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# A highly selective fluorescent turn-on probe for $Al^{3+}$ via $Al^{3+}$-promoted hydrolysis of ester

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ABSTRACT

A new reactive and highly selective fluorescent chemosensor (**1**) based on thiazole was synthesized for the quantification of aluminum ions in ethanol. The mechanism of fluorescence was based on the aluminum-promoted hydrolysis of the ester moiety and subsequent complexation.



## 1. Introduction

The developments of turn-on fluorescent probes that operate through chemical reactions triggered by the target analytes have attracted attention.[1–3] A range of chemical reactions have been implemented in the development of many reactive probes. This approach involves the use of highly selective and normally irreversible chemical reactions coupled with signal transduction induced by analytes. These reactive probes provide higher selectivity with larger spectroscopic changes than chemical probes. Previously, the synthesis and $Zn^{2+}$ or $Cu^{2+}$ sensing properties of several thiazole based chemosensors were reported.[4–7] Among them, the selectivity for cations can be controlled by changing the moiety at position-4 of the thiazole ring. Schiff base fluorescent sensors have attracted special attention owing to their versatile organic blockers possessing comparable accessibility and structure variable. On the other hand, few studies have examined Schiff base chemosensors for the detection of $Al^{3+}$ ion due to its weak coordination ability compared to transition metal ions[8–16] Therefore, considering the Schiff base and functional carboxylic moiety[17] affinity to $Al^{3+}$, probe **1** (Fig. 1) was prepared by introducing an ester and phenol group at positions-4 and -2 of the thiazole ring, respectively. This provided harder donors, such as oxygen and nitrogen atoms, in the molecular skeleton for the hard acid, $Al^{3+}$.

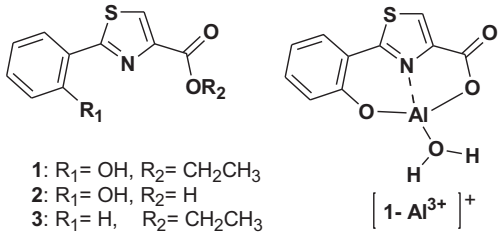


**Fig. 1.** Fluorescent thiazole probes, **1**–**3** synthesized in this study and aluminum complex of **1**.

Moreover, the hydroxyl group and ternary N atom as coordinating sites act as a bidentate ligand and show the same coordinating motif as the family of 8-hydroxyquinoline ligands that are used extensively in analytical chemistry for the detection of $Al^{3+}$.[18] Probes **2** and **3** were also prepared to understand the critical role of phenol at the 2-position of the thiazole rings and the mode of complexation with $Al^{3+}$.

## 2. Results and discussion

Probes **1** and **3** were obtained in good yield by a Hantzsch condensation reaction of 2-hydroxyphenylthiobenzamide and thiobenzamide with ethyl bromopyruvate in refluxing ethanol, and probe **2** was prepared in good yield by the hydrolysis of probe **1**.

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The structures of probes **1**, **2**, and **3** were confirmed by $^{1}H$ and $^{13}C$ NMR spectroscopy, and elemental analyses.

UV–vis study was carried out in ethanol at a concentration of 20 μM. The host solution was heated to 50 °C for 1 h after adding the guest to ensure complete complexation. Probe **1** displayed an obvious absorption band at 325 nm. This was attributed to a π–π transition, which is favored by the planar orientation enforced by intramolecular hydrogen bonding.[19] On the other hand, upon the addition of aluminum ions to a solution of probe **1**, the absorption band at 364 nm was enhanced gradually with a concomitant decrease in the absorption band at 325 nm, as shown in Fig. 2 with an isosbestic point at 339 nm. These findings are characteristic of phenol–thiazole derivatives when a complexation process is accompanied by the deprotonation of a hydroxyl group.[6,7] Moreover, there are three clear isosbestic points at 339, 304, and 286 nm, which clearly suggests the conversion of free chemosensor **1** to an $Al^{3+}$ complex of only one stoichiometry.[20,21]

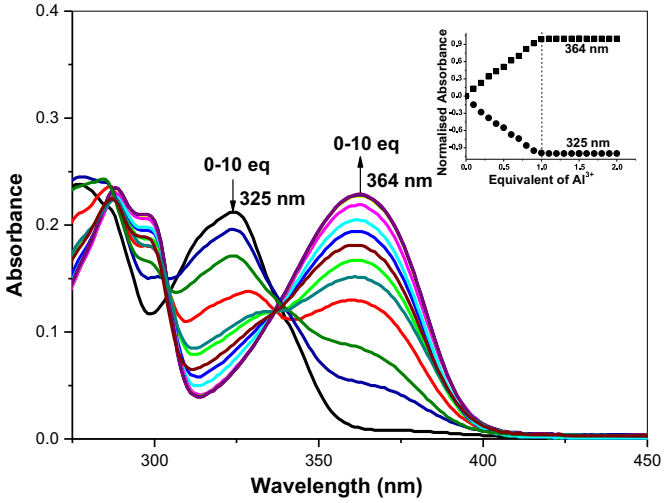



**Fig. 2.** UV–vis titration spectra of probe **1** (20 μM) upon the addition of 10 equiv of $Al(ClO_4)_3$ in EtOH on heating at 50 °C for 1 h.

The emission studies were carried in a similar manner at a concentration of 2 μM in ethanol. As a cation sensor, one of the important criteria for potential applications is the selectivity. To solutions of probe **1**, 10 equiv of a range of biologically and non-biologically relevant metal cations were added, and their complexation abilities were examined by fluorescence emission. None of the other cations except for $Al^{3+}$, which produced a prominent fluorescence peak at 434 nm, induced a distinct emission shift with probe **1** (Figs. 3 and 4). Even the addition of $Ga^{3+}$, which exhibits similar coordination behavior to $Al^{3+}$, and $Fe^{3+}$ did not produce any changes in the emission spectra. Fig. 5 shows the fluorescence spectrum of the free probe **1** and those in the presence of an incremental amount of $Al^{3+}$.

Probe **1** showed no emission peak when excited at 364 nm and the slow addition of $Al^{3+}$ elicited a large fluorescence peak at 434 nm. Therefore, in probe **1**, the fluorescence is turned on by binding with $Al^{3+}$. The inset in Fig. 5 shows the dependence of the normalized emission intensity ratio at 434 nm on the $Al^{3+}$ concentration. The linear enhancement of fluorescence was observed with increasing $Al^{3+}$ ion concentration when the $Al^{3+}$ to the probe **1** concentration ratio was ≤1:1. On the other hand, higher $Al^{3+}$ concentrations did not lead to any further emission enhancement. To determine the stoichiometry of probe **1** and $Al^{3+}$ in the complex, Job's method was employed using the emission changes at 434 nm as a function of the molar fraction of $Al^{3+}$. As shown in Fig. 6 maximum emission was observed when the molar fraction of

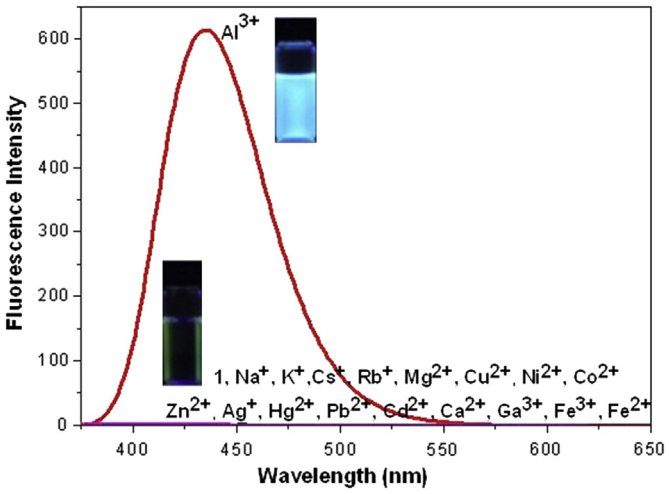



**Fig. 3.** Fluorescence spectra of probe **1** (2 μM) in EtOH upon heating at 50 °C for 1 h on the addition of 10 equiv of various cations. $\lambda_{ex}$=364 nm.

$Al^{3+}$ reached 0.5, which is indicative of 1:1 complexation between probe **1** and $Al^{3+}$. The binding constant for the complex between probe **1** and $Al^{3+}$ was determined by a non-linear fitting of the corresponding fluorescence titration data (Fig. 5) as $2.1\times10^{6}$ $M^{-1}$ with a satisfactory correlation coefficient value ($R$=0.9983) (Error estimated to be ≤10%).[22,23]

A competitive binding experiment with different cations and $Al^{3+}$ also shows that probe **1** is highly selective to $Al^{3+}$ (Fig. S-1). It was also found that probe **1** shows 0.39 μM of detection limit to sufficiently sense $Al^{3+}$ (Fig. S-2).[24] This unique selectivity of probe **1** toward $Al^{3+}$ could be interpreted in terms of the mechanism in Scheme 1. Aluminum is a well known Lewis acid[25] that is capable of hydrolyzing probe **1** and generating probe **2** that binds with $Al^{3+}$ resulting in the liberation of ethanol and emission peak at 434 nm due to a chelation effect.[26–28] At the initial stages, deprotonation of the phenolic proton occurs by the addition of $Al(ClO_4)_3$, which subsequently acts as a Lewis acid hydrolyzing the ester to generate acid **2**. This acid provides a better additional binding site for the chelation of $Al^{3+}$ and increases the fluorescence dramatically through a highly efficient chelation-enhanced fluorescence (CHEF) effect. Although there are some examples of $Cu^{2+}$-facilitated hydrolysis of an ester bond, there have been no reports of $Al^{3+}$-promoted ester hydrolysis, which is utilized here to improve the sensitivity and broaden the methodologies for designing a range of fluorescent probes.[29–31] This mechanism also helps explain why a solution of probe **1** (2 μM) in the presence of 20 μM of $Al^{3+}$ when allowed to stand at room temperature (25 °C), shows blue fluorescence that gradually grows more intense before reaching a maximum within 72 h, whereas an elevated temperature (50 °C) could promote the generation of fluorescence within 1 h.

To understand the mechanism by which probe **1** was hydrolyzed in the presence of $Al^{3+}$ a $^{1}H$ NMR titration of probe **1** with $Al(ClO_4)_3$ was checked in $CD_3OD$ as shown in Fig. 7. The $^{1}H$ NMR titration spectra showed the concomitant development of a $CH_3CH_2$ peak for ethanol and the disappearance of a $CH_3CH_2$ signal of the ester within 24 h. This supports the assumption that the fluorescence of complex **1**-$Al^{3+}$ is generated by ester hydrolysis **1** with $Al^{3+}$ as a promoter.

The above mechanistic proposal is further supported by the fluorescent and non-fluorescent behaviors of the control probes **2** and **3** in the presence of $Al^{3+}$ (Fig. S-4). Probe **2** produce identical changes in the photophysical properties with $Al^{3+}$ as probe **1** except that it showed emission selectivity toward $Ga^{3+}$, $Zn^{2+}$ and $Cd^{2+}$ along with $Al^{3+}$ (Fig. 8). On the other hand, probe **3** did not produce

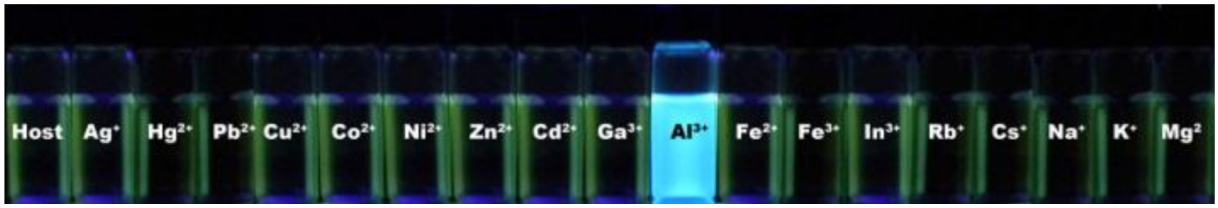



**Fig. 4.** Fluorogenic changes of a 2 μM solution of probe **1** in EtOH in the presence of 10 equiv of different cations upon illumination at 365 nm.

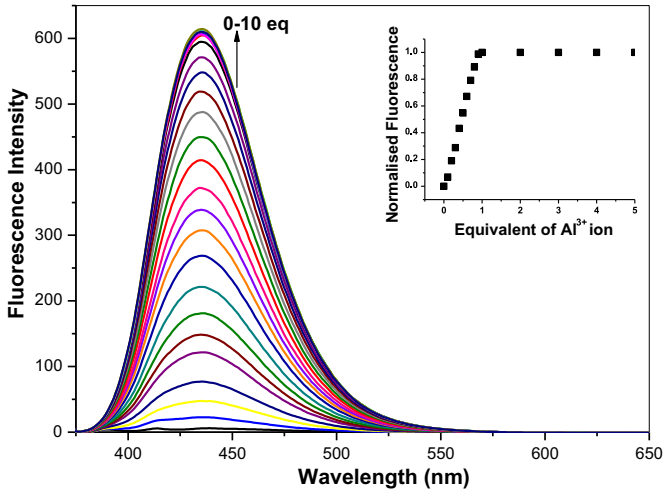



**Fig. 5.** Fluorescence titration spectra of probe **1** (2 μM) with $Al(ClO_4)_3$ in EtOH upon heating at 50 °C. $\lambda_{ex}$=364 nm. Inset: mol ratio plots of emission at 434 nm.

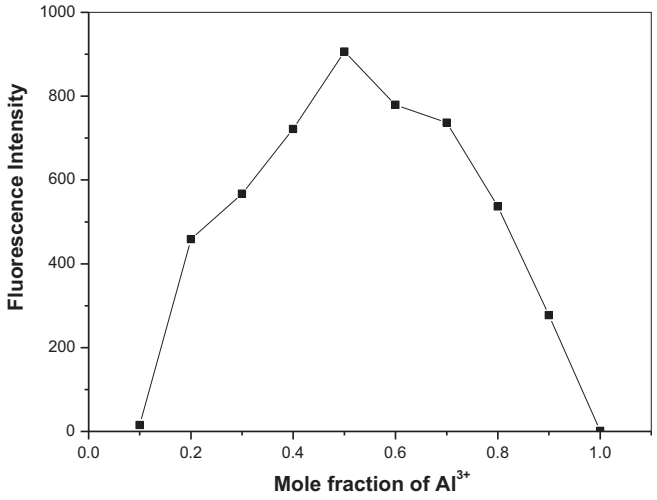



**Fig. 6.** Job's plot for probe **1** (20 μM) with $Al(ClO_4)_3$ (20 μM) in EtOH upon heating at 50 °C for 1 h. $\lambda_{ex}$=364 nm.

any change in absorption or emission upon the addition of 10 equiv of $Al^{3+}$ due to the absence of phenolic–OH because it is unable to exhibit three ways coordination with $Al^{3+}$ on a similar line of that observed with probes **1** and **2** (Fig. S-4). This suggests that $Al^{3+}$ first binds to the –OH of the phenol and causes the hydrolysis of the ester. A complex of probe **1** with $Al^{3+}$ in EtOH was also prepared and characterized by HR-FAB mass. The mass spectra of probe **1**-$Al^{3+}$ showed 1:1 stoichiometry (between probe **1** and $Al^{3+}$) with the molecular ion peak at *m*/*z*, 263.9903, which corresponds to (probe **1**+$Al^{3+}$–EtOH+$H_2O$–H)$^+$ (Fig. S-5). This also provides evidence that the ester is hydrolyzed to an acid by $Al^{3+}$ followed by complexation.

## 3. Conclusions

In summary, a thiazole based 'turn-on' fluorescence probe (**1**) for $Al^{3+}$ was prepared. For the first time, such high selectivity to $Al^{3+}$ over other cations was observed due to the $Al^{3+}$-promoted hydrolysis of the ester to give an acid that binds to $Al^{3+}$ resulting in a dramatic change in fluorescence by CHEF.

## 4. Experimental section

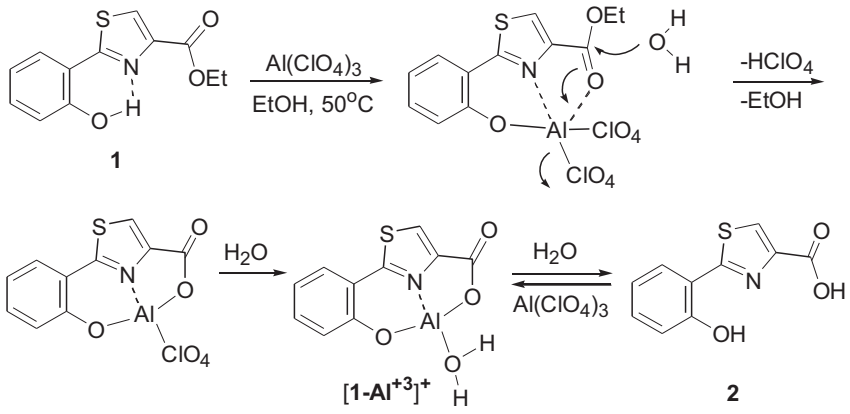
### 4.1. General

The melting points were determined using a Thomas-Hoover capillary melting point apparatus and were uncorrected. The $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker AM-400 spectrometer using $Me_4Si$ as the internal standard. The FAB mass was determined at KBSI Daegu branch. Infrared spectra were recorded using a Shimadzu Prestige-21 spectrometer on a KBr pellet. The UV–vis absorption spectra were determined on a Shimadzu UV-1650PC spectrophotometer. The fluorescence spectra were measured on a Shimadzu RF-5301 fluorescence spectrometer equipped with a xenon discharge lamp and 1 cm quartz cells with slit 3. All the measurements were taken at 298 K. Analytical grade ethanol was purchased from Merck. All other materials for syntheses were purchased from Aldrich Chemical Co. and used as received. 2-Hydroxyphenylthiobenzamide was prepared by the procedure reported in the literature.[6] Solutions of metal ions were prepared from their perchlorate salts of analytical grade, and subsequently diluted to prepare the working solutions. The quantum yield ($\Phi$) was calculated using the procedure reported in the literature.[4–7]

### 4.2. Synthesis of probe

*4.2.1. Ethyl 2-(2-hydroxyphenyl)thiazole-4-carboxylate (**1**).* A solution of 2-hydroxyphenylthiobenzamide **4** (300 mg, 1.96 mmol) and ethyl bromopyruvate (458 mg, 2.35 mmol) in ethanol (15 mL) was heated under reflux for 2 h. The reaction progress was monitored by TLC analysis. The solvent was removed in vacuo, and the residue was washed with water and extracted with EtOAc. The organic layer was dried over anhydrous $Na_2SO_4$ and concentrated. The residue was purified by column chromatography (EtOAc:hexane=1:4) to give compound **1** as a colorless needle shaped solid (350 mg, 1.40 mmol) in 71% yield. Mp 109–111 °C ($CH_2Cl_2$–hexane); IR (KBr, $cm^{-1}$) 3140, 2978, 1720, 1474, 1211; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.09 (s, 1H), 7.60 (dd, *J*=7.8, 8.8 Hz, 1H), 7.35 (m, 1H), 7.08 (dd, *J*=8.4, 8.4 Hz, 1H), 6.92 (m, 1H), 4.42 (q, *J*=7.1 Hz, 2H), 1.41 (t, *J*=7.4 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 169.8, 160.9, 157.4, 146.5, 132.9, 127.7, 125.4, 119.9, 118.5, 116.7, 62.0, 14.7; Anal. Calcd for $C_{12}H_{11}NO_2S$: C, 57.82; H, 4.45; N, 5.62; S, 12.86, found: C, 57.78; H, 4.36; N, 5.66; S, 13.12. HR-mass Calcd for: $C_{12}H_{11}NO_3S$ $[M+H]^+$: 249.0460; found: *m*/*z* 249.0457.

*4.2.2. 2-(2-Hydroxyphenyl)thiazole-4-carboxyic acid (**2**).* Compound **1** (100 mg, 0.65 mmol) and 5 mL of 1 N KOH in ethanol (25 mL) was heated under reflux for 2 h. The reaction progress was monitored by TLC. The solvent was removed in vacuo, and the




**Scheme 1.** $Al^{3+}$-promoted hydrolysis of probe **1**.

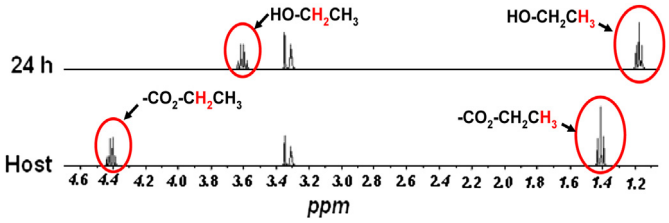



**Fig. 7.** $^1H$ NMR spectrum of probe **1** (0.04 mM) in the presence of 1.0 equiv of $Al^{3+}$ ion after 24 h at 25 °C in $CD_3OD$ (detail titration in Fig. S-3).

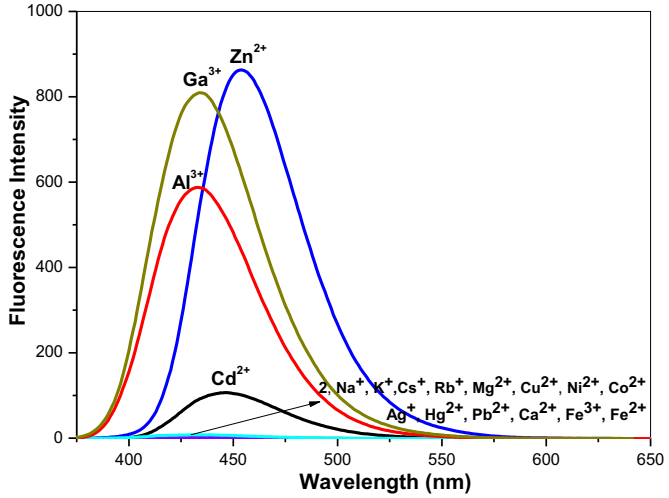



**Fig. 8.** Fluorescent spectra of probe **2** (2 μM) upon the addition of 10 equiv of various cations in EtOH. $\lambda_{ex}$=364 nm.

residue was washed with water, acidified with 10 mL of 1 N HCl and extracted with $CH_2Cl_2$. The organic layer was dried over anhydrous $Na_2SO_4$ and concentrated. The residue was purified by column chromatography (10% MeOH in $CH_2Cl_2$) to give compound **2** as a white solid (82 mg, 0.37 mmol) in 90% yield. Mp 249–251 °C ($CH_2Cl_2$–hexane); IR (KBr, $cm^{-1}$) 3450, 3125–2577, 1690, 1481, 1269; $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.98 (dd, $J$=7.8, 7.3 Hz, 1H), 7.05 (d, $J$=8.1 Hz, 1H), 7.34 (dd, $J$=8.0, 7.3 Hz, 1H), 8.13 (d, $J$=7.8 Hz, 1H), 8.46 (s, 1H), 11.33 (s, 1H), 13.05 (s, 1H); $^{13}C$ NMR (100 MHz, DMSO-$d_6$) $\delta$ 164.0, 162.6, 155.6, 146.4, 131.9, 128.8, 128.0, 112.0, 119.1, 116.9; Anal. Calcd for $C_{10}H_7NO_3S$: C, 54.29; H, 3.19; N, 6.33; S, 14.49, found: C, 54.57; H, 3.20; N, 6.45; S, 14.40. HR-mass Calcd for: $C_{10}H_7NO_3S$ $[M+H]^+$: 222.0225; found: $m/z$ 222.0221.

*4.2.3. Ethyl 2-(2-phenyl)thiazole-4-carboxylate (**3**).* This compound was obtained by the same procedure for synthesizing compound **1** using thiobenzamide (200 mg, 1.46 mmol) and ethyl bromopyruvate (341 mg, 1.75 mmol) in ethanol (15 mL). The product was purified by column chromatography (10% EtOAc in hexane) to give compound **3** as a colorless needle shaped solid in 70% yield. Mp 120–121 °C ($CH_2Cl_2$–hexane); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.78 (d, $J$=8.0 Hz, 2H), 7.77 (s, 1H), 7.31 (t, $J$=8.0 Hz, 3H), 4.34 (q, $J$=8.0 Hz, 2H), 1.34 (t, $J$=7.1 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 169.5, 162.0, 148.3, 133.0, 129.4, 129.13, 128.4, 127.8, 127.7, 127.3, 62.1, 14.8; Anal. Calcd for $C_{12}H_{11}NO_2S$: C, 61.78; H, 4.75; N, 6.00; S, 13.74; found: C, 61.72; H, 4.69; N, 6.03; S, 13.67.

*4.2.4. **1**-$Al^{3+}$ complex.* A mixture of compound **1** (100 mg, 0.45 mmol) and $Al(ClO_4)_3 \cdot 9H_2O$ (263 mg, 0.54 mmol) in ethanol (10 mL) was heated under reflux for 1 h. The mixture was cooled to room temperature, and the ethanol was evaporated and the residue was dried under vacuum to provide **1**-$Al^{3+}$ complex as a white solid extremely hygroscopic in nature (110 mg, 92% yield). HR-FAB Mass: Calcd for ($C_{10}H_7NO_4S{\cdot}Al$) 263.9911; found: 263.9903.

## Acknowledgements

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## Supplementary data

Figures of competitive binding of probe **1**-$Al^{3+}$, method of determination of detection limit of $Al^{3+}$ by probe **1**, $^1H$ NMR experiments spectra of probe **1**, absorbance (UV–vis), fluorescence spectra of probes **1**–**3**, and HR-FAB mass of probe **1**-$Al^{3+}$ complex are available. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.05.062.

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