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Synthesis and electronic absorption and fluorescence of 2-arylbenzothiazole derivatives

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Abstract

A series of new 2-arylbenzothiazoles have been prepared in high yields by Jacobson's cyclization condensation of 2-aminobenzenethiol with benzoyl chloride or benzaldehyde derivatives under three different routes. These compounds have been fully characterized by EA, IR, NMR and MS. The electronic absorption and fluorescence of these compounds have been systematically investigated for the first time. The relationships between their photophysical properties and structures have been discussed. The alteration of absorption and emission wavelengths can be elucidated by Hammett's substituent constants.

Keywords: 2-Arylbenzothiazole; Structure; Electronic absorption; Fluorescence; Hammett's substituent constants

1. Introduction

Benzothiazole derivatives have been well known for their biological and pharmaceutical activities, such as antitumor, antiviral, antimicrobial activities and potent inhibitory activity [1–3]. Recently, benzothiazole derivatives have also attracted increasing attention due to their application in the area of organic optoelectronic materials, such as second-order nonlinear optical (NLO) materials [4], two-photo absorption (TPA) chromophores [5], photoconducting materials [6], liquid crystals [7] and fluorophores [8]. Most recently, 2-arylbenzothiazoles have been used as cyclometalated ligands for heavy metal ions, such as Ir [9] and Pt [10], because of their strong chelating capability, and these complexes have been proven to be good phosphorescent dyes for organic light-emitting diodes (OLEDs).

Though benzothiazole derivatives have been widely investigated, surprisingly, the studies on their photoluminescent properties are very limited [8]. Moreover, to our knowledge, there are not any systematic surveys on the relationship between their structure and photophysical properties, which are closely related with the electronic characters of benzothiazole derivatives. Understanding the relationship will be benefit to design new fluorescent agent and benzothiazole-based ligands to tune luminescent properties of their corresponding complexes.

In this article, a series of 2-arylbenzothiazole compounds have been synthesized by condensation of 2-aminobenzenethiol with benzoyl chloride derivatives or benzaldehyde derivatives, and fully characterized by EA, NMR and MS. We will discuss how the substitutes with different electronic effect or position or number on the aryl ring of 2-arylbenzothiazole tune their electronic absorption and photoluminescent properties.

2. Experimental

2.1. General information

Melting points (uncorrected) were performed on WRS-2 Melting Point apparatus. ^{1}H NMR and ^{19}F NMR were recorded on Varian Mercury VX-300 MHz spectrometer in $CDCl_3$. Infrared spectra were obtained on a Nicolet SX Fourier transform spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Carlorerba-1106 microanalyzer. Mass Spectra (FAB-MS) were determined by VJ-ZAB-3F Mass Spectrometer. UV–vis absorption spectra were recorded on Schimadzu 160A spectrophotometer. PL spectra were recorded on Perkin-Elmer LS 55 luminescence spectrophotometer.

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All silica gel column chromatography was performed with use of silica gel (200–300 mesh). The intermediates, i.e. 4-cyanobenzoyl chloride [11], 4-iodobenzaldehyde [12], 3-bromobenzaldehyde [13], 2-methoxybenzaldehyde [14], 3-methoxybenzaldehyde [15], 2,4-dimethoxybenzaldehyde [16] and 2,4,5-trimethoxybenzaldehyde [17] were prepared according to literature procedure. Other materials were purchased and used without further purification.

2.2. Preparation of *1–3*

General procedure: 2-aminobenzenethiol (10 mmol) was dissolved into 20 ml of *N*-methyl-pyrrolidinone under argon atmosphere, and then the corresponding acid chloride (15 mmol) was slowly added at room temperature. The mixture was heated at 100 °C for 4 h. After cooling, the solution was poured into ice water and the solution was adjusted to pH 8–9 with 7N aqueous ammonia. A white precipitate was separated out and the crude product was filtered, washed with water several times, and further purified by column chromatography.

2-(4-Fluorophenyl)-benzothiazole 4-F-bt (**1**), white solid, yield: 93%. ^{1}H NMR: 8.05 (m, 3H), 7.88 (d, J = 7.8 Hz, 2H), 7.48 (t, J = 7.5 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.17 (t, J = 8.4 Hz, 1H). ^{19}F NMR: −109.3. mp = 99–100 °C. Anal. Calcd. for $C_{13}H_8NFS$: C, 68.10; H, 3.52; N, 6.11. Found: C, 68.20; H, 3.53; N, 6.23%. MS (FAB): *m/e*, 229 (M^+).

2-(4-Cyanophenyl)-benzothiazole 4-CN-bt (**2**): light yellow solid, yield: 91%. ^{1}H NMR: 8.06 (d, J = 7.5 Hz, 1H), 7.96 (d, J = 8.4 Hz, 2H), 7.90 (d, J = 7.5 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.50 (t, J = 7.5 Hz, 1H), 7.41 (t, J = 6.9 Hz, 1H). IR (KBr, cm^{-1}): 2206. (s, –CN). mp = 100–101 °C. Anal. Calcd. for $C_{14}H_8N_2S$: C, 71.16; H, 3.41; N, 11.86. Found: C, 71.08; H, 3.45; N, 11.67%. MS (FAB): *m/e*, 236 (M^+).

2-(4-*tert*-Butylphenyl)-benzothiazole 4-^{t}Bu-bt (**3**): white solid, yield: 87%. ^{1}H NMR: 8.02 (m, 3H), 7.82 (d, J = 7.2 Hz, 1H), 7.43 (m, 3H), 7.29 (t, J = 7.5 Hz, 1H), 1.30 (s, 9H). mp = 106–107 °C. Anal. Calcd. for $C_{17}H_{17}NS$: C, 76.36; H, 6.41; N, 5.24. Found: C, 76.24; H, 6.42; N, 5.26%. MS (FAB): *m/e*, 267 (M^+).

2.3. Preparation of *4–8*

General procedure: 2-aminothiophenol (10 mmol) and the corresponding benzaldehyde (10 mmol) were dissolved to 20 ml of DMSO under argon atmosphere. The mixture was heated at 200 °C for 0.5 h. After cooling, the solution was poured into ice water, and then adjusted the solution to pH 8–9 with 1N $NaHCO_3$ solution. The precipitate was filtered, washed with a great deal of water several times. After dried under vacuum, the crude product was recrystallized with ethanol.

2-(4-tolyl)-benzothiazole 4-Me-bt (**4**): white crystals, yield: 89%. ^{1}H NMR: 8.02 (d, J = 8.1 Hz, 1H), 7.95 (d, J = 8.1 Hz, 2H), 7.85 (d, J = 8.1 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.33 (t, J = 7.2 Hz, 1H) 7.26 (d, J = 8.1 Hz, 2H), 2.42 (s, 3H). mp = 85–86 °C. Anal. Calcd. for $C_{14}H_{11}NS$: C, 74.63; H, 4.92; N, 6.22. Found: C, 74.45; H, 4.82; N, 6.24%. MS (FAB): *m/e*, 225 (M^+).

2-(4-Chlorophenyl)-benzothiazole 4-Cl-bt (**5**): white crystals, yield: 90%. ^{1}H NMR: 8.03 (t, J = 8.4 Hz, 3H), 7.89 (d, J = 8.1 Hz, 1H), 7.48 (q, J = 7.2 Hz, 3H), 7.38 (t, J = 7.5 Hz, 1H). mp = 116–117 °C. Anal. Calcd. for $C_{13}H_8NClS$: C, 63.54; H, 3.28; N, 5.70. Found: C, 63.45; H, 3.19; N, 5.64%. MS (FAB): *m/e*, 245 (M^+).

2-(4-Bromophenyl)-benzothiazole 4-Br-bt (**6**): light green needle crystals yield: 92%. ^{1}H NMR: 8.04 (d, J = 7.8 Hz, 1H), 7.93 (m, 3H), 7.60 (d, J = 8.4 Hz, 2H), 7.44 (t, J = 8.4 Hz, 1H), 7.38 (t, J = 8.1 Hz, 1H). mp = 120–121 °C. Anal. Calcd. for $C_{13}H_8NBrS$: C, 53.81; H, 2.78; N, 4.83. Found: C, 53.65; H, 2.92; N, 4.96%. MS (FAB): *m/e*, 289 (M^+).

2-(4-Iodophenyl)-benzothiazole 4-I-bt (**7**): green crystals, yield: 86%. ^{1}H NMR: 8.04 (t, J = 8.1 Hz, 3H), 7.90 (d, J = 7.8 Hz, 1H), 7.48 (m, 3H), 7.39 (t, J = 8.1 Hz, 1H). mp = 134–135 °C. Anal. Calcd. for $C_{13}H_8NIS$: C, 46.31; H, 2.39; N, 4.15. Found: C, 46.35; H, 2.56; N, 4.06%. MS (FAB): *m/e*, 337 (M^+).

2-(3-Bromophenyl)-benzothiazole 3-Br-bt (**8**): green crystals, yield: 82%. ^{1}H NMR: 8.27 (s, 1H), 8.07 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 7.2 Hz, 1H), 7.61 (d, J = 7.2 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.38 (m, 2H). mp = 124–126 °C. Anal. Calcd. for $C_{13}H_8NBrS$: C, 53.81; H, 2.78; N, 4.83. Found: C, 53.75; H, 2.89; N, 4.86%. MS (FAB): *m/e*, 289 (M^+).

2.4. Preparation of *9–13*

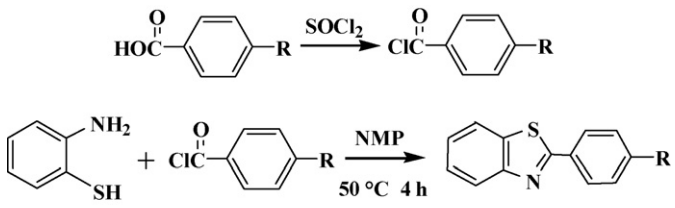
General procedure: 2-aminothiophenol (10 mmol) and methoxy substituted benzaldehyde (10 mmol) and *p*-toluenesulfonic acid monohydrate (PTSA) (1.0 mmol) were refluxed in chloroform (20 ml) under nitrogen for 24 h. After cooling, the mixture was extracted with water as well as ether and dried with Na_2SO_4. After removal of solvent, the crude product was recrystallized with ethanol to give pure product.

2-(2-Methoxyphenyl)-benzothiazole 2-MeO-bt (**9**): light green crystals, yield: 85%. ^{1}H NMR: 8.52 (d, J = 8.1 Hz, 1H), 8.08 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.46 (m, 2H), 7.36 (t, J = 7.5 Hz, 1H), 7.10 (m, 2H), 4.06 (s, 3H). mp = 118–119 °C. Anal. Calcd. for $C_{14}H_{11}ONS$: C, 69.68; H, 4.59; N, 5.90. Found: C, 69.72; H, 4.63; N, 6.01%. MS (FAB): *m/e*, 241 (M^+).

2-(4-Methoxyphenyl)-benzothiazole 4-MeO-bt (**10**): white crystals, yield: 86%. ^{1}H NMR: 8.03 (d, J = 7.2 Hz, 3H), 7.86 (d, J = 8.1 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H), 7.00 (d, J = 8.1 Hz, 2H), 3.88 (s, 3H). mp = 122–123 °C. Anal. Calcd. for $C_{14}H_{11}ONS$: C, 69.68; H, 4.59; N, 5.80. Found: C, 69.61; H, 4.45; N, 5.71%. MS (FAB): *m/e*, 241 (M^+).

2-(3-Methoxyphenyl)-benzothiazole 3-MeO-bt (**11**): white crystals, yield: 82%. ^{1}H NMR: 8.06 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.65 (m, 2H), 7.49 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 7.2 Hz, 2H), 7.04 (d, J = 7.8 Hz, 1H), 3.92 (s, 3H). mp = 120–121 °C. Anal. Calcd. for $C_{14}H_{11}ONS$: C, 69.68; H, 4.59; N, 5.80. Found: C, 69.57; H, 4.56; N, 5.76%. MS (FAB): *m/e*, 241 (M^+).

2-(2,4-Dimethoxyphenyl)-benzothiazole 2,4-MeO-bt (**12**): yellow green crystals, yield: 87%. ^{1}H NMR: 8.45 (d, J = 8.1 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.45 (t,



1 R = F;
2 R = CN;
3 R = ^{t}Bu.

Scheme 1. Synthesis of 2-arylbenzothiazoles **1**–**3** by route A.

J = 7.2 Hz, 1H), 7.32 (t, J = 7.2 Hz, 1H), 6.65 (d, J = 8.7 Hz, 1H), 6.56 (s, 1H), 4.01 (s, 3H), 3.86 (s, 3H). mp = 139–140 °C. Anal. Calcd. for $C_{15}H_{13}O_2NS$: C, 66.40; H, 4.83; N, 5.16. Found: C, 66.32; H, 4.76; N, 5.02%. MS (FAB): *m/e*, 271 (M^+).

2-(2,4,5-Trimethoxyphenyl)-benzothiazole 2,4,5-MeO-bt (**13**): green crystals, yield: 86%. ^{1}H NMR: 8.05 (t, J = 7.2 Hz, 2H), 7.88 (d, J = 7.8 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.33 (t, J = 7.2 Hz, 1H), 6.61 (s, 1H), 4.04 (s, 3H), 4.01 (s, 3H), 3.96 (s, 3H). mp = 198–199 °C. Anal. Calcd. for $C_{16}H_{15}O_3NS$: C, 63.77; H, 5.01; N, 4.65. Found: C, 63.66; H, 4.96; N, 4.62%. MS (FAB): *m/e*, 301 (M^+).

3. Results and discussion

3.1. Synthesis and characterization

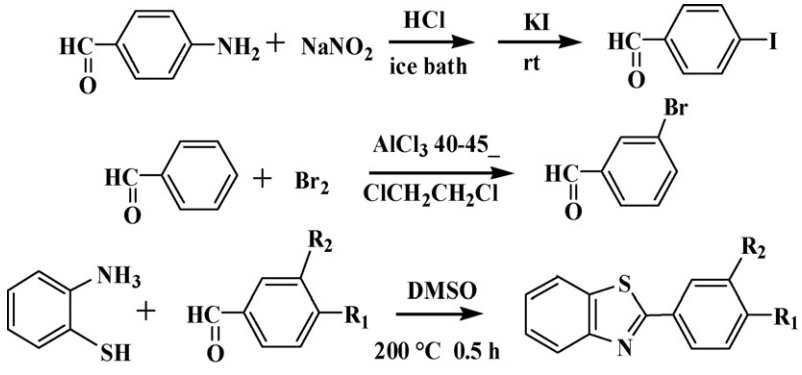
A lot of synthetic methods have been developed for preparing the benzothiazole derivatives, such as solid or liquid-phase combinatorial synthesis [18], C–C coupling reaction [19], radical cyclization [20] and microwave mediated reaction [21], etc. In this study, the 2-arylbenzothiazoles were synthesized by Jacobson's cyclization reaction of 2-aminobenzenethiol with benzoyl chloride or benzaldehyde derivatives [22]. In view of the easy availability of precursors, three synthetic routes were adopted as shown in Schemes 1–3.

In route A, 4-substituted benzoic acid was converted to corresponding acid chlorides, which subsequently underwent condensation with 2-aminobenzenethiol to afford the desired compounds **1**–**3**. The active acid chlorides make the reaction proceed under mild condition. The solvent of *N*-methylpyrrolidinone (NMP) provides a weak basic circumstance, which serves for the absorption reagent of hydrogen chloride produced during the reaction. It is noteworthy that the route A avoids the use of expensive 4-substitued benzaldehyde derivatives, such as 4-fluoro-benzaldehyde, 4-cyano-benzaldehyde and 4-*tert*-butyl-benzaldehyde.

In route B, the easy available substituted benzaldehydes were used as the precursors for cyclization reaction with 2-aminobenzenethiol. The solvent of dimethyl sulfoxide (DMSO) can provide not only the high temperature that speeds the reaction, but also its bibulous capability promotes the reaction process. The two factors make the reaction complete very quickly.

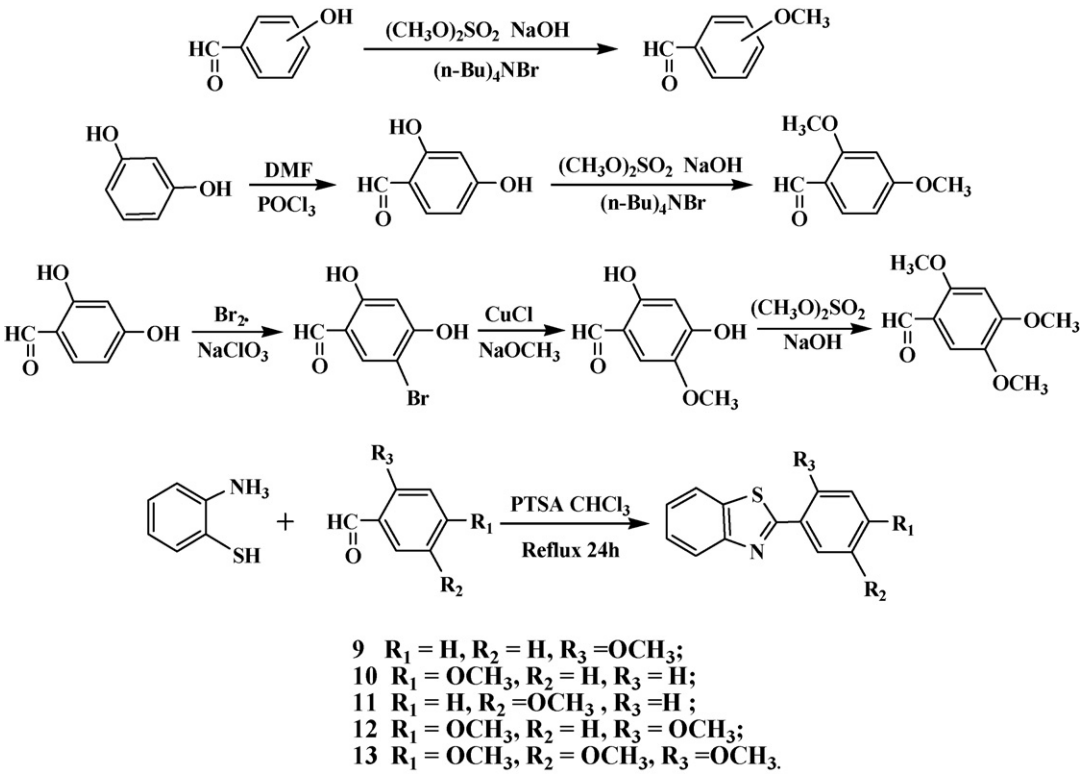
In route C, 1,3-benzenediol was converted to 2,4-dihydroxybenzaldehyde via Vilsmeier reactions, which then underwent bromination to give 5-bromo-2,4-dihydroxy-benzaldehyde. The bromine was subsequently replaced by methoxy under the CuCl as catalyst to afford the intermediate 2,4-dihydroxy-5-methoxy-benzaldehyde. All hydroxyls of these compounds were methylated by use of dimethyl sulfate. The methoxyl-substituted benzaldehydes finally reacted with 2-aminobenzenethiol under the *p*-toluenesulfonic acid (PTSA) as catalyst to afford the desired products **9**–**13**.

Elemental analyses of the compounds are consistent with the expected formulation of their structures. The mass spectra all give corresponding molecular ion peaks, respectively. ^{1}H NMR spectra show well-resolved multilets for the aryl protons. The protons of methoxyl appear a single peak at about 4.0 ppm. ^{19}F NMR of 4-F-bt (**1**) shows a single peak at −109.3 ppm. 4-CN-bt



4 R_1 =CH_3, R_2 = H;
5 R1 = Cl, R_2 = H;
6 R_1 = Br, R_2 = H;
7 R_1 =I, R_2 = H;
8 R_1 = H, R_2 = Br.

Scheme 2. Synthesis of 2-arylbenzothiazoles **4**–**8** by route B.



Scheme 3. Synthesis of 2-arylbenzothiazoles **9**–**13** by route C.

(**2**) displays a characteristic CN infrared stretching vibration at 2206 cm^{-1}.

3.2. Electronic absorption spectra

Figs. 1 and 2 show the absorption spectra of 2-arylbenzothiazoles in the solution of dichloromethane. All compounds show a wide absorption band in the region of 290–350 nm, with molar extinction coefficient at about 10,000 mol^{-1} cm^{-1}. With increasing the electron-donating ability of the 4-substituents on the phenyl ring, the absorption maximum shifts hyposochromically, while the electron-accepting CN group at the 4-position shifts the absorption maximum towards the red (refer to the corresponding data for compounds 4-MeO-bt (**10**), 4-^{t}Bu-bt (**3**), 4-Me-bt (**4**), 4-CN-bt (**2**) in Table 1). Similarly, the maximum absorption peak of stronger electron-donating methoxy at 3-position (3-MeO-bt (**11**)) blue shifts 12 nm comparing to the electron-withdrawing bromine at 3-position (3-Br-bt (**8**)). When changing the position of substitute from 4-position to 3- or 2-position, a marked bathochromic shift of the maximum absorption wavelengths is observed (refer to the corresponding data for compounds 4-

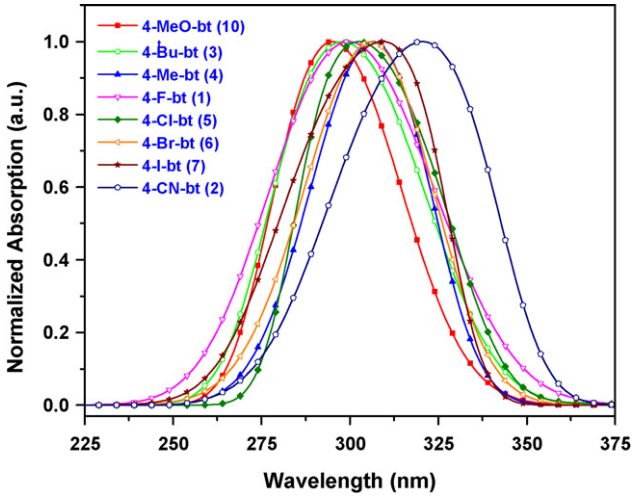


Fig. 1. Absorption spectra of 2-arylbenzothiazoles with different electronic effect of substitutes.

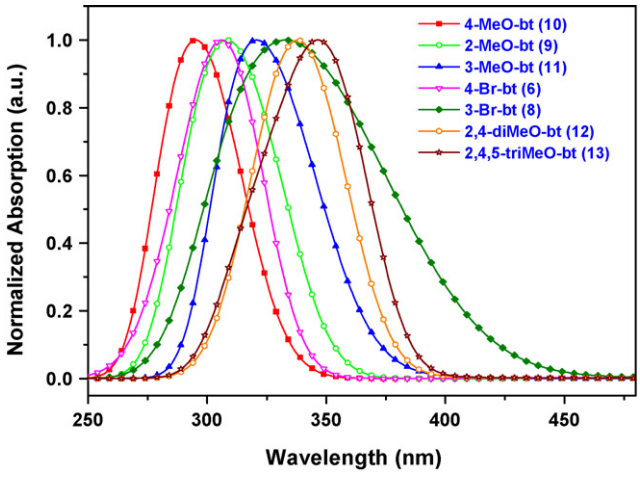


Fig. 2. Absorption spectra of 2-arylbenzothiazoles with different positions and number of substitutes.

Table 1
Photophysical data of 2-arylbenzothiazole derivatives

Compounds	λ_{max} (Abs)[a]		λ_{max} (Em) (nm)		Stoke's shift (nm)	Hammett's substituent constants, σ	Φ_f (%)[c]
	nm	log ε	Solution[a]	Film[b]			
4-MeO-bt (**10**)	295	4.0	355	358	60	−0.28	22.6
4-^{t}Bu-bt (**3**)	298	3.9	357	360	59	−0.19	22.4
4-Me-bt (**4**)	307	3.8	360	362	53	−0.17	21.0
4-F-bt (**1**)	300	4.1	368	371	68	0.062	24.1
4-Cl-bt (**5**)	303	3.8	371	376	68	0.227	26.4
4-Br-bt (**6**)	306	4.3	375	379	69	0.232	33.6
4-I-bt (**7**)	309	3.9	382	386	73	0.28	38.2
4-CN-bt (**2**)	322	3.9	419	421	97	0.66	25.5
3-Br-bt (**8**)	333	4.0	400	405	67	0.39	30.1
2-MeO-bt (**9**)	308	4.2	367	372	59		23.2
3-MeO-bt (**11**)	321	3.8	380	385	59	0.11	20.1
2,4-MeO-bt (**12**)	338	4.1	389	391	51		18.5
2,4,5-MeO-bt (**13**)	347	4.3	401	422	54		16.3

[a] In CH_2Cl_2 solution at 298 K.
[b] In PMMA film (5% weight ratio).
[c] Quantum yield of fluorescence was measured in CH_2Cl_2 solution relative to quinine bisulfate (10^{-5} M in 1.0N H_2SO_4 $\Phi_f = 0.546$, as standard).

MeO-bt (**10**), 2-MeO-bt (**9**), 3-MeO-bt (**11**), 4-Br-bt (**6**) and 3-Br-bt (**8**) in Table 1). For example, by changing the positions of methoxy substitute according to the order of 4-, 2-, and 3-position, the absorption peaks bathochromic shift 13 and 26 nm, respectively. It is obvious that the *meta* substitutes with respect to benzothiazole ring result a larger red shift on the absorption maximum than the *ortho* substitutes. This may be related to the electron-deficient property of benzothiazole moiety. The numbers of substitutes have also effect on their absorption maximum. The three methoxy substituted compound exhibits the maximum absorption peak at 347 nm.

3.3. Fluorescent properties

The photoluminescence spectra of 2-arylbenzothiazoles were measured in CH_2Cl_2 solution (Figs. 3 and 4) and in PMMA (polymethylmethacrylate) film (5% weight ratio) at 298 K, respectively. All compounds have good fluorescence quantum yields in solutions at room temperature, and large Stoke's shifts (50–97 nm) (Table 1). All compounds exhibit a broad structureless emission in the range 355–419 nm. Their emission spectra show the same trends with the absorption spectra when altering the kinds, positions or numbers of substitutes. On changing the kinds of 4-substituted group on the phenyl, the emission peaks hypsochromically shift with increasing the electron-donating ability of substitutes. 4-MeO-bt (**10**) shows emission peak at 355 nm, blue shifting 64 nm related to the 4-CN-bt (**2**). By changing the position of methoxy substitutes, according to the order of 3-, 2-, and 4-position, a systematically hypsochromic shift (∼25 nm) of the emission peaks is observed. As concerning the numbers of substitutes, the more the substitutes are, the lower energy emission occurs. The emission of these compounds in PMMA film displayed a little bit red shift comparing to their emission in solution, except the 2,4,5-MeO-bt (**13**), which has an significantly larger red shift (21 nm), presumably due to the strong π–π stacking interactions in its solid structure.

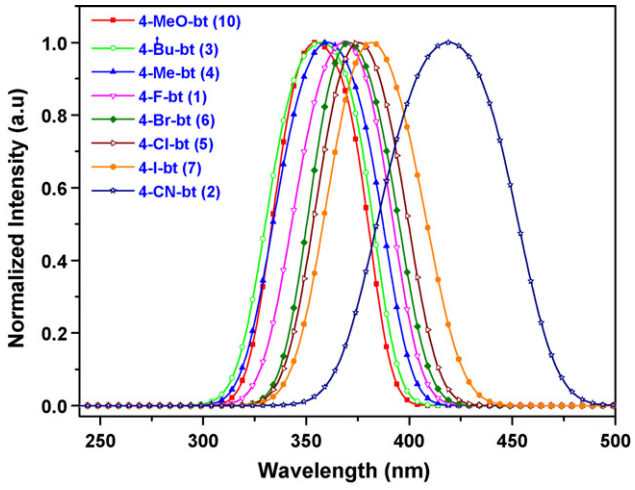


Fig. 3. PL spectra of 2-arylbenzothiazoles with different electronic effect of substitutes.

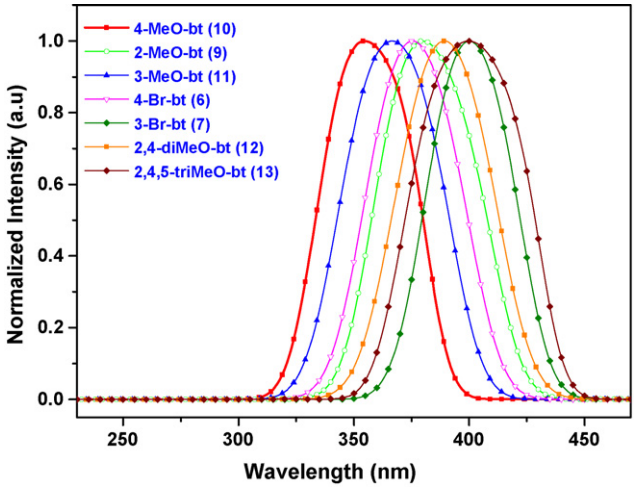


Fig. 4. PL spectra of 2-arylbenzothiazoles with different positions and number of substitutes.

3.4. Relationship between photophysical properties and structures

The above observations from electronic absorption and emission can be rationalized in terms of the Hammett's substituent constant σ, which is a characteristic of the electronic effect of substituted group [5,9d]. Generally, electron-accepting substituents exhibit positive σ values and electron-donating groups show negative values at *para*-position. The σ also varies with its position on the aryl ring relative to the reactive site. As given in Table 1, the σ values (at 4-position) have the following order: –CN > –I > –Br > –Cl > –F > –Me > –^{t}Bu > –MeO, which are correlated well with the maximum wavelengths of both electronic absorption and emission spectra. The larger the σ value is, the larger the maximum absorption and emission are (refer to the corresponding data for compounds 4-MeO-bt (**10**), 3-MeO-bt (**11**), 4-Br-bt (**6**), 4-Br-bt (**8**) in Table 1).

4. Conclusions

In summary, we have synthesized a series of 2-arylbenzothiazoles by use of Jacobson's cyclization of 2-aminobenzenethiol with benzoyl chloride or benzaldehyde derivatives in view of the easy availability of the precursors. The studies revealed that the maximum absorption and emission peaks could be systematic tuned by changing the kinds, positions and/or numbers of substituted groups on the phenyl ring of 2-arylbenzothiazoles. The alterations of absorption and emission wavelengths coincide well with the order of Hammett's substituent constants. This provides some clue to design and develop more fluorescent materials and novel cyclometalated ligands.

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