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Synthesis and optical properties of novel unsymmetrically substituted benzothiadiazole-based luminophores

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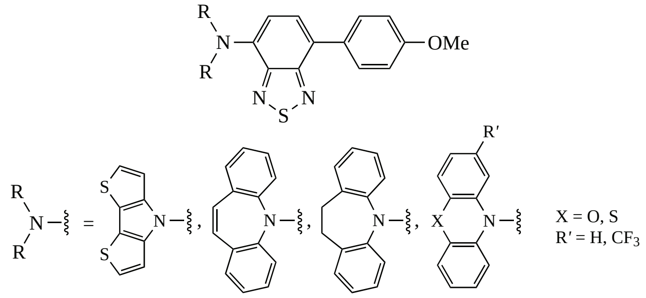
New unsymmetrically substituted benzothiadiazoles were synthesized from 4,7-dibromo-2,1,3-benzothiadiazole *via* the sequence of Pd-catalyzed Suzuki and Buchwald–Hartwig cross-coupling reactions with 4-methoxyphenylboronic acid and heterocyclic amines, respectively. Based on initially performed photophysical study as well as DFT calculation, these compounds, in particular with dibenzoazepine core, can be selected as promising scaffolds for further fine-tuning of their properties to be used in optoelectronics including OLED technologies.



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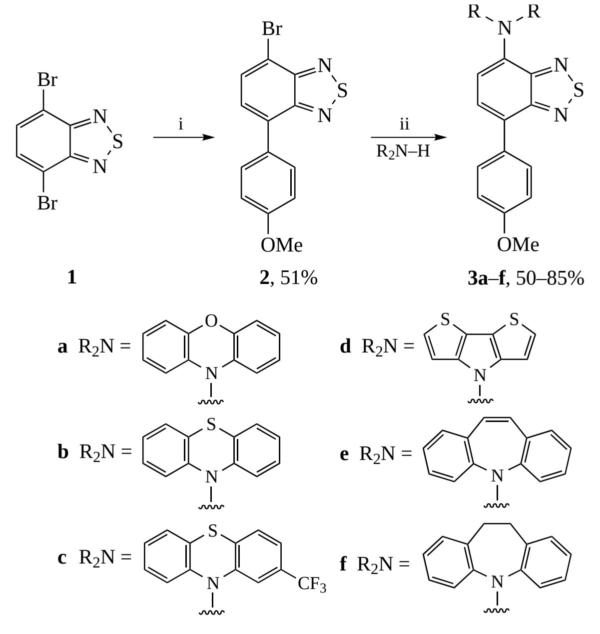
During the past decade, 4,7-disubstituted 2,1,3-benzothiadiazole (BTD) derivatives with extended π-conjugation owing to their outstanding electron affinity,[1] carrier transport abilities, thermal and chemical stabilities have been extensively studied as privileged scaffolds for the construction of different opto-electronic devices, *e.g.*, organic light emitting diodes (OLEDs),[2] field effect transistors (OFETs),[3] solar cells (OSCs),[4] bioprobes,[5] and chemsensors.[6] Despite prominent advances highlighting the great potential of these compounds, particularly attention is focused on direct substitution at the 4,7-positions with amino groups to afford unsymmetrical BTDs of donor–acceptor type. The most promising examples of such molecules were designed for dye-sensitized solar cells with an apparent increase in the power conversion efficiency[7] and for thermally activated delayed fluorescence (TADF) emitters with high external quantum efficiency.[8] Taking into account the fact that electronic and steric nature of substituents at positions 4 or/and 7 can dramatically affect performance and photophysical properties of the target molecules, herein we report on the synthesis of a series of novel unequally substituted BTD derivatives with phenoxazine, phenothiazine, dithienopyrrole and dibenzazepine as electron donor units as well as our initial investigation on their photophysical characteristics to estimate a potential application of these compounds in materials science.



Scheme 1 *Reagents and conditions*: i, 4-$MeOC_6H_4B(OH)_2$ (1 equiv.), $NaHCO_3$ (3 equiv.), 1,4-dioxane/water (3 : 1), $Pd(PPh_3)_2Cl_2$ (1 mol%), reflux, 24 h; ii, $R_2N–H$ (1.05 equiv.), $Pd(OAc)_2$ (5 mol%), RuPhos (10 mol%), Bu^tONa (1.5 equiv.), 1,4-dioxane, 100 °C, 24 h.

A synthetic route from commercially available 4,7-dibromo-2,1,3-benzothiadiazole **1** (Scheme 1) to the amino BTDs **3a–f** included a sequence of two Pd-catalyzed cross-coupling reactions. The first step, Suzuki mono-coupling of dibromide **1** with 4-metoxyphenylboronic acid, was accomplished by slightly modified procedure previously described for selective formation of monobromide **2**[9] under catalysis with significantly reduced

Table 1 Photophysical properties of compounds **3a**–**f**.

Compound	λ_{max}^{abs}/nm	λ_{max}^{PL}/nm	φ_{PL} (%)
3a	383	480	0.2
3b	384	540	0.1
3c	385	530	0.5–1
3d	437	542	2–3
3e	455	587	26–33
3f	467	591	32–40

amount of Pd-complex. For the next Buchwald–Hartwig coupling of compound **2** with selected cyclic amines, the combination of 5 mol% Pd(OAc)$_2$, 10 mol% RuPhos (2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl) and 1.5 equiv. Bu^{t}ONa has proved to be the most effective catalytic system among tested.

All compounds **3a**–**f** were isolated by flash chromatography on silica gel and additionally purified by sublimation (200–220 °C/0.1 Torr). Their structures were proved by ^{1}H NMR, ^{13}C NMR and HRMS (see Online Supplementary Materials).

Photoluminescent properties of compounds **3a**–**f** are summarized in Table 1. The optical spectra were recorded for nondeaerated 0.2–20 μM solutions in toluene at room temperature (see Online Supplementary Materials, Figures S1–S6). The fluorescence quantum yield was estimated by Parker–Rees method. Rhodamine B in ethanol solution (Q = 65–70%) was chosen as a standard.[10]

All compounds exhibit intense absorption bands at 383–467 nm and fluorescence emission in the green-yellow region (480–591 nm). Figure 1 shows the absorption and emission spectra for compound **3f**. Surprisingly, the phenoxazine, phenothiazine and dithienopyrrole derivatives **3a**–**d** showed very low quantum yields (0.1–3%). In contrast, the benzoazepine compounds **3e**,**f** have rather high fluorescence efficiency, with the best quantum yield being 40% for **3f**.

To make spectral assignments, we calculated the electronic absorption spectra and the frontier molecular orbitals using the TD-DFT method at the B3LYP/DZP level. Earlier we showed that B3LYP is the best exchange correlation functional for estimation of the differences in energy between the frontier orbitals of organic dyes.[11] The calculated absorption bands for all studied compounds are only 10–40 nm differ relative to experimental values (Table 2). In the case of the dibenzoazepine (**3e**) and dihydrodibenzoazepine (**3f**) derivatives, the most intense absorption band corresponds to the π → π* transition, which is formed by HOMO → LUMO orbitals. Both these frontier orbitals are mainly located at the benzothiadiazole moiety (see Online Supplementary Materials, Figure S7). In contrast, in the case of phenoxazine (**3a**) and phenothiazine (**3b**,**c**) compounds, HOMO is located at the phenoxazine and phenothiazine fragments, while LUMO remains at the benzothiadiazole. However, the band corresponding to this charge transfer transition has very low intensity because of the absence of conjugation between cyclic moieties in these compounds (for example, the dihedral angle phenoxazine/benzothiadiazole in molecule of **3a** is 86.4°). Therefore, for compounds **3a**,**b** the most intense absorption band is provided by HOMO−1 → LUMO transition, where the HOMO−1 orbital is mainly located at benzothiadiazole and 4-methoxyphenyl substituent. The introduction of the CF$_3$ group into the phenothiazine moiety leads only to a slight bathochromic shift of the most intense band and the increase of the HOMO–LUMO gap by 0.08 eV. Dithienopyrrole derivative **3d** exhibits closely related photophysical behavior involving HOMO−1 and HOMO−2 to the main transitions instead of HOMO.

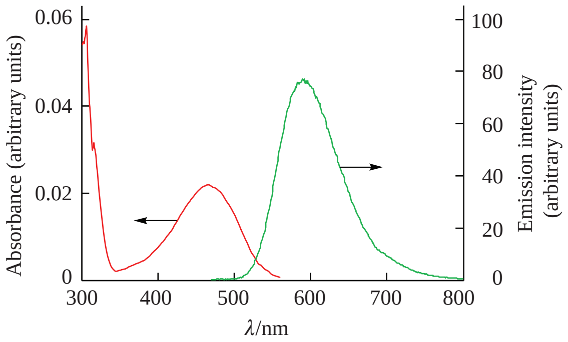


Figure 1 The absorption and emission spectra of compound **3f** in toluene ($C = 0.2\times10^{-5}$ M, λ_{ex} = 460 nm, 20 °C).

Table 2 General analysis of the absorption bands by TD DFT calculations at the B3LYP/DZP level.

Compound	Experimental absorption maxima/nm	Calculated absorption maxima/nm	Calculated oscillator strengths	Main MOs responsible for excitation[a]
3a	383	413	0.179106	HOMO–1 → LUMO (99%)
		665	0.000579	HOMO → LUMO (99%)
3b	384	408	0.185355	HOMO–1 → LUMO (99%)
		571	0.004237	HOMO → LUMO (99%)
3c	385	413	0.191621	HOMO–1 → LUMO (99%)
		549	0.007352	HOMO → LUMO (99%)
3d	437	399	0.070450	HOMO–2 → LUMO (99%)
		479	0.141245	HOMO–1 → LUMO (99%)
		528	0.000678	HOMO → LUMO (100%)
3e	455	403	0.003554	HOMO → LUMO + 1 (98%)
		446	0.15404	HOMO → LUMO (98%)
3f	467	334	0.004909	HOMO–1 → LUMO (99%)
		450	0.16546	HOMO → LUMO (98%)

[a] Values in parentheses give the percentage contribution of the corresponding orbitals to the total transition.

Noteworthy, according to DFT calculations, the heterocyclic moieties in all studied compounds are not coplanar that prevents its conjugation. It can be explained by the sterical hindrance between these moieties due to its bulkiness and close proximity. We propose that the addition of acetylene or phenyl spacer between them should prominently improve photophysical properties of the final compounds.

In conclusion, an efficient scheme for the preparation of a series of new unsymmetrically substituted benzothiadiazoles has been elaborated *via* sequence of two Pd-catalyzed cross coupling Suzuki and Buchwald–Hartwig reactions. Based on our results, these compounds, in particular with dibenzoazepine core, can be selected as promising scaffolds for further fine-tuning of their properties to be used in optoelectronics including OLED technologies.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.01.009.

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