



# Synthesis of highly soluble fluorescent $\pi$ -extended 2-(2-thienyl)benzothiazole derivatives via oxidative cyclization of 2-thienylthioanilide as the key step



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## ARTICLE INFO

### Article history:

Received 1 June 2013

Revised 3 October 2013

Accepted 15 October 2013

Available online 30 October 2013

### Keywords:

Benzothiazole

2-(2-Thienyl)benzothiazole

Oxidative cyclization

Push–pull dye

Fluorescence

## ABSTRACT

In this Letter, we synthesize highly soluble push–pull type fluorescent 2-(2-thienyl)benzothiazole dyes and evaluate their photophysical properties. The key step is the synthesis of 2-(5'-bromothien-2'-yl)-6-alkoxybenzothiazole (**2**) via oxidative cyclization of 2-thienylthioanilide using  $\text{PhI}(\text{OAc})_2$  as the oxidant. The target dyes could be easily synthesized by the Suzuki–Miyaura cross-coupling reaction of **2** and an appropriate  $\pi$ -donor. The photophysical properties of the 2-thienylbenzothiazole chromophore were controlled by the  $\pi$ -donor moiety. It was found that **2** exhibited large Stokes shifts ( $5345\text{ cm}^{-1}$ ) and a high quantum efficiency for fluorescence ( $\Phi_F = 0.94$  in  $\text{CH}_2\text{Cl}_2$ ). Therefore, it can be expected to be a useful photofunctional material in liquid crystal laser dyes and nonlinear optical materials.

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Benzothiazole is a thermally stable electron-withdrawing heterocyclic scaffold. Functional derivatives of benzothiazole with  $\pi$ -extended moieties at the 2-position (methyne substituents), that is, push–pull type 2-arylbenzothiazoles, have been extensively investigated.<sup>1–8</sup> In particular, systems containing various  $\pi$ -extended donor moieties with benzothiazole as the acceptor can be easily realized through  $\pi$ -conjugation. Such donor–acceptor systems have considerable potential for use in fluorescent dyes,<sup>5</sup> nonlinear optics (NLO),<sup>6</sup> electron-transport materials,<sup>7</sup> field-effect transistors,<sup>8</sup> and so on.

Among all these applications, we are interested in preparing fluorescent dyes for distributed-feedback liquid–crystal lasers.<sup>9,10</sup> For practical applications, the lasing threshold of a liquid–crystal laser must be lowered to nearly zero.<sup>10</sup> To achieve the desired low threshold, it is necessary to design a laser dye that exhibits high luminous efficiency (high molar absorption coefficient and high quantum yield)<sup>9,10</sup> and a large Stokes shift.<sup>11,12</sup>

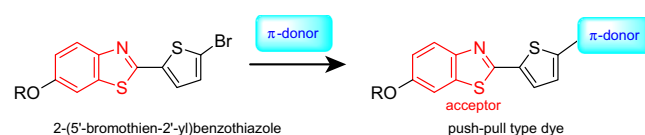
In order to develop such a laser dye, we focused on push–pull type  $\pi$ -extended 2-(2-thienyl)benzothiazole derivatives (chromophores) with a highly soluble substituent.<sup>13</sup> Thienyl groups with various donors can enhance the molecular hyperpolarizability of benzothiazole to produce appropriate Stokes shifts. The 2-ethylhexyl group, a branched long-chain alkyl group, has been adopted as an efficient substituent for achieving high solubility and good processability.<sup>10</sup>

To this end, we designed various  $\pi$ -extended 2-(2-thienyl)benzothiazole dyes from 2-(5'-bromothien-2'-yl)benzothiazole with appropriate  $\pi$ -donors via the Suzuki–Miyaura cross-coupling reaction (Scheme 1). In addition, to achieve high solubility, (2-ethylhexyl)oxy was chosen as the substituent at the 6-position of benzothiazole. However, to the best of our knowledge, a method for synthesizing 6-alkoxy-2-thienylbenzothiazole derivatives has not yet been developed.

In this study, we investigate the cyclization of 2-thienylthioanilide, which is a precursor of  $\pi$ -extended 2-(2-thienyl)benzothiazole, and optimize the reaction conditions. Then, we prepare push–pull-type dyes and evaluate their photophysical properties, with the aim of developing an efficient laser dye for future applications.

## Synthesis of 2-(5'-bromothien-2'-yl)-6-alkoxybenzothiazole

Various synthetic methodologies have been developed for the preparation of versatile 2-arylbenzothiazole derivatives.<sup>1</sup> These



Scheme 1. Synthetic route of  $\pi$ -extended 2-(2-thienyl)benzothiazole dyes.

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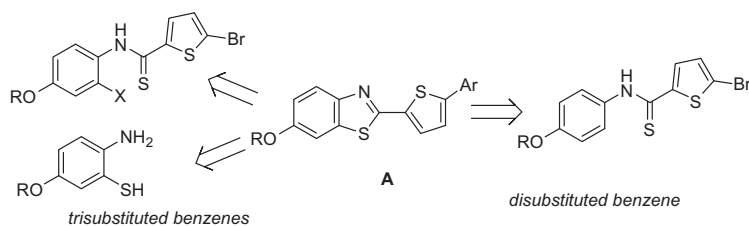


Figure 1. Retrosynthetic analysis of a benzothiazole.

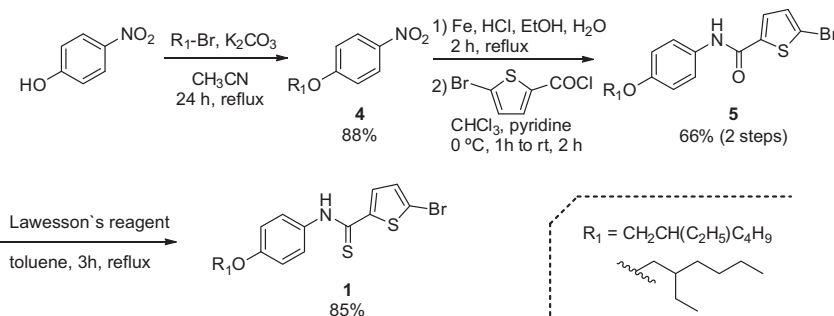
processes can be categorized into three types. The first approach involves the functionalization (arylation) of benzothiazoles.<sup>2</sup> In particular, the acidic protons of the thiazole moiety are susceptible to halogenation and direct arylation, and the halogenated benzothiazoles can be used in cross-coupling reactions. The second protocol is the cyclocondensation of aryl formates or aryl carboxylic acids with *ortho*-aminothiophenol, which is prepared by solvolysis of benzothiazoles.<sup>3</sup> Finally, the last approach is a cyclization route via aromatic substitution or oxidative functionalization.<sup>4</sup>

We focused on oxidative cyclization (Fig. 1) to synthesize the target product, 2-(5'-aryl-thien-2'-yl)-6-alkoxybenzothiazole (compound **A**). This route is advantageous for preparing the cyclization precursor. Synthesis of our target compound via this route involves the preparation of only the disubstituted benzene, whereas other routes require trisubstituted benzenes, which are not easy to prepare.<sup>14</sup> Although oxidative cyclization for the synthesis of a benzothiazole skeleton is an established process, we are the first to carry out the oxidative cyclization of 2-thienylthioanilide.

Scheme 2 summarizes the preparation of the cyclization precursor, 5-bromo-*N*-(4-((2-ethylhexyl)oxy)phenyl)thiophene-2-carbothioamide **1**. The starting material is 4-nitrophenol, to which 2-ethylhexyl bromide is added in the presence of  $K_2CO_3$  and  $CH_3CN$ . Then, the nitro group is transformed to an amino group using iron powder and ethanol, and subsequently, 5-bromo-2-thienyl chloride in  $CH_2Cl_2$  is obtained in 66% yield. **1** was prepared in 85% yield by using Lawesson's reagent.

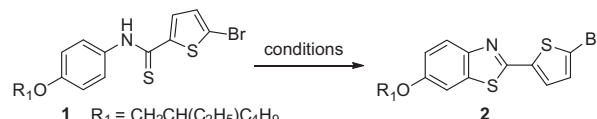
Next, we examined the oxidative cyclization of **1** using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in  $CH_2Cl_2$ . However, despite the previously reported high yields (>80%)<sup>4d</sup> of 2-(2-phenyl)benzothiazole derivatives under the same conditions, we observed low conversion to 2-(5'-bromothien-2'-yl)benzothiazole **2** (only 10% yield) (Table 1, entry 1), and the starting compound **1** was not recovered even though a stoichiometric amount of DDQ was utilized.

The use of other cyclization agents also led to undesirable results (Table 1). In the case of chloranil,<sup>15</sup> **2** was obtained in <10% yield (entry 2), and large amounts of **1** was recovered. When  $K_3[Fe(CN)_6]$ <sup>16</sup> or halogens (i.e.,  $Br_2$  or  $I_2$ )<sup>17</sup> were used as oxidants, **1** decomposed immediately (entries 3–5). On the other hand, when  $PhI(OCOCF_3)_2$  was used, **2** was isolated in 20% yield (entry 6).



Scheme 2. Synthetic route of the cyclization precursor **1**.

Table 1  
Cyclization Reaction of **1** to afford **2**



Entry	Oxidant	Temperature (°C)	Solvent (0.1 M)	Yield (%)
1	DDQ	rt	$CH_2Cl_2^a$	10
2	Chloranil	110	Toluene <sup>a</sup>	Trace amount
3	$K_3[Fe(CN)_6]$	80	$EtOH^a$	Trace amount
4	$Br_2$	0	$CH_2Cl_2^a$	0 <sup>c</sup>
5	$I_2$	0	$CH_2Cl_2^a$	0 <sup>c</sup>
6	$PhI(OCOCF_3)_2$	rt	$CF_3CH_2OH^a$	20
7	$PhI(OAc)_2$	rt	$CF_3CH_2OH^a$	44
8	$PhI(OAc)_2$	rt	$CH_2Cl_2^a$	22
9	$PhI(OAc)_2$	rt	$CF_3CH_2OH^b$	68

<sup>a</sup> The reaction was carried out with 0.1 M of **1**.

<sup>b</sup> 0.04 M of **1**.

<sup>c</sup> Decomposition.

Furthermore, with  $PhIOAc_2$  as the oxidant, **2** was obtained in 44% yield (entry 7). Thus, although the yield of **2** could be improved by selecting the appropriate oxidant, it was still low.

To improve the yield further, the reaction conditions were varied and optimized. When  $CH_2Cl_2$  was used as a solvent, the yield decreased to 22% (entry 8). On the other hand, the yield increased to 68% when a lower concentration (0.04 M) of **1** was used (entry 9).

Jackson and co-workers reported that  $PhI(OCOCF_3)_2$  was more appropriate than  $PhIOAc_2$  for the cyclization of thioanilides.<sup>13</sup> They mentioned that the oxidant  $PhI(OCOCF_3)_2$  enabled 2-phenylbenzothiazole to be prepared efficiently because of its radical property,<sup>18</sup> whereas in the case of  $PhIOAc_2$ , oxidative cyclization proceeded with little conversion, resulting in the recovery of the corresponding benzanilide. However, in our case, radical conditions were not effective in constructing a benzothiazole skeleton (Table 1, entries 1, 3–5). Under our conditions, the radicals enhance the decomposition of **1** at the electron-rich benzene ring<sup>21</sup> or thiophene moiety.<sup>22</sup> In contrast,  $PhIOAc_2$  functions as a two-electron oxidant for oxygen and sulfur nucleophiles.<sup>19,20</sup> This is the reason

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