



Novel fluorescent N,O-chelated fluorine-boron benzamide complexes containing thiadiazoles: Synthesis and fluorescence characteristics

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ARTICLE INFO

Article history:

Received 9 May 2017

Received in revised form

13 August 2017

Accepted 14 August 2017

Available online 17 August 2017

Keywords:

BF₂ complexes

Blue fluorescence

Solid state

Stokes shifts

Quantum yield

AIEE

ABSTRACT

A series of N-(5-phenyl-1,3,4-thiadiazol-2-yl)benzamide derivatives and their corresponding BF₂ complexes were synthesized, and their photophysical properties were determined. The effect of the derivatives with various substituents on the benzamide ring and phenyl-1, 3, 4-thiadiazole ring were examined in different organic solvents and in the solid state. These dyes enjoy a series of excellent photophysical properties including the large Stokes shift, solid-state fluorescence, and aggregation-induced emission effect (AIEE).

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1. Introduction

Organic fluorine-boron complexes carrying the BF₂ moiety are known to be fluorescent [1]. Among them, the boron-dipyrromethene (BODIPY) as the best-known example, are a family with excellent fluorescent properties [2]. They exhibit high fluorescence quantum yield, outstanding optical properties and sharp fluorescence spectra [3,4] and are often applied to electroluminescent devices [5], dye-sensitized solar cells [6,7], liquid crystals [8], biological imaging [9] and laser dyes [10]. Among these, heterocyclic azo dyes have been widely investigated mostly due to they are versatile chromophores that can provide bright strong shades tunable for absorption spectrum [11]. And azo dyes are of particular interest because the planarity of the azo bridge combines with benzoyl or other systems should contribute to larger π electron transmission effects and lead to higher optical activity [12,13]. These previous studies prompted us to the synthesis and the characterization of new thiadiazoles N-O BF₂ as suitable candidates for potential use in fluorescent dyes.

In recently years, BF₂ fluorescence complexes have attracted significant attention due to their outstanding optical properties [14]. However, in many cases, these dyes exhibit decreased

fluorescence in the solid state as a result of aggregation-caused quenching (ACQ) [15], which owing to the formation of delocalized excitons or excimers cause enhanced non-radiative deactivation of the excited state [16,17]. We design these boron fluoride complexes of thiadiazoles (**3b**) have showed nice fluorescence in solution state and solid state, however, we also find these boron fluoride complexes (**3a,3d**) exhibit intense solid fluorescence but weak in solution. In contrast of aggregation-caused quenching (ACQ) [18], the unusual phenomenon of the luminescence aggregate state stronger than that in the solution state [19], called aggregation-induced emission effect (AIEE) [20], which is now attracting increasing research attention. These compounds (**3a,3d**) which have the AIEE characteristics exhibit weak luminescence in solution state, but show highly emissive behaviour in their aggregated and solid states. The results showed that thiadiazoles derivatives and their BF₂ complexes displayed attractive luminescent properties [21,22].

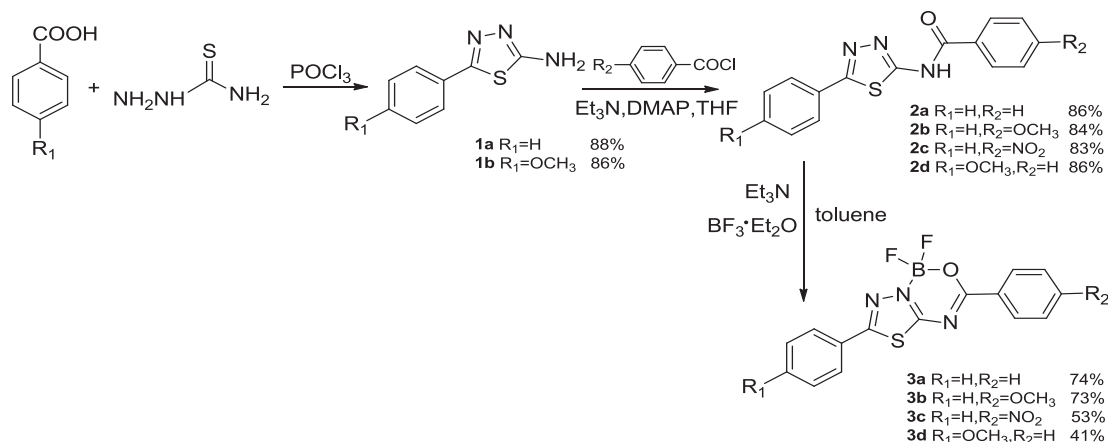
2. Results and discussion

2.1. Synthesis

Preparation of the N-(5-phenyl-1, 3, 4-thiadiazol-2-yl)benzamide derivatives **2** and their corresponding BF₂ complexes **3** were shown in Scheme 1. Benzamide derivatives **2** were prepared following a patent method [23] by amidation of 2-

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Scheme 1. Synthesis of benzamide **2**, BF_2 complexes **3**.

aminobenzothiazole with benzoyl chloride (1.2 equiv.) at room temperature which resulted in more than 83% yields. The BF_2 complexes **3** were produced, with the yields of 41%–74%, by using an excess of $BF_3 \cdot OEt_2$ in toluene with Et_3N as the base and purification by column chromatography. All the structures of boron complexes were fully characterized by FTIR, 1H NMR, ^{13}C NMR and HRMS analysis.

2.2. Fluorescence detection

2.2.1. UV–Vis and fluorescence of **3a** in solution

The end product BF_2 complexes **3** showed good solubility and stability in organic solvents such as dichloromethane (DCM), chloroform, toluene, EtOH, THF and *N,N*-dimethylformamide. By testing, no observable color and fluorescence fading was found over months. The solvent effect on the absorption and fluorescence properties of **3a** were examined. As shown in Table 1 and Fig. 1, complex **3a** exhibited a sharp absorption peak at about 330 nm in organic solvents, and the λ_{max} was barely affected by solvent polarity, suggesting that the dipole moments of the molecules in their ground and excited states were almost equal [24]. While the fluorescence intensity were strongly dependent on solvents and reduced with the increase in solvent polarity. In Fig. 1(b), **3a** showed the highest emission curve in toluene. So we chose toluene to examine the absorption and fluorescence properties of all the BF_2 complexes **3**.

2.2.2. Optical properties of complexes **3** in solution

The UV–vis absorption and normalized fluorescence spectra of **3a–3d** in toluene are shown in Fig. 2. The maximum absorption wavelength of complex **3** compared to that of amide **2** (Table 1), although amide **2** did not show fluorescence, complex **3** exhibited blue fluorescence at 410 nm–436 nm. The fluorescence quantum yields (Φ_F) of **3a** in toluene was 0.06 and the Stokes shift was 73 nm. The λ_{max} of **3b** (356 nm), **3c** (343 nm), **3d** (349 nm) was slightly red-shifted, and ϵ_{max} (**3b**) was higher (46667) compared to that of **3a** (337 nm and 36000), respectively. But, **3c** (25000), **3d** (25333) showed decrease in ϵ_{max} . It is worth noting that the fluorescence quantum yields were highly dependent on the substituents on the aromatic ring. In the absence of substitution at the right aromatic ring, low quantum yield (0.06) was observed and introducing electron-withdrawing (NO_2) onto the *para*-position of right phenyl ring (**3c**) got lower quantum yield (<0.01). However, introducing an electron-donating methoxy group onto the *para*-position of right phenyl ring (complex **3b**), the quantum yield increased to 0.29. In addition, we could observe high quantum yield 0.16 (**3d**) which introducing electron-donating methoxy group onto the *para*-position of left phenyl ring. This suggested that we could construct push-pull-type architecture through the introduction of an electron-donating group onto the phenyl ring (see Figs. 3 and 4).

2.2.3. Optical properties of complexes **3** in the solid state

The BF_2 complexes **3** were also emissive in the solid state and their emission data were shown in Table 1. Generally, the high

Table 1
Optical data of **3a–3d** in solvents and in the solid state.

Dye	Matrix	UV–Vis		Fluorescence		Stokes shift (nm)
		λ_{abs} (nm)	ϵ_{max} ($M^{-1} cm^{-1}$)	λ_{em} (nm)	Φ_F	
3a	$CHCl_3$	335	33667	413	0.05	78
	toluene	337	36000	410	0.06	73
	DCM	333	33000	412	0.03	79
	THF	332	32333	402	0.02	70
	EtOH	328	29667	409	0.01	81
	MeCN	330	34000	415	<0.01	85
	EA	331	33333	411	0.01	80
	DMF	334	36667	419	0.01	85
	solid	367		429		62
3b	toluene	356	46667	414	0.29	58
	solid	369		446		77
3c	toluene	343	25000	409	<0.01	66
3d	toluene	349	25333	436	0.16	87
	solid	370		456		86

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