

New Fluorescent Heterocyclic Materials: Synthesis, Solvatochromic and Fluorescence Properties

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Abstract. Thienyl- and bithienyl-1,3-benzothiazoles *1* and *2* were synthesised by reacting various formyl thienyl and bithienyl derivatives with *o*-aminobenzenethiol in moderate to excellent yields. Evaluation of the solvatochromic and fluorescence properties of these compounds was carried out. Due to their strong fluorescence and also the strong push-pull character, benzothiazole derivatives *1* and *2* can be used as potential NLO materials or as fluorescent markers.

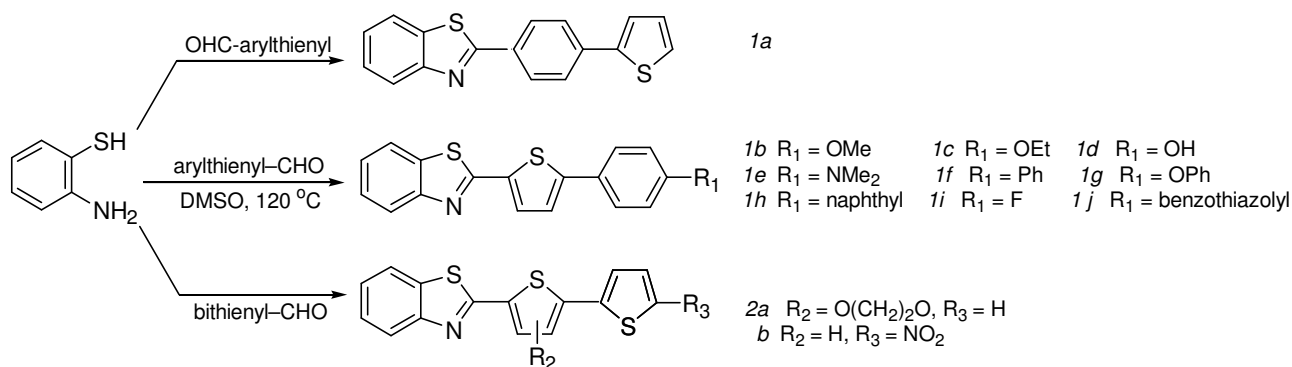
Introduction

The benzothiazole nucleus appears in many fluorescent compounds that have useful applications as a result of the ease of synthesis of this heterocycle and the high fluorescence quantum yields obtained when this small, rigid moiety is present [1]. The practical interest upon benzothiazole derivatives (2-aryl-benzothiazole, 2-(2-phenylethenyl)-benzothiazole, 2-indolyl-benzothiazole, 2-carbazolyl-benzothiazole and thiazole push-pull alkenes, etc.) is based on their widespread application [2]. In addition to intense fluorescence, some compounds of this type have interesting biological properties. They have been investigated for their clinical efficacy as cytotoxic, antimicrobial, antifungal, anti-tumour and anti-HIV activity. Such compounds can also have application as polidentate ligands, in laser technology as laser dyes, organic luminophores, thermo- and LTV-stabilizers for polymer materials, diazotype materials, for organic electroluminescent devices and materials with non-linear optical (NLO) properties [3-5]. As part of our continuing interest in heterocycles with non-linear optical and fluorescent properties [6-13] we describe here the synthesis, the UV-visible, the solvatochromic and fluorescence studies of a series of heterocyclic fluorophores of the benzothiazole type.

Results and discussion

Synthesis. A series of benzothiazoles *1* and *2* were synthesized with either fluoro-, alkoxy- or *N,N*-dialkylamino- donors or with a nitro acceptor on the thienylaryl or on the bithienyl moiety across a conjugated π -bridge containing a thienylaryl or a bithienyl moiety (Scheme 1). Formyl precursors were synthesized by Suzuki cross-coupling reaction of thienyl- or aryl boronic acid with bromoaryl or bromothienyl compounds, catalyzed by Pd(PPh₃)₄. These compounds were synthesized with different π -bridges and several donor and acceptor groups in order to evaluate the effect of the π conjugating bridge and the donating and accepting strength of these groups on the solvatochromic and fluorescent properties of benzothiazoles *1* and *2*. The benzothiazole moiety was obtained by the simple reaction of *o*-aminobenzenethiol with formyl precursors, in DMSO at 120 °C for 30-60 min.

Purification of the crude products by column chromatography gave the pure benzothiazoles *1* and *2* in fair to excellent yields (40-91%) (Table 1).



Scheme 1- Synthesis of benzothiazoles *1* and *2*.

Table 1- Yields, UV-visible absorption and emission data for benzothiazoles *1* and *2*.

| Entry | Compd. | R ₁ | R ₂ , R ₃ | Yield [%] | Absorption $\lambda_{\text{max}}^*[\text{nm}]$ (ϵ) | Emission $\lambda_{\text{max}}^*[\text{nm}]$ | Stokes' shift [nm] | Quantum Yield Φ |
|-------|-----------|--------------------|---|-----------|---|--|--------------------|----------------------|
| 1 | <i>1a</i> | H | --- | 85 | 340 (4.59) | 406 | 66 | 0.43 |
| 2 | <i>1b</i> | OMe | --- | 86 | 372 (4.49) | 454 | 82 | 0.68 |
| 3 | <i>1c</i> | OEt | --- | 83 | 372 (4.50) | 454 | 82 | 0.46 |
| 4 | <i>1d</i> | OH | --- | 40 | 378 (4.22) | 463 | 85 | 0.96 |
| 5 | <i>1e</i> | N(Me) ₂ | --- | 49 | 406 (4.51) | 548 | 142 | 0.97 |
| 6 | <i>1f</i> | Ph | --- | 89 | 369 (4.63) | 446 | 77 | 0.59 |
| 7 | <i>1g</i> | OPh | --- | 91 | 365 (4.55) | 445 | 80 | 0.66 |
| 8 | <i>1h</i> | naphthyl | --- | 77 | 339 (4.50) | 446 | 93 | 0.17 |
| 9 | <i>1i</i> | F | --- | 90 | 355 (4.51) | 427 | 72 | 0.59 |
| 10 | <i>1j</i> | benzothiazolyl | --- | 84 | 386 (4.58) | 452 | 66 | 0.80 |
| 11 | <i>2a</i> | --- | R ₂ = O(CH ₂) ₂ O R ₃ = H | 84 | 388 (4.57) | 458 | 70 | 0.89 |
| 12 | <i>2b</i> | --- | R ₃ = NO ₂ R ₂ = H | 77 | 416 (4.45) | 593 | 177 | 0.19 |

*All the UV-visible and fluorescence spectra were run in degassed absolute ethanol.

UV-visible study. Electronic absorption spectra of all benzothiazole derivatives *1* and *2* in absolute ethanol show an intense lowest energy charge-transfer absorption band in the UV-visible region. The position of this band is strongly influenced by the structure of the compounds, for example by the type of π system (aryl or heteroaryl groups) linked to the benzothiazole moiety and the substitution pattern in the aryl or thienyl rings (Table 1). The reason for the substantial red shift in the investigated compounds *1b-e* ($\lambda_{\text{max}} = 372\text{-}406$ nm) and *1g* ($\lambda_{\text{max}} = 365$ nm) relative to those of unsubstituted 2-(5'-phenyl-2'-thienyl)-1,3-benzothiazole [6] ($\lambda_{\text{max}} = 359$ nm) and *1a* ($\lambda_{\text{max}} = 340$ nm) is the strong inductive and conjugative effect of the alkoxy or the *N,N*-dialkylamino substituent in the *para* position of the phenyl ring. The influence of the strength of the donor group is demonstrated by comparison of the absorption maxima of compounds *1b* and *1e* as the longest

wavelength transition is shifted from 372 nm in *Ib* (Table 1, entry 2) to 406 nm in *Ie* (Table 1, entry 5). The influence of the strength of the acceptor group is demonstrated by comparison of the absorption maxima of 2,2'-bithienyl-benzothiazole [11] and *2b*, as the longest wavelength transition is shifted from 378 nm in 2,2'-bithienyl-benzothiazole to 416 nm in *2b* (Table 2, entry 12). The influence of the benzothiazole moiety is demonstrated by comparison of the absorption maxima of compounds *Ia* and *Ij* as the longest wavelength transition is shifted from 340 nm in *Ia* (Table 1, entry 1) to 386 nm in bis-benzothiazole *Ij* (Table 1, entry 10). The shifts of the absorption maxima are proportional to the intramolecular charge-transfer between the electron-releasing and withdrawing groups. In general, the stronger the donor and/or acceptor group, the smaller the energy difference between ground and excited states, and the longer the wavelength of absorption. According to Zyss [14], the increase of the β values characteristic of the NLO effects is accompanied by an increase of the λ_{\max} in the UV-vis spectra.

Solvatochromic study. To evaluate the intermolecular forces between the solvents and the solute molecules and in order to determine the best indicator dye, we made a preliminary study of the absorption spectra of compounds *I-2* in 4 selected solvents of different solvation character (diethyl ether, ethanol, chloroform and DMSO). We found that compounds *Ie* and *2b* show the longest shift in wavenumber maxima ($\Delta\nu_{\max} > 1000 \text{ cm}^{-1}$), so a full solvatochromic study involving 14 solvents was carried out. The wavelength maxima λ_{\max} and wavenumber maxima ν_{\max} of compounds *Ie* and *2b* are listed in Table 2 and compared with π^* values for each solvent, determined by Kamlet and Taft [15].

Table 2- Solvatochromic data [λ_{\max} (nm) and ν_{\max} (cm^{-1}) of the charge-transfer band] for compounds *Ie* and *2b* in various solvents with π^* values by Kamlet and Taft [15].

| Solvent | π^* | Compound | | | |
|------------------|---------|------------------|--------------|------------------|--------------|
| | | <i>Ie</i> | <i>2b</i> | <i>Ie</i> | <i>2b</i> |
| | | λ_{\max} | ν_{\max} | λ_{\max} | ν_{\max} |
| <i>n</i> -hexane | -0.08 | 388.6 | 25,733 | 408.8 | 24,462 |
| diethyl ether | 0.27 | 394.8 | 25,329 | 413.0 | 24,213 |
| ethanol | 0.54 | 402.6 | 24,839 | 416.0 | 24,038 |
| toluene | 0.54 | 400.8 | 24,950 | 417.0 | 23,981 |
| 1,4-dioxane | 0.55 | 402.2 | 24,863 | 417.8 | 23,935 |
| ethyl acetate | 0.55 | 401.8 | 24,888 | 418.0 | 23,923 |
| THF | 0.58 | 403.8 | 24,765 | 419.2 | 23,855 |
| methanol | 0.60 | 405.5 | 24,661 | 420.0 | 23,810 |
| acetone | 0.71 | 405.2 | 24,679 | 419.6 | 23,832 |
| acetonitrile | 0.75 | 405.6 | 24,655 | 421.6 | 23,719 |
| chloroform | 0.76 | 406.0 | 24,631 | 423.0 | 23,641 |
| DCM | 0.82 | 408.0 | 24,510 | 423.8 | 23,596 |
| DMF | 0.88 | 411.2 | 24,319 | 426.6 | 23,441 |
| DMSO | 1.00 | 414.2 | 24,143 | 430.6 | 23,223 |

For compounds *Ie* and *2b*, the highest energy transitions are found with *n*-hexane, a nonpolar solvent, and more polar solvents such as DMSO result in lower energy transitions, thus indicating a positive solvatochromic response ($\Delta\nu_{\max} = 1590 \text{ cm}^{-1}$ for *Ie* and $\Delta\nu_{\max} = 1238 \text{ cm}^{-1}$ for *2b*) that is related to a greater stabilization of the excited state relative to the ground state with increasing

polarity of the solvent. Compounds *1e* and *2b* show excellent correlation between wavenumber maxima and π^* values for the 14 solvents tested. Due to the evident solvatochromism and the good correlation with π^* values ($r = 0.9857$ for *1e* and $r = 0.9605$ for *2b*), compounds *1e* and *2b* could be used as a solvent polarity indicator dyes.

Fluorescence study. A fluorescence study was carried out with benzothiazoles *1* and *2* in order to relate the fluorescence properties to the nature of the aryl- and heteroaryl- bridge and the nature of the donating and the acceptor groups attached to these moieties. Fluorescence spectra of 3×10^{-6} M solutions of compounds *1-2* were measured, excitation and emission maxima and fluorescence quantum yields are also reported (Table 1). Emission spectra of compounds *1-2* were run in degassed absolute ethanol, using 9,10-diphenylanthracene as standard ($\Phi = 0.95$ in ethanol). The combination of thienylaryl or bithienyl with a benzothiazole results in a red shift of the emission maxima of the thienylaryl- or bithienyl moiety, owing to the electron-withdrawing nature of the benzothiazole. There is also a pronounced improvement in the quantum yield when a second benzothiazole group is introduced into the molecule (compare *1a* and *1j*, $\Phi = 0.43$ and 0.80 , respectively). The nature of the donating group (alkoxy- or *N,N*-dialkylamino-) affects both the position of the maxima of long-wavelength fluorescence and the quantum yield, which are shifted from $\lambda_{em} = 454$ nm, $\Phi = 0.68$ for *1b* (Table 1, entry 2) to $\lambda_{em} = 548$ nm, $\Phi = 0.97$ for *1e* (Table 1, entry 5). For amino substituents, the bathochromic shift of the fluorescence as well of the absorption band is due to the larger electron-releasing ability of the nitrogen in amine groups [16].

All the compounds exhibit high fluorescence quantum yields, especially *1d* and *1e* ($\Phi = 0.96$ and 0.97 , respectively) and *2a* ($\Phi = 0.89$) and it appears that thienylarylbenzothiazoles *1a-j* have higher quantum yields than bithienylbenzothiazoles *2a* and *2b* and related [11], regardless of the substituents, thus revealing the influence of the conjugating bridge in fluorescence properties (Figure 1). The synthesized compounds show large Stokes' shift (the lowest being 66 nm for *1a* and *1j* and the highest 177 nm for *2b*) (Table 1, entries 1, 10 and 12). There seems to be a relationship between the substituent group, its electron-donating character and the magnitude of the Stokes' shift, as *N,N*-dimethylamino- group in compound *1e* show larger Stokes' shift (142 nm) in comparison with methoxy- group in compound *1b* (82 nm) and the unsubstituted compound *1a* (66 nm).

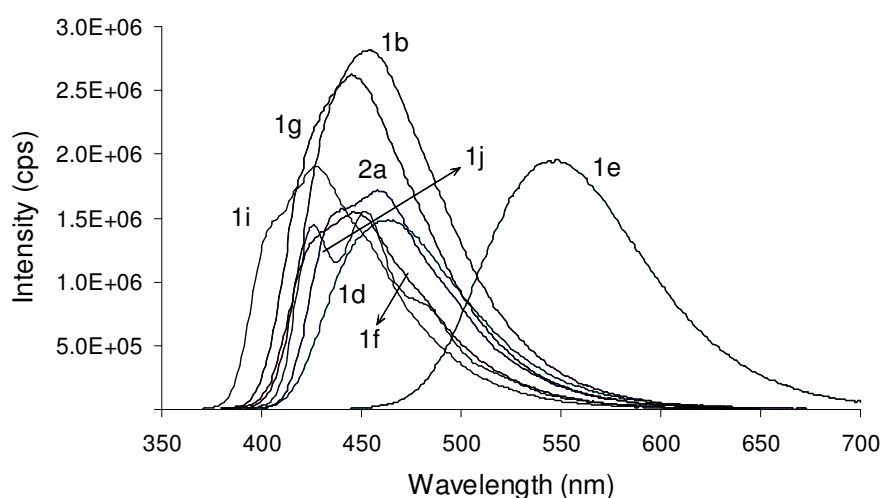


Figure 1 – Fluorescence spectra of compounds *1* and *2* with quantum yield higher than 0.5.

Conclusions

In summary, we have achieved the first synthesis of a series of benzothiazole derivatives *1* and *2* in fair to excellent yields. By comparing the several derivatives synthesised, it can be seen that the π -conjugating bridge and the electron donating or withdrawing group on the phenyl, thienyl or bithienyl moieties have significant influence on the solvatochromic and fluorescence properties. In agreement with the results obtained from the UV-visible, fluorescence and solvatochromic studies and also with previous findings, the new 2-thienylaryl- and 2-(2',2''-bithienyl)-1,3-benzothiazoles *1* and *2* synthesized can be applied for the manufacture of new materials with non-linear optical properties [17], as fluorescent markers, due to their strong fluorescence, or as light emitters in organic light emitting devices (OLEDs) [4].

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