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Substituent and solvent effects on excited state intramolecular proton transfer in novel 2-(2′-hydroxyphenyl)benzothiazole derivatives

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ABSTRACT

A group of novel 2-(2′-hydroxyphenyl)benzothiazole derivatives **1–5** were synthesized with electron-donating or -withdrawing substituent introduced in *para* position of N atom in benzothiazolyl ring. The excited state intramolecular proton transfer (ESIPT) in **1–5** along with non-substituted 2-(2′-hydroxyphenyl)benzothiazole **6** was studied by means of UV–vis absorption and steady-state fluorescence in solutions. Compounds **1–6** exhibit dual fluorescences including purple normal emission and green tautomer emission. Systematical comparison of the fluorescence of any analogue in a series of solvents ranging from protic ethanol to non-polar hexane demonstrated that polar solvents favor the normal emission while non-polar solvents facilitate ESIPT process and tautomer formation and emission. In either protic or non-polar solvent the tautomer emission intensity of **1–6** decreases consecutively in the order of decreasing electron-donating ability or increasing electron-withdrawing ability of the substituents, on the premise of identical normal emission intensity. This indicates that electron-donating substituents in these derivatives favor ESIPT process and tautomer emission. Competition of intra- and intermolecular hydrogen bonding was studied in dioxane-water binary solvent. It is demonstrated that intermolecular hydrogen bonding with protic solvent impedes ESIPT and tautomer emission. The fluorescent behaviors of **1–6** were interpreted in terms of the population of ground-state rotamers responsible for normal and tautomer emission respectively.

1. Introduction

Excited state intramolecular proton trasfer (ESIPT) phenomena have been intensively investigated [1–13] in the past decades due to the practical applications of ESIPT-exhibiting molecules as laser dyes [1], photostabilizers [11], fluorescent probes in biology [13], and light-emitting materials for electroluminescent devices [6,7]. ESIPT typically occurs in aromatic molecules having a phenolic hydroxy group with an intramolecular hydrogen bond to a nearby heteroatom of the same chromophore. The proton in the hydroxy group, upon photoexcitation, migrates to the heteroatom at a distance <2 Å to form the excited state of a tautomer. In the general family of typical ESIPT-exhibiting 2-(2′-hydroxyphenyl)benzazole derivatives, two distinct intramolecular hydrogen bonded rotamers I and II (Fig. 1) have been detected experimentally in the ground-state [3]. It is established that only rotamer II undergoes ESIPT to form the excited state of phototautomer III, which transmits a long-wavelength emission with an anomalously large Stokes shift of typically 200 nm, while rotamer I (sometimes along with other possible conformers) is responsible for the short-wavelength normal emission. It is therefore possible for the ESIPT-exhibiting substances to have dual fluorescences, depending on the molecular nature and the external factors such as solvent polarity and temperature. ESIPT proceeds on a time scale of about 100 fs since it involves very slight movement of a light hydrogen atom without energy barrier, as shown by the potential energy curve in Fig. 1. This extreme speed of tautomer formation implies that the contents of normal and tautomer emission in the overall fluorescence are determined by the population of rotamer I and II in the ground-state. In protic solvents, the intramolecular hydrogen bonding is competed by the intermolecular hydrogen bonding of the hydroxy group with the solvent molecules (case IV in Fig. 1), definitely resulting in the decrease of tautomer formation and consequently the long-wavelength emission.

A variety of 2-(2′-hydroxyphenyl)benzazole compounds have been created for ESIPT investigations [3,8–12], most of which have substituents in the different position of hydroxyphenyl ring. However, few works on ESIPT and related behaviors of 2-(2′-hydroxyphenyl)benzothiazole derivatives with substituents introduced in benzothiazolyl ring were reported. In present paper, we report the synthesis of a group of novel 2-(2′-hydroxyphenyl)benzothiazole derivatives (Fig. 2), with different

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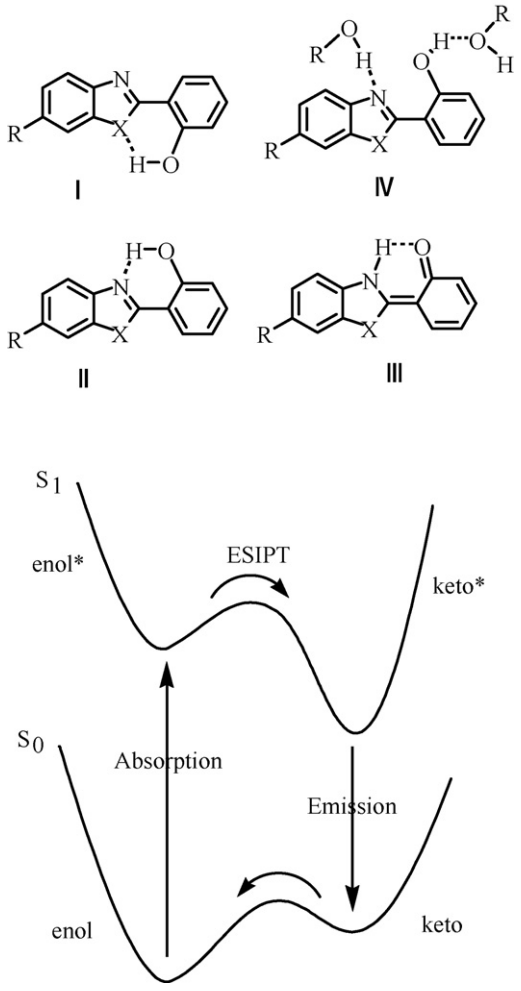

Fig. 1. ESIPT mechanism of 2-(2′-hydroxyphenyl)benzazole dyes (X = N, O, S).

electron-donating group (CH_3, OCH_3) or -withdrawing group (Br, F, CF_3) introduced into the 6-position in benzothiazolyl ring. The substituent effect on the ESIPT process and photophysical properties of these dyes were studied systematically in solutions by means of UV–vis absorption and steady-state fluorescence spectroscopy. In addition, a series of solvents, ranging from non-polar hydrocarbon to strongly polar and protic ethanol and even water, were used to study the solvent effect on the spectroscopy properties of the present novel derivatives. The substituent and solvent effects on ESIPT and spectroscopy behaviors were compared and discussed. To the best of our knowledge, this is the first report on the ESIPT study of 2-(2′-hydroxyphenyl)benzothiazole derivatives with substituent in benzothiazolyl ring.

2. Experimental

2.1. Materials, instruments, and method

All the chemicals for the synthesis or solvents for the spectrum measurement are of analytical or spectroscopy grade and used as received without further purification. ^{1}H NMR spectra were recorded on a Varian INOVA spectrometer (400 MHz), with peak frequencies referenced versus an internal standard (TMS) shifts at 0 ppm. The Infra-red (IR) spectra were measured as KBr pellets on a JASCO FT/IR 430 spectrophotometer. Mass spectra were recorded on a Micromass Q-Tof (Micromass, Wythenshawe, UK) mass spectrometer equipped with an orthogonal electrospray source (Z-spray). The fluorescence and UV–vis absorption spectra measurements were performed on a Perkin-Elmer LS55 fluorescence spectrometer and a Perkin-Elmer Lambda 35 UV-Visible spectrophotometer respectively, with non-degassed solutions at room temperature. The optimised geometries and energies of 2-(2′-hydroxyphenyl)benzothiazole derivatives were calculated without any symmetrical restriction at B3LYP/6-31G(d) level. The solvent effects were calculated by a static isodensity surface polarized continuum model [14] at the same level. All calculations were carried out with GAUSSIAN 03 [15].

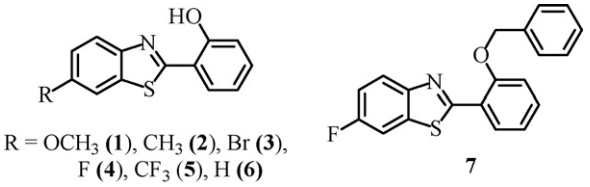

Fig. 2. Chemical structures of compounds **1–7**.

2.2. Synthesis of compounds

2.2.1. N-(4′-substitutedphenyl)-2-hydroxybenzamide (*1a–5a*)[16,17]

1a–5a were synthesized according to the literature method. To a solution of 4-substituedaniline (0.1 mol) and salicylic acid (0.11 mol) in 100 mL of chlorobenzene in a 250 mL flask was added PCl_3 (0.05 mol) within 20 min at room temperature. The mixture was then refluxed for 1.5 h. The resulted solution, apart from the yellow residue adhered to the flask bottom, was poured into cracked ice. The precipitate was filtered and dried in a vacuum oven. Recrystallization of the crude powder in mixed chloroform and ethanol (1:1) gives pure white product, the chemical structure of which was confirmed by melting point and ^{1}H NMR.

1a: Yield: 88%. Mp 160.2–160.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 12.07 (s, 1H), 7.92 (s, 1H), 7.51–7.49 (d, 1H), 7.45–7.40 (m, 3H), 7.02–7.00 (d, 1H), 6.93–6.87 (m, 3H), 3.80 (m, 3H).

2a: Yield: 84%. Mp 157.3–157.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 12.04 (s, 1H), 7.90 (s, 1H), 7.50–7.48 (d, 1H), 7.44–7.41 (m, 3H), 7.19–7.17 (d, 2H), 7.02–7.00 (d, 1H), 6.91–6.88 (m, 1H), 2.34 (s, 3H).

3a: Yield: 90%. Mp 175.3–175.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 11.81(s, 1H), 7.91 (s, 1H), 7.52–7.43 (m, 6H), 7.04–7.02 (d, 1H), 6.94–6.90 (m, 1H).

4a: Yield: 82%. Mp 163.5–164.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 11.90 (s, 1H), 7.94 (s, 1H), 7.54–7.50 (m, 3H), 7.47–7.43 (m, 1H), 7.11–7.06 (m, 2H), 7.04–7.03 (d, 1H), 6.94–6.89 (m, 1H).

5a: Yield: 92%. Mp 210.2–210.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 11.70 (s, 1H), 8.05 (s, 1H), 7.75–7.73 (d, 2H), 7.67–7.65 (d, 2H), 7.55–7.53 (d, 1H), 7.50–7.46 (m, 1H), 7.07–7.05 (d, 1H), 6.97–6.93 (m, 1H).

2.2.2. N-(4′-substitutedphenyl)-2-tertbutyldimethylsilyloxy-thiobenzamide (*1b–5b*) [18,19]

A solution composed of **1a–5a** (0.01 mol), tertbutyldimethylsilyl chloride (1.1 mol equiv), imidazole (1.05 mol equiv) and dichloromethane (150 mL) located in 500 mL flask was stirred at room temperature for 10 h, and washed with aqueous HCl (0.1 M) and water. Distillation of solvent with rotary evaporator afforded the crude product of corresponding silyl ether, which was directly put into next reaction without any purification due to little contamination by organic components.

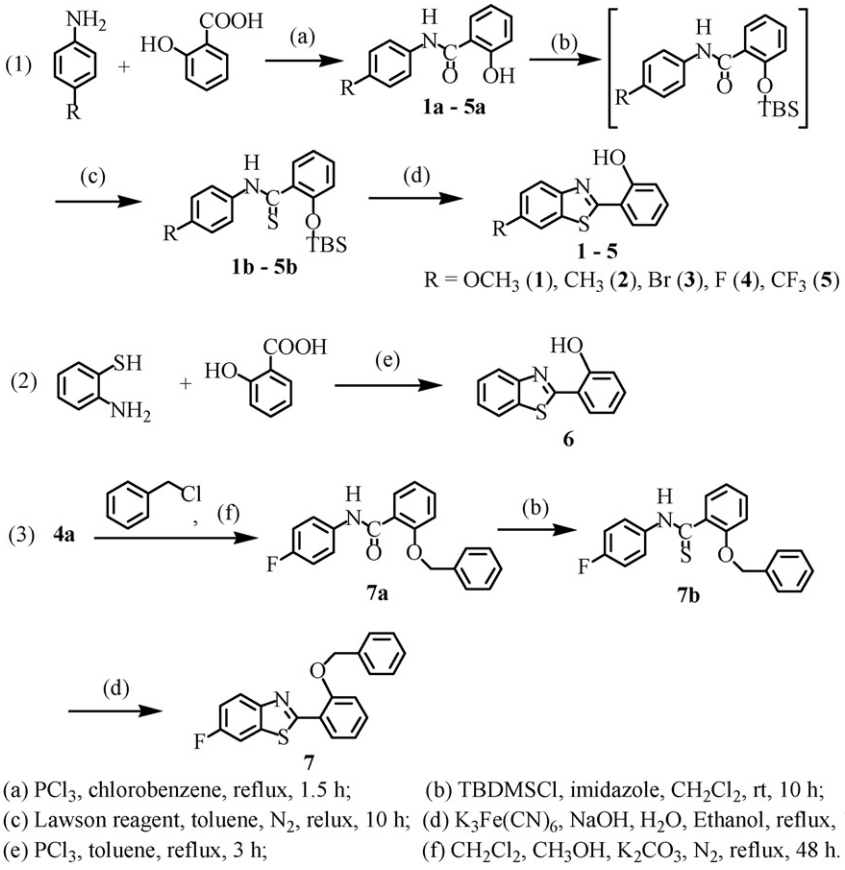

Fig. 3. Syntheses of compounds **1–7**.

To the protected product silyl ether obtained as above, were added Lawesson's reagent (1.5 mol equiv.) and 120 mL toluene. The solution was refluxed under an atmosphere of nitrogen for 9 h. After evaporation of solvent under reduced pressure, the residue was isolated through column chromatography over silica with mixed petroleum ether and dichloromethane (5:4) as eluent to yield yellow pure products.

1b: Yield 76.5% (calcd. from **1a**). Mp 124.5–124.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 10.162 (s, 1H), 8.32–8.29 (d, 1H), 7.70–7.67 (d, 2H), 7.33–7.29 (m, 1H), 7.08–7.04 (m, 1H), 6.95–6.93 (d, 2H), 6.88–6.85 (d, 1H), 3.82 (s, 3H), 0.94–0.92 (s, 9H), 0.25 (s, 6H). LRMS (ESI, positive): found *m*/*z* 374 (calcd. for [M + H]).

2b: Yield 85% (calcd. from **2a**). Mp 83.7–87.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 10.143 (s, 1H), 8.30–8.28 (d, 1H), 7.68–7.66 (d, 2H), 7.33–7.29 (m, 1H), 7.23–7.21 (d, 2H), 7.08–7.04 (m, 1H), 6.88–6.86 (d, 1H), 2.36 (s, 3H), 0.93–0.89 (s, 9H), 0.25 (s, 6H). LRMS (ESI, positive): found *m*/*z* 358 (calcd. for [M + H]).

3b: Yield 79% (calcd. from **3a**). Mp 127.9–129.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 10.172 (s, 1H), 8.27–8.25 (d, 1H), 7.76–7.74 (d, 2H), 7.55–7.52 (d, 2H), 7.35–7.31 (m, 1H), 7.09–7.05 (m, 1H), 6.88–6.86 (d, 1H), 0.92 (s, 9H), 0.24 (s, 6H). LRMS (ESI, positive): found *m*/*z* 424 (calcd. for [M + H]).

4b: Yield 89% (calcd. from **4a**). Mp 68.4–71.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 10.221 (s, 1H), 8.31–8.28 (d, 1H), 7.77–7.73 (m, 2H), 7.35–7.30 (m, 1H), 7.13–7.07 (m, 3H), 6.89–6.86 (d, 1H), 0.93–0.92 (s, 9H), 0.25 (s, 6H). LRMS (ESI, positive): found *m*/*z* 362 (calcd. for [M + H]).

5b: Yield 71% (calcd. from **5a**). Mp 121.7–122.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 10.277 (s, 1H), 8.26–8.24 (d, 1H), 8.04–8.02 (d, 2H), 7.69–7.67 (d, 2H), 7.37–7.33 (m, 1H), 7.11–7.07 (m, 1H), 6.90–6.88 (d, 1H), 0.92 (s, 9H), 0.24 (s, 6H). LRMS (ESI, positive): found *m*/*z* 412 (calcd. for [M + H]).

*2.2.3. 2-(2′-hydroxyphenyl)-6-substitutedbenzothiazole (**1–5**) [16,20]*

To the thiobenzamide **1b–5b** (0.01 mol) wetted with small amount of ethanol beforehand was added 30% aqueous sodium hydroxide (8 mol equiv.). The mixture was diluted by water to provide a final suspension of 10% aqueous sodium hydroxide. The diluted sample was added within 10 min to a stirred solution of potassium ferricyanide (4 equiv.) in water (20 wt%) at 80–90 °C. After stirred for 1.5 h and then cooled to room temperature, the reaction solution was poured into water and neutralized with dilute aqueous HCl. Extraction of the solution with dichloromethane followed by evaporation of solvent produced the crude product residue, which was isolated by column chromatograph over silica using petroleum ether and dichloromethane (3:1) as eluent to yield the pure target product **1–5** as white solid.

1: Yield 15% (cal. from **1b**). Mp 150.6–151.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 12.492 (s, 1H), 7.86–7.84 (d, 1H), 7.67 (s, 1H), 7.65–7.65 (d, 1H), 7.38–7.34 (m, 1H), 7.31–7.29 (d, 1H), 7.10–7.08 (d, 1H), 6.96–6.92 (m, 1H). LRMS (ESI, positive): found *m*/*z* 258 (calcd. for [M + H]). FT-IR: 3434, 2943, 1625, 1600, 1585, 1485, 1469, 1266, 1231, 826, 743 cm^{-1}.

2: Yield 25% (cal. from **2b**). Mp 185.3–185.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 12.383 (s, 1H), 7.85–7.83 (d, 1H), 7.63–7.60 (d, 1H), 7.36–7.32 (m, 2H), 7.09–7.06 (m, 2H), 6.95–6.91 (m, 1H), 3.88 (s, 3H). LRMS (ESI, positive): found *m*/*z* 242 (calcd. for [M + H]). FT-IR: 3422, 3049, 2974, 1584, 1483, 1457, 1272, 1223, 817, 745 cm^{-1}.

3: Yield 19% (cal. from **3b**). Mp 204.5–205.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 12.165 (s, 1H), 8.02 (s, 1H), 7.83–7.81 (d, 1H), 7.66–7.64 (d, 1H), 7.61–7.58 (d, 1H), 7.41–7.37 (m, 1H), 7.10–7.08 (d, 1H), 6.97–6.93 (m, 1H). LRMS (ESI, positive): found *m*/*z* 303 (calcd. for [M + H]). FT–IR: 3436, 3079, 2924, 1619, 1577, 1480, 1444, 1270, 1251, 1220, 825, 752 cm^{-1}.

4: Yield 21% (cal. from **4b**). Mp 178.0–178.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 12.196 (s,1H), 7.94–7.91 (m, 1H), 7.66–7.63 (d, 1H), 7.59–7.56 (d, 1H), 7.40–7.36 (m, 1H), 7.24–7.21 (d, 1H), 7.10–7.08 (d, 1H), 6.97–6.93 (m, 1H). LRMS (ESI, positive): found *m*/*z* 246 (calcd. for [M + H]). FT-IR: 3434, 3061, 1623, 1583, 1484, 1456, 1265, 1247, 1219, 1198, 824, 744 cm^{-1}.

5: Yield 20% (cal. from **5b**). Mp 213.3–215.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 12.236 (s, 1H), 8.19 (s, 1H), 8.08–8.06 (d, 1H), 7.76–7.70 (m, 2H), 7.44–7.41 (m, 1H), 7.13–7.11 (d, 1H), 7.00–6.96 (m, 1H).). LRMS (ESI, positive): found *m*/*z* 296 (calcd. for [M + H]). FT-IR: 3432, 3046, 2924, 1622, 1603, 1500, 1483, 1320, 1246, 1217, 1115, 1085, 839, 753 cm^{-1}.

2.2.4. 2-(2′-Hydroxyphenyl)benzothiazole (**6**)

6 was prepared according to the literature method, and the spectral data for the structure characterization are identical with those reported previously. [21]

2.2.5. 2-(2′-Benzyloxyphenyl)-6-fluorobenzothiazole (**7**) [18–20]

To a solution of compound **4a** (2 g, 8.65 mmol) in anhydrous dichloromethane (20 mL) and anhydrous methanol (20 mL) were added potassium carbonate (2.39 g, 17.3 mmol) and benzyl chloride (2 mL, 17.3 mmol). The reaction mixture was refluxed for 48 h under nitrogen atmosphere. After cooling and filtration, the filtrate was concentrated, and the residue was purified by flash column chromatography over silica gel using mixed dichloromethane and petroleum ether (2:1) as eluent to give pure compound **7a** (2.64 g, 8.22 mmol).

7b and **7** were synthesized using the same methods described in Section 2.2.2. and Section 2.2.3. respectively.

7a: Yield 94%. Mp 121.5–122.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 9.96 (s, 1H), 8.34–8.32 (d, 1H), 7.54–7.47 (m, 6H), 7.22–7.13 (m, 4H), 6.92–6.87 (m, 2H), 5.22 (s, 2H).

7b: Yield 92.7%. Mp 103.2–104.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 10.848 (s, 1H), 8.56–8.54 (d, 1H), 7.48–7.35 (m, 8H), 7.15–7.08 (m, 2H), 6.97–6.93 (d, 2H), 5.20 (s, 2H). MS (TOF, ES, positive): found *m*/*z* 338 (calcd. for [M + H]).

7: Yield 75%. Mp 110.9–111.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.569 (s, 1H), 8.07–8.03 (m, 1H), 7.54–7.52 (d, 3H), 7.44–7.36 (m, 4H), 7.24–7.19 (m, 1H), 7.16–7.10 (m, 2H), 5.34 (s, 2H). MS (API-ES+) found *m*/*z* 396 (100, calcd. for [M + H]) and 417 (50, calcd. for [M + Na]).

3. Results and discussion

3.1. Synthesis

The compound **6** was prepared by one-step cyclization reaction between salicylic acid and 2-aminothiophenol according to the literature method [21]. Different from **6** and other reported 2-(2′-hydroxyphenyl)benzothiazole derivatives with substituents located in hydroxyphenyl ring, analogs **1**–**5** were synthesized through the procedure described in Fig. 3 partially due to commercial source limit of most substituted 2-aminothiophenol. Condensation of 4-substituted aniline with salicylic acid in the presence of PCl_3 generates the corresponding amide **1a**–**5a**. In order to avoid the participation of the phenolic hydroxy group in the following reactions, it is necessary to convert **1a**–**5a** by reacting with tert-butyldimethylchlorosilane to their silyl ether, which was directly put into the next thionation reaction with Lawesson's reagent [22] without strict purification. Jocobson reaction of thiobenzamide **1b–5b** with potassium ferricyanide in the presence of sodium hydroxide not only resulted in the formation of benzothiazole skeleton, but also the deprotection of phenolic hydroxy group [23,24].

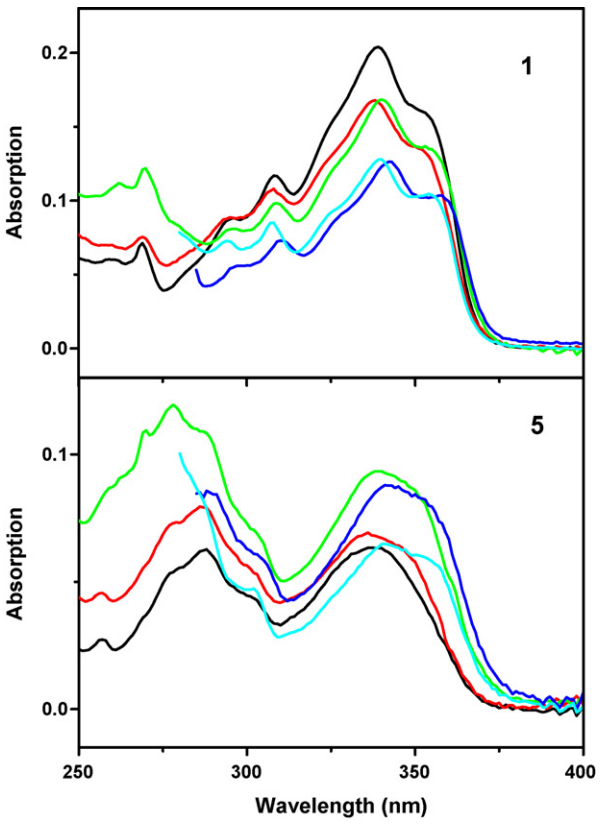

Fig. 4. Absorption spectra of **1** and **5** in different solvents. (black: ethanol, red: acetonitrile, green: dichloromethane, blue: toluene, and cyan: hexane.) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

Finally the target compounds **1–5** were obtained at acceptable yields.

In order to verify the influence of the intramolecular hydrogen bonding to the ESIPT process and consequently the spectroscopic behaviors of the titled substances, **4a** was selected to undergo three-step reactions under similar conditions to those for **1–5** (as shown in Fig. 3) to prepare **7**, in which the absence of a free phenolic hydroxy group blocks the formation of an intramolecular hydrogen bond.

3.2. Absorption spectra

Fig. 4 illustrates the electronic absorption spectra of **1** and **5**, as examples, in dilute solutions of different solvents. For the sake of spectral comparison and accurate acquisition of fluorescence quantum yields next, the optical density for the long-wavelength band of each solution was adjusted to a value of around 0.1 [25,26]. The detailed absorption data of each compound in different solvents are summarized in Table 1. Most dyes exhibit two obvious absorption bands with absorption maxima (λ_{max}) at 270–290 nm and 320–340 nm, respectively. The molar extinction coefficient (ε_{max}) of the longer wavelength band of each compound indicates that it is associated with the π–π^* transition of the molecular skeleton. As shown in Fig. 4, the long-wavelength absorption band of analog **1**, with λ_{max} at around 340 nm, shows the vibrational structure, and the absorbance of each band at shorter wavelength region is much weaker than that of 340 nm band. Analog **5** exhibit a structureless long-wavelength absorption band in each solution. The solvatochromic effect is much pronounced for **5** since the absorption spectrum has a 10 nm red shift if the solvent goes from polar and protic ethanol to non-polar hexane or toluene. This is probably because the possible conformational equilibrium of **5** in solution

Table 1
Photophysical properties of **1–7** in different solvents.

Sample	Solvent	Absorption		Fluorescence	
		λ_{max} (nm)/$\varepsilon_{max} \times 10^4$ (L mol^{-1} cm^{-1})	λ_{max} (nm)/$\varepsilon_{max} \times 10^4$ (L mol^{-1} cm^{-1})	λ_N (nm)/Φ_N[a]	λ_T (nm)/Φ_T[a]
1	Ethanol	339/3.88		384/0.0923	511/0.0004
	CH_2Cl_2	340/4.66		396/0.0012	508/0.0061
	Hexane	339/2.88		388/0.0005	511/0.0115
2	Ethanol	334/2.47	291/2.08	378/0.0174	510/0.0008
	CH_2Cl_2	336/1.76	280/1.31	395/0.0033	509/0.0070
	Hexane	336/1.94	278/1.97	389/0.0005	513/0.0108
3	Ethanol	337/1.86	291/1.51	382/0.0262	510/0.0001
	CH_2Cl_2	338/3.64	291/3.31	395/0.0016	516/0.0016
	Hexane	340/3.63	291/3.78	388/0.0003	517/0.0014
4	Ethanol	331/1.44	286/1.00	380/0.0940	0
	CH_2Cl_2	334/2.05	276/1.97	396/0.0021	514/0.0018
	Hexane	336/2.92	286/2.87	388/0.0004	518/0.0021
5	Ethanol	337/1.85	288/1.83	387/0.0354	0
	CH_2Cl_2	339/1.91	278/2.43	395/0.0029	520/0.0009
	Hexane	341/2.25	278/3.09	378/0.0006	520/0.0012
6	Ethanol	333/2.16	289/1.725	379/0.0239	510/0.0002
	CH_2Cl_2	334/3.14	276/3.51	396/0.0013	513/0.0021
	Hexane	336/2.10	277/2.46	388/0.0005	513/0.0059
7	Ethanol	322/2.67			
	CH_2Cl_2	324/3.4		385	
	Hexane	320/2.55			

λ_N: normal emission wavelength, λ_T: tautomer emission wavelength, Φ_N: Fluorescence quantum yield of normal emission, Φ_T: Fluorescence quantum yield of tautomer emission

[a] Φ_N and Φ_T were measured and calculated relative to quinine sulfate in 0.1 N sulfuric acid as standard ($\Phi = 0.55$).

in the ground-state is more sensitive to solvent polarity than other analogs [12].

3.3. Photoluminescence

3.3.1. Correlation between intramolecular hydrogen bonding and ESIPT

The existence of the intramolecular hydrogen bond in molecules of **1–6** is confirmed by the observation of the peak at 12–13 ppm in the ^{1}H NMR spectra (Section 2), which is a typical signal for hydrogen bonded hydrogen atom.

In order to reveal the remarkable contribution of the intramolecular hydrogen bonding to the optical properties of benzothiazole derivatives, the fluorescence spectra of compound **4** and its derivative **7** were measured in dilute dichloromethane solutions under identical condition and depicted in Fig. 5. A dual fluorescence character was detected for **4** with emission peaks centered at 395 and 515 nm respectively. It is safe to assign the structureless normal emission at 395 nm to rotamer I (Fig. 1) and long-wavelength band at 515 nm to phototautomer III and finally to rotamer II [3]. While compound **7** exhibits a well-resolved purple fluorescence with peak at 385 nm and two shoulders at 367 and 350 nm. The absence of intramolecular hydrogen bond in molecules of **7**, together with the fact that covalent linking of benzyl to oxygen atom should not change the luminescent property of the molecular skeleton essentially, evidently confirms that intramolecular hydrogen bonding is the essential driving force for ESIPT process and dual fluorescence behavior of 2-(2′-hydroxyphenyl)benzazole derivatives.

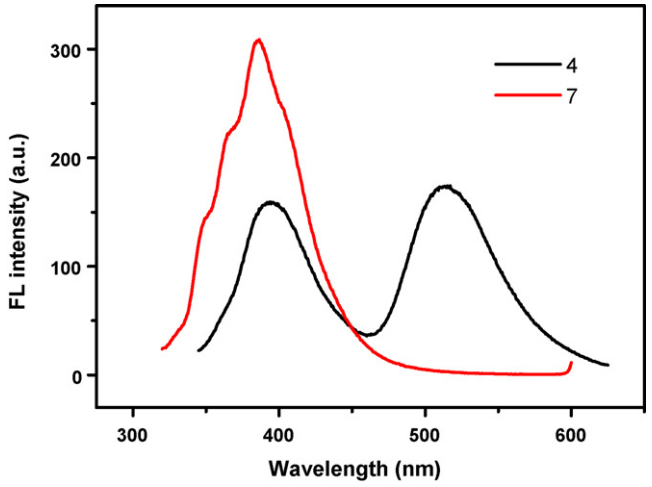

Fig. 5. Fluorescence spectra of **4** (3×10^{-6} mol L^{-1}, $\lambda_{exc} = 330$ nm) and **7** (3×10^{-6} mol L^{-1}, $\lambda_{exc} = 310$ nm) in dichloromethane solutions.

3.3.2. Solvent effect on ESIPT and fluorescence

A series of common organic solvents, ranging from protic and polar ethanol to non-polar hexane, were selected to make dilute solutions of **1–6** and measure fluorescence. To ensure the intrinsic single molecular properties are not disturbed by any unnecessary intermolecular interaction in concentrated solutions, the samples used in fluorescence measurements are identical to those for absorption spectra acquisition with concentration in the order of 10^{-6} mol L^{-1}. Fig. 6 shows the fluorescence spectra of analog **1** in different solvents. In protic solvent ethanol, two fluorescence bands at 384 and 511 nm have been detected. The former with much higher intensity should be assigned to the normal emission and the latter with lower intensity to tautomer emission respectively. As solvent going from ethanol to acetonitrile, the tautomer emission intensity increases at the expense of the normal one as indicated by the fluorescence quantum yields of these two bands in Table 1. The further decrease in solvent polarity results in further increase of the tautomer emission. In non-polar solvents like toluene or hexane, the normal emission band is hardly discerned and the tautomer band predominates the overall fluorescence spectra. The fluorescence curves evolution especially at short-wavelength region in Fig. 6, with tautomer emission intensity normalized, clearly describes the solvent effect.

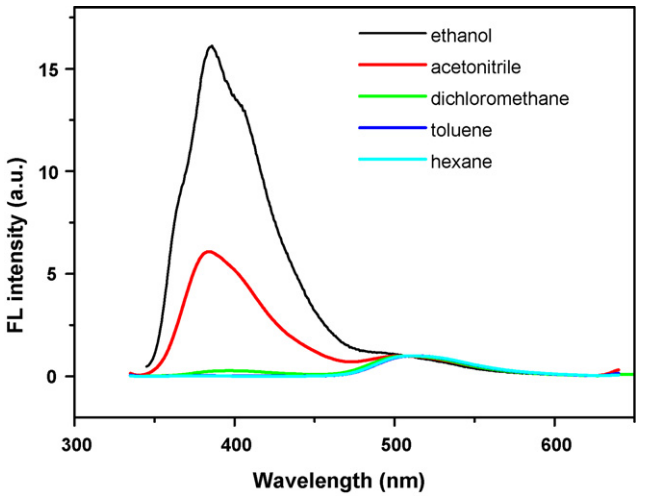

Fig. 6. Normalized fluorescence spectra of **1** in different solvents (3×10^{-6} mol L^{-1}, λ_{exc} = 330 nm).

All other derivatives, **2**–**6**, were studied in a similar way, and similar results were observed. In order to show the influence of solvent polarity to the emission properties semi-quantificationally, the ratio of normal emission peak intensity to the tautomer emission peak intensity (I_n/I_t) was plotted as a function of the normalized solvent polarity parameter E_T^N [27] in Fig. 7. It is obvious that non-polar hydrocarbon favors the tautomer emission while the protic and polar solvent favors the normal emission in spite of the electron-withdrawing or donating nature of the substituent R in molecules of **1–6**, in agreement with previous observation [3]. This is because rotamer II, which exclusively undergoes ESIPT process and is responsible for the tautomer emission, is intrinsically more stable than rotamer I for all the present 2-(2′-hydroxyphenyl)benzothiazole derivatives. Normal emission increase with solvent polarity should be because rotamer I, which has slightly higher dipole moment than II, is stabilized more than II in polar solvents.

3.3.3. *Substituent effect on ESIPT and fluorescence*

Systematical comparison of the fluorescence properties of **1–6** under identical condition can reveal the function of the substituent R which was introduced into these molecules on purpose. Fig. 8a

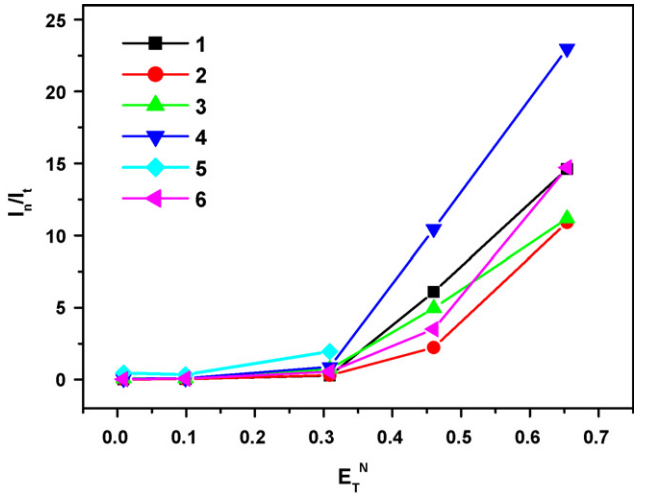

Fig. 7. Plot of I_n/I_t as a function of solvent polarity parameter E_T^N for derivatives **1–6**. (E_T^N values are as follows: hexane 0.009, toluene 0.099, dichloromethane 0.309, acetonitrile 0.46 and ethanol 0.654.).

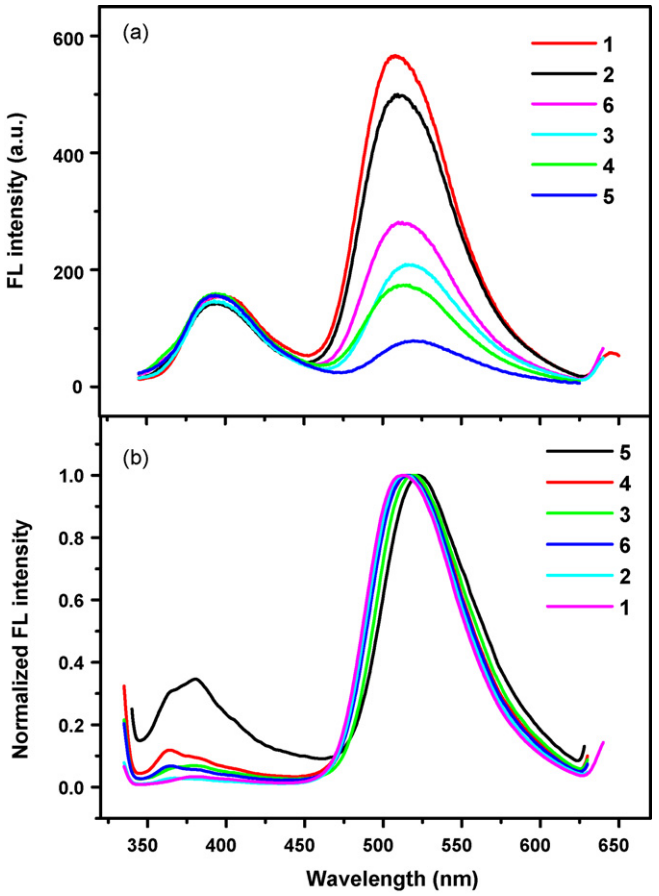

Fig. 8. Fluorescence spectra of **1–6** in dichloromethane (a) and toluene (b). (3×10^{-6} mol L^{-1} and λ_{exc} = 330 nm for all samples).

illustrates the fluorescence spectra of **1–6** in dichloromethane solutions under identical measurement condition. The concentration of each sample was controlled as ca. 3×10^{-6} mol L^{-1}. All the substances exhibit both normal emission and tautomer emission in such a dipolar solvent. The normal emission intensity of each sample is roughly equal to each other, while the tautomer emission intensity decreases in the order of **1**, **2**, **6**, **3**, **4**, and **5**, which is just the order decreasing the electron donating ability of the substituents (OCH_3, CH_3, H, Br, F, CF_3) or the order increasing the electron-withdrawing ability of them. In polar solvents such as acetonitrile and ethanol, same spectral trends were observed (figures not shown). In non-polar toluene solutions, similar results were obtained and displayed in Fig. 8b. If normalizing the tautomer emission intensity, the normal emission intensity decreases in the order of increasing electron donating ability of substituents.

In order to understand the relationship between molecular structure and the spectroscopic properties of substance **1–6**, theoretical calculation was carried out with *ab initio* calculation. The O–H bond length of present 2-(2′-hydroxyphenyl)benzothiazole derivatives was calculated at B3LYP/6-31G(d) level as 0.99343, 0.99328, 0.99315, 0.99232, 0.99229, 0.99216 Å for **1**, **2**, **6**, **3**, **4**, and **5**, respectively. The consecutive decrease in O–H bond length in the order of **1**, **2**, **6**, **3**, **4**, and **5** implies a continuous decrease in the strength of intramolecular hydrogen bond between N–H and consequently a decrease in the ground-state population of rotater II and tautomer emission. The calculated result is consistent with the observed substituent effect in experiments.

In addition, the ground-state energy of rotamer I and II for each derivative was calculated in both gas phase and in weakly polar solvent such as dichloromethane. The calculated data were summa-

Table 2
The calculated ground-state energy and energy difference of rotamer I and rotamer II of 2-(2′-hydroxyphenyl)benzothiazole derivatives at B3LYP/6-31G(d) level.

	In gas phase			In dichloromethane		
R	E_I (hartree)	E_{II} (hartree)	ΔE_{I-II} (Kcal)	E_I (hartree)	E_{II} (hartree)	ΔE_{I-II} (Kcal)
OCH_3	−1143.4989763	−1143.5144034	9.68	−1143.5101054	−1143.5240975	8.78
CH_3	−1068.295441	−1068.3106129	9.52	−1068.3038346	−1068.3177523	8.73
H	−1028.9773832	−1028.9928457	9.70	−1028.9860923	−1029.002763	10.46
Br	−3600.080813	−3600.0961968	9.65	−3600.0922342	−3600.10098	5.49
F	−1128.2092875	−1128.2246198	9.62	−1128.2189201	−1128.2334277	9.10
CF_3	−1366.0141052	−1366.029462	9.63	−1366.0281204	−1366.0346706	4.11

E_I, E_{II}: ground-state energy of rotamer I, II.
$\Delta E_{I-II} = E_I - E_{II}$.

rized in Table 2. The ground-state energy of rotamer II is lower than that of rotamer I for all present derivatives in gas phase, indicating that rotamer II is intrinsically more stable than rotamer I. This helps to interpret that the tautomer emission predominates over normal emission in non-polar solvents such as hexane and toluene for all derivatives regardless of substituents, as shown in Fig. 8b, since the solvent effect on substance molecules is so tiny that this case can be approximated to gas phase. In weakly polar dichloromethane, the ground-state energy of rotamer II keeps to be lower than I for most derivatives, in agreement with that the tautomer emission still be stronger than normal emission for most derivatives, as shown in Fig. 8a. However, the energy difference between rotamer I and II is decreased in comparison to those in gas phase, implies that the dipole constant of rotamer I is bigger than II and the former can be more stabilized by polar solvent. This is in agreement with that the normal emission from rotamer I increased if the solvent goes from nonpolar to polar one, as shown in Fig. 6.

3.3.4. *Substituent effect and solvent effect, which dominates?*

As discussed in above two subsections, both solvent and substituent play important roles to influence the photoluminescent properties of the present 2-(2′-hydroxyphenyl)benzothiazole derivatives **1–6**. A question arises accordingly. Among these external and internal factors, i.e. solvent effect and substituent effect, which one dominates to determine the spectroscopic behavior? The answer can be easily found in Fig. 7. In non-polar hydrocarbon or toluene, the peak intensity ratio I_n/I_t is near to zero and tautomer emission predominates the overall fluorescence spectrum for all derivatives **1–6**, while in polar solvents, I_n/I_t is much higher than 1 and the normal emission turns to dominate the whole emission regardless of the substituent, although it did help to adjust the I_n/I_t in both polar and non-polar mediums. To some extent, it can be concluded that solvent effect, rather than substituent factor, plays essential role to determine the fluorescent behaviors of ESIPT-exhibiting molecules such as 2-(2′-hydroxyphenyl)benzothiazole derivatives, i.e. the solvent polarity determines the emission color of the ESIPT-exhibiting substances. This merit makes ESIPT-exhibiting substances suitable for many practical applications, e.g. as polarity probe of mediums.

3.3.5. *Competition of intra- and intermolecular hydrogen bonding: In dioxane-water binary solvent*

The competition of intra- and intermolecular hydrogen bonding in present 2-(2′-hydroxyphenyl)benzothiazole derivatives were studied in dioxane-water binary-solvent solutions, in which dioxane is a weakly polar and hydrogen bonding solvent while water is a typically protic but poor solvent for most organic molecules. Analog **1** was selected as an example for this purpose, and a series of solutions in dioxane-water mixture with different water fraction but identical concentration of **1** (7.5×10^{-6} mol L^{-1}) were made for spectroscopic measurements. As shown by the normalized fluorescence spectra in Fig. 9, **1** exhibits both normal and tautomer emission bands with peaks at 395 and 520 nm respectively in pure dioxane. With the addition of water, the tautomer emission intensity decreases relatively to that of the normal emission. When water fraction is increased to 20% v/v, the tautomer emission almost vanished. With further increasing water fraction to 40% v/v, a new emission band at 445 nm appeared in addition to the normal emission. This band intensity increased with increasing water fraction and turned to be the main emission when water fraction is high up to 80% v/v.

It is understandable that the tautomer emission decreases with increasing water fraction in mixed solvent if the intermolecular hydrogen bonding between **1** and water is taken into account. In the initial stage, the presence of small amount of water in the dioxane solution must give rise to solvation of the molecules of **1**. The intermolecular hydrogen bonding between **1** and water definitely disrupts the ground-state intramolecular hydrogen bonding rotamers I and II but increases the quantity of species IV, in which ESIPT and tautomer formation are inhibited. Consequently the tautomer emission decreases with addition of water and finally vanished.

In order to assign the new emission band at 445 nm at high water contents in the mixed solvent, both the excitation and absorption spectra of all samples used for Fig. 9 were measured. It is observed that the excitation spectra features with emission at 445 nm were nearly identical to those at 395 nm for all samples. In addition, no new absorption band has been detected with varying water contents. It is reasonable, therefore, to assign the emission band at 445 nm to an excited species which was formed only after photoexcitation of **1**. It is suggested that the 445 nm band arose from the excited phenolate anion (*[PhO^-]) of **1**, which is formed by dissociation of the hydroxy group in the presence of protonic solvent and much more stable in water. It is understandable that the phenolate anion of **1** was formed only in excited state in this neutral

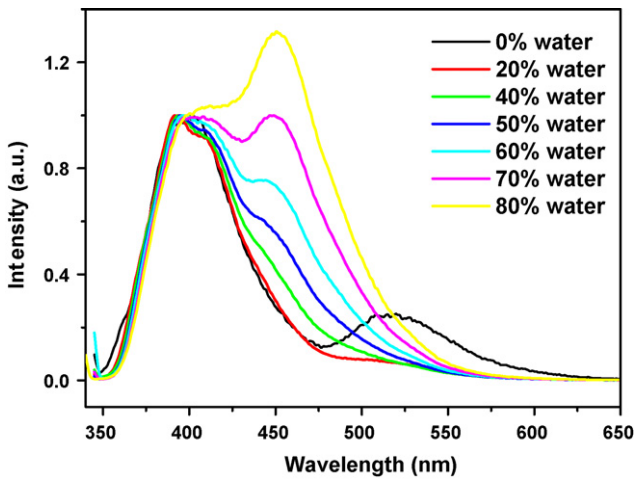

Fig. 9. Fluorescence spectra of **1** in dioxane-water mixed solvents.

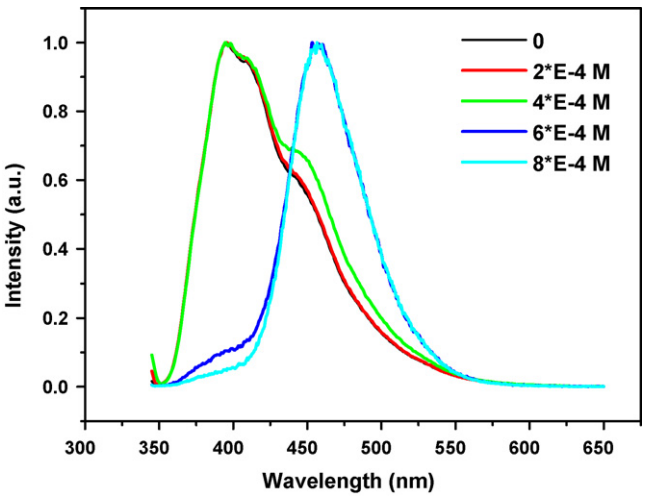

Fig. 10. Normalized fluorescence of **1** in dioxane-water (50% water) solutions with different sodium hydroxide concentration.

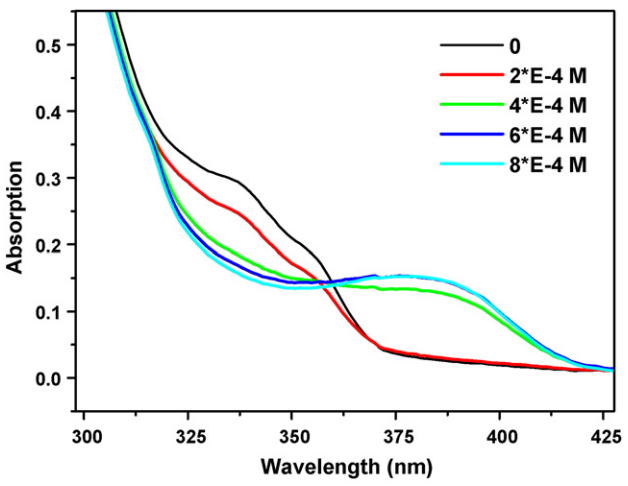

Fig. 12. Absorption spectra of **1** in dioxane-water (50% water) with different sodium hydroxide concentration.

medium since the pK_a of excited state is usually much higher than that of ground-state.

To verify the generation of phenolate anion**,** the fluorescence of **1** was measured by adding sodium hydroxide and varying alkali concentration while keeping both the water fraction in dioxane-water (50% water) and the concentration of **1** (7.5×10^{-6} mol L^{-1}) constant. As shown in Fig. 10, the original 445 nm band in the neutral solution increased at the expense of the normal emission at 395 nm with addition of alkali, and dominated the whole emission spectra when alkali concentration is high up to 6×10^{-4} mol L^{-1}. This indicates that the presence of alkali is favourable for the phenolate anion formation and its emission at 445 nm. The excitation spectra of the alkali samples with emission at 445 nm (Fig. 11) started to show one additional band at 380 nm with addition of sodium hydroxide. Accordingly, a new absorption band at 380 nm was observed in the absorption spectra of same samples as shown in Fig. 12, which can be assigned to the absorption of phenolate anion. The detection of 380 nm band in both excitation and absorption spectra with addition of alkali implies that the phenolate anion was formed in the ground-state if in the presence of alkali. The coexistence of the 380 nm band and the original 340 nm band in both the excitation and absorption spectra at low alkali concentration such as 2 to 4×10^{-4} mol L^{-1} implies that the phenolate anions

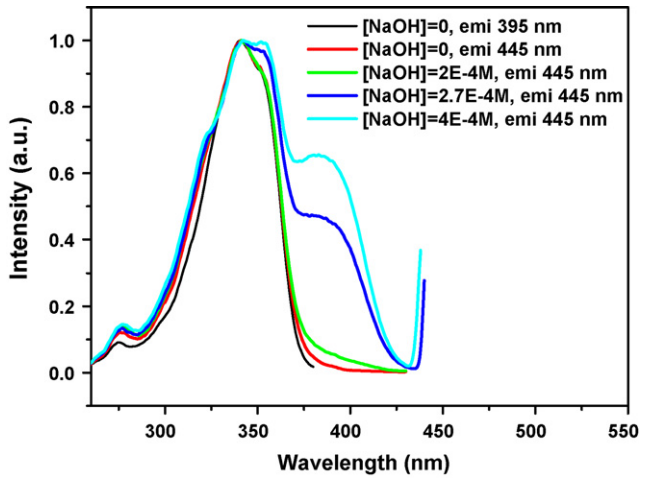

Fig. 11. Excitation spectra of **1** with emission at 395 and 445 nm in dioxane-water (50% water) solutions with different sodium hydroxide concentration.

responsible for the 440 nm emission band were generated not only in ground-state but also in excited state. When alkali concentration was high enough (6×10^{-4} mol L^{-1}), the majority of neutral molecules of **1** were converted in the ground-state to their phenolate anions and consequently the 445 nm band dominated the emission spectra and the 380 nm band dominated the excitation (the excitation line for 6×10^{-4} mol L^{-1} case not shown in Fig. 11 due to the 380 nm peak intensity out of detection range of the instrument) and the absorption spectra.

4. Conclusions

Novel 2-(2′-hydroxyphenyl)benzothiazole derivatives with electron-donating or withdrawing substituent in benzothiazolyl ring, **1–5**, were prepared for the first time. Spectroscopy investigation demonstrated that these compounds are possible to undergo ESIPT and exhibit dual fluorescences in solutions. The reported solvent effect on ESIPT is applicable to all compounds **1–5** in spite of the substituent, i.e. polar solvents favor the short-wavelength normal emission while non-polar solvents favor the long-wavelength tautomer emission. Introduction of substituent in benzothiazolyl ring of **1–5** did influence the ESIPT efficiency and their fluorescence through adjusting the O–H bond length and thus intramolecular hydrogen bond strength. Electron-donating groups such as methyl or methoxyl facilitate ESIPT and tautomer emission, while electron-withdrawing groups such as F or trifluoromethyl are not favorable to ESIPT process. The systematical study on both substituent effect and solvent effect in present paper indicates that the solvent is the first factor to determine the fluorescence properties of ESIPT-exhibiting substances, although substituents have important influences to ESIPT process and fluorescence behaviors as well. The experiments in dioxane-water binary solvents proved once again that the intermolecular hydrogen bonding involving protic solvent impedes ESIPT process and tautomer formation and emission, instead favors dissociation of hydroxy group and phenolate anion formation. The present study suggests that novel compounds **1–6** can be spread in many practical applications, e.g. as emitting component to fabricate white light-emitting diodes based on their wide emission spectra or as fluorescence probe to indicate media polarity.

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