Original Communication

2-(5-Amino-2-methoxyphenyl)benzothiazole as a fluorophore responding to metal cations

Kiyoshi Tanaka*, Sanami Hara, Satoru Iwata, and Takashi Takeyama

Laboratory of Molecular Control, Faculty of Science and Technology, Seikei University, Musashino-shi, Tokyo 180-8633, Japan

ABSTRACT

The fluorescence of 2-(5-amino-2-methoxyphenyl) benzothiazole (**1**) is affected by the solvent polarity and by the protonation; red shifts of the fluorescence are observed with an increase of the solvent polarity, and the fluorescent quenching is caused by the protonation at the amino group. Because the fluorescence intensity is sensitive to the association at the amino group, **1** is expected to work as a framework for fluorophores responding to metal cations by the association at the amino moiety. The benzothiazole **2**, having the pyridylmethyl-modified amino group as a powerful association site, is found to respond to Mg^{2+}, giving rise to blue shift of the fluorescence, and to Zn^{2+}, Hg^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, and H^+, causing fluorescent quenching.

KEYWORDS: cation recognition, bis(2-pyridylmethyl)amine, Mg^{2+}-responding fluorophore, 2-(5-amino-2-methoxyphenyl) benzothiazole

INTRODUCTION

A large red shift in fluorescence of *meta*-amino substituted phenylbenzazoles, where the amino group is nonconjugated with the electron-withdrawing benzazole group, is well established. This is explained by the dipole moment of the fluorophore becoming larger in the S_1 state upon excitation, that is, by intramolecular charge transfer at the excited state [1-3]. In a continuing research on applications of excited state intramolecular proton transfer of 2-hydroxyphenyl-benzazoles to a chemical sensor [4-7], we found out that 2-(5-amino-2-methoxyphenyl)benzothiazole indicates a redshifted fluorescence with relatively high fluorescence intensity. This fluorescent property shows the possibility of using this compound as a framework of fluorophore responding to some chemical species such as metal cations, because intramolecular electron transfer from the amino group may be controlled by its ligation of metal cations. We identified bis(2-pyridylmethyl)amino group as a recognizing site for metal cations, which is generally used as a ligand of Zn^{2+} due to its high affinity [8-16].

In this paper, we wish to describe fluorescent properties of 2-(5-amino-2-methoxyphenyl) benzothiazole (**1**) and the recognizing ability of bis(2-pyridylmethyl)amino- modified 2-(2-methoxyphenyl)benzothiazole (**2**).

MATERIALS AND METHODS

The FT/IR spectra were recorded on a JASCO FTIR-460 plus spectrophotometer and samples were run as potassium bromide pellets. The UV-vis and fluorescence spectra were recorded with JASCO V-530 and JASCO FP-6500 spectrometers, respectively, and measured in solvents of the highest quality for spectroscopy (KOKUSAN Chemical Co.) without further purification. Absolute fluorescence quantum yield was obtained using JASCO FP-6500 spectrometer with an integrating sphere unit (JASCO ILF-533). The

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*Corresponding author
tanaka@st.seikei.ac.jp

^{1}H NMR and ^{13}C NMR spectra were recorded with a JEOL JNM-LA400 or JEOL ECA-500 spectrometer and the chemical shifts are given in δ / ppm downfield from tetramethylsilane as an internal standard; *J* values are given in Hz. The elemental analyses were measured with a Perkin Elmer 2400 II CHN Analyzer.

2-(5-amino-2-methoxyphenyl)benzothiazole (1). A mixture of 2-methoxy-5-nitrobenzaldehyde (0.80 g, 4.4 mmol), 2-aminobenzenethiol (0.70 g, 5.6 mmol), and acetic acid (0.5 mL) in 45 mL of ethanol was refluxed for 1.5 h. After the mixture was cooled to room temperature, the formed precipitate was collected on a filter to give a yellow powder of 2-(2-methoxy-5-nitrophenyl) benzothiazole (0.24 g). Manganese dioxide (0.28 g, 3.2 mmol) was added to the filtrate and the mixture was stirred at room temperature for 18 h. After the heated mixture was filtered, the filtrate was cooled to room temperature. The formed precipitate was collected on a filter and was recrystallized from ethyl acetate to give 0.18 g of 2-(2-methoxy-5-nitrophenyl)benzothiazole: total yield 0.42 g (33%); yellow crystals; mp 208-210°C; FT/IR (KBr): ν 3097 (C-H), 1523 (NO$_2$), 1275 (C-O-C) cm^{-1}; UV-vis (acetonitrile): λ$_{max}$ (log ε / L mol^{-1} cm^{-1}) 293 (4.35), 315 (4.25) nm; ^{1}H NMR (CDCl$_3$): δ 4.19 (s, 3H), 7.16 (d, *J* = 9.0 Hz, 1H), 7.43 (dd, *J* = 8.2, 8.0 Hz, 1H), 7.56 (dd *J* = 8.2, 8.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 8.36 (dd, *J* = 9.0, 2.7 Hz, 1H), 9.47 (d, *J* = 2.7 Hz, 1H).

A mixture of 2-(2-methoxy-5-nitrophenyl) benzothiazole (0.60 g, 2.1 mmol) and tin dichloride dihydrate (3.26 g, 14.5 mmol) in 72 mL of 12 N-hydrochloric acid was stirred at room temperature for 24 h. Water (40 mL) was added to the mixture and the pH of the mixture was adjusted to 9 with 6 N-aqueous sodium hydroxide. The mixture was extracted with ethyl acetate and the extracts were washed with water and with brine, and dried over magnesium sulfate. After the evaporation of the solvent, the resulting residue was chromatographed on silica gel (hexane / ethyl acetate = 1 / 1) to give 0.42 g (78% yield) of **1**, which was recrystallized from hexane-ethyl acetate; orange crystals; mp 143-144°C; FT/IR (KBr): ν 3395, 3310 (N-H), 3060 (C-H), 2917 (C-H), 1268 (C-O-C) cm^{-1}; UV-vis (acetonitrile): λ$_{max}$ (log ε / L mol^{-1} cm^{-1})

366 (3.86), 301 (4.21), 309 (4.21) nm; ^{1}H NMR (CDCl$_3$) δ 3.71 (s, 2H), 4.19 (s, 3H), 6.83 (dd, *J* = 8.5, 2.9 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 2.9 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (CDCl$_3$): δ 163.16, 151.98, 150.84, 140.40, 136.16, 125.83, 124.51, 122.72, 122.60, 121.20, 118.89, 115.21, 113.60, 56.44. Anal. Calcd for C$_{14}$H$_{12}$N$_2$OS: C, 65.60; H, 4.72; N, 10.93. Found: C, 65.81; H, 4.72; N, 10.73.

2-{2-methoxy-5- bis (2-pyridylmethyl) aminophenyl}benzothiazole (2) and 2-{2-methoxy-5- (2-pyridylmethyl)aminophenyl}benzothiazole (3). A mixture of **1** (0.28 g, 1.1 mmol), 2-chloromethylpyridine hydrochloride (0.54 g, 3.3 mmol), and sodium carbonate (0.69 g, 6.5 mmol) in 20 mL of ethanol was refluxed for 80 h under an atmosphere of argon gas. After the evaporation of the solvent, water was added to the mixture. The aqueous mixture was extracted with ethyl acetate and the extracts were washed with water and with brine, and dried over magenesium sulfate. After the evaporation of the solvent, the resulting residue was chromatographed on silica gel (ethyl acetate as an eluent) to give 0.17 g (45% yield) of **3** and further eluted with ethyl acetate including of 1% of triethylamine, affording 0.22 g (46% yield) of **2**. Both compounds were purified by the recrystallyzation from hexane-ethyl acetate.

2: mp 138-140°C; FT/IR (KBr,): ν 3044 (C-H), 1233 (C-O-C-) cm^{-1}; UV-vis (acetonitrile) λ$_{max}$ (log ε / L mol^{-1} cm^{-1}) 386 (3.83), 300 (4.35) nm; ^{1}H NMR (CDCl$_3$): δ 3.94 (s, 3H), 4.87 (s, 4H), 6.82 (dd, *J* = 9.0, 3.2 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 7.17 (dd, *J* = 6.8, 5.1 Hz, 2H), 7.32 (d, *J* = 7.1 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.63 (ddd, *J* = 7.1, 6.8, 1.5 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 2H), 8.02 (d, *J* = 7.8 Hz, 1H), 8.04 (br.s, 1H), 8.60 (dd, *J* = 5.1, 1.5 Hz, 2H); ^{13}C NMR (CDCl$_3$): δ 163.21, 158.90, 152.14, 150.02, 149.61, 143.00, 136.83, 136.27, 125.73, 124.49, 123.06, 122.88, 122.06, 121.20, 121.13, 116.70, 113.66, 113.48, 57.56, 56.47. Anal. Calcd for C$_{26}$H$_{22}$N$_4$OS: C, 71.21; H, 5.06; N, 12.78. Found: C, 70.96; H, 5.03; N, 12.56.

3: mp 114-119°C; FT/IR (KBr): ν 3379 (N-H), 3009 (C-H), 1232 (C-O-C) cm^{-1}; UV-vis

(acetonitrile): λ_{max} (log ε / L mol^{-1} cm^{-1}) 377 (3.94), 305 (4.41) nm; ^{1}H NMR (CDCl$_3$): δ 3.94 (s, 3H), 4.51 (s, 2H), 4.85 (s, 1H), 6.78 (dd, J = 8.8, 2.9 Hz, 1H), 6.92 (d, J = 8.8 Hz, 1H), 7.15 (dd, J = 7.6, 4.2 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 8.1 Hz, 1H), 7.47 (t, J = 8.1 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.90 (d, J = 2.9 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 8.08 (d, J = 8.1 Hz, 1H), 8.58 (d, J = 4.2 Hz, 1H). Anal. Calcd for C$_{20}$H$_{17}$N$_3$OS: C, 69.14; H, 4.93; N, 12.09. Found: C, 68.87; H, 5.20; N, 11.79.

2-(5-acetamido-2-methoxyphenyl)benzothiazole (4). A solution of **1** (0.10 g, 0.39 mmol) in 10 mL of acetic anhydride and 10 mL of acetic acid was stirred at room temperature for 4 h. The reaction mixture was poured into ice-water and the resulting solid was collected on a filter to give crude **4** (0.09 g, 77%), which was purified by the recrystallization from hexane and ethyl acetate; white crystals; mp 176-178°C; FT/IR (KBr): ν 3246 (N-H), 3075 (C-H), 1659 (C=O), 1261 (C-O-C) cm^{-1}; UV-vis (acetonitrile) λ_{max} (log ε / L mol^{-1} cm^{-1}) 339 (4.13), 297 (4.25) nm; ^{1}H NMR (CDCl$_3$): δ 2.19 (s, 3H), 4.06 (s, 3H), 7.07 (d, J = 8.8 Hz, 1H), 7.27 (s, 1H), 7.40 (t, J = 8.1 Hz, 1H), 7.49 (t, J = 8.1 Hz, 1H), 7.94 (d, J = 8.1 Hz, 1H), 8.04 (dd, J = 8.8, 2.7 Hz, 1H), 8.07 (d, J = 8.1 Hz, 1H), 8.26 (d, J = 2.7 Hz, 1H). Anal. Calcd for C$_{16}$H$_{14}$N$_2$O$_2$S: C, 64.41; H, 4.73; N, 9.39. Found: C, 64.04; H, 4.74; N, 9.25.

2-(3-aminophenyl)benzothiazole (5). Similarly to the above, **5** was prepared.

2-(3-nitrophenyl)benzothiazole: 40% yield; yellow crystals; mp 185-186°C; FT/IR (KBr): ν 3086 (C-H), 1530 (NO$_2$) cm^{-1}; UV-vis (acetonitrile): λ_{max} (log ε / L mol^{-1} cm^{-1}) 283 (4.35) nm; ^{1}H NMR (CDCl$_3$) : δ 7.46 (t, J = 8.0 Hz, 1H), 7.56 (t, J = 8.0 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 8.35 (dd, J = 8.0, 0.8 Hz, 1H), 8.44 (dd, J = 8.0, 0.8 Hz, 1H), 8.95 (t, J = 0.8 Hz, 1H).

5: 27% yield; yellow crystals; mp 138-139°C; FT/IR (KBr): ν 3437, 3319 (N-H), 3214 (C-H) cm^{-1}; UV-vis (acetonitrile): λ_{max} (log ε / L mol^{-1} cm^{-1}) 330 (sh), 295 (4.25) nm; ^{1}H NMR (CDCl$_3$): δ 3.84 (br.s, 2H), 6.81 (dd, J = 7.8, 2.2 Hz, 1H), 7.27 (t, J = 7.8 Hz, 1H), 7.38 (dd, J = 8.2, 7.6 Hz, 1H), 7.43 (d, J = 7.8 Hz, 1H), 7.46 (br.s, 1H), 7.49 (dd, J = 8.2, 7.6 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 8.06 (d, J = 8.2 Hz, 1H).
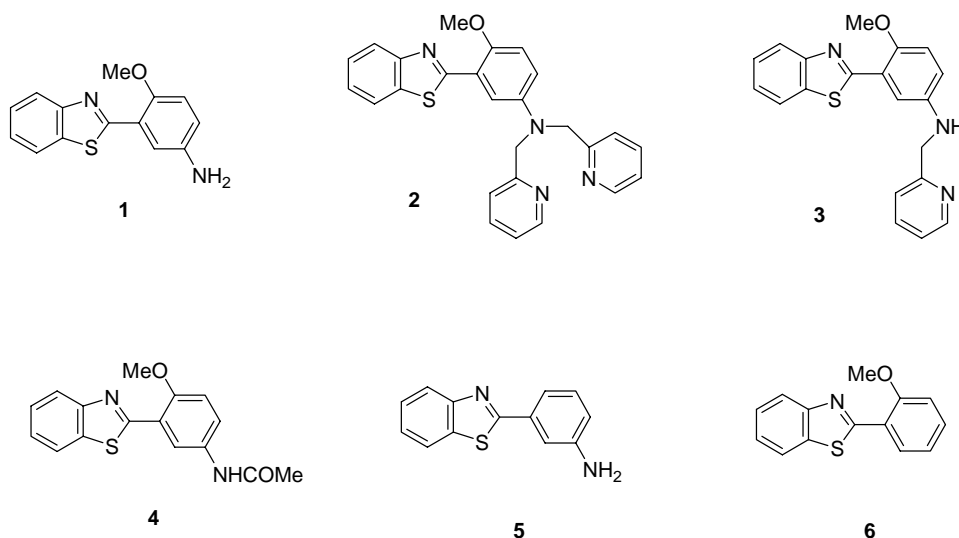
The structure was identified on the basis of the reported spectral data [1].

2-(2-methoxyphenyl)benzothiazole (6). A mixture of 2-methoxybenzaldehyde (2.17 g, 16.0 mmol), 2-aminobenzenethiol (2.00 g, 16.0 mmol), and acetic acid (1.5 mL) in 60 mL of ethanol was refluxed for 1.5 h. After the evaporation of the solvent, the mixture was extracted with ethyl acetate and the extracts were washed with 20% of aqueous sodium hydrogensulfite, with water, and with brine, and dried over magnesium sulfate. After the evaporation of the solvent, the resulting residue was recrystallized from hexane-ethyl acetate to give yellow crystals of **6** (1.31 g, 34%); mp 102-105°C (lit. [27] mp 106-108°C); FT/IR (KBr): ν 3015 (C-H), 2831 (C-H), 1247 (C-O-C) cm^{-1}; UV-vis (acetonitrile): λ_{max} (log ε / L mol^{-1} cm^{-1}) 322 (4.22), 296 (4.08) nm; ^{1}H NMR (CDCl$_3$): δ 4.07 (s, 3H), 7.08 (d, J = 8.3 Hz, 1H), 7.14 (t, J = 7.8 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.47 (m, 2H), 7.93 (d, J = 7.8 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 8.53 (dd, J = 7.8, 1.5 Hz, 1H). Anal. Calcd for C$_{14}$H$_{11}$NOS: C, 69.68; H, 4.59; N, 5.80. Found: C, 70.01; H, 4.66; N, 5.79.

RESULT AND DISCUSSION

Compound **1** was obtained by the reduction of 2-(2-methoxy-5-nitrophenyl)benzothiazole; pyridylmethylation of **1** with 2-chloromethylpyridine produced **2** in 46% yield together with monosubstituted 2-(2-methoxyphenyl)benzothiazole **3** in 45% yield. Acetamido-substituted 2-(2-methoxyphenyl)benzothiazole **4** was obtained by the acetylation of **1** with acetic anhydride. 2-(3-Aminophenyl)benzothiazole (**5**) was similarly prepared by the reduction of 2-(3-nitrophenyl)benzothiazole. 2-(2-Methoxyphenyl)benzothiazole (**6**) was directly obtained by the reaction of 2-aminobenzenethiol with 2-methoxybenzaldehyde in moderate yield.

Comparing spectral data of **1** and **6** in acetonitrile, one finds that introduction of amino group to *meta*-position in the phenyl ring causes red shifts in both the absorption and fluorescence spectra, accompanied by the increase of fluorescence intensity, as shown in Figure 1. A similar trend

Compounds 1, 2, 3, 4, 5, and 6

was observed with **5** and 2-phenylbenzothiazole [17]. Introduction of methoxy group to *ortho*-position of the phenyl ring of **5** induced red shifts in both the absorption and fluorescence spectra and increased the fluorescence intensity; although the wavelength of maximum absorption of **5** appears at 330 nm as a shoulder, that of **1** is redshifted to 366 nm and the fluorescent wavelength changes from 445 nm to 480 nm. It should be noted that the excitation spectra at 480 nm is consistent with the absorption spectra. Meanwhile, reducing electron density of the amino-nitrogen of **1** by the acetylation causes blue shifts in both the absorption and fluorescence spectra to 345 nm and 410 nm, respectively (the spectra of **4** in Figure 1).

Effects of solvent polarity and protonation on absorption and fluorescence of **1** were next investigated. Because of a wide range of permittivity, spectral data were taken in dioxane-water mixtures. Large blue shifts of the absorption and red shifts of the fluorescence are observed, and the fluorescence intensity is decreased with an increase of the solvent polarity (Figure 2). A plot of fluorescence maxima versus permittivity shows large dependence of the fluorescence wavelength on the solvent polarity (Figure 2). Protonations were performed in a dioxane-water (95:5) mixture using hydrochloric acid. Changes of the absorption of **1** by protonation are quite similar to those caused by the solvent polarity; wavelength of maximum absorption is blueshifted with an increase

of hydrochloric acid. Meanwhile, the fluorescence intensity at 490 nm is gradually decreased, and the small but distinct band at 370 nm becomes enlarged (Figure 3). A Job plot of this protonation supports the 1:1 complexation and curvefitting of the titration using absorption changes shows the association constant of $K = (1.5\pm0.1)\times10^4$ M^{-1} (Figure 4). From the blue shift of the absorption in the addition of hydrochloric acid, we concluded that protonation could take place at the amino group; the formed ammonium complex emits at 370 nm but its intensity is quite small. Therefore, the benzothiazole **1**, the phenyl group of which is modified by amino group and methoxy group at *meta-* and *ortho*-positions, respectively, is expected to work as a fluorophore responding to some chemical species such as metal cations by the association with the amino moiety.

The recognition ability of **2**, where bis (2-pyridylmethyl)amino group is used as a powerful association site, was investigated in acetonitrile. Compared to **1**, the absorption of **2** is redshifted by a range of 22 nm (from 366 nm to 388 nm) but the fluorescence wavelength 480 nm is the same (Figure 5). The absolute fluorescence quantum yield of **2** was estimated to be $\Phi = 0.36$ in acetonitrile. Changes in absorption and fluorescence of **2** induced by the addition of Zn^{2+} were first evaluated. The absorption is blueshifted and the fluorescence quenches with an increase of Zn^{2+} (Figure 5). A job plot supports the 1:1 complexation and the titration-curvefitting using absorption changes shows a very
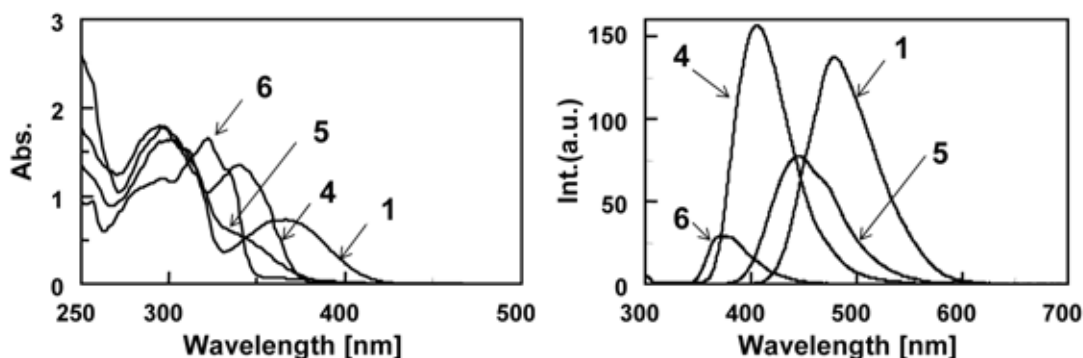
Figure 1. Absorption and fluorescence spectra of benzothiazoles **1**, **4**, **5**, and **6** in acetonitrile. [Benzothiazole] = 1×10^{-4} M for absorption and 1×10^{-5} M for fluorescence, λ_{ex} = 298 nm.
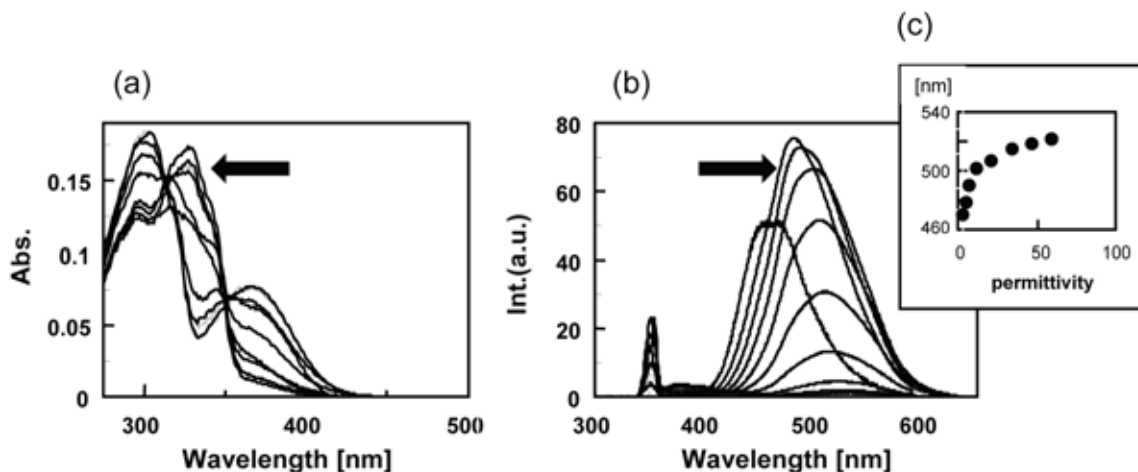

Figure 2. Changes of absorption (a) and fluorescence (b) of **1** with an increase of solvent polarity. [**1**] = 1×10^{-4} M for absorption and 1×10^{-5} M for fluorescence, λ_{ex} = 350 nm. Solvent (vol%); dioxane/water = 100/0, 95/5, 90/10, 80/20, 65/35, 50/50, 35/65, 20/80. (c) Relationship between λ_{em} and permittivity of the solvent.

Figure 3. Spectral changes of **1** with an increase of HCl in dioxane-water (95/5). [**1**] = 1×10^{-4} M, [HCl] = 0~30 eq., λ_{ex} = 310 nm.

high association constant, $K = (2.4\pm0.3)\times 10^6\,M^{-1}$ (Figure 6). A similar quenching is observed in the cases of Hg^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, and H^+; however, the fluorescence and absorption remain unchanged under the presence of Li^+, Na^+, K^+, and Ca^{2+}. The fluorescent behavior caused by Mg^{2+} is quite different from these cations; although the 480 nm fluorescence is quenched, the 424 nm fluorescence is gradually increased. Changes of the fluorescence at 480 nm and 424 nm under the presence of 10 eq. of cation are summarized in Figure 7.

Spectral changes caused by Mg^{2+} are depicted in Figure 8, which shows the blueshifts of the absorption similarly to the case of Zn^{2+} and the
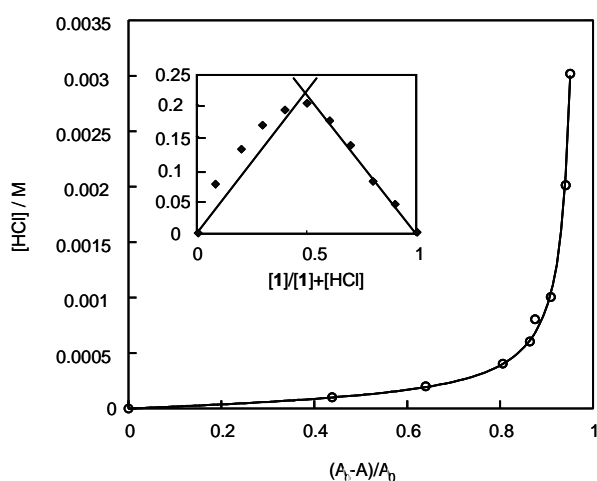
enhancement of the fluorescence at 424 nm with an increase of Mg^{2+}. The 1:1 complexation was confirmed by Job plot and its association constant was determined to be $K = (8.0\pm1.0)\times10^4\,M^{-1}$ on the basis of the titration-curvefitting using absorption changes (Figure 9). The fluorescence at 424 nm was confirmed to be from the complex on the basis of the matching of the excitation spectra at this wavelength with the absorption spectra. A powerful association site, bis (2-pyridylmethyl) amino moiety, is necessary for this blueshifted fluorescence because both amino- and mono (2-pyridylmethyl) amino-substituted benzothiazoles **1** and **3** do not emit the similar fluorescence by the addition of Mg^{2+}. Indeed, the ^{1}H NMR spectra of **2** under the presence of an equivalent of Mg^{2+} in CD_3CN show the deshielded protons adjacent to the pyridine nitrogen atom; however, this deshielding effect of Mg^{2+} is thought to be less than that of Zn^{2+} (Figure 10). Although the methyl protons are slightly deshielded in both cases, a large difference in the ^{1}H NMR spectra between Mg^{2+} and Zn^{2+} is found for the methylene protons; the protons split into two peaks under the presence of Mg^{2+}, in contrast to the singlet peak slightly upfield under the presence of Zn^{2+}. The splitting peak of the methylene protons under the presence of Mg^{2+} may be ascribed to the differences in the magnetic circumstances between methylene hydrogens of the Mg^{2+} complex. Although the reason why the methylene protons is singlet under the presence of Zn^{2+} is ambiguous, a similar situation is reported in the literature [9]. From these spectral changes, the deshielded pyridine hydrogens and methyl
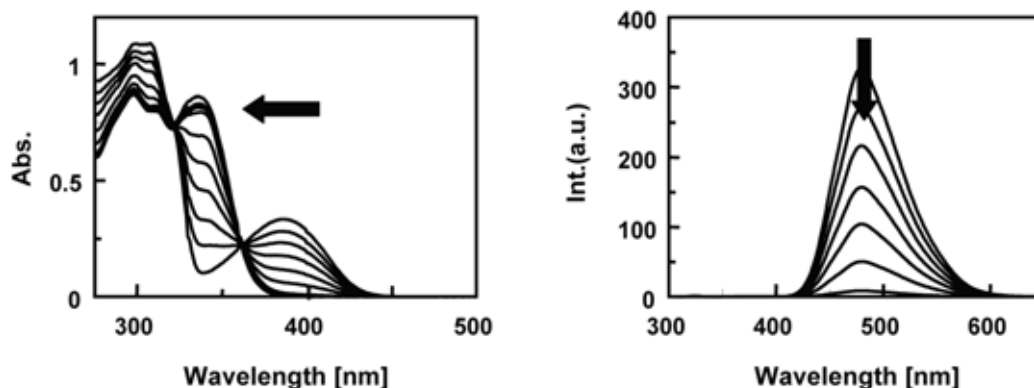

Figure 4. Titration curve of **1** with HCl in dioxane-water (95/5). $[1] = 1\times10^{-4}$ M, [HCl] = 0~30 eq.. Inset shows Job plot.

Figure 5. Spectral changes of **2** with an increase of Zn^{2+} in acetonitrile. $[2] = 5\times10^{-5}$ M. $[Zn(SCN)_2] = 0$~5 eq., $\lambda_{ex} = 323$ nm.
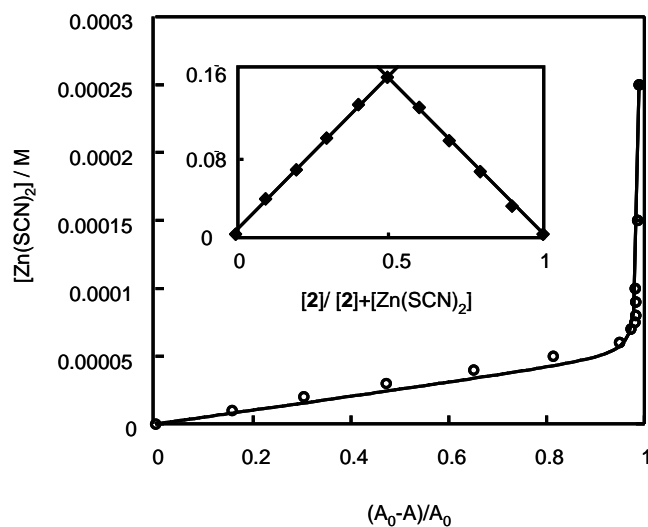
Figure 6. Titration curve of **2** with Zn^{2+} in acetonitrile.
$[\mathbf{2}] = 5\times10^{-5}$ M, $[Zn(SCN)_2] = 0\sim5$ eq.. Inset shows Job plot.

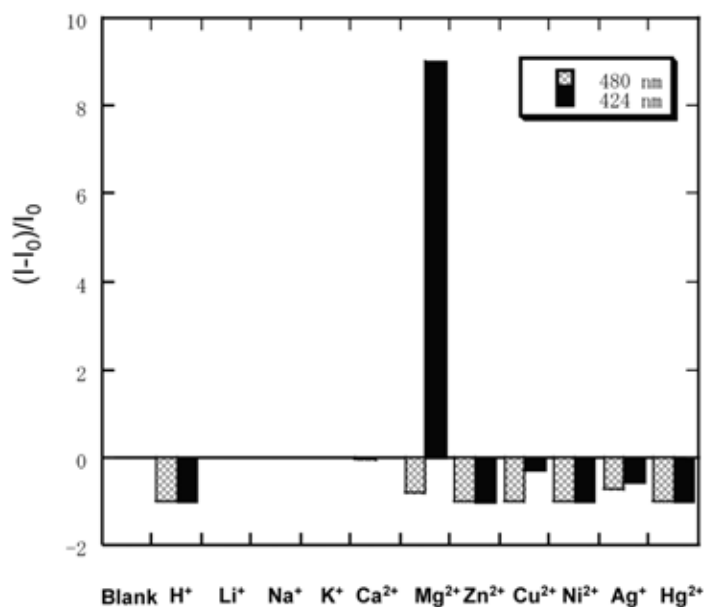**Figure 7.** Effects of metal cations on emissions at 424 nm and 480 nm.
Solvent; acetonitrile, $[\mathbf{2}] = 1\times10^{-5}$ M, [cation] = 10 eq., counter anion; SCN^- for
Li^+, Na^+, Ca^{2+}, Mg^{2+}, Zn^{2+}; ClO_4^- for Ni^{2+}, Cu^{2+}, Ag^+, Hg^{2+}; CF_3COO^- for H^+.

protons and the shielded methylene protons, it is suggested that the three nitrogen atoms participate in Zn^{2+} and Mg^{2+} coordination directly.

The enhancement of the blueshifted fluorescence by the ligation of Mg^{2+} with nitrogen atoms is a unique instance. The bonding of Mg^{2+} with oxygen atom has been utilized in the complexations of Mg^{2+}-sensing fluorophores [18-26]. The bonding of Mg^{2+} with the nitrogen atoms of **2** is anticipated to be not so strong because of the mismatch in the hardness. Actually, the similar Mg^{2+} induced fluorescence change is not observed in methanol, and the fluorescence at 424 nm under the presence
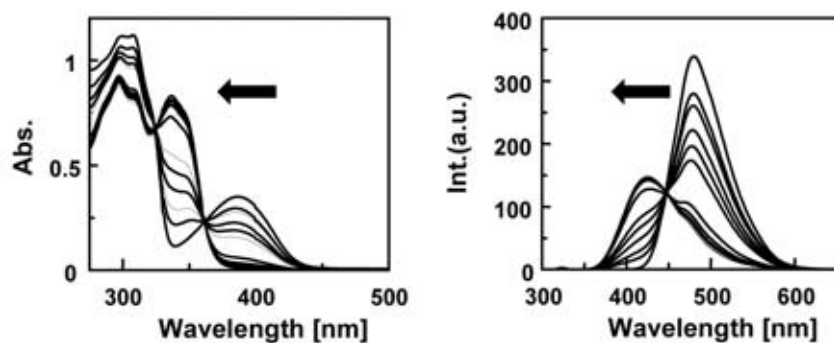
Figure 8. Spectral changes of **2** with an increase of Mg^{2+} in acetonitrile. [**2**] = 5×10^{-5} M. [$Mg(SCN)_2$] = 0~20 eq., λ_{ex} = 323 nm.

Figure 9. Titration curve of **2** with $Mg(SCN)_2$ in acetonitrile.
[**2**] = 5x10-5 M, [$Mg(SCN)_2$] = 0~20 eq.. Inset shows Job plot.

Figure 10. ^{1}H NMR spectra of **2** in the presence of Mg^{2+} and Zn^{2+}.
[**2**] = [$Zn(SCN)_2$] = 1×10^{-3} M, [$Mg(SCN)_2$] = 2×10^{-3} M in CD_3CN.

of Mg^{2+} is sensitive to the coexistent water; its fluorescence disappears even in 1% water-acetonitrile and the fluorescence at 480 nm comes back. The absorption and fluorescence of the Mg^{2+} complex of **2** could be compared with those of the amide **4**, and so the electronic effects of Mg^{2+} in the complex might be comparable to the amide group.

CONCLUSIONS

The benzothiazole **1**, the phenyl group of which is modified by amino group and methoxy group at *meta-* and *ortho*-positions, respectively, is easily prepared and indicates the fluorescence at long wavelength (480 nm) with relatively high fluorescence intensity. The fluorescence was affected by the solvent polarity and by the protonation; red shifts of the fluorescence are observed with an increase of the solvent polarity, and the protonation with hydrochloric acid causes its quenching. From these fluorescent behaviors, **1** is expected to work as a fluorophore responding to metal cations by the association with the amino moiety. The fluorescence of **2**, modified by bis (2-pyridylmethyl) amino group as a powerful association site, was found to respond to various cations; the quenching of the 480 nm fluorescence is observed in the cases of Zn^{2+}, Hg^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, and H^+ but the fluorescence remains unchanged under the presence of Li^+, Na^+, K^+, and Ca^{2+}. Among the evaluated cations, only Mg^{2+} causes the enhancement of the blueshifted fluorescence at 424 nm.

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