# 1,3,5,2-OXADIAZABORININES AS A CLASS OF FLUORESCENT ORGANOBORON DYES

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***Abstract.*** *Organoboron complexes are one of the most investigated class of fluorescent dyes. Among them, 1,3,5,2-oxadiazaborinines, due to their unsymmetric structures, exhibit relatively large values of Stokes shift, which is attractive for optoelectronic applications of such compounds. The synthesis of oxadiazaborinines fluorescent dyes is based on the use of amide ligands, formed from different nitrogen-containing 2-aminoheterocycles (amidopyrazines, naphthyridine-2-amines, 2-aminopyridines, 2-aminopyridazines, 2-aminopyrimidines, 2-aminothiadiazoles, 2-aminothiazoles, and benzo[d]thiazol-2-amines). Among heteroaryl-fused oxadiazaborinines, (benzo)thiazolo[3,2-c][1,3,5,2]oxadiazaborinines demonstrate a remarkable chemical stability and can be efficiently postfunctionalized by organolithium-mediated electrophilation or Pd-catalysed cross-coupling reactions.*

**Contents**



## 1. Introduction

Tetracoordinated organoboron complexes are one of the most important and widely used class of fluorescent dyes.[1] These compounds demonstrate practically useful electronic and optical properties (*e.g.* strong absorption bands in UV-VIS-NIR regions, high fluorescent quantum yields, photostability, relatively long excited-state lifetime, good solubility in common organic solvents, insensitivity to the environment).[2] As a result, they can serve many application areas, such as fluorescent probes,[3-15] photosensitizer in photodynamic therapy,[16-19] photoactive element in organic solar cells (OSC),[20-24] and supramolecular systems[25-31], emitter in optoelectronic devices,[32,33] cholesteric liquid crystal laser,[34] etc.

Currently, the most investigated organoboron fluorescent dyes are boron-dipyrromethene (BODIPY) derivatives, which are based on di-pyrrolo annulated 1,3,2-diazaborine scaffold.[3,35] However, despite the intensive fluorescence of BODIPYs in solutions, they usually demonstrate narrow Stokes shifts, which limits their optoelectronic applications.[1] To tackle this scientific challenge, in the last few years, modification of BODIPY core was the subject of great research interest. Therefore, organoboron complexes, including other than pyrrole heterocyclic units annulated to 1,3,2-diazaborinine **II**,[36-38] as well as, 1,2-azaborinine **I**,[39] and 1,3,5,2-triazaborinine **III**[40-45] ring, have been developed (Figure 1). Another class of six-membered ring organoboron complexes has been synthesized from *O*,*O*-chelating ligands, forming 1,3,2-dioxaborinine derivatives **IV**.[46-50]

One of the factors that leads to increasing the Stokes shift of the organoboron complexes is unsymmetrisation of the ligand structures.[1] In this context, complexes with hybrid ligands, having simultaneously nitrogen and oxygen coordinating centres, look very attractive. Organoboron dyes, based on 1,3,2-oxazaborinine **V** scaffold, have been widely investigated as complexes formed from $\beta$-ketoiminate[51-55] and phenolic[56-63] ligands. On the other hand, over the last decade, it was also elaborated the generation of 1,3,5,2-oxadiazaborinines **VI**, formed from amide ligands, as the novel class of fluorescent organoboron dyes.

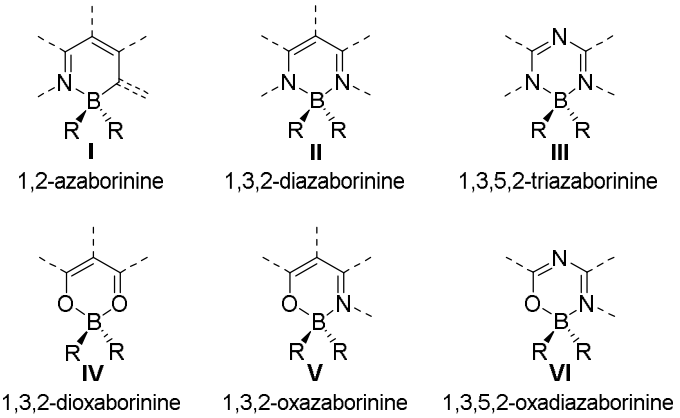
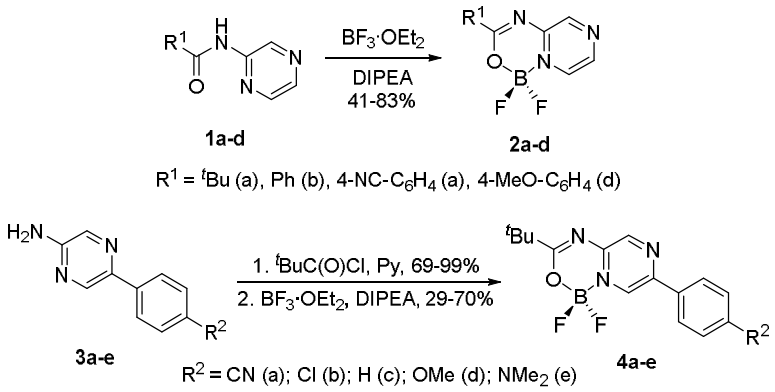



**Figure 1.** Six-membered ring organoboron complexes.

In this review, the synthesis of 1,3,5,2-oxadiazaborinine derivatives will be described and their photophysical properties will be analysed and compared.

## 2. Pyrazino[1,2-*c*][1,3,5,2]oxadiazaborinines

The first example of 1,3,5,2-oxadiazaborinine dyes was published in 2010 by Hirano and co-workers.[64] They demonstrated that treatment of amidopyrazines **1a-d** with boron trifluoride etherate ($BF_3 \cdot OEt_2$) in the presence of *N*,*N*-diisopropylethylamine (DIPEA) at room temperature gave pyrazino[1,2-*c*][1,3,5,2]oxadiazaborinines **2a-d** in 41-83% yield (Scheme 1). Compound **2a** with *tert*-butyl group at position C-8 exhibited absorption spectra with lower energy maximum ($\lambda_{abs}$) at 332 nm and molar absorption coefficient (ε) of 8600 $M^{-1}cm^{-1}$ in diluted cyclohexane solutions (Table 1). It exhibited single emission peak, maximized at 384 nm. The change of *tert*-Bu group on aromatic substituents (dyes **2b-d**) resulted in an increase of the value of ε and bathochromic shift in the absorption and emission spectra. Compounds **2b,c** with phenyl and *p*-cyanophenyl substituents demonstrated very similar absorption and emission profile ($\lambda_{abs}$=351 nm; $\lambda_{em}$=398, 404 nm). Meanwhile, the incorporation of *p*-methoxyphenyl substituent (dye **2d**) caused the more significant bathochromic shifts ($\lambda_{abs}$=382 nm; $\lambda_{em}$=429 nm). Moreover, donor effect of methoxy group in compound **2d** caused a positive solvatofluorochromism (*e.g.* in MeCN, $\lambda_{em}$=478 nm), which was not observed for compounds **2a-c**. The cyclohexane solutions of dyes **2a-d** showed weak to moderate fluorescent quantum yield (Φ) ranging from 0.013 (for cyano-derivative **2c**) to 0.29 (for methoxy analogue **2d**).




**Scheme 1.** Synthesis of pyrazino-oxadiazaborinines **2a-d** and **4a-e**.

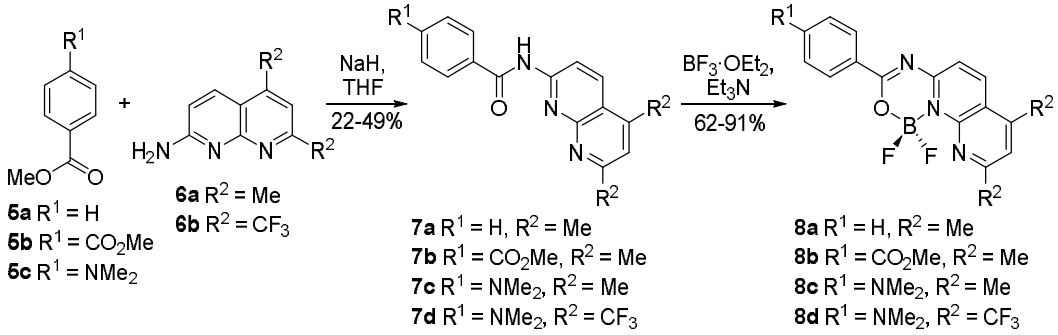
Hirano's group also explored the pyrazino[1,2-*c*][1,3,5,2]oxadiazaborinine class with the aromatic substituents at the pyrazine ring using the amines **3a-e**: after two-step transformation, the corresponding products **4a-e** were obtained (Scheme 1).[65] The introduction of aromatic group resulted the bathochromic shift in the lower energy absorption band and fluorescent spectra, compared with those of unsubstituted analogue **2a**. Derivatives **4a-c** with phenyl, *p*-chlorophenyl and *p*-cyanophenyl substituents exhibited similar spectroscopic properties ($\lambda_{abs}$=354-366 nm; $\lambda_{em}$=411-420 nm in diluted cyclohexane solutions), while the incorporation of the electron-donating groups (OMe and $NMe_2$) effectively affected the corresponding data ($\lambda_{abs}$=384 and 442 nm; $\lambda_{em}$=470 and 494 nm for dyes **4d** and **4e**, respectively) (Table 1).

**Table 1.** Absorption and emission properties of pyrazino[1,2-*c*][1,3,5,2]oxadiazaborinines **2a-d** and **4a-e**.

| Dye | Solvent | $\lambda_{abs}$, nm | ε, $M^{-1}cm^{-1}$ | $\lambda_{em}$, nm | Stokes shift, nm | Φ |
|---|---|---|---|---|---|---|
| **2a** | cyclohexane | 332 | 8600 | 384 | 52 | 0.078 |
| **2b** | cyclohexane | 351 | 26000 | 398 | 47 | 0.18 |
| **2c** | cyclohexane | 351 | 20000 | 404 | 53 | 0.013 |
| **2d** | cyclohexane | 382 | 30000 | 411 | 29 | 0.29 |
| **2d** | MeCN | 363 | 29000 | 478 | 115 | 0.062 |
| **4a** | cyclohexane | 354 | 21000 | 411 | 57 | 0.27 |
| **4b** | cyclohexane | 366 | 19000 | 420 | 54 | 0.28 |
| **4c** | cyclohexane | 363 | 17000 | 414 | 51 | 0.25 |
| **4d** | cyclohexane | 382 | 18000 | 470 | 88 | 0.34 |
| **4d** | MeCN | 379 | 18000 | 511 | 132 | 0.52 |
| **4e** | cyclohexane | 442 | 14000 | 494 | 52 | 0.70 |
| **4e** | $CHCl_3$ | 443 | 13000 | 611 | 168 | 0.08 |

### 3. [1,3,5,2]Oxadiazaborinino[3,4-*a*][1,8]naphthyridines

Subsequently, Fu and co-workers used naphthyridine building block for the construction of oxadiazaborinine-fused molecules. Reaction of esters **5a-c** with naphthyridine-2-amines **6a,b** under basic conditions gave amides **7a-d** in moderate (22-49%) yields. Condensation of ligands **7a-d** with $BF_3{\cdot}OEt_2$ in the presence of triethylamine ($Et_3N$) gave organoboron complexes **8a-d** in good (62-91%) yields (Scheme 2). Naphthyridine-fused oxadiazaborinine **8a** showed bathochromic shifted absorption maximum ($\lambda_{abs}$=384 nm, Table 2), compared with pyrazine-fused analogue **2b** ($\lambda_{abs}$=351 nm), which caused smaller value of Stokes shift (8 and 47 nm for compounds **8a** and **2b**, respectively). The presence of acceptor substituent at phenyl side ring (dye **8b**) did not make significant influence on the photophysical properties of such compounds. On the other hand, the incorporation of a donor ($Me_2N$) group in that position (compounds **8c,d**) changed the properties. Compound **8c** demonstrated bathochromic shift in both absorption and emission spectra as well as higher Stokes shift (97 nm) and decreased Φ. The change of two methyl groups at naphthyridine moiety on trifluorometyls resulted in structure **8d** with strong *push-pull* properties: $\lambda_{abs}$=480 nm, $\lambda_{em}$=642 nm, Stokes shift 162 nm, Φ<0.01 (Table 2).[66]



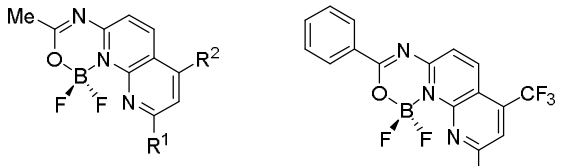

**Scheme 2.** Synthesis of [1,3,5,2]oxadiazaborinino[3,4-*a*][1,8]naphthyridines **8a-d**.

Additionally, this research group synthesised compounds **9a–d** with methyl substituents at the oxadiazaborinine ring.[55] These dyes exhibited relatively low fluorescent quantum yields (0.02-0.20), except analogue **9d** (Φ=0.98) (Table 2).

**Table 2.** Optical properties of compounds **8a-d**, **9a-d**, **10a-d**, **11a-g**, and **12a,b** in dichloromethane.

| Dye | $\lambda_{abs}$, nm | ε, $M^{-1}cm^{-1}$ | $\lambda_{em}$, nm | Stokes shift, nm | Φ |
|---|---|---|---|---|---|
| **8a** | 366, 384 | 36870, 41200 | 392 | 8 | 0.54 |
| **8b** | 370, 389 | 32010, 30230 | 397 | 8 | 0.20 |
| **8c** | 313, 440 | 15460, 63030 | 527 | 97 | 0.22 |
| **8d** | 355, 480 | 21190, 41050 | 642 | 162 | <0.01 |
| **9a** | 344, 361 | 23930, 30740 | 384 | 23 | 0.02 |
| **9b** | 343, 360 | 19100, 23250 | 383 | 23 | 0.03 |
| **9c** | 345, 362 | 27600, 34550 | 385 | 23 | 0.20 |
| **9d** | 365, 382 | 29250, 31500 | 408 | 25 | 0.98 |
| **10a** | 374, 392 | 15571, 17564 | 452 | 60 | 0.129 |
| **10b** | 382, 400 | 12337, 13327 | 455 | 55 | 0.109 |
| **10c** | 374, 394 | 18127, 16564 | 454 | 60 | 0.116 |
| **10d** | 402, 418 | 13415, 18139 | 457 | 39 | 0.168 |
| **11a** | 389, 410 | 10965, 13489 | 419, 443 | 9 | 0.183 |
| **11b** | 389, 410 | 16218, 20417 | 432, 451 | 22 | 0.495 |
| **11c** | 372, 391 | 13804, 15849 | 403, 423 | 12 | 0.421 |
| **11d** | 352, 367 | 8913, 9772 | 392, 410 | 25 | 0.277 |
| **11e** | 427 | 18197 | 489 | 62 | 0.519 |
| **11f** | 389, 410 | 6760, 7.943 | 422, 442 | 12 | 0.302 |
| **11g** | 408, 430 | 17783, 22387 | 465 | 35 | 0.256 |
| **12a** | 427 | 16596 | 624 | 197 | 0.620 |
| **12b** | 396, 417 | 6310, 7413 | 637 | 220 | 0.542 |

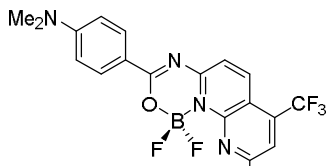
Bonacorso and co-workers expanded the library of [1,3,5,2]oxadiazaborinino[3,4-*a*][1,8]naphthyridines with the $CF_3$ substituent at position 7 of the naphthyridine unit (Figure 2). Such complexes were synthesized from corresponding 2-aminonaphthyridines by acylation reaction and following complexation of the formed amides with $BF_3 \cdot OEt_2$. Complexes **10a-d** exhibited single blue emission light ($\lambda_{em}$=452-457 nm) in chloroform with moderate fluorescent quantum yields (Φ=0.109-0.168).[67] This indicates the bathochromic emission shifts and slight increase of the fluorescence efficiency, compared with the emission of analogous **9a-c** (Table 2).



**9a** $R^1 = R^2 = Me$
**9b** $R^1 = Me$, $R^2 = H$
**9c** $R^1 = Cl$, $R^2 = H$
**9d** $R^1 = OH$, $R^2 = H$
**10a** $R^1 = Ph$, $R^2 = CF_3$
**10b** $R^1 = 4\text{-}CH_3\text{-}C_6H_4$, $R^2 = CF_3$
**10c** $R^1 = 4\text{-}F\text{-}C_6H_4$, $R^2 = CF_3$
**10d** $R^1 = 2\text{-thienyl}$, $R^2 = CF_3$



**15a-g** $R^1$
**11a** $R^1 = Ph$
**11b** $R^1 = 4\text{-}CH_3\text{-}C_6H_4$
**11c** $R^1 = 4\text{-}F\text{-}C_6H_4$
**11d** $R^1 = 4\text{-}Br\text{-}C_6H_4$
**11e** $R^1 = 4\text{-}MeO\text{-}C_6H_4$
**11f** $R^1 = 4\text{-}O_2N\text{-}C_6H_4$
**11g** $R^1 = 2\text{-thienyl}$

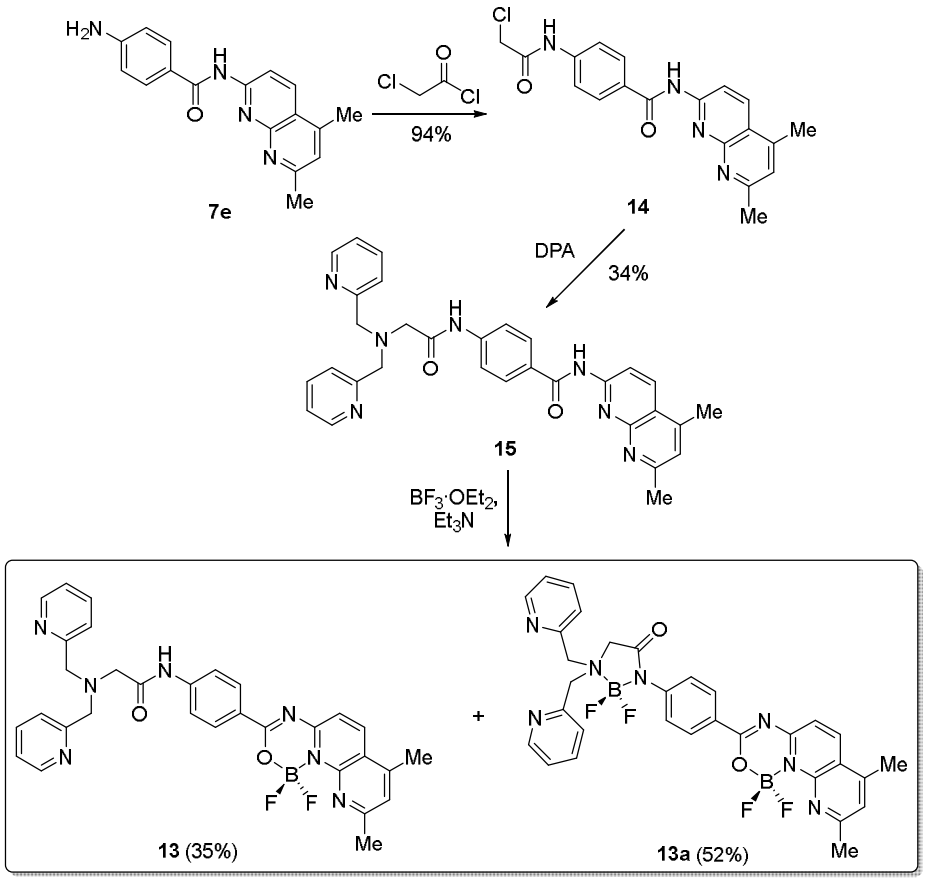


**12a** $R^2 = OMe$
**12b** $R^2 = NO_2$

**Figure 2.** [1,3,5,2]Oxadiazaborinino[3,4-*a*][1,8]naphthyridines **10a-d**, **15a-g**, and **12a,b**.

The change of methyl onto phenyl substituents at amide side of molecular scaffold provided complexes **11a-g**, which exhibited hypsochromically shifted double-band emission. Furthermore, *push-pull* analogous **12a,b** with *para*-dimethylaminophenyl substituents at the oxadiazaborinine side and donor (4-$MeOC_6H_4$) or acceptor (4-$O_2NC_6H_4$) substituents at position 7 of the naphthyridine ring demonstrated a large Stokes shifts (197 and 220 nm, respectively) in dichloromethane with relatively good fluorescent quantum yields (62/54%, Table 2).[68] Besides, dye **12b** demonstrated largest two-photon absorption cross-sections of 268 GM at 990 nm.[69]

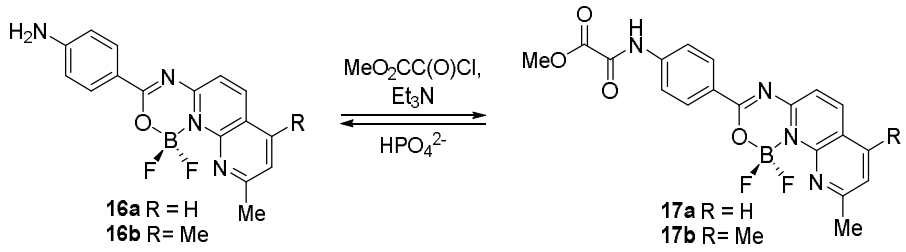
Based on the previous results, Fu's group developed amide-containing di-2-picolylamine (DPA) receptor **13**. The synthesis of compound **13** is shown in Scheme 3. Acylation reaction of amine **7e** with chloroacetic chloride gave compound **14** in 94% yield, which was converted into ligand **15** (in 34% yield) *via* interaction with DPA. Finally, treatment of compound **15** with $BF_3{\cdot}OEt_2$ in the presence of $Et_3N$ gave mixture of complexes **13** and **13a** in 35 and 52% yields, respectively. Compound **13** demonstrated complexing ability with $Pd^{2+}$, $Cd^{2+}$, $Hg^{2+}$, and $Zn^{2+}$ cations.[70]




**Scheme 3.** Synthesis of amide-containing di-2-picolylamine (DPA) receptor **13**.

Zhang, Zhou and co-workers designed phosphate ion (Pi) probes, based on a methoxy oxalyl group reaction site. Thus, complexes **16a,b** were acylated with methyl chlorooxoacetate to give amides **17a,b** (Scheme 4). Probes **17a,b** demonstrated high selectivity for Pi detection without interference from adenosine mono-, di-, triphosphate (AMP, ADP, ATP), guanosine mono-, di-, triphosphate (GMP, GDP, GTP), thymidine mono-, di-, triphosphates (TMP, TDP, TTP), uridine mono-, di-, triphosphates (UMP, UDP,

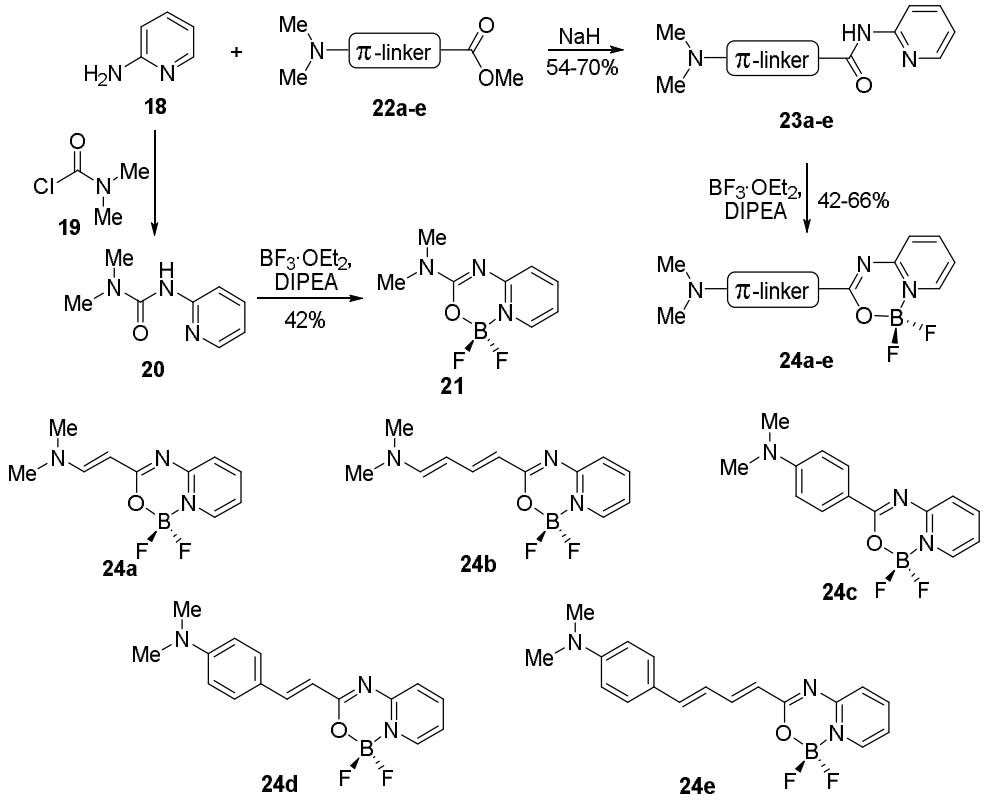
UTP), pyrophosphate (PPi) or other anions. The in vivo imaging experiments showed the ability of probes **17a,b** to permeate into the HeLa cells and *Caenorhabditis elegans* to detect Pi via a strong fluorescence intensity change.[71]




**Scheme 4.** Phosphate ion (Pi) probes **17a,b**.

**4. Pyrido[1,2-*c*][1,3,5,2]oxadiazaborinines**

Ośmiałowski and co-workers elaborated donor-acceptor (D-A) dyes based on pyrido-fused oxadiazaborinines conjugated with dimethylamino donor group *via* $\pi$-linker with different D-to-A lengths varied from 1.5 to 4.5 Å.[72] The synthesis of such compounds was started from 2-aminopyridine **18** (Scheme 5).




**Scheme 5.** Synthesis of pyrido[1,2-*c*][1,3,5,2]oxadiazaborinines **21** and **24a-e**.

Acylation reaction of amine **18** with dimethylcarbamoyl chloride **19** resulted in tri-substituted urea **20**, which reacted with $BF_3 \cdot OEt_2$ under basic conditions to give organoboron complex **21** in 42% yield. To create $\pi$-elongated ligand **23a-e**, direct amidation reaction between esters **22a-e** and 2-aminopyridine was used. The obtained amides were treated with $BF_3 \cdot OEt_2$/DIPEA to perform complexes **24a-e** in 42-66% yield.[72] In the case of these compounds, increasing the $\pi$-conjugation length between donor and acceptor units resulted in a bathochromic displacement of the absorption ($\lambda_{abs}$ ranged from 335 to 461 nm in chloroform), and emission bands ($\lambda_{em}$ ranged from 382 to 595 nm in chloroform). Organoboron complex **21** exhibited Stokes shift of 47 nm, while the corresponding values in the cases of analogous **24a-e** increased from 31 nm for dye **24b** to 134 nm for compound **24e** (Table 3). The fluorescence quantum yields were comparatively high for solutions of complexes **21** ($\Phi$=0.648) and **24c** ($\Phi$=0.685), and weak for analogous **24a,b,d,e** with vinyl-containing $\pi$-linkers (Table 3).

These authors also prepared first analogue of pyrido-thiodiazoborinine dyes. Thus, amide **23c** was converted into thioanalogue **25** in 78% yield by thionation with Lawesson reagent. Treatment of thioamide **25** with $BF_3 \cdot OEt_2$ under basic conditions resulted in the formation of thiodiazoborinine **26** in 67% yield (Scheme 6).[73] Sulfur-containing compound **26** exhibited bathochromically shifted adsorption and emission spectra ($\lambda_{abs}$=432 nm, $\lambda_{em}$=508 nm) and a smaller emission quantum yield (0.53) than its oxygen counterpart **24c** ($\lambda_{abs}$=404 nm, $\lambda_{em}$=459 nm, $\Phi$=0.685) (Table 3).

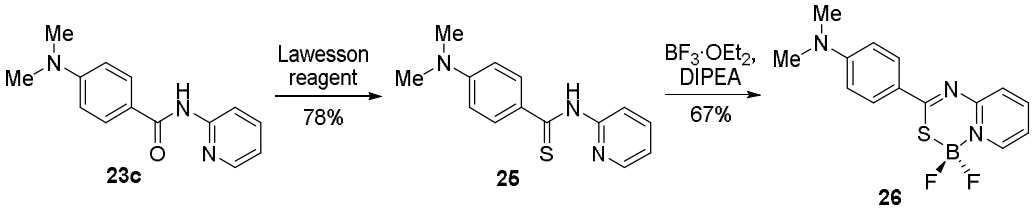
Next, Bonacorso and co-workers expanded the pyrido[1,2-*c*][1,3,5,2]oxadiazaborinine library, elaborating compounds **27a-e** with different aryl(heteroaryl) substituents at position 3 of the oxadiazaborinine ring (Figure 3).[74] Comparatively to analogue **24c**, complexes **27a-d** demonstrated hypsochromic shift in absorption and emission spectra and much lower fluorescent quantum yields (Table 3).

**Table 3.** Optical properties of pyrido[1,2-*c*][1,3,5,2]oxadiazaborinines

| Dye | Solvent | $\lambda_{abs}$, nm | $\varepsilon$, $M^{-1}cm^{-1}$ | $\lambda_{em}$, nm | Stokes Shift, nm | $\Phi$ | Ref. |
|---|---|---|---|---|---|---|---|
| **21** | $CHCl_3$ | 335 | 13500 | 382 | 47 | 0.648 | 72 |
| **24a** | $CHCl_3$ | 390 | 50100 | 421 | 31 | 0.325 | 72 |
| **24b** | $CHCl_3$ | 455 | 56200 | 492 | 37 | 0.038 | 72 |
| **24c** | $CHCl_3$ | 404 | 51000 | 459 | 55 | 0.685 | 72 |
| **24d** | $CHCl_3$ | 442 | 45800 | 527 | 105 | 0.186 | 72 |
| **24e** | $CHCl_3$ | 461 | 48000 | 595 | 134 | 0.098 | 72 |
| **26** | $CHCl_3$ | 432 | 35900 | 508 | 76 | 0.53 | 73 |
| **27a** | $CHCl_3$ | 335 | 2869 | 422 | 87 | 0.003 | 74 |
| **27b** | $CHCl_3$ | 339 | 5577 | 409 | 70 | 0.140 | 74 |
| **27c** | $CHCl_3$ | 402 | 3074 | 454 | 51 | 0.217 | 74 |
| **27d** | $CHCl_3$ | 336 | 3237 | 423 | 87 | <0.001 | 74 |
| **27e** | $CHCl_3$ | 341 | 3814 | 404 | 63 | 0.167 | 74 |
| **27f** | $CHCl_3$ | 351 | 4429 | 411 | 60 | 0.176 | 74 |
| **27a** | $CHCl_3$ | 335 | 19500 | N/A | – | 0 | 75 |
| **27a** | solid | – | – | 412 | – | 0.66 | 75 |
| **28** | $CHCl_3$ | 328 | 15000 | 392 | 64 | 0.05 | 75 |
| **28** | solid | – | – | 397 | – | 0.18 | 75 |
| **2b** | $CHCl_3$ | 354 | 19800 | 403 | 49 | 0.13 | 75 |
| **2b** | solid | – | – | 426 | – | 0.16 | 75 |
| **32a** | $CH_2Cl_2$ | 394 | 28000 | 456 | 62 | 0.20 | 76 |
| **32b** | $CH_2Cl_2$ | 394 | 43200 | 457 | 63 | 0.30 | 76 |
| **32c** | $CH_2Cl_2$ | 399 | 71500 | 460 | 61 | 0.39 | 76 |
| **32d** | $CHCl_3$ | 452 | 47800 | 484 | 32 | 0.385 | 72 |

Yamaji and co-workers investigated comparative properties of pyrido-, pyridazino- and pyrimidino-fused oxadiazaborinines **27a**, **28**, and **2b** (Figure 3) both in the chloroform solutions and in the solid states.[75] In contrast to pyridine-containing compound **27a**, which showed almost no fluorescence in the

solution, pyridazine and pyrimidine analogous **28** and **2b** emitted blue fluorescence with quantum yields of 0.05 and 0.13, respectively (Table 3). Moreover, organoboron complexes **28** and **2b** also demonstrated the triplet formation, while little transient signal was observed for dye **27a**. For the contrary, in the solid state, pyrido[1,2-*c*][1,3,5,2]oxadiazaborinine **27a** intensively emitted with a high quantum yield (0.66), while organoboron complexes **28** and **2b** showed fluorescence with quantum yields of 0.18 and 0.16, respectively.




**Scheme 6.** Synthesis of pyrido[1,2-*c*][1,3,5,2]thiadiazaborinine **24**.

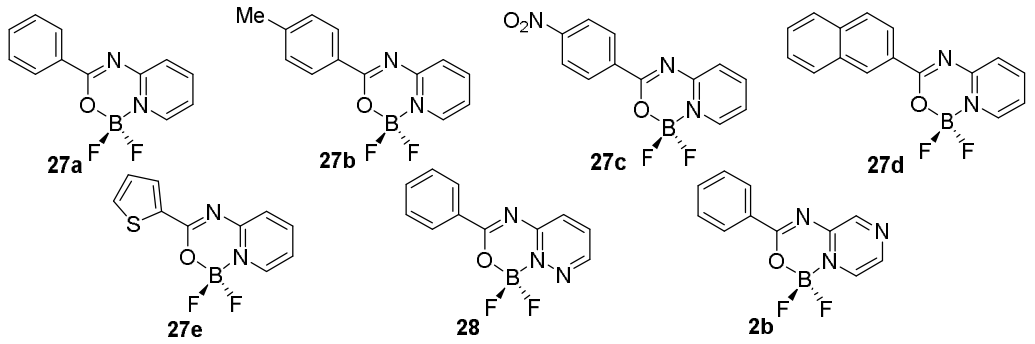
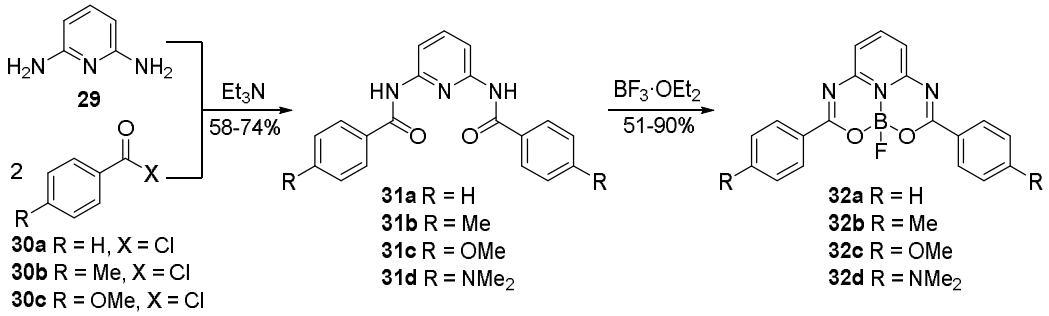



**Figure 3.** Oxadiazaborinines **27a–e**, **28**, and **2b**.

An analogous synthetic strategy was used to obtain organoboron dyes with two annulated oxadiazaboronine rings.[76] Acylation of 2,6-diaminopyridine **29** with two equivalent of chlorides **30a-c**[76] or ester **5c**[72] gave diamides **31a-d** in 58-74%, which played role of tridentate ligands for the complexation with $BF_3 \cdot OEt_2$. Complexes **32a-d** were obtained in 51-90% yields (Scheme 7).




**Scheme 7.** Synthesis of organoboron complexes **30a-d**.

Compounds **32a-c** exhibited similar absorption ($\lambda_{abs}$=394-399 nm) and emission ($\lambda_{em}$=456-460 nm) profiles with moderate fluorescent efficiency (Φ=0.20-0.39) in dichloromethane solutions (Table 3). Furthermore, these dyes showed also comparatively good solid-state quantum yields (0.38-0.41).[76] On the

other hand, analogue **32d** with two *p*-dimethylamino donor groups characterized by bathochromically shifted absorption ($\lambda_{abs}$=452 nm) and emission ($\lambda_{em}$=484 nm) spectra, with fluorescent quantum yield of 0.39 in the diluted chloroform solution (Table 3).[72]

**5. Pyrimido[1,2-*c*][1,3,5,2]oxadiazaborinines**

Bonacorso and co-workers synthesized also pyrimidine-based organoboron complexes **33a-f** (Figure 4) from corresponding *N*-(pyrimidine-2-yl)benzamides.[77] Chloroform solutions of compounds **33a,c-f** demonstrated absorption band in ultraviolet region with the maxima at 319-342 nm (Table 4). Meanwhile, the solution of organoboron complex **33b** (containing *p*-dimethylaminophenyl donor group) had an intense bathochromically shifted absorption band ($\lambda_{abs}$=412 nm ), which could be attributed to the intramolecular charge transfer (ICT) transition. In the fluorescent spectra, dyes **33a-f** demonstrated single-band emission properties with the maxima in the 399-452 nm range and moderate fluorescent quantum yields (0.12-0.22) in chloroform solution.

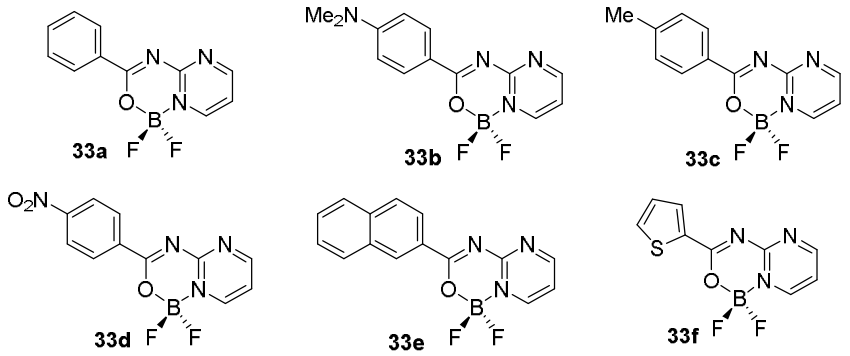



**Figure 4.** Pyrimido[1,2-*c*][1,3,5,2]oxadiazaborinines **33a-f**.

**Table 4.** Optical properties of pyrido[1,2-*c*][1,3,5,2]oxadiazaborinines **33a-f** in $CHCl_3$.

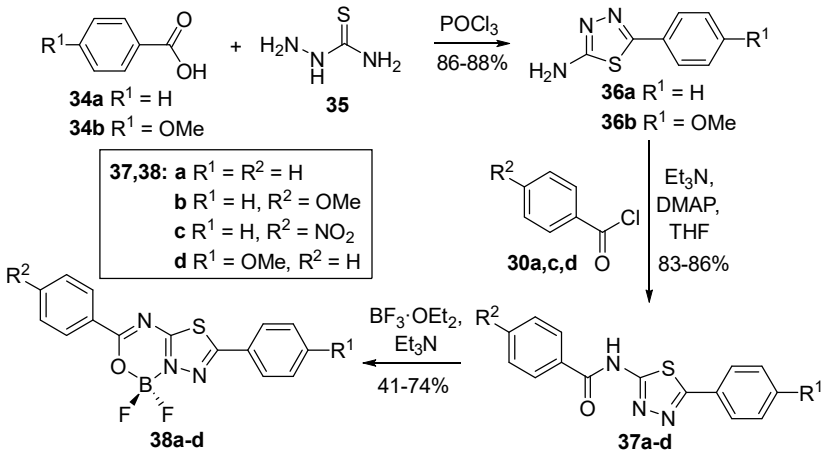
| Compound | $\lambda_{abs}$, nm | $\lambda_{em}$, nm | Stokes Shift, nm | Φ |
|---|---|---|---|---|
| **33a** | 322 | 422 | 100 | 0.12 |
| **33b** | 412 | 452 | 42 | 0.22 |
| **33c** | 328 | 403 | 75 | 0.16 |
| **33d** | 319 | 427 | 108 | 0.13 |
| **33e** | 335 | 411 | 76 | 0.20 |
| **33f** | 342 | 399 | 57 | 0.13 |

**6. [1,3,4]Thiadiazolo[3,2-c][1,3,5,2]oxadiazaborinines**

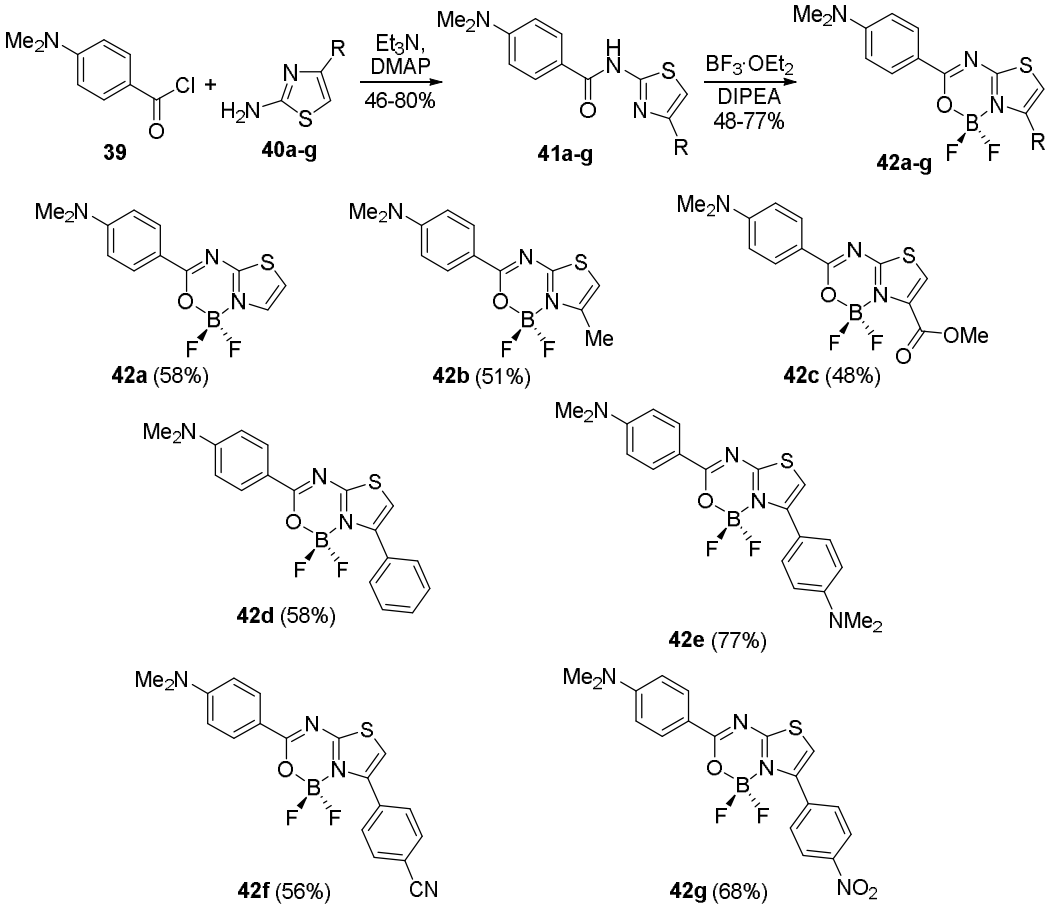
Li and co-workers synthesised four 1,3,4-thiadiazolo-fused oxadiazaborinines **38a-d**. The synthesis (Scheme 8) was started from benzoic acids **34a,b** and thiosemicarbazide **35**. Treatment of substrates **34a,b** and **35** with phosphorus oxychloride gave 5-aryl-2-amino-thiadiazoles **36a,b** in very good yields (86-88%). Acylation of amines **40a,b** with benzoyl chlorides **30a,c,d** under basic conditions led corresponding amides **37a-d** (83-86%), which were successfully converted into boron complexes **38a-d** (in 41-74% yields) by standard procedure using $BF_3 \cdot OEt_2$ as a borylation agent and $Et_3N$ as a base.[78] In toluene solutions, dyes **38a-d** exhibited absorption properties centred at 337-356 nm (ε=25000-46667 $M^{-1}cm^{-1}$) and emission band located at 409-436 nm with the weak to moderate quantum yield (0.01-0.29).

**7. (Benzo)thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinines**

In 2018, we reported the first synthesis of thiazole-fused oxadiazaborinines conjugated with dimethylamine donor via rotatable *p*-phenylene linker (Scheme 9).[79]




**Scheme 8.** Synthesis of [1,3,4]thiadiazolo[3,2-c][1,3,5,2]oxadiazaborinines **38a-d**.




**Scheme 9.** Synthesis of thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinines **42a-g**.

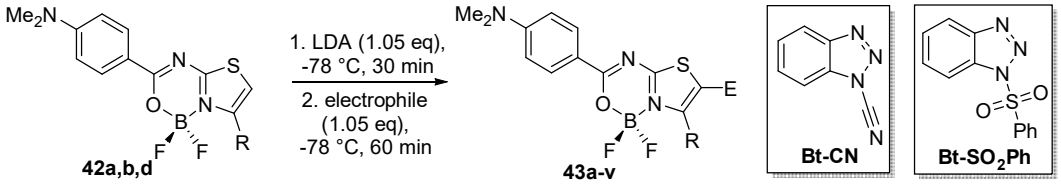
The thiazole ring was selected as the electron-rich heterocyclic moiety, which decrease the acceptor character of the oxadiazaborinine core. The synthesis of these compounds includes only two simple steps. Firstly, acylation reaction of *(para*-dimethylamino)benzoyl chloride **39** with 4-*R*-2-aminothiazoles **40a-g** in basic media gave amides **41a-g** in 46-80% yields. Secondly, ligands **41a-g** were transformed into boron complexes **42a-g** by treatment with $BF_3 \cdot OEt_2$ and DIPEA in moderate to good (48-77%) yields. The obtained organoboron complexes have different substitutes at position 4 of 1,3-thiazole ring, including donor and acceptor groups. The absorption and emission data of the toluene solutions of compounds **42a-g** are summarized in Table 5. All these dyes exhibited characteristic absorption peak with the maximum absorption wavelengths at 402-415 nm (ε=47300-63100 $M^{-1}$ $cm^{-1}$) and showed almost no variation with changing solvent polarity. Emission spectra of the dilute toluene solutions of dyes **42a-d,f-g** demonstrated one band with the maxima at 437-448 nm. On the other hand, the corresponding spectrum of complex **42e** is characterized by a bathochromic shift ($\lambda_{em}$=518 nm), which causes a significant increase of the value of Stokes shift (Δν=5386 $cm^{-1}$ for **42e**, and Δν=1647-1927 $cm^{-1}$ for **42a-d,f-g**). Organoboron complexes **42a-d** exhibited very high values of fluorescent quantum yield in toluene (Φ=0.94–0.99). Whilst, the incorporation of donor (*p*-dimethylaminophenyl in dye **42e**) or acceptor (*p*-cyanophenyl in dye **42f**) group caused the decrease of fluorescent efficiency (Φ=0.66 and 0.62, respectively). Moreover, compound **42g** with strong acceptor (*p*-nitrophenyl) substituent demonstrated very high fluorescent quenching (Φ=0.02 in toluene).

**Table 5.** Absorption and emission properties of thiazolo[3,2-c][1,3,5,2]oxadiazaborinines in toluene.

| Compound | $\lambda_{abs}$, nm | ε, $M^{-1}cm^{-1}$ | $\lambda_{em}$, nm | Δν, $cm^{-1}$ | Φ |
|---|---|---|---|---|---|
| **42a** | 405 | 56600 | 439 | 1912 | >0.99 |
| **42b** | 407 | 59300 | 437 | 1687 | >0.99 |
| **42c** | 406 | 63100 | 439 | 1851 | 0.94 |
| **42d** | 409 | 56600 | 444 | 1927 | 0.94 |
| **42e** | 405 | 47300 | 518 | 5386 | 0.66 |
| **42f** | 414 | 59900 | 448 | 1833 | 0.62 |
| **42g** | 415 | 62900 | 447 | 1725 | 0.02 |
| **43a** | 416 | 62000 | 449 | 1767 | 0.83 |
| **43b** | 416 | 58300 | 449 | 1767 | 0.77 |
| **43c** | 418 | 57500 | 451 | 1750 | 0.21 |
| **43d** | 406 | 57900 | 437 | 1747 | 0.83 |
| **43e** | 425 | 36300 | 464 | 1978 | 0.79 |
| **43f** | 430 | 32700 | 470 | 1979 | 0.66 |
| **43g** | 437 | 43100 | 481 | 2093 | 0.79 |
| **43h** | 407 | 59700 | 440 | 1843 | 0.85 |
| **43i** | 420 | 62500 | 457 | 1927 | 0.84 |
| **43j** | 429 | 68700 | 471 | 2079 | 0.83 |
| **43k** | 417 | 76100 | 454 | 1954 | 0.70 |
| **43l** | 406 | 56100 | 438 | 1799 | 0.84 |
| **43m** | 395 | 58000 | 439 | 2537 | 0.79 |
| **43n** | 407 | 48000 | 439 | 1791 | 0.82 |
| **43o** | 419 | 51200 | 449 | 1595 | 0.76 |
| **43p** | 419 | 59300 | 449 | 1595 | 0.79 |
| **43q** | 420 | 68500 | 457 | 1928 | 0.80 |
| **43r** | 424 | 63700 | 458 | 1751 | 0.82 |
| **43s** | 409 | 51700 | 441 | 1774 | 0.84 |
| **43t** | 418 | 62500 | 447 | 1552 | 0.63 |
| **43u** | 421 | 64200 | 462 | 2108 | 0.70 |
| **43v** | 423 | 87500 | 458 | 1807 | 0.85 |

Unexpectedly, in the solid state, compound **42a** exhibited very high emission ($\Phi_{solid}$=0.94). This phenomenon was caused by poorly organized molecular packing, which was confirmed by the X-ray analysis. The investigation of the fluorescence properties of dye **42a** in THF-water mixtures of various ratios showed that this compound exhibits aggregation induced emission (AIE) activity. On the other hand, due to the well-organized molecular packing of substituted derivatives **42b-f**, their solid-state emission was much lower ($\Phi_{solid}$=0.07-0.25).

To obtain thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinine derivatives with substituted at position 5 of 1,3-thiazole ring, we developed a transition-metal-free C–H postfunctionalization method, based on direct lithiation of compounds **42** (Scheme 10, Table 6).[80]




**Scheme 10.** Organolithium-mediated postfunctionalization of thiazolo[3,2-c][1,3,5,2]oxadiazaborinines.

**Table 6.** Scope for the LDA-mediated electrophilic postfunctionalization of complexes **42a,b,d**.

| entry | R | Electrophile | E | Product | Yield, % |
|---|---|---|---|---|---|
| 1 | H | $CCl_4$ | Cl | **43a** | 67 |
| 2 | H | $CBr_4$ | Br | **43b** | 64 |
| 3 | H | $Br_2$ | Br | **43b** | 60 |
| 4 | H | $I_2$ | I | **43c** | 60 |
| 5 | H | MeI[a] | Me | **43d** | 71 |
| 6 | H | $ClCO_2Me$ | $CO_2Me$ | **43e** | 76 |
| 7 | H | Br-CN | Br | **43b** | 71 |
| 8 | H | **Bt-CN**[a] | CN | **43f** | 70 |
| 9 | H | DMF | CHO | **43g** | 76 |
| 10 | H | $Me_3SiCl$ | $SiMe_3$ | **43h** | 85 |
| 11 | H | $(PhS)_2$ | SPh | **43i** | 73 |
| 12 | H | $PhSO_2Cl$ | Cl | **43a** | 65 |
| 13 | H | **Bt-$SO_2$Ph**[a] | $SO_2Ph$ | **43j** | 80 |
| 14 | H | $(PhSe)_2$ | SePh | **43k** | 73 |
| 15 | H | $Bu_3SnCl$ | $SnBu_3$ | **43l** | 64 |
| 16 | Me | MeI[a] | Me | **43m** | 80 |
| 17 | Me | $Me_3SiCl$ | $SiMe_3$ | **43n** | 88 |
| 18 | Me | $CCl_4$ | Cl | **43o** | 86 |
| 19 | Me | $CBr_4$ | Br | **43p** | 85 |
| 20 | Me | $(PhS)_2$ | SPh | **43q** | 82 |
| 21 | Me | $ClCO_2Et$ | $CO_2Et$ | **43r** | 67 |
| 22 | Ph | $Me_3SiCl$ | $SiMe_3$ | **43s** | 88 |
| 23 | Ph | $CBr_4$ | Br | **43t** | 81 |
| 24 | Ph | $(PhS)_2$ | SPh | **43u** | 68 |
| 25 | Ph | $ClCO_2Et$ | $CO_2Et$ | **43v** | 72 |

[a]With HMPA addition.

Organolithium-mediated electrophilic substitution of 1,3-thiazole is depended on the acidity of thiazole protons (H-2>H-5>H-4).[81] Accordingly to this rule, the electrophilation of 4,5-unsubstituted 1,3-thiazole derivatives occurs favorably at position 5 of the thiazole ring. However, the substitution at position 4 could be possible in the presence of excess of organolithium reagent for halogenation reaction caused by

"halogen-dance".[82-85] With this in mind, we investigated the organolithium-mediated electrophilation reaction of complex **42a** with the 4,5-unsubstituted 1,3-thiazole unit. As an effective mediator of the thiazole ring modification, lithium diisopropylamide (LDA) was selected. It is noteworthy that *N*,*O*-coordinated organoboron complexes exhibit low stability under basic reaction conditions.[86] Fortunately, thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinines demonstrated high chemical stability in LDA-mediated electrophilation at low temperature (-78 °C) (Scheme 10). First of all, the electrophilic halogenating reagents (carbon tetrachloride, carbon tetrabromide, bromine, and iodine) were tested (Table 6, entries 1-4). Regioselective mono-halogenation at position 5 of the thiazole ring with the highest yields of product **43a-c** (60-67%) was achieved when the molar ratio of the thiazole substrate/LDA/electrophile was 1.00:1.05:1.05 (Scheme 10).

Then, the elaborated reaction conditions were applied for several C-electrophiles. However, to successfully provide a methylation reaction, the addition of cation-complexing agent (hexamethylphosphoramide, HMPA) was necessary; compound **43d** was isolated with 71% yield (Table 6, entry 5). Ester **43e** and aldehyde **43g** were synthesized in 76% yield in both cases using methyl chloroformate and dimethylformamide (DMF) as electrophiles (Table 6, entries 6 and 9). Surprisingly, the use of cyanogen bromide as the electrophilic agent led halogene-substituted product **43b** (entry 7 in Table 6). To obtain cyano derivative **43f**, benzotriazole-carbonitrile (Bt-CN)[87] was used as an effective electrophilic cyanation reagent. Product **43f** was isolated with 70% yield (Table 6, entry 8). Besides, applying this methodology for reaction of compound **42a** with Si-, S-, Se-, and Sn-electrophiles, we synthesized organoboron dyes **43h-l** in good yields (64-85%, Table 6, entries 10, 11, and 13-15). Noticeably, similarly to the cyanation reaction, sulfonation did not occur with electrophilic halogenide (phenylsulfonyl chloride, entry 12 in Table 6); chloro derivative **43a** in 65% yield was obtained in this case. Meanwhile, to synthesize complex **43j** with sulfone group (entry 13 in Table 6), phenylsulfonyl-benzotriazole (Bt-$SO_2$Ph)[88] was used as the electrophile.

Possessing the developed conditions for the effecient organolithium-mediated electrophilation of compound **42a**, we expanded this reaction for complexes **42b,c**. The use of methylating, silylating, halogenating, sulfenylating, and ethoxycarboxylating reagents allowed to synthesize dyes **43m-v** with the 4,5-disubstituted thiazole unit in very good yields (67-88%, Table 6, entries 16-25).

Taking together, the LDA-mediated reaction of thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinine derivatives **42** with electrophilic reagents allows valuable regioselective C−H modification of these organoboron chromophores incorporating different groups, including C-, Hal-, Si-, S-, Se-, and Sn-substituents. As a result, a library of novel 1,3-thiazole-based organoboron complexes **47a-v** was synthesized (Scheme 10) in good yields (60-88%, Table 6).

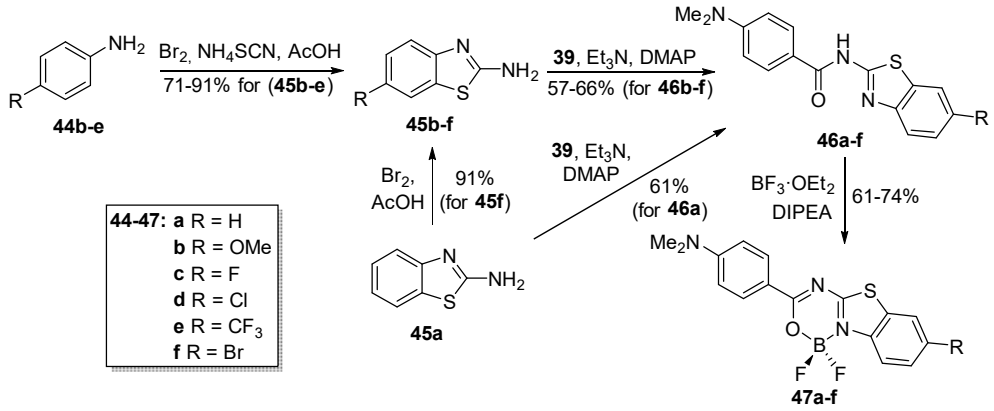
Such obtained thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinines **43a-v** generally exhibited a strong absorption band and intense single emission properties. In toluene solutions, the wavelengths of absorption and emission maxima were dependented on the donor/acceptor strength of the substituent E. The maxima were bathochromically shifted with increasing acceptor strength. Consequently, compared to the absorption and emission maxima of complexes **42a,b,d** ($\lambda_{abs}$=405-409 nm and $\lambda_{em}$=437-444 nm), the corresponding parameters of compounds **43a-c,o,p,t** with halogen substituents at the thiazole ring demonstrated slightly increased the wavelengths of absorption and emission maxima ($\lambda_{abs}$=416-421 nm; $\lambda_{em}$=447-451 nm). Much stronger bathochromic shifts were observed in the case of compounds with electron-withdrawing ester (**43e,r,v**, $\lambda_{abs}$=423-425 nm; $\lambda_{em}$=458-464 nm), nitryl (**43f**, $\lambda_{abs}$=430 nm and $\lambda_{em}$=470 nm), aldehyde (**43g**, $\lambda_{abs}$=437 nm and $\lambda_{em}$=481 nm), and sulfone (**43j**, $\lambda_{abs}$=429 nm and $\lambda_{em}$=471 nm) group (Table 5). This dependency also resulted a growth of the Stokes shifts (Δν) from 1747 $cm^{-1}$ for dye **43d** to 2093 $cm^{-1}$ for aldehyde **43g**.

It should be highlighted that substituents E (at position 5 of the thiazole ring) make definitely much higher influence on the value of absorption and emission maxima of the thiazolo[3,2-c][1,3,5,2]oxadiazaborinines, comparatively with that of substituents R (at position 4).

Dyes **43a-v** mainly showed high fluorescence quantum yields in non-polar solvents (Φ=0.63-0.85 in toluene). While iodo derivative **43c** due to “heavy atom effect” exhibited a significant decrease of fluorescence efficiency (Φ=0.21 in toluene, Table 5). However, in the solid state, they demonstrated relatively weak fluorescence quantum yields (up to 0.20), which were apparently predetermined by

aggregation-caused quenching (ACQ), generated by $\pi$–$\pi$/$\pi$–n interactions between the parallelly orientated complex molecules. The exception was observed for organoboron complex **43l**, which exhibited an increased solid-state fluorescence quantum yield ($\Phi_{solid}$=0.44). This caused by the presence of bulky lipophilic $SnBu_3$ substituent, which reduced the intermolecular $\pi$–$\pi$ stacking in the solid state and restrained the ACQ effect.

Continuing our research, we investigated the influence of annulation of aromatic unit to 1,3-thiazole ring on the photophysical properties of such type of complexes. To achieve this goal, we have designed the *N*,*O*-coordinated $BF_2$ complexes using benzo[*d*]thiazole as a heterocyclic *N*-coordinating centre. The modification of position 6 in benzo[*d*]thiazole moiety was selected to provide the best $\pi$-conjugation between the *N*-coordinated centre of a ligand (following boron unit) and substituents R. Unsubstituted benzo[*d*]thiazol-2-amine **45a** is commercially available. Benzo[*d*]thiazol-2-amines **45b-e** with substituent R (OMe, F, Cl, $CF_3$) at position 6 of the benzothiazole scaffold were synthesised in 71-91% yields by a one-pot method starting 4-substituted anilines **44b-e** and bromine/$NH_4SCN$ in acetic acid.[89,90] On the other hand, to synthesize 6-bromobenzo[*d*]thiazol-2-amine **45f**, unsubstituted analogous **45a** was selectively brominated in glacial acetic acid medium at position 6 of the benzothiazole with very good (91%) yield (Scheme 11). Next, the two-step methodology, containing acylation reaction of amines **45a-f** with chloride **39** and followed complexation of amides **46a-f** with boron trifluoride, was applied to the synthesis of benzo[4,5]thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinines **47a-f** (Scheme 11).[91]

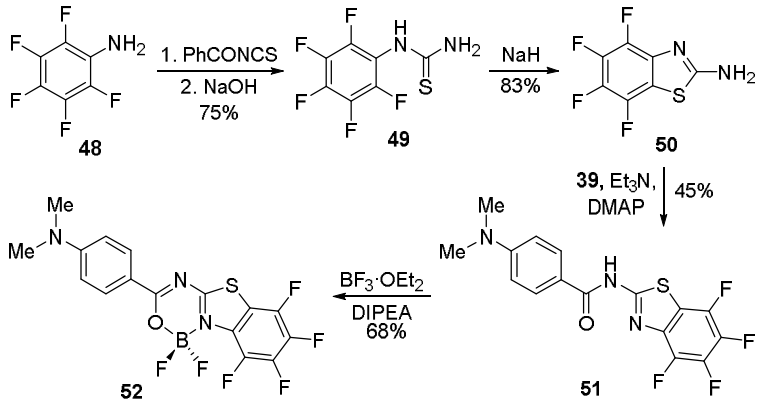



**Scheme 11.** Synthesis of benzo[4,5]thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinines **47a-f**.

Such obtained benzo[4,5]thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinines **47a-f** had different substituents at the 6-position of the benzothiazole unit, including donor (OMe), weak acceptor (F, Cl, Br), and strong acceptor ($CF_3$) groups. To compare photophysical properties of these dyes with those of an analogue, modified by a much stronger acceptor strength in the benzothiazole moiety, we designed a boron complex based on a perfluorinated benzothiazole synthon. In order to attain this objective, we developed the synthetic pathway starting from pentafluoroaniline **48** (Scheme 12). Thus, amine **48** was converted into 1-(perfluorophenyl)thiourea **49** in 75% yield by treatment with benzoyl isothiocyanate and followed hydrolysis with NaOH. Next, reaction of thiourea **49** with a strong base (NaH) in dry DMF resulted in hydrofluoric acid elimination and benzothiazole cyclization, to give 4,5,6,7-tetrafluorobenzo[*d*]thiazol-2-amine **50** in good (83%) yield. After that, using the previously elaborated methodology, amine **50** was converted into amide **51** in 45% yield, which in turn was successfully transformed into final complex **52** in 68% yield.

The annulation of phenyl ring (compounds **47a-f**, and **52**) resulted in a bathochromic shift of the absorption ($\lambda_{abs}$=421-431 nm in toluene, Table 7) and emission ($\lambda_{em}$=450-464 nm) bands, and increase the molar absorption coefficient (ε=62600-88400 $M^{-1}cm^{-1}$), as compared to the corresponding photophysical parameters of unfused thiazole derivative **42a** ($\lambda_{abs}$=405 nm, $\lambda_{em}$=439 nm, ε=56600 $M^{-1}cm^{-1}$). Complexes

**47a-f** also exhibited high fluorescence efficiency (Φ=0.74-0.93) in toluene. Meanwhile, the toluene solution of complex **52** demonstrated a little less efficient emission (Φ=0.65). Conversely, in the solid state, due to the strong ACQ effect, the fluorescent quantum yield values of complexes **47a-f** were low ($\Phi_{solid}$=0.02-0.06), while dye **52** exhibited solid-state emission with an enhanced fluorescence quantum yield ($\Phi_{solid}$=0.34).



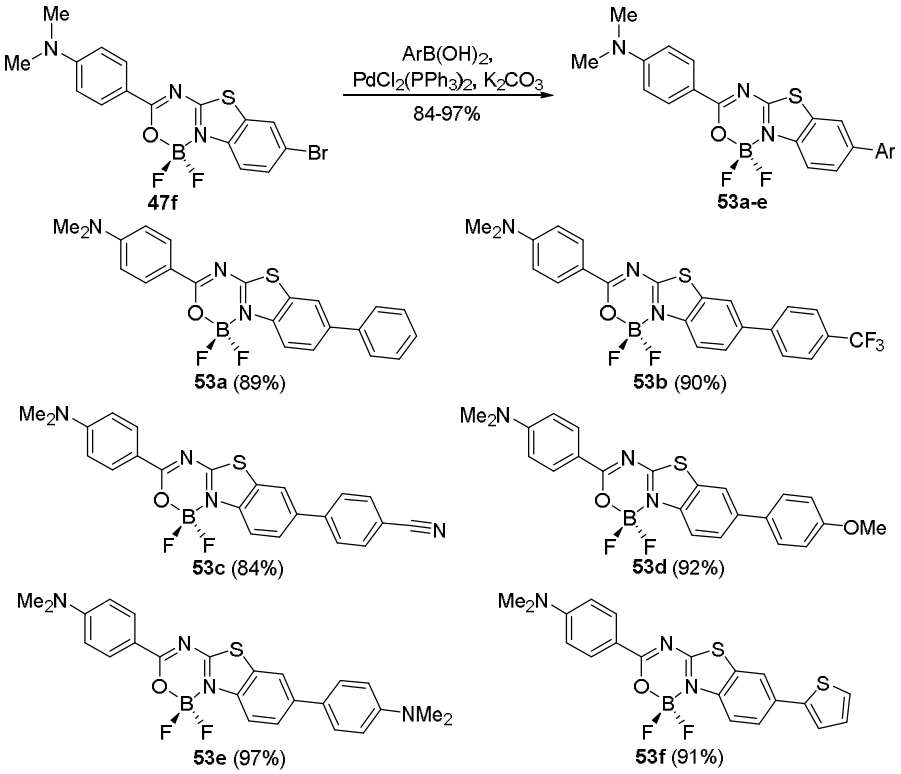

**Scheme 12.** Synthesis of benzo[4,5]thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinine **52**.

**Table 7.** Absorption and emission properties of benzo[4,5]thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinines.

| Compound | $\lambda_{abs}$, nm | ε, $M^{-1}cm^{-1}$ | $\lambda_{em}$, nm | Δν, $cm^{-1}$ | Φ |
|---|---|---|---|---|---|
| **47a** | 421 | 62600 | 450 | 1531 | 0.84 |
| **47b** | 411/427 | 82500/88400 | 454 | 1392 | 0.88 |
| **47c** | 423 | 71700 | 452 | 1516 | 0.85 |
| **47d** | 427 | 73200 | 456 | 1489 | 0.91 |
| **47e** | 428 | 86000 | 460 | 1625 | 0.93 |
| **47f** | 427 | 66700 | 450 | 1197 | 0.74 |
| **52** | 431 | 84900 | 464 | 1650 | 0.65 |
| **53a** | 430 | 78100 | 457 | 1373 | 0.92 |
| **53b** | 431 | 69500 | 459 | 1415 | 0.80 |
| **53c** | 434 | 89000 | 459 | 1255 | 0.99 |
| **53d** | 431 | 70900 | 459 | 1415 | 0.95 |
| **53e** | 430 | 64800 | 523 | 4135 | 0.78 |
| **53f** | 436 | 73600 | 462 | 1291 | 0.84 |

Complex **47f** with bromo-substituent at the benzothiazole unit (R=Br) was investigated in Suzuki-Miyaura reaction with (het)arylboronic acids. $PdCl_2(PPh_3)_2$ was used as an effective catalyst. The optimized procedure (with 1.00:1.50:0.05 molar ratio of bromo substrate/arylboronic acid/Pd catalyst) allowed to obtain products **53a-f** in very high yields (89-95%, Scheme 13).[92] Such synthesised complexes **53a-f** had different aromatic substituents at position 6 of the benzo[*d*]thiazole unit, including electron-acceptor (*p*-trifluoromethylphenyl and *p*-cyanophenyl) and electron-donor (*p*-dimethylaminophenyl, *p*-methoxyphenyl, and 2-thienyl) groups.

The absorption wavelength maxima of complexes **53a-f** in toluene solution were ranged from 430 to 436 nm (Table 7) and characterized by high molar absorption coefficients (ε=64800-89000 $M^{-1}\cdot cm^{-1}$). The corresponding emission wavelength maxima were located in the range 457-462 nm for dyes **53a-d,f**. Strikingly, the large bathochromic shift was observed in the emission spectrum of compounds **53e** (Ar=4-$C_6H_4NMe_2$, $\lambda_{em}$=523 nm). The toluene solutions of dyes **53a-f** showed high fluorescent quantum yields (Φ=0.78-0.99). Meanwhile, in the solid state, these compounds exhibited weak fluorescence ($\Phi_{solid}$ up to 0.17), except complex **53c** ($\Phi_{solid}$=0.31).




**Scheme 13.** Suzuki-Miyaura reaction of compound **47f** with aryl(thienyl)boronic acid.

After obtaining the information about the relation between the (benzo)thiazole unit and the electronic and optical properties of the (benzo)thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinine dyes, we demonstrated that the replacement of $Me_2N$ group by a carbazole moiety (dyes **54a,b**, Figure 5) resulted in a remarkable increase of solvatofluorochromism, and, due to the restriction of intramolecular rotation, in enhanced AIE activity. Strikingly, attachment of two $^t$Bu groups to the carbazole unit (dye **54b**) stimulated the significant mechanofluorochromic properties.[93]

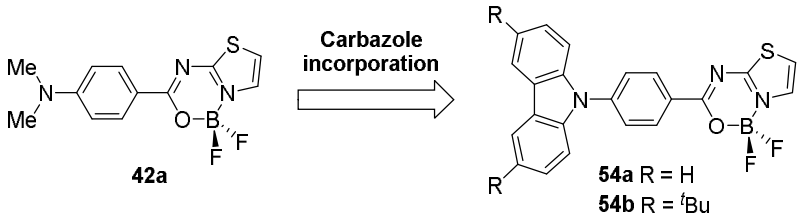
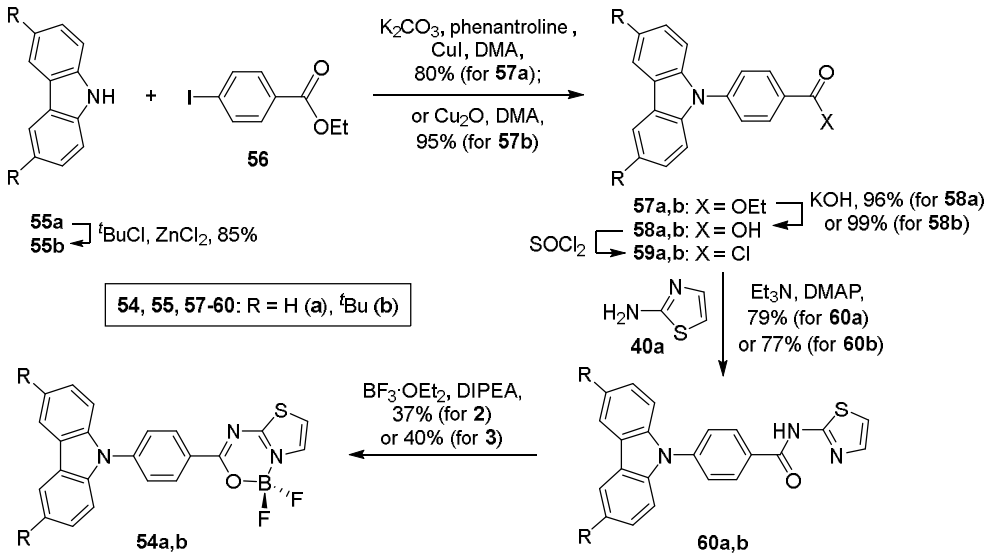



**Figure 5.** Thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinines **42a** and **54a,b**.

According to the synthetic route shown in Scheme 13, complexes **54a,b** were easily prepared in four steps, confirming the efficient and convenient strategy to attain the thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinine dyes with sterically hindered donor groups. As the starting materials were used commercially available carbazole **55a** and 3,6-di-*tert*-butylcarbazole **55b**, which was obtained by standard *tert*-butylation of compound **55a** in 85% yield. Firstly, amines **55a,b** were coupled with ethyl 4-iodobenzoate **56** under

Ullmann amination conditions giving products **57a** and **57b** in 80 and 95% yields, respectively. Secondly, hydrolysis of the ester **57a,b** gave 4-(9*H*-carbazol-9-yl)benzoic acid **58a** and 4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)benzoic acid **58b** in nearly quantitative yields (96 and 99%). Thirdly, acids **58a,b** were converted into corresponding chlorides **59a,b** by treatment with thionyl chloride in the hot toluene medium; chlorides **59a,b** were introduced in acylation reaction with 2-aminothiazole **40a** under basic conditions to give amides **60a** and **60b** in very good yields (79 and 77%). Lastly, transformation of these compounds into organoboron complexes **54a,b** were realized by condensation with boron trifluoride in the presents of DIPEA, giving the final products in moderate yields (37 and 40%).




**Scheme 13.** Synthesis of carbazole-modified thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinines **54a,b**.

In comparison to corresponding parameters of complex **42a** (Table 5), the solutions of carbazole-modified dye **54a** in toluene exhibited hypsochromic shift in absorption spectrum ($\lambda_{abs}$=384 nm) with decreased molar absorption coefficient (ε=23600 $M^{-1}cm^{-1}$), and bathochromic shift in emission spectrum ($\lambda_{em}$=462 nm). This indicates the increase of intramolecular charge transfer (ICT) with the structural changing of $Me_2N$ donor group on carbazole unit. The incorporation of two *tert*-butyl groups at the positions C-3 and C-6 of the carbazole moiety caused the bathochromic shifts in absorption and emission spectra of compound **54b** ($\lambda_{abs}$=399 nm, ε=22300 $M^{-1}cm^{-1}$, $\lambda_{em}$=489 nm, in toluene), compared with those of analogue **54a**.

The presence of carbazole donor unit, linked with oxadiazaborinine acceptor *via* phenyl linker, restricted the intramolecular rotation, causing enhanced aggregation-induced emission properties of the compounds: in the THF/water mixtures with the large water percentage, they demonstrated the formation of emissive nanoaggregates with the average size of 79 and 89 nm for complexes **54a** and **54b**, respectively.

The solid-state fluorescent quantum yields of compounds **54a** and **54b** was 0.26 and 0.34, respectively. Moreover, dye **54b** exhibited also mechanofluorochromic properties. The crystal sample of complex **54b** exhibited bright blue fluorescence maximized at 496 nm. Meanwhile, after mechanical grinding this sample exhibited yellowish emissions centered at 534 nm. Afterwards, the DCM-fuming of the same sample resulted in the hipsochromic shift of the emission spectra ($\lambda_{em}$=491 nm).

## 8. Conclusion

In this review, the recent research works on the design of 1,3,5,2-oxadiazaborinine dyes have been summarized. To construct oxadiazaborinine-based fluorescent dyes, different nitrogen-containing

2-aminoheterocycles (amidopyrazines, naphthyridine-2-amines, 2-aminopyridines, 2-aminopyridazines, 2-aminopyrimidines, 2-aminothiadiazoles, 2-aminothiazoles, and benzo[*d*]thiazol-2-amines) have been used. The studies demonstrated that 1,3,5,2-oxadiazaborinine core exhibits electron-acceptor properties. Therefore, the conjugation of this organoboron heterocycle with strong donor (such as *p*-dimethylaminophenyl) group results in the formation of fluorescent dyes with intramolecular charge transfer character, causing significant bathochromic shifts in absorption and emission spectra. Organoboron dyes, based on 1,3,5,2-oxadiazaborinine fused with electron-withdrawing heterocycles (pyrazine, naphthyridine, pyridine, pyrimidine, thiadiazole), exhibited relatively lower fluorescence. On the other hand, the (benzo)thiazole-fused analogues demonstrated much higher fluorescent quantum yield due to the decreased acceptor character of (benzo)thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinine core. Another advantage of (benzo)thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinine derivatives is their chemical stability. Such dyes can be modified by organolithium-mediated electrophilation or Pd-catalysed cross-coupling reactions. In addition, the conjugation of thiazolo[3,2-*c*][1,3,5,2]oxadiazaborinine scaffold with carbazole donor unit results in the formation of AIE-active organoboron dyes.

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