

New azaborine-thiophene heteroacenes†

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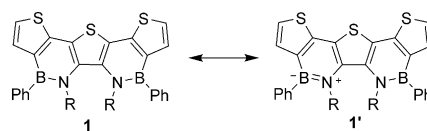
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A new class of heteroacenes containing B, N and S elements in the 22-electron aromatic nucleus has been synthesized by reaction of diaminoterthiophenes with dichlorophenylborane. Their structure was studied by X-ray crystallography and DFT calculations. UV-Vis absorption /emission spectroscopy shows high rigidity and deep-blue fluorescence of these compounds.

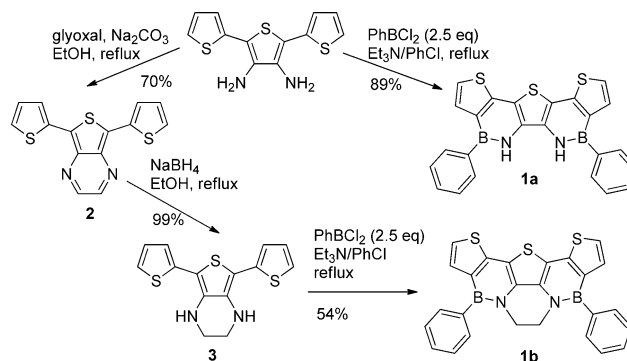
For several decades conjugated oligo- and polythiophenes have been extensively investigated as promising materials for organic electronics. A great number of conjugated thiophene derivatives has been synthesized and studied leading to materials with high charge and exciton mobility, tunable band-gap, high conductivity in the doped state, photochromic switching, *etc.*¹ For most of these derivatives, however, a relatively low luminescent efficiency limits their use in applications where light-emitting properties are required (*e.g.*, emissive diodes and transistors, fluorescent sensors).² From this perspective, thiophene derivatives incorporating boron atom, featuring an empty p-orbital are of particular interest due to strong electron-acceptor ability of boron and highly emissive properties of many of its derivatives. This offers a number of materials design opportunities, including non-linear optical chromophores,³ low band-gap polymers,⁴ ambipolar semiconductors,⁵ white-color⁶ and tunable light-emitters.⁷ Boron-containing conjugated materials have only started to be actively explored in the last 5–10 years.⁸ One of the reasons is that strong Lewis acidity (electrophilicity) of boron translates into chemical instability of organoboron compounds, which is an obvious drawback for materials application. The major approach to suppress this reactivity was steric screening of the boron atom, usually with crowded aryl substituents.⁸ A number of stable boron-contained oligothiophenes have been prepared in this way,^{3,5–10} although bulky substituents also suppress π -stacking in these materials, which is detrimental for charge mobility. Another possible approach to stabilize the boron center is through orbital interaction of the boron's empty orbital with a lone pair of an adjacent atom (such as nitrogen). Diazaborole-substituted¹¹ and *B,B*-diaminodiborine-fused¹² thiophenes that are stabilized by B–N interactions rather than steric substituents have been reported as stable compounds with photoluminescence quantum yield $\Phi_{PL} = 16$ –59%. Even

better stabilization can in principle be achieved by incorporating a BN fragment in an aromatic ring to form azaborines which are isoelectronic to corresponding polyaromatic hydrocarbons, but these are still few.¹³



Herein we describe synthesis, crystallographic, spectral and electrochemical properties of novel polycyclic 22-*e* aromatic compounds **1** consisting from alternating azaborine and thiophene rings. We note that related thienoazaborine¹⁴ and dithienoazaborine¹⁵ have been synthesized earlier but their properties were not reported.

Bis-azaborine **1a** was obtained with 89% yield by heating the known diaminoterthiophene with excess of PhBCl_2 in the presence of Et_3N (Scheme 1). The reaction most likely starts as an electrophilic borylation of the amino group to yield chloroaminoborane intermediate. The following intramolecular cyclization occurs with the neighboring thiophene ring to form an azaborine cycle rather than with the second amino group (which would give a diazaborole derivative). No diazaborole was formed even when strictly 1 equiv. of PhBCl_2 was used and the only isolated product was the corresponding mono-azaborine fused terthiophene (ESI†). As the strong expected acidity of N–H protons (consider resonance form **1'**) could be problematic for applications and further functionalization, we decided to protect them with an ethylene bridge which fits well between the two nitrogen centers and does not distort the planarity of the ring system. The required ethylenediaminoterthiophene **3** was prepared by reduction of the pyrazine **2** with NaBH_4 . Its borylation with excess of PhBCl_2 yields bis-azaborine **1b** with 54% yield. Both **1a** and **1b** showed thermal stability to ~ 300 °C in TGA.



Scheme 1 Synthesis of azaborines **1a** and **1b**.

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† Electronic supplementary information (ESI) available: Experimental part, quantitative fluoride binding experiments; TGA curves for **1a** and **1b**; copies of NMR spectra. CCDC 782155 and 782156. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc01963a

The molecular structures of azaborines **1a** and **1b** were studied by X-ray crystallography and density functional theory (DFT) calculations at B3LYP/6-311G(d,p) level. Azaborine **1a** crystallizes with two inequivalent molecules and includes the molecule of solvent (acetone) that is hydrogen-bonded to two NH sites ($N \cdots O$ distance 3.04 Å). The B–N length of the azaborine cycles in **1a** and **1b** (1.405–1.460 Å from X-ray, 1.43 Å from DFT) is similar to that of other azaborines¹³ and confirms a significant contribution of the zwitter-ionic form **1'**. According to DFT calculations, and in agreement with the structure of **1'**, there is a significant HOMO density on the boron atom (but none on the nitrogen) and significant LUMO density on the nitrogen (but none on the boron) (Fig. 1).

The introduction of azaborine moieties rigidifies the oligothiophene backbone: the molecules are almost planar with an angle between the planes defined by the terminal thiophene rings is 4.3° (twisting) and 7° (bending) for **1a** and **1b**, respectively. The two phenyl rings are out of the plane (dihedral angle 26–33° for **1a** and 51–56° for **1b**) which limits their conjugation with the polycyclic moiety. Both compounds form slipped π -stacks with alternating head-to-tail orientation (Fig. 2). No π – π interaction was observed between the phenyl substituents, either within or across the stacks. In the stack, the interplanar distances between the parallel terthiophene ring system is 3.47 Å and 3.62 Å for two unequivalent molecules of **1a**. For **1b**, the ethylene bridge causes some expansion of the π -stack and the molecules appear dimerized (interplanar distances of 3.58 Å and 3.83 Å).

The rigidity and efficient conjugation in azaborines **1** explains a relatively low reorganization energy λ for the transfer of the hole, which, together, with π -stacking, in an important attribute of an efficient semiconductor. At B3LYP/6-311G(d,p) level of theory azaborine **1b** shows $\lambda = 0.27$ eV, which is lower than that of linear and *S*-fused oligothiophene (thienoacenes) of a similar size.¹⁶ While device fabrication with **1a** and **1b** was hampered by poor film-forming properties, this should not be an issue for corresponding polymers.

UV-Vis absorption spectra of azaborines **1a** and **1b** shows vibronically splitted bands, yet another indication of their structural rigidity. The spacing between the vibronic features (~ 1470 cm⁻¹) corresponds well to the thiophene C–C vibrations. The ethylene bridge in **1b** does not significantly affect the electronic structure and both compounds display almost identical absorption spectra. The λ_{abs} (395 and 397 nm for 0–0 transition of **1a** and **1b**, respectively, Table 1) is red-shifted compared to the non-fused terthiophene ($\lambda_{\text{abs}} = 354$ nm) and an *S*-bridged analogue pentathienoacene ($\lambda_{\text{abs}} = 357$ nm).¹⁷ The optical gaps deduced from the absorption maxima (3.14 and 3.12 eV for **1a** and **1b**, respectively) are somewhat smaller

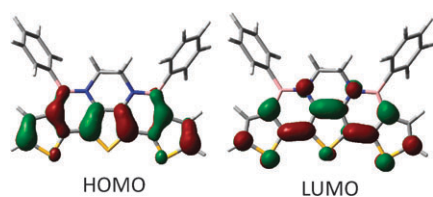


Fig. 1 Calculated HOMO/LUMO topologies of **1b**.

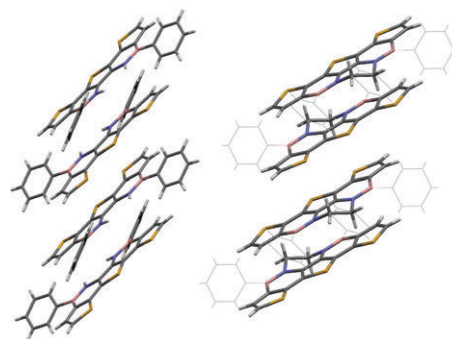


Fig. 2 Solid state packing of azaborines **1a** (left) and **1b** (right).† The solvating molecules of acetone are removed from the structure of **1a** and the Ph rings in **1b** are dimmed for clarity.

than gas-phase calculated HOMO–LUMO gaps (3.55 and 3.53 eV, respectively).

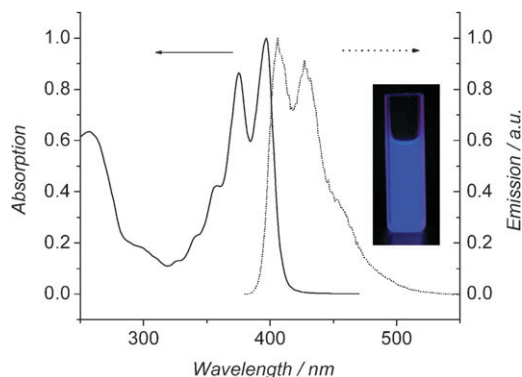
The compounds **1a** and **1b** exhibit deep-blue photoluminescence at $\lambda_{\text{max}} = 407$ –410 nm, with $\Phi_{\text{PL}} = 25$ –34% (Fig. 3, Table 1). This is a moderately high value in thiophene series. High rigidity of the azaborinethiophenes is further manifested in a small Stokes shift of ~ 0.1 eV which is much smaller than that of non-fused terthiophene (0.64 eV) and even sulfur-bridged pentathienoacene (0.28 eV).¹⁷ Together with insignificant solvatochromism (λ_{max} shift of < 3 nm for solvents range from CHCl_3 to acetonitrile), this also suggests that there is no significant charge transfer upon excitation.

Redox properties of azaborines **1a** and **1b** have been studied by cyclic voltammetry (ESI†). Both compounds undergo irreversible electrochemical oxidation with anodic peak potential E_{pa} at 0.48 V vs. Fc/Fc^+ . This is *ca.* 0.2 V more positive than the oxidation of diaminoterthiophene,¹⁸ in line with the electron withdrawing effect of boron. The HOMO energy, estimated from the redox potential at -5.3 eV (assuming Fc/Fc^+ at -4.8 eV), is in a good agreement with DFT calculated values (Table 1). In accord with the HOMO–LUMO gap, no reduction processes were observed. The electron-donating ethylene bridge in **1b** does not significantly affect its oxidation potential, which is consistent with the HOMO located on the boron rather than on the nitrogen.

The intramolecular Lewis acid–base interaction in **1a,b** (represented by the resonance structure **1'**) reduces the electrophilicity of the boron stabilizing the structure. No complexation was detected with weak or moderate Lewis bases, *e.g.* H_2O , THF, amines, Cl^- , Br^- , I^- , OH^- or OCH_3^- . A specific binding of the fluoride ion, characteristic of boronic derivatives,¹⁹ was, nevertheless, found in absorption and emission spectra (Fig. 4). Adding Bu_4NF to solutions **1b** leads to appearance of a long-wavelength absorption band at 470 nm and extenuates of the original absorption at ~ 400 nm. Two isosbestic points at 408 nm and 353 nm observed throughout the titration, even when a very large excess of F^- is added, indicate a clear transformation between the **1b** and one single product.‡ Expectedly, the binding constant $\log K_{\text{a}} = 3.3 \pm 0.1$ (in CH_2Cl_2) is lower than that of triarylboranes without electronic stabilization of the empty orbital (*e.g.* $\log K_{\text{a}} = 6.3$ for dithienylmesitylborane in CH_2Cl_2).¹⁹ The fluoride adduct is also characterized by a pronounced red-shifted emission band at 540 nm. The fluorescence change from blue to green

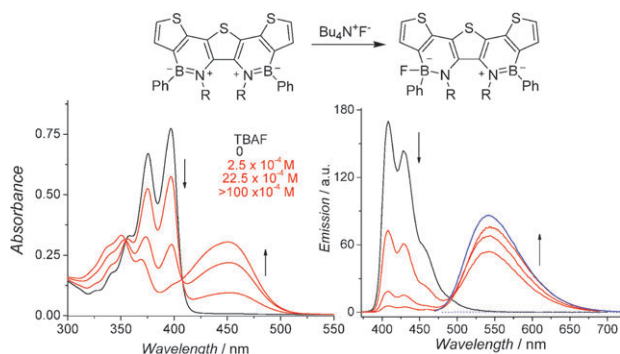
Table 1 Electronic properties of azaborines **1a** and **1b**

	$\lambda_{\text{abs}}/\text{nm}$ (log ϵ)	$\lambda_{\text{em}}/\text{nm}$	Φ_{PL} [%]	HOMO/eV electrochem (<i>calc</i>)	E_{g}/eV opt (<i>calc</i>)
1a	395 (4.58)	407	34	-5.3 (-5.42)	3.14 (3.55)
1b	397 (4.74)	410	25	-5.3 (-5.36)	3.12 (3.53)

**Fig. 3** UV-Vis absorption and emission spectra of **1b**.

color can be easily observed with a naked eye. Fluoride addition can also be monitored by ^{11}B NMR causing chemical shift change from 34 ppm to 4 ppm due to formation of tetracoordinate boron center. Fluoride sensing by conjugated boron derivatives is not rare, most of these undergo a *blue* shift of the absorbance and quenching of the fluorescence.²⁰ A pronounced *red*-shifted absorbance and emission observed for our azaborines **1**, is more desirable for high sensitivity detection. § If excited at 450 nm, the system can be used as “off-on” sensor since the emission occurs only upon addition of F^- .

In conclusion, we have synthesized novel deep-blue emissive fused azaborine-thiophenes through a facile borylation reaction. The method should be applicable to other amino-substituted oligothiophenes paving a way to a new class of π -functional

**Fig. 4** Absorption (left, [**1b**] = 3.1×10^{-5} M) and emission (right, [**1b**] = 4×10^{-6} M) spectra of **1b** in CH_2Cl_2 upon addition of Bu_4NF ($\lambda_{\text{exc}} = 356$ nm (red) or 458 nm (blue)).

aromatic molecules and polymers. An interaction of the boron empty orbital with the lone pair of the nitrogen suppresses the Lewis acidity of the former, leading to increased stability of these materials. This interaction is confirmed by X-ray crystallography and DFT calculations. Planarity and rigidity of azaborine-fused oligothiophenes as well as π -stacking ordering in the solid state make them potential candidates for semiconducting applications.

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Notes and references

‡ Prolonged (more than a few minutes) exposure to air leads to oxidation of the fluoride addition product resulting in radical species. It is, however, completely stable in the nitrogen atmosphere.
§ A weaker red-shift upon F^- addition was previously reported for boryl-substituted dithienophospholes.⁹

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