10^{-5} M) and **N3B3** (1.3×10^{-5} M) in THF upon stepwise addition of TBAF solution. Excited at 370 nm.

Theoretical calculations on compounds **N3B6** and **N3B3** using density functional theory (B3LYP/6-31G*)¹⁸ indicated similar HOMO and LUMO orbital energies for both molecules and thus similar energy gaps. Although the calculated LUMO levels (−1.82 and −1.63 eV, respectively) are higher than the experimental values, there is good agreement between calculated HOMO levels (−5.19 and −5.10 eV, respectively) and experimental data (see Table 1).

In conclusion, we have synthesized and characterized the first multichromophore π -conjugated dendrimers bearing phenylene bridged boron and nitrogen moieties with different D-A ratio. Optical investigations revealed that changing the D-A ratio did not influence significantly the ground state

properties of the B–N containing dendrimers. In contrast, the excited state characteristics, such as emission wavelength can be tuned. In the case of a 1:1 ratio of D-A a more efficient charge transfer occurred as compared to a 1:2 ratio. As a result, a red shift of the emission bands and a stronger solvent dependence were observed for compound **N3B3**. Synthesized dendritic molecules will be further tested as materials for blue OLED and NLO. Synthesis of higher generations of dendritic structures is in progress.

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Supporting Information Available: Experimental procedures, characterization, and spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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