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New thiazolothiazole derivatives as fluorescent chemosensors for Cr^{3+} and Al^{3+}

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ABSTRACT

Two new 2,5-diarylthiazolo[5,4-*d*]thiazole derivatives bearing ethylene oxide moieties were synthesized. Their photophysical and electrochemical properties as well as binding properties towards various metal ions were examined. Thiazole derivative **1** showed large fluorescent enhancements with Cr^{3+} and Al^{3+}. On the other hand, thiazole derivative **2** displayed a selective fluorescent change with Cr^{3+} among the metal ions examined. As far as we are aware of, these are the first examples of thiazolothiazole derivatives as fluorescent chemosensors for metal ions.

1. Introduction

Numerous organic molecules and polymers that exhibit electroluminescence (EL) or have electron transporting properties have been reported [1,2]. Especially, 2,5-diarylthiazolo[5,4-*d*]thiazoles have been actively utilized for field-effect transistors [3], two-photon-absorption (TPA) active materials as nonlinear optical chromophores [4], electroluminescent polymer [5], etc [6]. However, thiazolothiazole derivatives have not been explored as fluorescent chemosensors [7–14] for metal ions.

Chromium (Cr^{3+}) ion is not only an essential nutrient for humans, but also plays an important role in the metabolism of carbohydrates, lipids, proteins, and nucleic acids [15]. The deficiency of chromium is known to lead to a variety of disease, including diabetes and cardiovascular disease [16]. At the mean time, chromium is an environmental pollutant and its build-up due to various industrial and agricultural activities is a matter of concern [17]. In spite of the biological and environmental importance of Cr^{3+}, only few reports are available regarding fluorescent detection of Cr^{3+} [18–23]. On the other hand, the widespread use of aluminum in food additives and aluminum-based pharmaceuticals often expose people to Al^{3+}. There are a few fluorescent chemosensors have been reported for the detection of Al^{3+} [24–29].

Herein, two new thiazolothiazole derivatives (**1** and **2**) were synthesized, in which ether binding units were introduced (Fig. 1). Photophysical and electrochemical properties of these new derivatives were examined. In addition, compound **2** displayed selective fluorescence "*Off-On*" change upon the addition of Cr^{3+}. On the other hand, compound **1** bearing shorter ethylene oxide unit showed large fluorescent enhancements with Cr^{3+} and Al^{3+} among the metal ions examined.

2. Experimental

2.1. Materials and equipments

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Flash chromatography was carried out on silica gel 60 (230–400 mesh). ^1H NMR and ^{13}C-NMR spectra were recorded using 250 MHz NMR or 500 MHz NMR. Compound **3** was synthesized following the reported procedure [30].

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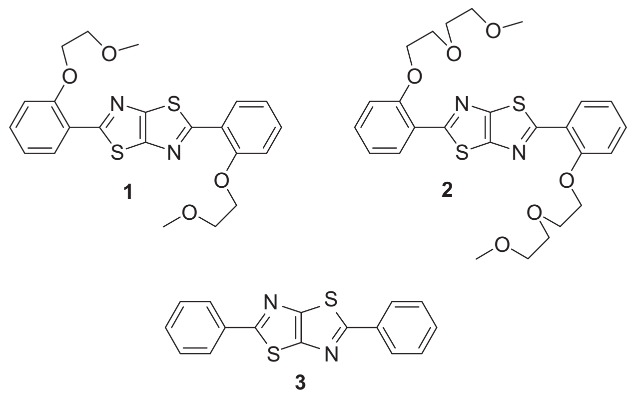


Fig. 1. Structures of the thiazolothiazole derivatives **1**–**3**.

2.2. Synthesis

*2.2.1. Compound **1***

Procedure A. 2-(2-Methoxyethoxy)benzaldehyde (0.75 g, 4.16 mmol) was added to dithiooxamide (0.25 g, 2.08 mmol) in 20 mL DMF. The reaction was refluxed for 20 h, then the solvent was evaporated. The crude product was purified by column chromatography using ethyl acetate-hexane (2:1) as eluent to give compound **1** as yellow powder (0.31 g, 34%). Mp: 203 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.40 (dd, 1H, J = 9.0 Hz and 2.0 Hz), 7.33 (m, 1H), 7.05 (dd, 1H, J = 17.3 Hz and 1.2 Hz), 7.00 (t, 1H, J = 11.6 Hz), 4.31 (t, 2H, J = 5.3 Hz), 3.92 (t, 2H, J = 5.75 Hz), 3.58 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.7, 155.9, 152.1, 131.1, 128.7, 123.3, 121.6, 112.6, 71.1, 68.7, 59.6; HRMS (FAB) $C_{22}H_{23}O_4N_2S_2$ = 443.1099, found 443.1104 $(M + H)^+$.

*2.2.2. Compound **2***

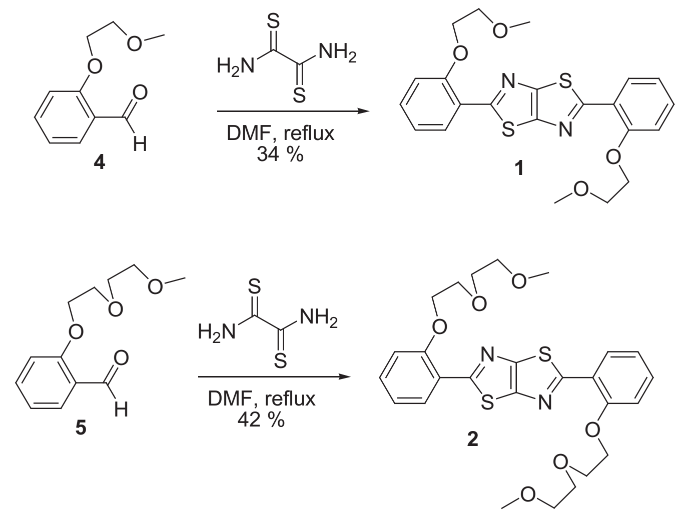
Procedure A was applied to 2-[2-(2-methoxyethoxy)ethoxy] benzaldehyde **5** (1.47 g, 6.57 mmol) and dithiooxamide (0.15 g, 1.13 mmol) in 20 mL DMF to give compound **2** as yellow powder (1.46 g, 42%). Mp: 134 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.38 (dd, 1H, J = 9.0 Hz and 2.0 Hz), 7.35 (t, 1H, J = 8.9 Hz), 7.04 (m, 2H), 4.41 (t, 2H, J = 5.3 Hz) 3.84 (t, 2H, J = 5.75 Hz), 3.83 (m, 2H) 3.63 (m, 2H) 1.49 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.7, 155.6, 152.2, 131.1, 128.7, 123.3, 121.6, 112.6, 72.2, 71.1, 69.7, 68.7, 59.3; HRMS (FAB) $C_{26}H_{21}O_6N_2S_2$ = 531.1624, found 531.1630 $(M + H)^+$.

2.3. Electrochemical study

Cyclic voltammetry (CV) experiments were carried out in the appropriate solutions containing electroactive compounds and 0.1 M tetrabutylammonium perchlorates at room temperature using a BAS 100B electrochemical analyzer in a glove-box. A Pt disk (dia. 1.6 mm) and Pt wire, and Ag|$AgNO_3$ (0.1 M) were used as working, counter, and reference electrodes, respectively. All the potential values were calibrated versus the ferrocene/ferrocenium (Fc|Fc^+) redox couple and then corrected to the saturated calomel electrode (SCE) on the basis of an Fc|Fc^+ redox potential of 0.28 V and 0.16 V versus SCE in CH_3CN/DMSO mixed solution and CH_2Cl_2, respectively. The potential scan rate was 0.1 V/s.

2.4. UV and fluorescent study with metal ions

Stock solutions (0.01 M) of the perchlorate salts of Al^{3+}, Cr^{3+}, Ag^+, Fe^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+}, K^+, Li^+, Cs^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Zn^{2+} ions in CH_3CN were prepared. Stock solutions of **1** and **2** (0.1 mM) were also prepared in CH_3CN and $CHCl_3$, respectively. Test solutions were prepared by placing 300 μL of the probe stock solution into a test tube, adding an appropriate aliquot of each metal stock, and diluting the solution to 3 mL with CH_3CN and $CHCl_3$. The absorption and fluorescence properties of **1** were tested in CH_3CN:$CHCl_3$ (4:1, v/v) and those of **2** were examined in CH_3CN.



Scheme 1. Synthesis of the thiazolothiazole derivatives **1**–**2**.

3. Results and discussion

3.1. Synthesis

The synthetic routes of new thiazolothiazole derivatives **1** and **2** are shown in Scheme 1. The corresponding aldehyde, such as 2-(2-methoxyethoxy)benzaldehyde (for **1**) was added to dithiooxamide in 20 mL DMF, which was then refluxed for 20 h. After the solvent was evaporated, the crude product was purified by column chromatography using ethyl acetate-hexane (2:1) as eluent to give compound **1** as yellow powder in 34% yield. For compound **2**, the corresponding aldehyde 2-[2-(2-methoxyethoxy)ethoxy]benzaldehyde **6**, was synthesized following the reported procedure [24]. In a similar way, the corresponding aldehyde **6** was reacted with dithiooxamide to give **2** in 42% yield. Compounds **1** and **2** were fully characterized by ^{1}H NMR, ^{13}C NMR (see supporting information) and high resolution FAB mass spectroscopy.

3.2. Quantum efficiencies and CV data

The absorption and fluorescence spectra of compounds **1** and **2** were examined in DMSO and CH_2Cl_2 solutions at room temperature. The relative quantum efficiencies were determined using 9,10-

Table 1
Cyclic voltammetric data for **1**–**3**.[a,b]

	E_{pa}/E_{pc}		E_g (eV)	λ_{max} (nm)[f]	1240/λ_{max} (eV)
	E_{red}	E_{ox}			
1	−1.76/−1.83[a]	…[c]/−1.96[b]	3.13[d]	390	3.18
2	−1.76/−1.83[a]	…[c]/−1.96[b]	3.13[d]	390	3.18
3	−1.60/−1.67[a]	…[c]/−1.83[b]	3.43[e]	371	3.33

[a] CVs were recorded in CH_3CN:DMSO (1:1)/0.1 M TBAP.
[b] CVs were recorded in CH_2Cl_2/0.1 M TBAP.
[c] It is hard to measure the value because of lack of reversibility.
[d] Calculated from the CVs in CH_3CN:DMSO (1:1)/0.1 M TBAP.
[e] Calculated from the CVs in CH_2Cl_2/0.1 M TBAP.
[f] Measured in CH_2Cl_2.

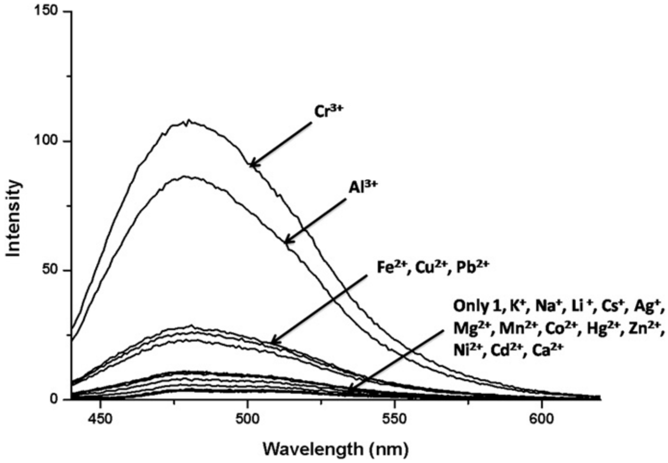


Fig. 2. Fluorescent spectra (excitation at 420 nm) of **1** (1×10^{-5} M) in CH_3CN:$CHCl_3$ (4:1, v/v) upon addition of 5 equiv. of metal ions.

diphenylanthracene in degassed hexane ($\Phi = 0.96$) as a reference compound. In DMSO, the relative quantum efficiencies and maximum wavelength for fluorescence were 33% ($\lambda_{max} = 423$ nm) and 23% ($\lambda_{max} = 423$ nm) for compound **1** and **2**, respectively. In CH_2Cl_2, those were observed as 38% ($\lambda_{max} = 428$ nm) and 43% ($\lambda_{max} = 428$ nm) for compound **1** and **2**, respectively. Quantum efficiencies of these derivatives were in the range of 23%–43%.

The electrochemical properties of compounds **1-3** by CV measurements are summarized in Table 1, where the E_{ox} and E_{red} values are known to be related to the HOMO and LUMO energy levels, respectively [31,32]. CVs were carried out both in CH_3CN/DMSO mixture and CH_2Cl_2 due to the potential window and solubility where reduction was well-defined in the former solvent while oxidation in the latter one as shown in Figs. S5 and S6. The CV of **3** and that of **1** resemble each other bearing the same electroactive structural body except ether linkage. It is notable that electron-donating properties of ether substituents in **1** and **2**, where reduction and oxidation waves shifted to the negative potential by 0.16 V (recorded in CH_3CN/DMSO mixture) and 0.30 V (recorded in CH_2Cl_2), respectively. The reversibility of the oxidation wave of **3** was also improved by electron-donating substituent of **1** due to stabilization of radical cation of **1** (Fig. S6). Overall, the band gap values from CV reveal good agreement with those from absorption wavelength within 0.1 eV.

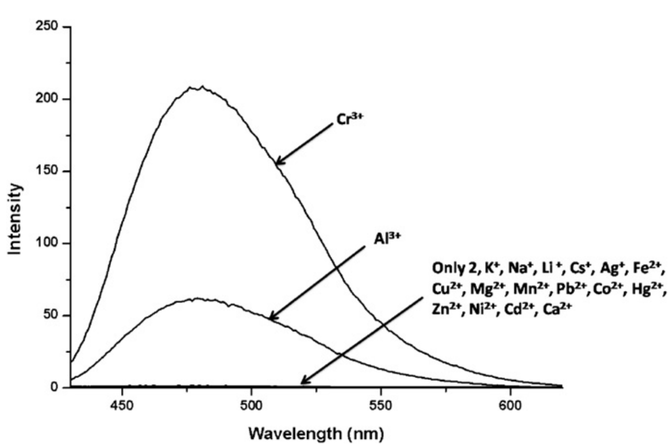


Fig. 3. Fluorescent spectra (excitation at 420 nm) of **2** (1×10^{-5} M) in CH_3CN upon addition of 5 equiv. of metal ions.

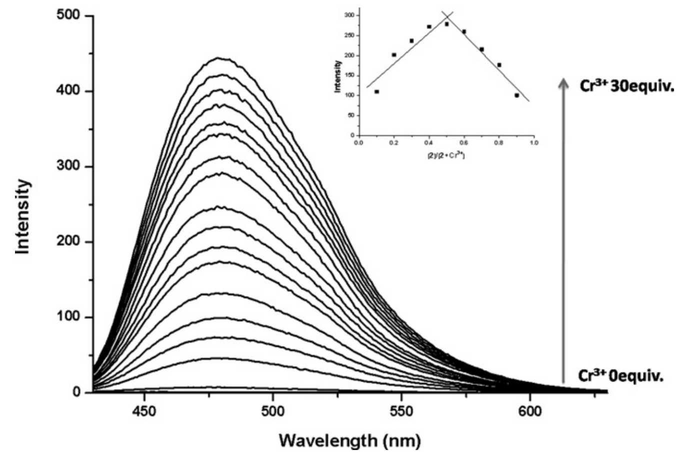


Fig. 4. Fluorescent change of **2** (1×10^{-5} M, CH_3CN) upon adding of 0–30 equiv. of Cr^{3+} ion, excitation at 420 nm (Inset: Job plot for **2** with Cr^{3+} ion. The line show 1:1 stoichiometry.).

3.3. UV absorption and fluorescence study with metal ions

The absorption and fluorescence properties of **2** were tested in CH_3CN. On the other hand, compound **1** was examined in CH_3CN:$CHCl_3$ (4:1, v/v) due to the solubility problem. Compound **1** and **2** showed major absorption bands at 368 nm (Fig. S1) and at 367 nm (Fig. S2), respectively. Perchlorate salts of Al^{3+}, Cr^{3+}, Ag^+, Fe^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+}, K^+, Li^+, Cs^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Zn^{2+} were used for the metal ion binding study. Cr^{3+} and Al^{3+} induced internal charge transfer peaks around 420 nm in UV spectra of **1** and **2** as shown in Figs. S1 and S2. The fluorescence spectra were obtained by exciting thiazole derivatives **1** and **2** at 420 nm. When 5 equiv. of metal ions were added, **1** showed large fluorescence enhancements with Cr^{3+} and Al^{3+} while Fe^{2+}, Cu^{2+} and Pb^{2+} induced relatively smaller enhancements (Fig. 2). On the contrary, compound **2** showed a selective "*Off-On*" fluorescence change (~200 fold) with Cr^{3+} among the various metal ions examined even though there was a small fluorescence enhancement with Al^{3+} (Fig. 3).

The fluorescence titrations of **1** with Cr^{3+} and Al^{3+} are explained in Figs. S11 and S12. The association constants (K_a) of **1** with Cr^{3+} and Al^{3+} were calculated as 6.99×10^{-4} M^{-1} and 9.29×10^{-4} M^{-1},

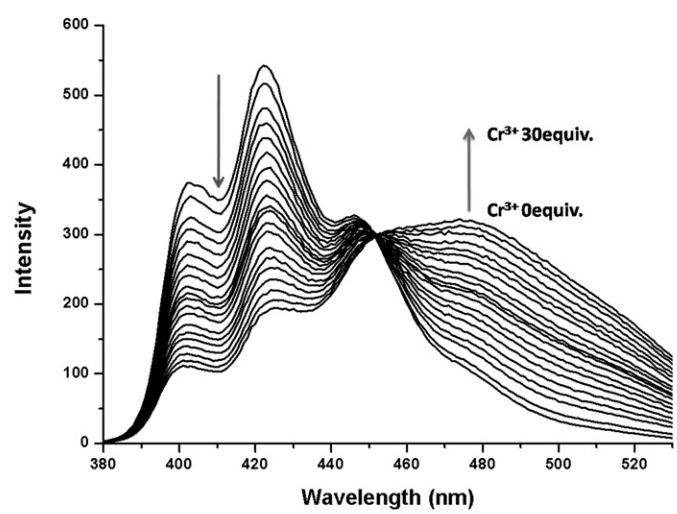


Fig. 5. Fluorescent change of **2** (1×10^{-5} M, CH_3CN) upon adding of 0–30 equiv. of Cr^{3+} ion, excitation at 370 nm.

respectively [33]. Fig. 4 explains the fluorescence titrations of **2** with Cr^{3+} and those with Al^{3+} are explained in Fig. S13. K_a values of **2** with Cr^{3+} and Al^{3+} were calculated as 9.61×10^{-4} M^{-1} and 2.95×10^{-4} M^{-1} [33]. Job plots for **1** and **2** with Cr^{3+} and Al^{3+} showed 1:1 stoichiometry (Fig. 4, Fig. S11–13). On the other hand, when 370 nm was used for excitation, compound **2** showed nice ratiometric changes with Cr^{3+} (Fig. 5). Ratiometric fluorescent chemosensors have an important advantage, such as signal rationing, which can allow to increase the dynamic range and provide built-in corrections [34–41]. As the concentration of Cr^{3+} increases, the peak at 422 nm quenched, while the peak at 476 nm increased with an isosbestic point of 452 nm (Fig. 5).

4. Conclusions

In current study, we synthesized two new thiazolothiazole derivatives (**1** and **2**), in which ether binding units were introduced. Photophysical and electrochemical properties of these new derivatives were examined. In addition, compound **2** displayed a selective fluorescence "*Off-On*" change upon the addition of Cr^{3+}. On the other hand, compound **1** bearing shorter ethylene oxide unit showed large fluorescent enhancements with Cr^{3+} and Al^{3+} among the metal ions examined. As far as we are aware of, these are the first examples of thiazolothiazole based fluorescent chemosensors for metal ions.

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Appendix. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.dyepig.2012.02.005.

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