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Controlling the Charge Transfer in Phenylene-Bridged Borylene−Amine π-Conjugated Systems

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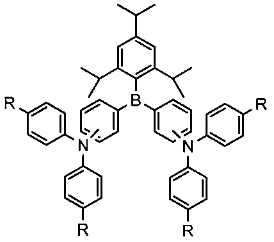
ABSTRACT



1p *para*-phenylene, R = Me
2p *para*-phenylene, R = OMe
1m *meta*-phenylene, R = Me
2m *meta*-phenylene, R = OMe

Novel boron−nitrogen-containing π-conjugated compounds 3,3′- and 4,4′-((2,4,6-triisopropylphenyl)borylene)bis(*N*,*N*-diarylbenzenamine) (1−2), *m*- and *p*-phenylene bridged to the boron center, respectively, have been synthesized and characterized. Optical studies by means of UV−vis absorption and emission measurements as well as DFT calculations reveal a different charge transfer behavior between the para series and the meta series at ground and excited states.

Boron-containing π-conjugated systems have recently attracted attention[1] due to their extensive applications in material science, e.g., as emission and electron conduction layers in organic light-emitting diodes (OLEDs),[2] fluoride sensors,[3] and in components for nonlinear optics.[4] The intriguing properties of boron-containing compounds, which include low-lying LUMO orbitals, ease of reduction, and a bathochromic shift of the absorption and emission spectra, result from the efficient overlap between an empty p orbital on the boron center and the π-conjugated framework. When an appropriate electron donor is in conjugation with a boron acceptor unit, an intense intramolecular charge transfer from the electron-rich moiety to the boron center occurs (Figure

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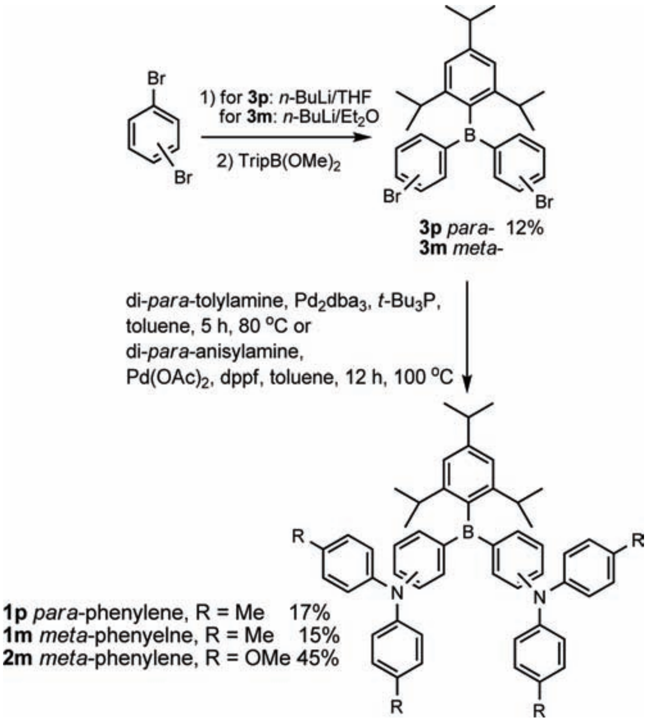
S1, Supporting Information).[2c] The electronic properties and the geometry of the linker have a significant impact on the optical characteristics of organoboron compounds. Yamaguchi et al.[5] showed that incorporation of a strong electron-donating group into boron-containing systems results in efficient charge transfer, and therefore a bathochromic shift in both absorption and emission spectra is observed. Recently, Wang et al.[6] investigated the absorption and emission spectra of linear boron- and nitrogen-containing molecules with different shape and conjugation type. This study revealed that the most efficient charge transfer was present in the linear system due to the conjugative interaction.

During our research into π-conjugated donor−acceptor triarylboron compounds,[7] we noticed a significant lack of systematic studies in terms of the effect of the position of the donor substituents with respect to the boron center. The change in the location of the donor moiety influences the properties of the resulting compounds, especially their charge transfer behavior. Such investigations offer a promising route to understanding the effects of conjugation in these systems, and thereby controlling the absorption and emission characteristics as well as the HOMO−LUMO gap of different oligomeric or polymeric donor−acceptor systems. To investigate the impact of the electronic properties of linkers and donors on the intramolecular charge transfer interaction in organoboron compounds, we studied model compounds 3,3′- and 4,4′-((2,4,6-triisopropylphenyl)borylene)bis(*N*,*N*-diarylbenzenamine) (**1**−**2**), which are *m*- (**1m**, **2m**) and *p*- (**1p**, **2p**) phenylene bridged to the boron center, respectively. Different amino groups were incorporated to probe the influence of the strength of the donor moiety on the optical properties of the resulting compounds. The charge transfer interaction between the amino center and the boron center was studied by means of UV−vis absorption and emission spectroscopy and density functional theory (DFT) calculations. Additionally, fluoride sensing properties were investigated.

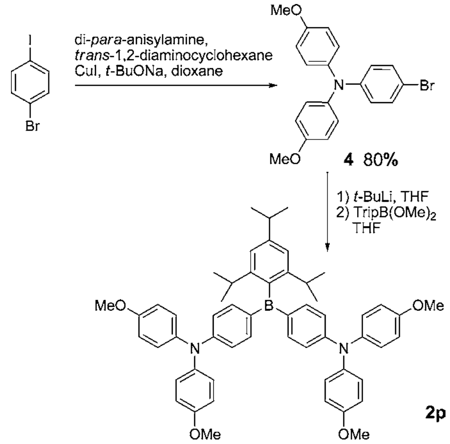
Bis(4-bromophenyl)-2,4,6-triisopropylphenylborane (**3p**) and bis(3-bromophenyl)-2,4,6-triisopropylphenylborane (**3m**) were obtained by treating commercially available 1,4- or 1,3-dibromobenzene with *n*-butyllithium (*n*-BuLi) followed by addition of dimethyl 2,4,6-triisopropylphenylboronate (TripB(OMe)$_2$),[8] respectively (Scheme 1). Surprisingly, different conditions had to be used to synthesize these two compounds. In the case of the para-substituted species (**3p**), halogen−metal exchange was completed after stirring at −78 °C in tetrahydrofuran (THF) for 1 h and the product was acquired as colorless crystals which were stable against air and moisture. For the meta-isomer **3m**, reaction at room temperature in diethyl ether was required and the product was obtained as a pale viscous oil after column chromatography.

Scheme 1. Syntetic Route for Compounds **1p**, **1m**, and **2m**



As shown in Scheme 1, compounds **1p**, **1m**, and **2m** were synthesized via Hartwig−Buchwald amination[9] of **3p** and **3m** with either di-*p*-tolylamine or di-*p*-anisylamine. Moreover, in this amination step, varying conditions were required. The meta-substituted compounds **1m** and **2m** were achieved with palladium(II) acetate and 1,1′-bis(diphenylphosphino)ferrocene (dppf) as the catalytic system.[10] Synthesis of compound **1p** was performed by using tris(dibenzylideneacetone)dipalladium (Pd$_2$dba$_3$) and tri-*tert*-butylphosphine (*t*-Bu$_3$P) as catalyst. It was not possible to synthesize **2p** via amination. To synthesize compound **2p**, an alternative approach was introduced as demonstrated in Scheme 2. The

Scheme 2. Synthetic Route for Compound **2p**



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first step involved the synthesis of bromo-substituted amine **4**.[11] This was treated with *tert*-butyllithium (*t*-BuLi), followed by addition of TripB(OMe)$_2$ to furnish the target compound **2p**.

Compounds **1**−**2** are yellow-greenish oils and well soluble in common organic solvents. Figure 1 shows UV−vis absorption and emission spectra of **1**−**2**. The optical band gap was calculated by using the onset of the absorption spectra. All four compounds exhibit two absorption bands around 295 and 400 nm, respectively. The former one can be identified as a band originating from the aromatic backbone, while the latter one is attributed to a charge transfer transition from the amino group to the boron center. To confirm this charge transfer interaction, titration experiments with fluoride ions were investigated, as F$^-$ can convert a boron center from an acceptor to a donor species.[7] Upon addition of tetrabutylammonium fluoride (TBAF) to the dichloromethane (DCM) solution of compound **1p**, the band at 397 nm disappeared and the intensity of the band at 295 nm significantly increased (Figure 2). This result indicates occupation of the empty orbital of the boron atom by F$^-$ and inhibition of the charge transfer from the nitrogen center to the boron center. This was further confirmed by an hypsochromic shift of 60 nm in the corresponding emission maximum after binding to F$^-$. The sensing behavior of the meta-substituted compound **1m** is almost the same (Supporting Information) as described for **1p**, which suggests that the B−N containing compounds **1**−**2** can be used as fluoride sensors.[4b,12]

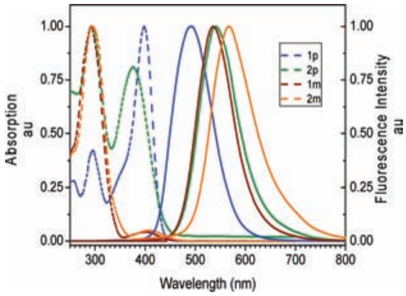

Figure 1. UV−vis absorption (dash lines) and emission (solid lines) spectra of compounds **1**−**2** in DCM.

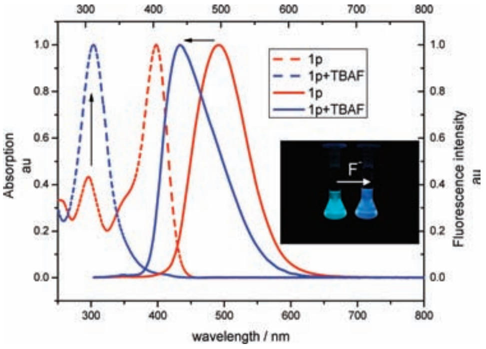

Figure 2. UV−vis absorption (dash lines) and emission (solid lines) spectra of compound **1p** (red) upon treatment with TBAF (blue) in DCM (1.3×10^{-5} mol/L). Inset photograph: Change of color of the DCM solution of **1p** upon treatment with TBAF. The flasks were illuminated with a hand-held UV lamp.

Interestingly, the relative intensity of the absorption bands around 295 and 400 nm changes dramatically upon changing the position of the donor substituents on the phenylene linkers at the boron moiety (Figure 1).

The much smaller intensity of the charge transfer band in the case of meta-substituted compounds **1m** and **2m** as compared to para-substituted compounds **1p** and **2p** can be attributed to the weaker donor−acceptor interactions in the ground states. This is a result of the position of substitution, since *m*-phenylene positioning of N relative to B interrupts the conjugation. Increasing the strength of the donor substituents in the meta-series, by introducing methoxy groups on the amine moieties (compound **2m**), resulted in only a small bathochromic shift in the absorption spectra (from 398 to 409 nm).

Much lower fluorescence quantum yields (Table 1) were observed for *m*-phenylene bridged compounds **1m** and **2m** compared to para-linked compound **1p**. This also can be attributed to the less efficient conjugation pathway.[6] Time-resolved fluorescence measurements revealed that compound **1p** has a lifetime of approximately 2 ns in hexane and a considerably longer lifetime in DCM due to the charge transfer character of the excited state. Compound **2m** in both hexane and DCM has a fluorescence lifetime that is on the order of tenths of nanoseconds indicating the much slower relaxation of the excited state due to the meta substitution.

Table 1. Photophysical Data for Compounds **1**−**2**

compd	abs λ_{max} (nm) (log ε)	optical band gap (eV)	emission λ_{max}(nm)	QY[b]
1p	295 (4.46)			
	397 (4.85)	2.86	492	0.40
2p	292 (−)[a]			
	376 (−)[a]	2.84	542	
1m	292 (4.88)			
	398 (3.51)	2.76	537	0.09
2m	295 (4.75)			
	409 (3.45)	2.67	568	0.06

[a] Pure sample obtained by analytical HPLC. [b] In cyclohexane.

In contrast to the very weak solvatochromism in the absorption spectra, the difference in emission spectra is

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significant (Figures S6−S9, Supporting Information).[13] Bathochromic shifts of 97, 86, 99, and 100 nm were observed for compounds **1p**, **2p**, **1m**, and **2m**, respectively, when the polarity of the solvent changed from hexane to acetonitrile. Such a remarkable bathochromic shift is characteristic for an efficient charge transfer from the nitrogen donor to the boron acceptor.[14]

One can notice a larger effect of solvatochromism for methoxy series (compounds **2p** and **2m**) (14 nm) than for the methyl one (**1p** and **1m**) (2 nm) probobly due to the strong donating character of methoxy groups. Comparison of the emission maxima of compound **1p** (492 nm) and compound **1m** (537 nm) in DCM (Figure 1) indicated a stronger charge transfer in the excited state in the case of meta substitution. This can be explained by the more electron-deficient character of the meta-substituted boron as compared to the para-substituted example. When a more electron-rich amine is introduced as in compound **2m**, a further bathochromic shift of 40 nm is observed compared with compound **1m**.

For a better understanding of the optical properties displayed by **1**−**2**, we have investigated the geometry and electronic structure of these molecules using density functional theory calculation (B3LYP/6-31G*).[15] Calculated HOMO and LUMO orbitals of compounds **1**−**2** are shown in Figure S11 in the Supporting Information. These calculations reveal that in all compounds the LUMO orbitals are localized on the boron subunit and the HOMO orbitals reside on the amine moieties. In contrast, the HOMO orbitals in compounds **1m** and **2m** are located on one and the HOMO-1 orbitals on the other donor subunit.[16] In all compounds the dihedral angles of the aryl rings attached to the boron are about 23°, which is in agreement with the results of Marder et al.[17] According to our calculations shown in Figure 3, the energies of HOMO and LUMO levels, and thus the energy gap, can be tuned simply by changing the position of the donor substituent in the boron−nitrogen system. Compound **2m** has the smallest calculated gap, although optical gaps are smaller than those calculated, in agreement with the experimentally observed trend for compounds **1**−**2**. In the case of meta-substituted compounds **1m** and **2m**, significant decreases of LUMO levels were observed compared to the corresponding para-substituted compounds **1p** and **2p**. This phenomenon is consistent with the stronger acceptor properties of boron in **1m** and **2m**, due to the weak electronic communication between the amine and boron centers.

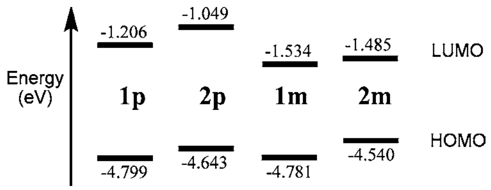

Figure 3. Calculated (B3LYP/6-31G*) energy levels for compounds **1**−**2**.

In conclusion, novel boron-containing donor−acceptor compounds **1**−**2** have been synthesized and characterized. UV−vis absorption and emission spectroscopic measurements as well as performed calculations confirm that (i) compounds **1p** and **2p**, with *p*-phenylene bridges, show much stronger charge transfer abilities at the ground state, due to a favorable position of substitution compared to the meta-series **1m** and **2m**, and (ii) compounds **1m** and **2m**, with *m*-phenylene bridges, possess stronger electron acceptor abilities in the excited states compared to **1p** and **2p** because the donor moiety cannot compensate for the electron-accepting character of the boron center. Additionally, fluoride sensing behavior of these compounds was proven by a strong hypsochromic shift of the emission spectra and disappearance of the charge transfer band in the absorption spectra upon treatment with F^-. Our studies offer an effective protocol to understand and control the conjugation effect, and therefore photophysical properties of different D−A systems.

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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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