

Synthesis of fluorescent 2-(2',2''-bithienyl)-1,3-benzothiazoles

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Summary: Eight new bithienyl benzothiazole derivatives **1** were synthesised by reacting various 5-formyl-5'-alkoxy- or 5-formyl-5'-amino-2,2'-bithiophenes **2** with ortho-aminobenzenethiol in good to excellent yields. Compounds **1a-h** were completely characterised by spectroscopic methods. Absorption and fluorescence spectra of these compounds were also recorded. In agreement with previous findings concerning the fluorescence studies of 2-(2'-thienyl)-1,3-benzothiazoles, the new compounds prepared can find application for additives in textile dyeing and plastics, tunable dye lasers, biological stains, fluorescent markers, materials science and optoelectronics.

Keywords: fluorescence, bithiophenes, benzothiazoles, bithienyl-benzothiazoles
Category: 2 (Materials and technology)

1 Introduction

Fluorescent compounds have found widespread use in scientific and industrial areas, for example as fluorescent brightening agents, for textile and plastics, additives in textile dyeing, inks and paints, tunable dye lasers and biological stains. Other applications include electroluminescent and liquid crystals displays, solar collectors, materials science and optoelectronics. The benzothiazole nucleus appears in many fluorescent compounds that have useful applications, which results from the ease of synthesis of this heterocycle and the high fluorescence quantum yields obtained when this small, rigid moiety is present in the compounds [1].

Thiophenes and oligothiophenes substituted by donor/acceptor groups have been extensively investigated. These compounds are often used as energy transfer and light-harvesting systems and for optical and electronic devices [2-4]. Oligothiophene derivatives are also characterised by important electroluminescence properties. Due to their strong fluorescence, these compounds can also find application as fluorescent markers [5-7].

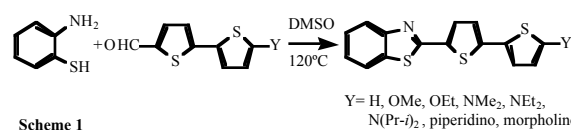
2 Results and discussion

In recent years we have been interested in the synthesis and study of the fluorescence properties of a series of heterocyclic compounds of the benzothiazole type, substituted with several groups such as indolyl, carbazolyl, coumaryl and thienyl [8-10]. The

most promising results were obtained for the 2-(2'-thienyl)benzothiazoles [8], substituted in position 5' with electron donating groups, and these findings prompted us to evaluate the bithiophene moiety, with various groups such as alkoxy- or *N,N*-dialkylamino.

Our recent reported synthesis of 5-formyl-5'-alkoxy- and 5-formyl-5'-amino-2,2'-bithiophenes **2** made these compounds available in reasonable amounts, ready for further applications [11]. Indeed, we were able to use these compounds with success as substrates for the synthesis of 1,3-benzothiazole derivatives **1a-h**. The 5-formyl bithiophene **2a** was synthesised by a standard Suzuki coupling [12] between 2-bromo-5-formylthiophene and 2-thiophene boronic acid in 85% yield. Therefore the synthesis, UV/Vis and fluorescence properties of a series of heterocyclic fluorophores of the benzothiazole type containing a bithienyl moiety have been investigated.

The benzothiazole moiety was obtained by the simple reaction of *o*-aminobenzenethiol with 5-formyl-substituted bithiophenes **2a-h**, in DMSO at 120 °C for 30-60 min (Scheme 1). Purification of the crude products by column chromatography gave the pure benzothiazoles **1a-h** in good to excellent yields (57-96%).



Scheme 1

The reaction is initiated by the formation of the corresponding imine that cyclises spontaneously, yielding the benzothiazoline, which is oxidised to the benzothiazole, aided by the oxidising character of DMSO. The yields for compounds **1d-h** are lower than for compounds **1a-c**, due to the higher electron-donating character of *N,N*-dialkylamino groups, which makes the carbonyl of the formyl group less prone to nucleophilic attack by the amino group. Some reagent degradation during reaction was also detected in these cases.

The fluorescence spectra of compounds **1a-h** were measured, excitation and emission maxima and fluorescence quantum yields are also reported (Table 1). Absorption and emission spectra of 3×10^{-6} M solutions of compounds **1a-h** were run in degassed absolute ethanol, using 9,10-diphenylanthracene as standard ($\phi=0.95$ in ethanol). All the compounds are very fluorescent, especially **1b**

and **1c** ($\phi= 0.58$ and 0.56 , respectively) and show large Stokes shift (the lowest being 108 nm for **1b** and the highest 176 nm for **1a**).

In Fig. 1, the various emission spectra for **1a-h** are compared, showing that the nature of the substituent group influences the fluorescence quantum yield, as well as the wavelength of maximum emission.

Fluorescence data was also collected for precursors **2a-h** (Table 2 and Fig. 2). They show lower Stokes shift and lower quantum yield, except for **2b** and **2c** which have quantum yields similar to that of the corresponding benzothiazoles **1b** and **1c**. In these cases, when the substituent is methoxy or ethoxy, the introduction of the benzothiazole moiety does not affect much the quantum yield, whereas with all other substituents the presence of the benzothiazole increases fluorescence quantum yield dramatically.

Table 1. Yields, UV/Vis and fluorescence data for compounds **1a-h**

Compound	Y	Yield (%)	UV/Vis		Fluorescence	
			λ_{\max}/nm	$\log \epsilon$	$\lambda_{\text{em}}/\text{nm}$	ϕ
1a	H	92	378	4.55	454	0.25
1b	OMe	96	390	4.43	498	0.58
1c	OEt	94	391	4.50	500	0.56
1d	NMe ₂	65	440	4.19	587	0.48
1e	NEt ₂	56	455	4.20	587	0.46
1f	N(<i>Pr-i</i>) ₂	59	452	4.12	588	0.41
1g	piperidino	81	432	4.31	593	0.52
1h	morpholino	65	420	4.29	582	0.48

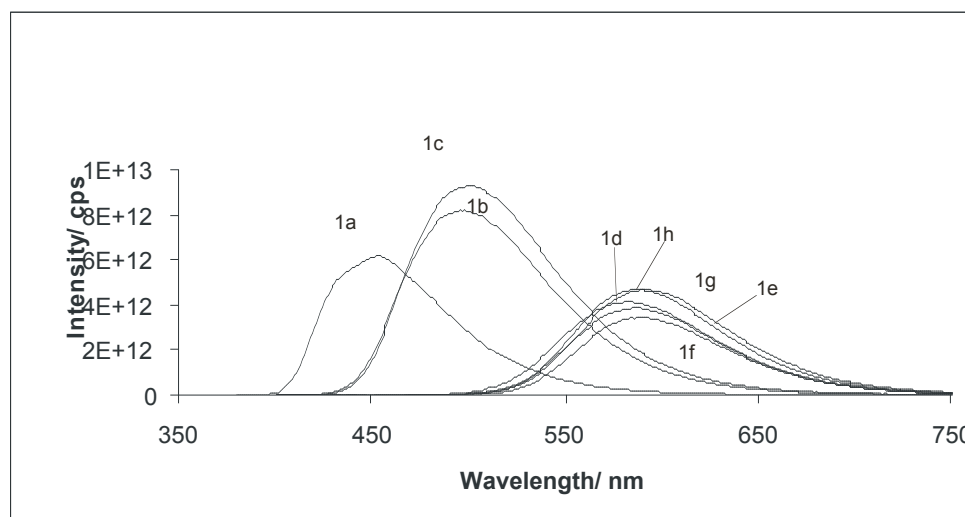


Fig. 1. Emission spectra for compounds **1a-h**.

All the synthesized compounds show good stability in solid state and in solution. Currently we are investigating the introduction of other substituents on the thienyl and

bithienyl moiety and also the substitution on the benzothiazole ring to modulate the fluorescence quantum yield and the wavelength of maximum emission.

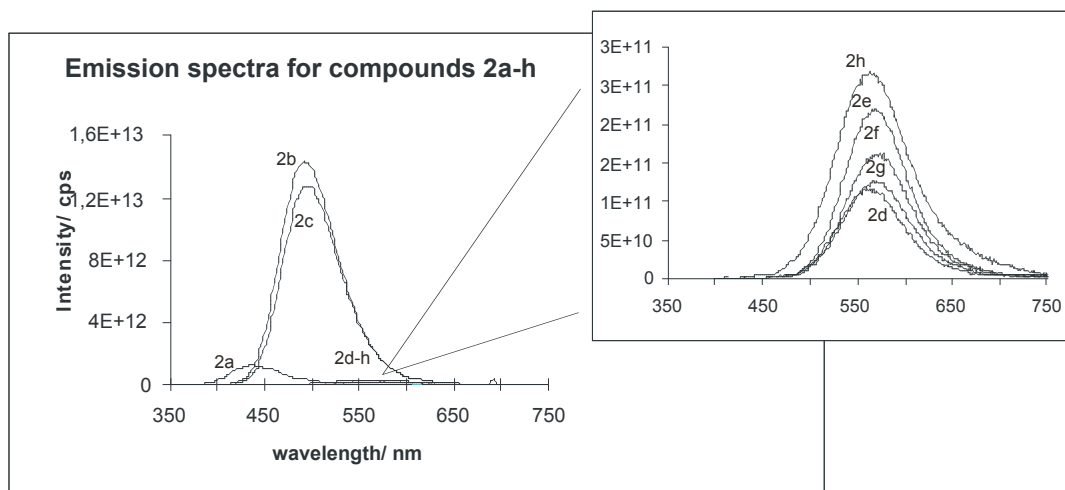


Fig. 2. Emission spectra for compounds **2a-h**.

Table 2. UV/Vis and fluorescence data for compounds **2a-h**

Compound	Y	UV/Vis		Fluorescence	
		λ_{\max}/nm	$\log \epsilon$	$\lambda_{\text{em}}/\text{nm}$	ϕ
2a	H	347	4.36	435	0.04
2b	OMe	381	4.31	492	0.51
2c	OEt	379	4.37	496	0.47
2d	NMe ₂	449	4.37	559	0.01
2e	NEt ₂	463	4.43	569	0.005
2f	N(Pr- <i>i</i>) ₂	465	4.35	573	0.01
2g	piperidino	440	4.35	570	0.01
2h	morpholino	421	4.25	562	0.02

3 Experimental details

The new compounds **1a-h** were completely characterised by elemental analysis or high resolution mass spectrometry, ¹H and ¹³C NMR spectroscopy and UV/Vis spectroscopy. The synthesis of formyl bithiophenes **2a-g** has been described elsewhere [11].

Method for the synthesis of **1a-h** (described for **1b**)

5-Formyl-5'-methoxybithiophene **2b** (30 mg, 0.13 mmol) and *o*-aminobenzenethiol (0.014 ml, 0.134 mmol) were heated in DMSO (2 mL)

at 120 °C in an oil bath with magnetic stirring for 30-60 min. Reaction was followed by TLC using chloroform/hexane 1:1 as eluent. When the reaction was completed, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was dried with magnesium sulphate and evaporated in vacuum. The crude residue was submitted to silica gel column chromatography using mixtures of hexane and chloroform of increasing polarity. The fractions containing the purified product were collected and

evaporated. The product was then recrystallised.

Spectroscopic data for compound 1b

¹H NMR (CDCl₃, 300 MHz): δ 3.94 (3H, s, OCH₃), 6.18 (1H, d *J* 4 Hz, 4'-H), 6.96 (1H, d *J* 4 Hz, 3'-H), 7.01 (1H, d *J* 4 Hz, 3''-H), 7.36 (1H, dt *J* 7 and 1.2 Hz, 5-H), 7.47 (1H, dt *J* 7 and 1.2 Hz, 6-H), 7.51 (1H, d *J* 4 Hz, 4''-H), 7.84 (1H, dd *J* 7 and 1.2 Hz, 7-H), 8.00 (1H, dd *J* 7 and 1.2 Hz, 4-H).

¹³C NMR (CDCl₃, 75.4 MHz): δ 60.31 (OCH₃), 104.75 (4'-C), 121.39 (7-C), 122.53 (3''-C), 122.74 (4-C), 122.85 (2'-C + 3'-C), 125.06 (5-C), 126.42 (6-C), 129.28 (4''-C), 134.06 (2-C), 134.54 (4a-C), 142.09 (2''-C), 153.67 (7a-C), 161.05 (5''-C), 166.68 (5'-C).

High resolution mass spectrometry HRMS (EI)
Calculated for C₁₆H₁₁NOS₃: 329.0003; Found: 329.0008.

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