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A Highly Sensitive Fluorescent Probe for Selective Detection of Al^{3+} Cation by Switching the Solvent from Aprotic to Protic Environment

JUNEMIN PARK,† SATHESHKUMAR ANGUPILLAI,† AND YOUNG-A SON*

Department of Advanced Organic Materials Engineering, Chungnam National University, Yuseong-gu, Daejeon, South Korea

*We have designed and synthesized known coumarin-rhodamine (**CR1**) derivative for sensing the Al^{3+} ion in the presence of aprotic (CH_3CN/H_2O) medium via TBET mechanism. The results of the photo physical studies revealed that the sensing mechanism involves Al^{3+} induced change from non-fluoroscent (spirolactam form) to fluorescent (ring opening form) in **CR1** leading to the visible color change. The Job's plot indicated the formation of 2:1 complex between **CR1** and Al^{3+} with limit of detection is 1.78×10^{-8} M. Various spectroscopy techniques and theoretical calculation have been employed to investigate the mechanism of the sensing property of **CR1** with Al^{3+}.*

Keywords Rhodamine; Coumarin; TBET; FRET; Energy band gap

Introduction

In very recently organic dye molecules are predominantly used for cation sensing. Among the various dye molecules, rhodamine and coumarin moieties are most prominently used as a chemosensors, owing to their high fluorescence quantum yield and emission bands at the red region of the spectrum. Generally, rhodamine 6G derivatives are non-fluorescent and colorless, whereas when they coordinate with metal ions, ring-opening of the corresponding spirolactam gives rise to a strong florescence emission and a pink color. However, small Stokes shifts limit their applications in certain cases [1]. Forster Resonance Energy Transfer (FRET) is generally the most adopted methodology for addressing this issue. For FRET to be effective, a substantial spectral overlap for the donor emission and acceptor absorption bands is required, which sometimes restrict the choice and the design of the FRET-based probe molecules. While in the case of through-bond energy transfer (TBET) based chemosensors, does not required the spectral overlap between donor emission and acceptor absorption band, though it exhibits fast energy transfer rates and large pseudo-Stokes

†These authors contributed equally to this work.

*Address correspondence to Young-A Son, Department of Advanced Organic Materials Engineering, Chungnam National University, 220 Gung-dong, Daejeon, 305-764, South Korea. E-mail: yason@cnu.ac.kr

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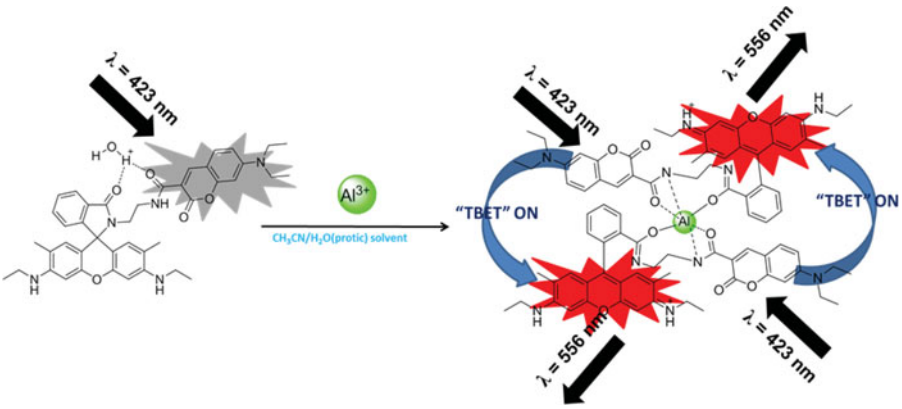
shifts. Moreover, the TBET cassettes shows obviously higher energy transfer efficiency than that of the classical FRET system [4–5]. Despite such flexibility, reports on TBET cassettes for developing biomarkers and/or fluorescent probes for intracellular imaging applications are actually rare [6].

Al^{3+} is the third most abundant metal in the earth's crust, accounting for approximately 8% of its mass. Due to the acid rain, the free Al^{3+} concentration is increasing in the environment and surface water, which is deadly to growing plants [7]. In addition, it has been widely used in the many field such as water treatment, food additive, aluminum based pharmaceuticals, occupational dusts, aluminum containers and cooking tools. Al^{3+} ions are producing neurotoxic issues to humans, such as Alzheimer's and Parkinson's disease [8]. Therefore, the detection and to controlling of Al^{3+} levels in the biosphere is essential. Up to date, numbers of techniques are available for Al^{3+} estimation [9]. However, these methods are time-consuming and expensive, as they require tedious sample pretreatment and sophisticated instrumentation. While in the case of colorimetric and fluorimetric detection methods have several advantages than that of the other methods. Hence, the design and construction of chemosensors with high selectivity and sensitivity towards Al^{3+} have become the focus in numerous studies in the field of supramolecular chemistry. Until recently, only a few fluorescent chemosensors have been developed for detection of Al^{3+} [10–12]. Most fluorescent sensors for Al^{3+} have good selectivity, but this approach has several disadvantages including complicated synthetic procedures and poor water solubility.

In this paper, we report the synthesis and colorimetric/fluorometric properties of conformationally constrained coumarin-rhodamine ligand **CR1** for selective detection of Al^{3+} based on TBET mechanism. Recently, Guangjie He et al., [13] have developed same chemosensor **CR1** for Cu^{2+} sensing in CH_3CN medium. The spectroscopic studies revealed that the sensing mechanism of **CR1** in CH_3CN is due to the existence of FRET between coumarin and rhodamine. On the contrary, during the course of our work, the chemosensor **CR1** has been selectively sense the Al^{3+} ion in CH_3CN/H_2O medium. In general, the molecule composed by two unit such as donor and acceptor (D-A), the sensing property of chemosensors have been followed by the two different mechanism such as FRET/TBET [14]. It is well known that the spirolactam ring opening is solvent assisted in protic environment (Scheme 1) and also hydrogen bonding between solvent and acceptor



Scheme 1. Solvent facilitated TBET transition on **CR1** with Al^{3+} ion.

molecules prevent donor and acceptor fragment from becoming plannar and thus the TBET process is facilitated [14].

Experimental

Instrument

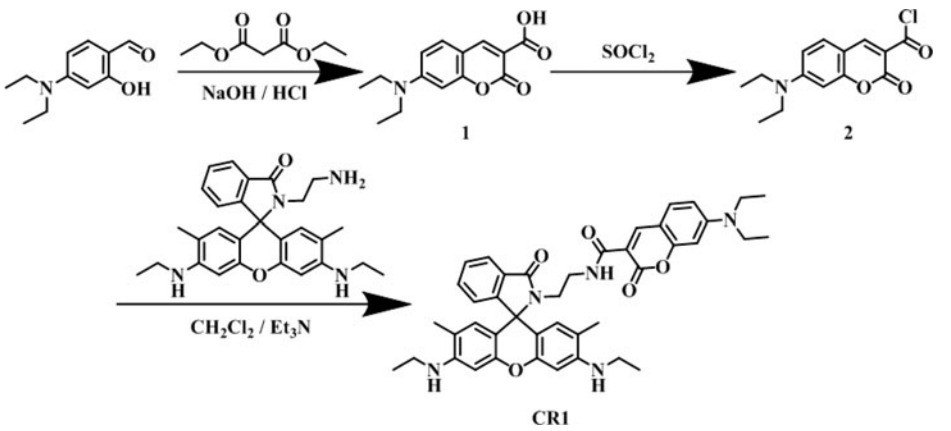
UV-Vis spectral studies were carried out on Agilent 8453 single beam spectrophotometer. Steady state fluorescence spectra were obtained on a spectrofluorometer, Shimadzu RF-5301PC. The excitation and emission slit width (1.5 nm) was kept constant for all of the experiments. FT-IR spectra were obtained as KBr pellets on an FT-IR spectrometer (FTS-175C, Bio-laboratories, Cambridge, USA). Nuclear magnetic resonance spectra were recorded in $CDCl_3$ (Bruker, ^1H NMR 600 MHz). Electrospray ionization mass spectrometry (ESI-MS) spectra were measured on a 4000 Q TRAP [AB SCIEX] and elemental analyses were performed by EA112 [Thermo Fisher Scientific].

Chemicals

All the reagents and solvents, used for synthesis of **CR1**, were purchased from Aldrich (St.Louis, USA) and used without further purification. Rhodamine 6G is purchased from the Sigma-Aldrich Company, 4-diethylamino sacylaldehyde is purchased from Alfa-Aesar. Various metal ion solutions of $LiClO_4$, $NaClO_4$, $CsClO_4$, $Mg(ClO_4)_2$, $Fe(ClO_4)_2 \bullet XH_2O$, $Ni(ClO_4)_2 \bullet 6H_2O$, $Cu(ClO_4)_2 \bullet 6H_2O$, $AgClO_4$, $Hg(ClO_4)_2 \bullet XH_2O$, and $Al(ClO_4)_3 \bullet 9H_2O$ were purchased from Sigma-Aldrich, and $Co(ClO_4)_2 \bullet 6H_2O$, $Zn(ClO_4)_2 \bullet 6H_2O$, $Cd(ClO_4)_2 \bullet 6H_2O$ and $Pb(ClO_4)_2 \bullet 3H_2O$ were purchased from Alfa-Aesar Chemical Reagent Co.

Synthetic Procedures

Compounds **CR1** (the product of the reaction of CR with Al^{3+}) was efficiently synthesized following the synthetic methodology shown in Scheme 2. Rhodamine 6G ethylamine, and 7-diethylamino-3-carboxylic chloride coumarin, were synthesized according to the literature methods [15].



Scheme 2. Synthesis of chemosensor **CR1**.

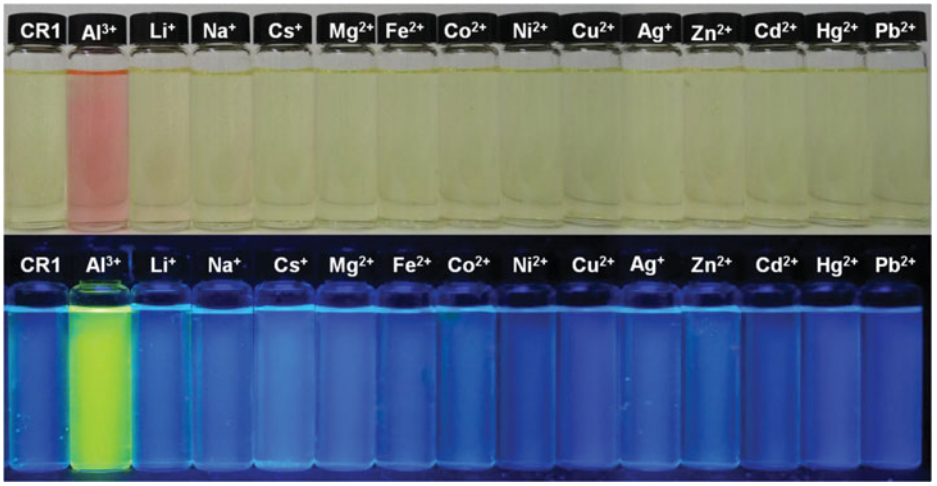


Figure 1. Visible and fluorescence color change of **CR1** in CH_3CN/ H_2O (1:1) in the presence of Al^{3+}, Li^{+}, Na^{+}, Cs^{+}, Mg^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^{+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+}.

Synthesis of Compound CR1

A Et_3N (0.42 ml,0.003 mol) was added in to a stirred solution of N-(rhodamine-6G) lactam-ethylenediamine (1.14 g, 0.0025 mol) in CH_2Cl_2 (20 mL). A solution of **2** (0.70 g, 0.0025 mol) in CH_2Cl_2 (60 mL) was added drop wise to the stirred reaction mixture. The reaction mixture was stirred at RT under nitrogen atmosphere for 24 h. The organic layer was washed with water (200 mL) and dried over anhydrous Na_2SO_4 and filtered. The organic layer was removed under reduced pressure. The crude product was purified by column chromatography on alumina (ethyl acetate) to afford 1.44 g of yellow solid **CR1** in 82% yield. ^{1}H-NMR (600MHz, $CDCl_3$) : 8.579 (s, 1H), 8.565(t, 1H), 7.945(m, 1H), 7.433(m, 2H), 7.385(d, 1H), 7.035(m, 1H), 6.624(q, 1H), 6.467(d, 1H), 6.324(s, 2H), 6.289(s, 2H), 3.449(q, 4H), 3.397(t, 4H), 3.186(m, 4H), 3.136(t, 2H), 1.592(s, 6H), 1.270(t, 6H), 1.232(t, 6H) ^{13}C-NMR (150MHz, $CDCl_3$) : 169.09, 161.41, 154.79, 149.23, 142.06, 139.07, 129.52, 129.49, 129.47, 129.20, 101.43, 101.19, 97.28, 96.48, 80.09, 46.01, 44.9, 39.28, 24.02, 17.37, 15.03, 13.06 ppm ; ESI-MS: [M]+, 700.5 Anal. Calcd for CR1 $C_{42}H_{45}N_5O_5$: C, 72.08; H, 6.48; N, 10.01%. Found : C, 71.97; H, 6.78; N, 9.77%

Results and Discussion

Visual Detection

The colorimetric/fluorimetric sensitivity of **CR1** toward various cations such as Li^{+}, Na^{+}, Cs^{+}, Mg^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^{+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+} and Al^{3+} in their perchlorate form was monitored visually. As depicted in Fig.1 solutions of **CR1** in CH_3CN/H_2O (1/1; v/v) turn pale yellow to intense pink color (Top) and the fluorescence change from blue to yellowish green (Bottom) after the addition of Al^{3+}. However, their color remained unchanged after the addition of other chosen cations. This is indicate that the selectivity of **CR1** toward Al^{3+} ion.

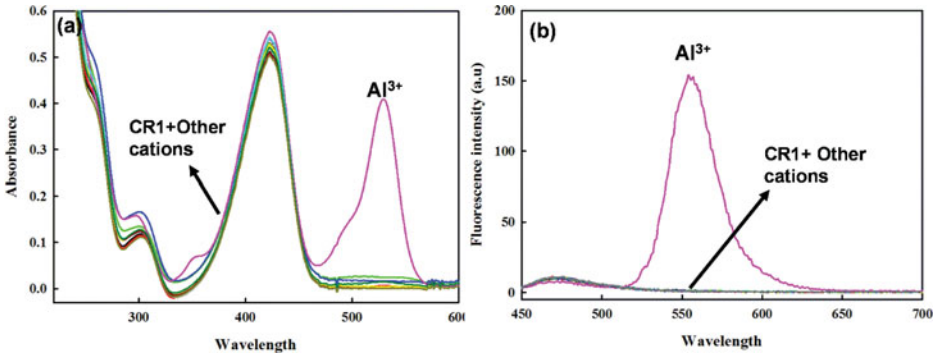


Figure 2. UV-Vis (a) and fluorescence spectra (b) of **CR1** (10 μM) with various metal ion (10 μM) in CH_3CN/H_2O (1:1).

Photo Physical Property

To further investigate the selectivity of **CR1** to Al^{3+}, we performed the UV-Vis absorbance and fluorescence spectroscopic techniques. As shown in the figure 2a, the electronic spectrum of the free **CR1** has been appeared at 301 and 423 nm, which is corresponding to the spirolactam ring and comurin respectively, [13] the addition of Al^{3+} ions to the **CR1**, a new absorption band centred at 524 nm accompanying a remarkable increasing intensity, corresponds to the absorption of rhodamine, which induced a clear color change from pale yellow to pink (Fig. 2a). This confirms that **CR1** was induced to the ring-opened structure from the spirolactam by Al^{3+} which possessed a long absorption wavelength and high molar extinction coefficient. While in the case of other chosen competitive metal ions, such as Li^+, Na^+, Cs^+, Mg^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} does not produce any significant color or spectral change under identical conditions. Likewise, in the fluorescence spectra (Fig 2b), a pure **CR1** (10 μM, CH_3CN:H_2O (1:1, v/v)) solution displayed very weak emission peak at 472 nm. While the addition of Al^{3+} to **CR1** solution, the new emission peak was observed at 556 nm. In the case of other metal ions, the peak at 556 nm does not appear. These results demonstrated that **CR1** has high selectivity toward Al^{3+} over other competitive metal ions. As spelt in to the introduction section, our molecule **CR1** has followed the TBET mechanism instead of FRET mechanism. In the case of simple CH_3CN solvent (polar-aprotic), **CR1-**Cu^{2+} complexes showed the weak emission peak at 472 and 556 nm due to the presence of FRET between coumarin and rhaodamine moiety [13]. While in the case of polar-protic solvent (CH_3CN/H_2O), coumarin shows very weak emission peak at 472 nm, consequently the new strong peak (8 fold higher than that of aprotic solvent) has been appeared in the range of 556 nm due to the spirolactom ring opening followed by the TBET transition [14]. The result of fluorescence study clearly indicated that the sensing property of **CR1** in CH_3CN/H_2O medium is mainly due to the prescence of TBET mechanism. Moreover, it shows slight spectral overlap with the acceptor's excitation with a negligible FRET process which is favorable for the investigation with the TBET

To gain more insight into the chemosensing properties and mechanism of **CR1** toward Al^{3+}, absorption and fluorescence titration (Fig. 3) with Al^{3+} were recorded. With the addition of incremental amounts of Al^{3+} ions to **CR1** in CH_3CN/H_2O the absorption peak at 321 nm enhanced gradually accompanying the formation of a new peak at 524 nm

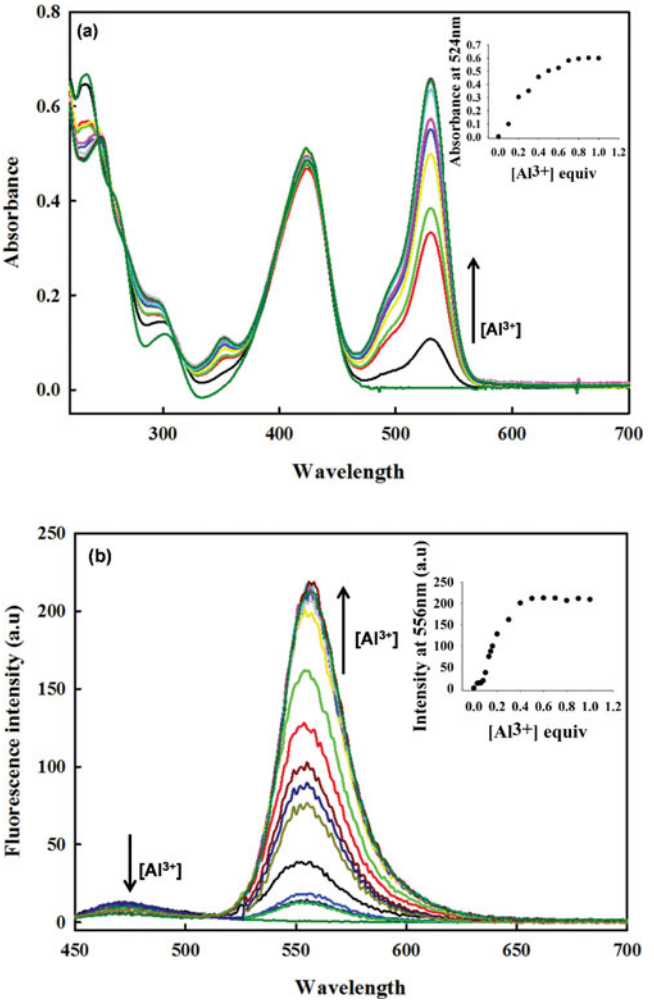


Figure 3. Change in UV-Vis (a) and fluorescence spectra (b) for **CR1** (10μ M) in CH_3CN/H_2O upon the incremental addition of (0–10 μM) of Al^{3+} ion.

(Fig. 3a). This new band observation is due to the ring opening of spiro lactam unit by Al^{3+}. The Al^{3+} binding ability of the **CR1** was also evaluated by fluorescence titration studies at an excitation wavelength of 423 nm and emission wavelength of 450–700 nm, results given in Figure 3. For the free **CR1** the emission peak was exhibits at 472 nm (Figure 3b), and no characteristic emission peak was appeared at 556 nm. Upon gradual addition of Al^{3+} ions to the **CR1** solution, the donor emission at 472 nm slowly decreased, and a new emission band with a maximum at 556 nm (rhodamine 6G) appeared and gradually increased. From the fluorescence enhancement binding constant of the **2CR1-**Al^{3+} complex was calculated as 4.904×10^{-10} using the B-H equation [16].

The stoichiometry of the **CR1** and Al^{3+} was determined using the UV-Vis spectral data. As shown in figure 4, a curve with a maximum at near

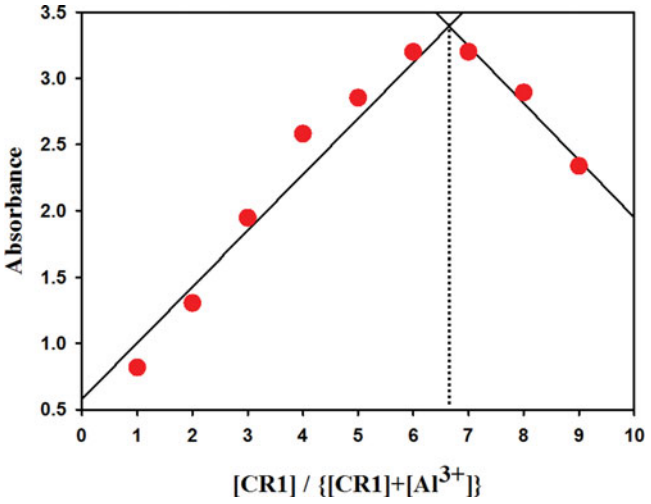


Figure 4. Job's plot for **CR1** with Al^{3+}.

0.7 mole fraction, this is indicated the formation of 2:1 (**CR1**: Al^{3+}) complex [17].

Competitive Experiments

To check the practical knack of chemosensor **CR1** to Al^{3+} ion, we have carried out competitive experiments in the presence of Al^{3+} ions mixed with other chosen metal. Both the electronic absorbance and fluorescence response of the **2CR1-**Al^{3+} system remains the same by comparison with or without the other metal ions (Fig. 5). These findings confirmed the selectivity and effective interaction of probe **CR1** with Al^{3+}. For practical applications, the detection limit of **CR1** was also estimated. The fluorescence titration profile of **CR1** (10 μM) with Al^{3+} demonstrated that the detection limit of Al^{3+} is 1.17×10^{-8} M which is far below the WHO acceptable limit (0.05 mg L^{-1} or 1.85×10^{-3} M of Al^{3+}) in drinking water.

Sensing Mechanism

In order to ascertain the complexation between **CR1** and Al^{3+}, the FT-IR spectrum of **CR1** and **2CR1**-Al^{3+} was recorded (Fig. 6). For free **CR1**, the peaks at 1683 and 1618 cm^{-1} are corresponds to spirolactam ring carbonyl (C═O) and amide (NH-C═O) stretching vibrations respectively and also two sharp peak appear at 3346 and 2970 $cm^{-1}$are assigned to the NH stretching peaks. While in the case of **2CR1**-Al^{3+} complexes, characteristic stretching frequencies for the spirolactam ring carbonyl, that appeared at 1683 cm^{-1}completely disappeared, this is confirming the spirolactam ring opening, which led to a new peak at 1605 cm^{-1} representing the oxygen of the spiro ring attached to the Al^{3+}ion. In addition with that the amide carbonyl peak was shifted from 1618 to 1567, these results indicate that the oxygen from the spirolactam and amide carbonyl has involved the complexation

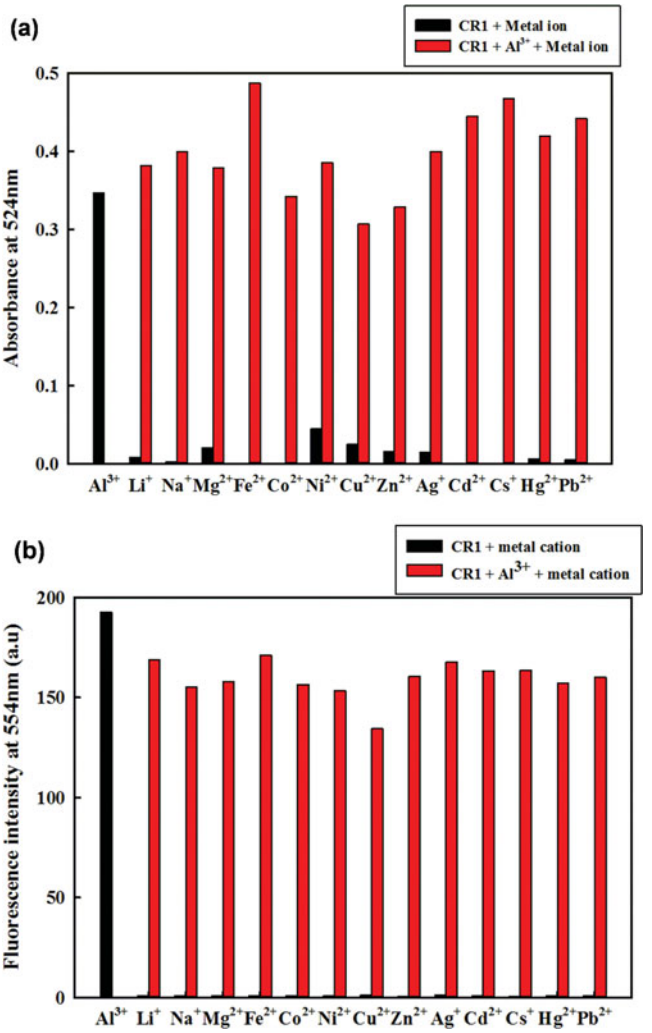


Figure 5. Absorption (a) and fluorescence response (b) of **CR1** (10 μM) in the presence of Al^{3+} and other metal ions (1 equiv.) in $CH_3CN:H_2O$ (1;1, v/v); the black bar correspond to the **CR1** with all chosen cation and the red bar represents the **CR1** in addition to other metal ions with Al^{3+}.

with Al^{3+}. However, broad new peaks at 3373 and 2977 cm^{-1} provide information regarding the formation of a quaternary ammonium salt in the rhodamine xanthene moiety [18–19].

^{1}H-NMR spectra of **CR1** and **2CR1**-Al^{3+} in $CDCl_3$ were recorded to determine the binding mode and mechanism. The signal at 3.5 ppm (triplet) is corresponds to the xanthene terminal -NH- proton and two singlet around at 6.2 – 6.3 ppm are due to the xanthene ring hydrogen (Fig. 7A). While in the case of **2CR1**-Al^{3+}, xanthene NH peak is separated into two sets(Fig. 7B). One set of protons is shifted up field and the second set of amine protons is shifted downfield. This separation in to two sets of (—NH—) protons is due to the formation of a quaternary amine salt after the

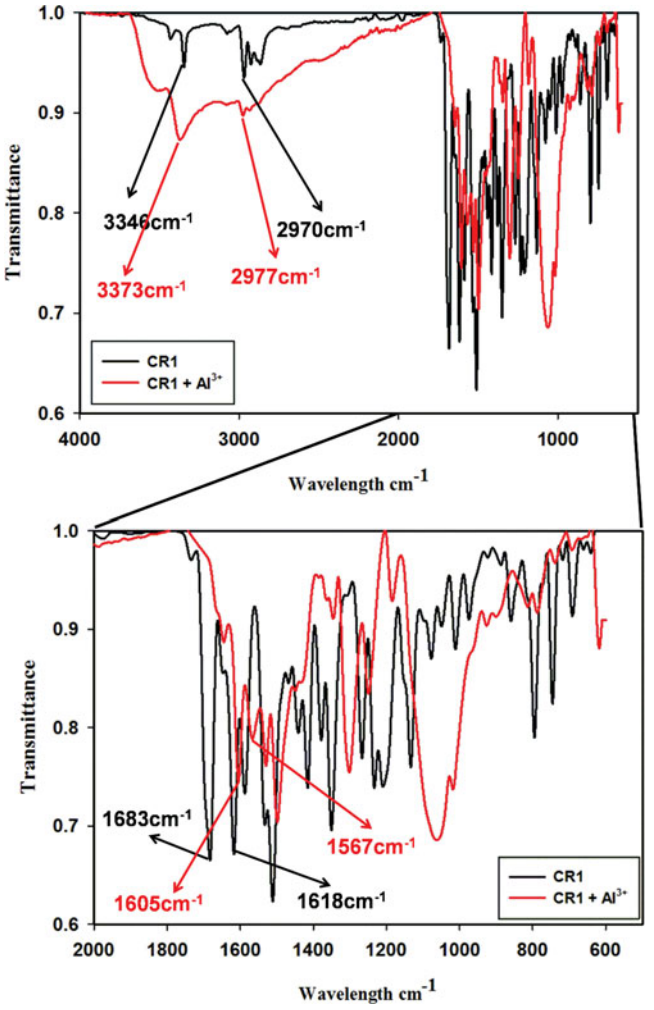


Figure 6. FT-IR spectra of **CR1** and **2CR1**-Al^{3+}.

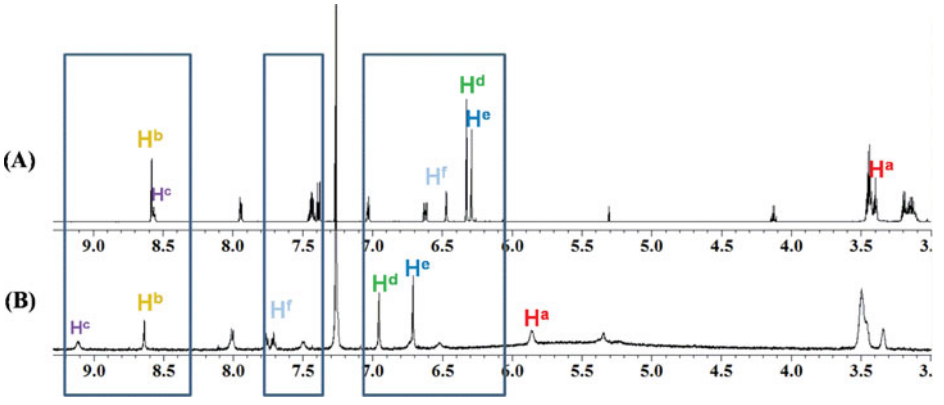
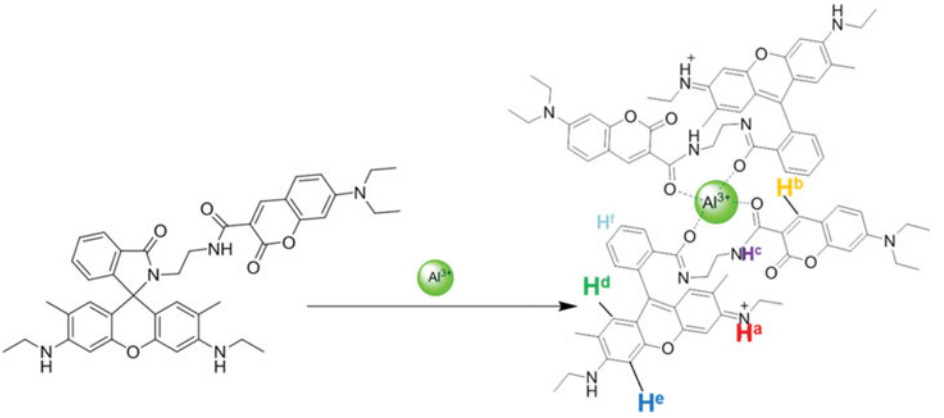


Figure 7. ^{1}H NMR spectra of **CR1**(A) and **2CR1**-Al^{3+}(B) complexes.

spirolactam ring is opened by the Al^{3+}ion. Subsequently, in **2CR1**-Al^{3+} complex, the xanthene protons are shifted to the deshielding area and due to the complexation of Al^{3+} the amide NH was appear with down field shift [20–21]. Based on the FT-IR and ^{1}H-NMR studies, we proposed the binding sites on **CR1** with Al^{3+} ion as shown in Scheme 3.



Scheme 3. Proposed binding mechanism of **CR1** with Al^{3+}.

Conclusion

In summary, **CR1** has been selectively sense the Al^{3+} ion based on TBET mechanism in CH_3CN/H_2O medium. We modulated the selectivity of **CR1** to Al^{3+} metal ion by switching the sensing media. **CR1** gives a turn-on colorimetric and fluorometric signal toward Al^{3+} in CH_3CN-H_2O. To the best of our knowledge, this is the first example of a chemosensor based on D-A molecule that can change their selectivity by switching the solvent systems. Because of the simplicity of the analysis, we believe that the proposed probe may find application in a variety of real samples.

Acknowledgments

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