



A Novel Fluorescent Chemosensor Based on β -(2-Pyridyl)acrolein-Rhodamine B Derivative: Polymer Particle Interaction with an Enhanced Sensing Performance[†]

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Abstract

A novel, fluorescent chemosensor based on β -(2-pyridyl)acrolein-rhodamine B (RB-AC) derivative was synthesized and its sensing performance with poly(ethylene glycol) dimethacrylate (PEGDMA) polymer particle was investigated. The prepared β -(2-pyridyl)acrolein-rhodamine B/poly(ethylene glycol)dimethacrylate (PEGDMA/RB-AC) particle was used for sensing of Al^{3+} . The PEGDMA/RB-AC particles showed immediate “off-on” fluorescent responses toward Al^{3+} . The fluorescent response was attributed to the spirolactam ring opening of RB-AC. This sensor particle showed high selectivity towards Al^{3+} in the presence of other competing metal ions. The sensitivity of PEGDMA/RB-AC particle was demonstrated by confocal laser scanning microscopy (CLSM) and scanning electron microscopy (SEM). The binding stoichiometry and binding mode of the metal complex was established by Job's plot and FT-IR spectroscopy.

Keywords: β -(2-pyridyl)acrolein-rhodamine B derivative, rhodamine/polymer particles, aluminium sensing, fluorescent sensor

1. Introduction

The development of selective and sensitive probe for the detection of biologically and environmentally important species has emerged as a significant goal in the field of chemical sensors (Zhou et al., 2014; Xu et al., 2010; Wang et al., 2014). So far, a number of fluorescent probes with different excitation and emission wave lengths have been used as signal receptors of chemosensors such as coumarin (Chen et al., 2014), pyrene (Wang et al., 2013), 1,8-naphthalimide (Dai and Xu, 2011), xanthenes (Chen et al., 2012), squaraine (Akkaya, 1997), cyanine (Zheng et al., 2012) and boron dipyrromethene difluoride (BODIPY) (Li et al., 2012). Among these, xanthene derivatives are of great interest due to their excellent photophysical properties such as long absorption and emission wavelengths, large absorption co-efficient and high fluorescence quantum yield (Beaumont et al., 1993). Rhodamine is a well known dye of xanthenes derivative having spirolactam ring which is color less and non-fluorescent, whereas its

ring opened amide form gives strong color and fluorescent emission. Based on this, many rhodamine derivatives have been used as a fluorescent probe for the detection of various metal ions (Kim et al., 2008). The sensing behavior of most of the rhodamine based fluorescent probes was studied in the solution (Zhang et al., 2012; Lee et al., 2015; Lee et al., 2010; Weerasinghe et al., 2009; Ju et al., 2011). In order to use these probes in the fields, it should be materialized. In recent years, the preparation of rhodamine functionalized fluorescent particles for the removal of metal ions received much interest (Jung et al., 2011).

Molecular imprinting polymerization (MIP) is also known as template polymerization and widely used method for synthesizing host polymer which has been recognizing target species. Due to their chemical and mechanical stability, simple preparation, low cost and high selectivity, MIP has been used in wide range of fields such as chromatographic separation, solid-phase extraction, catalysts and sensors (Yang et al., 2009; Andersson, 2000; Li and Husson, 2006). The imprinting mechanism is explained as the trapping of template molecule into the polymer matrix during polymerization as a result the molecular information of the template is retained in the polymeric material in the cross linked powders after complete extraction of the template from the matrix membranes. Two types of interactions between the template

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molecule and functional monomers have been explained such as covalent and non-covalent interactions. The covalent interaction (Wulff and Sarhan, 1972) creates bonds between the template and polymer whereas non-covalent interaction (Haupt and Mosbach, 2000) creates electrostatic interactions such as π - π interaction and hydrogen bonds. The non-covalent technique has been preferentially used for different reasons such as easily conducted, the removal of the template is achieved through continuous extraction and a substantial number of functionalities can be introduced into the binding sites (Yan and Row, 2006). Immobilization of the indicators in matrices has substantial effects on the performance of the optical sensors in terms of selectivity, sensitivity, and stability. Keeping these factors in mind, in this study, we have retained the template in polymer matrices as a recognizing unit instead of extraction of template from polymer matrices.

Recently, our research group involves the development of colorimetric/fluorogenic chemosensors for selective detection of different types of analytes (So et al., 2014; Jeong et al., 2015). It is well documented that the spirolactam ring of the rhodamine derivative is open when it interacts with the metal ions and in turn it shows the fluorescence. Thus, in this article we have made an attempt to synthesis a simple new rhodamine derivative and used this as a template for the preparation of PEGDMA/rhodamine solid sensory particles. The prepared PEGDMA-rhodamine particles have been used for the sensing of Al^{3+} . The particle shows fluorescent turn on when it interact with Al^{3+} . The prepared rhodamine template was characterized using ^1H NMR and mass spectroscopy and the PEGDMA/rhodamine solid sensory particles were characterized confocal image and scanning electron microscopy.

2. Experimental section

2.1. Materials

The chemicals for the synthesis of β -(2-pyridyl)acrolein-rhodamine B derivative (RB-AC) were purchased from Aldrich and Kanto Chemicals Japan and were used without further purification. All reagents and solvents are of analytical grade and used without further purification. The metal ions such as Li^+ , Na^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , Hg^{2+} , Pb^{2+} , Al^{3+} as perchlorate salts were purchased from commercial suppliers and used without further purification. Ethylene glycol dimethacrylate (EGDMA) was obtained from the Sigma Chemical Company, USA, and was used as received without purification. Azobisisobutyronitrile (AIBN) and poly(vinylpyrrolidone) (PVP) were obtained from Acros Organics, New Jersey, USA. Ethylene gly-

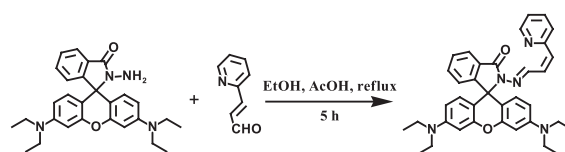
col dimethacrylate (EGDMA) was used as the monomer. 2,2-Azobisisobutyronitrile (AIBN) and poly(vinyl pyrrolidone) (PVPK-85-95, $M_w = 1,300,000$) were used as the initiator and stabilizer, respectively.

2.2. Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded in CDCl_3 unless otherwise stated, with tetramethylsilane (TMS) as internal reference at ambient temperature, mainly on a BRUKER AVANCE III 300 Magnet: Ascend TM series, 14.1 Tesla, ^1H resonance frequency 300 MHz, Top Spin 3.1 (software) spectrometer Germany spectrometers. HR-MS spectrum was recorded with Bruker autoflex III mass spectrometer. FT-IR spectra were recorded with an FTS-175C spectrometer. UV-Visible absorption spectra were recorded on an Agilent 8453 spectrophotometer. Fluorescence emission spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. The slit width was 1.5 nm for both excitation and emission. Samples were contained in 10.0 nm path length quartz cuvettes (3.5 mL volume). Fluorescence imaging was performed by confocal fluorescence microscopy on LSM5Live, (Germany) with Zeiss LSM5 Live Release version 4.2.SP1 Image Browser software were used. The scanning electron microscope (SEM) images were obtained by JEOL, JSM-7000F.

2.3. Synthesis of RB-AC

Rhodamine B hydrazide and β -(2-pyridyl)acrolein were prepared following the literature method (Zhang et al., 2011; Krasnaya et al., 1997). The synthesis of RB-AC is shown in **Scheme 1**. In a 100 mL three necked round bottom flask, rhodamine B hydrazide (1.23 g, 2.6 mmol) was dissolved in hot ethanol (30 mL). Then, a solution of 0.5 g (3 mmol) of β -(2-pyridyl)acrolein in 20 mL of ethanol was added drop wise to the flask in 1 h. After the addition of β -(2-Pyridyl)acrolein, 1 mL of acetic acid was added to the reaction mixture. Under stirring, the reaction mixture was refluxed for 5 h. After 5 h, the reaction mixture was cool to room temperature and the formed precipitate was filtered and washed with cold ethanol. The crude product was purified by column chromatography using hexane-ethyl acetate (60:40) as eluent to get pure product (1.01 g, yield = 69.1 %). The Product was confirmed by ^1H NMR and mass spectroscopy (**Fig. S1 and S2**).



Scheme 1 Synthesis of RB-AC.

2.4. Synthesis of PEGDMA/RB-AC particles

The dispersion medium (stabilizer) was prepared by dissolving 1.5 g of poly(vinyl pyrrolidone) (PVP) in de-ionized water (150 mL). The synthesis was performed in a three-necked flask equipped with a stirrer, water condenser and thermometer. A mixture containing 17 g of ethylene glycol dimethacrylate (EGDMA), initiator, 0.255 g of azobisisobutyronitrile (AIBN) and 0.0017 g of RB-AC was diluted with a mixed solvent (toluene (8 mL)/butanol (8 mL)). The reaction mixture transferred to the PVP dispersion medium and this reaction mixture was purged with N_2 gas for 10 min after that the reaction mixture was sealed under this nitrogen atmosphere and heated at 80 °C for overnight. The produced polymer was filtered using a Whatman filter number 1 and washed with acetone and methanol to get the RB-AC encapsulated PEGDMA (PEGDMA/RB-AC) as white powder.

3. Results and discussion

3.1. Preliminary studies

In order to evaluate the sensing behavior of PEGDMA/RB-AC, we have examined the absorbance, fluorescence and visible color change of the RB-AC in solution in the presence of various metal ions including alkali, alkaline-earth and transition-metal ions such as Li^+ , Na^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , Hg^{2+} , Pb^{2+} and Al^{3+} , in ethanol/DMF (v/v = 9/1). The absorbance spectrum of RB-AC doesn't show any peaks longer than 500 nm which was attributed to the ring closed spirolactam form of RB-AC (**Fig. 1**) (Chen et al., 2012). As shown in **Fig. 1**, the absorbance intensity of RB-AC was significantly increased at 560 nm upon the addition of Al^{3+} whereas no changes in absorbance intensity of RB-AC were observed upon the addition of other competitive metal ions. **Fig. 2** shows the fluorescence changes of RB-AC in the presence of different metal ions. The RB-AC alone doesn't show any fluorescence peak around 580 nm. The addition of Al^{3+} into RB-AC showed the considerable enhancement in fluorescence intensity at 580 nm. Further the addition of other competitive metal ions doesn't lead the fluorescence enhancement of the RB-AC.

Furthermore, the sensing behavior of RB-AC with different significant metal ions was checked by 'naked eye' detection methods. As shown in **Fig. 3**, the synthesized RB-AC displays a 'naked-eye' color change from colorless to pink (**Fig. 3, top**) after the addition of 10 μM of Al^{3+} in ethanol/DMF (9:1) mixture. While in the case of other cations such as Li^+ , Na^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , Hg^{2+} and Pb^{2+} does not produce any significant color changes. Further, the addi-

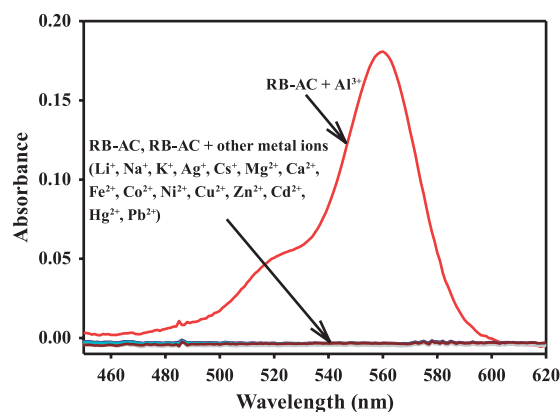


Fig. 1 Absorbance spectra of 10 μM of RB-AC in ethanol/DMF (9:1) in the presence of 10 μM of different metal ions.

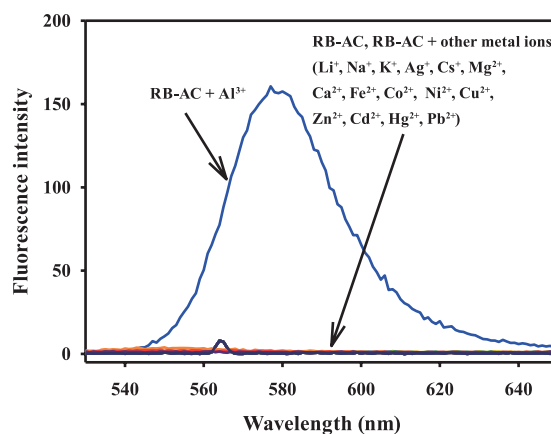


Fig. 2 Fluorescence spectra of 10 μM of RB-AC in ethanol/DMF (9:1) in the presence of 10 μM of different metal ions.

tion of Al^{3+} exhibits intense yellow fluorescence under illumination of UV-light (**Fig. 3, bottom**). Thus, the sensing of Al^{3+} by RB-AC can be detected by the naked eye without the assistance of any instrument.

3.2. Spectroscopic recognition of RB-AC towards Al^{3+}

UV-Vis and fluorescence spectral methods were used to study the recognition of RB-AC towards Al^{3+} . UV-vis spectra of RB-AC in ethanol/DMF (9:1) mixture in the presence of different concentrations of Al^{3+} are shown in **Fig. S3**. In the absence of Al^{3+} , the absorption spectrum of RB-AC doesn't exhibit any characteristic absorption of rhodamine moiety whereas upon the addition of Al^{3+} , a new absorption band centered at 560 nm was observed. Further addition of Al^{3+} into RB-AC leads to the increase in absorbance at 560 nm. This indicated a clear and gradually color change from colorless to pink due to the opening of the closed rhodamine spirolactam ring.

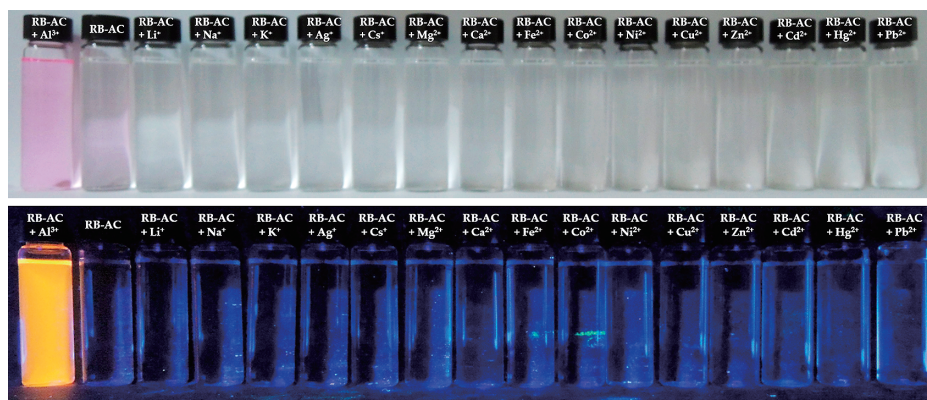


Fig. 3 Photographs of color changes of RB-AC (10 μM) in ethanol/DMF (9:1) in the presence of various metal ions detected by naked eye (top) and by UV-lamp (bottom).

Due to its high sensitivity, fluorescence spectroscopy has been widely used in the study of molecular interactions between rhodamine and metal ions (Chen et al., 2009). **Fig. S4** shows the fluorescence spectra of RB-AC in ethanol/DMF (9:1) mixture was recorded against the different concentrations of Al^{3+} . As shown in **Fig. S4**, while increasing the concentration of Al^{3+} the fluorescence intensity at 580 nm was gradually increased. The binding constant of RG-HN with Al^{3+} was determined using Benesi-Hildebrand equation (**Fig. S5**). It was found to be 4.70×10^4 which was within the range of reported Al^{3+} chemosensors (Kim et al., 2014).

The detection limit of the receptor RB-AC towards Al^{3+} was calculated based on $3\delta/k$ (Lohani et al., 2010). Where, δ is the standard deviation of the blank solution and k is the slope of the calibration plot. A linear response was observed when the concentration of Al^{3+} is plotted against fluorescence intensity with a correlation coefficient of 0.982 (**Fig. S6**). The detection limit was calculated from slope and it was found to be 5.4×10^{-8} M.

3.3. Sensing property of PEGDMA/RB-AC particles towards Al^{3+}

The results discussed in previous sections indicated that the synthesized RB-AC has good recognition towards Al^{3+} and it can be used for the preparation of sensing probe for Al^{3+} . In order to improve the sensing performance of RB-AC, we have addressed the task of designing of RB-AC encapsulated PEGDMA particles. To demonstrate the encapsulation of RB-AC by PEGDMA, we have studied the color change of PEGDMA/RB-AC particles in ethanol/DMF (9:1) mixture with and without Al^{3+} . In the absence of Al^{3+} , PEGDMA/RB-AC particles in ethanol/DMF (9:1) mixture doesn't show any color. After the addition of Al^{3+} to the PEGDMA/RB-AC particles in ethanol/DMF mixture (9:1), the color of the particles was changed colorless to pink and the particle

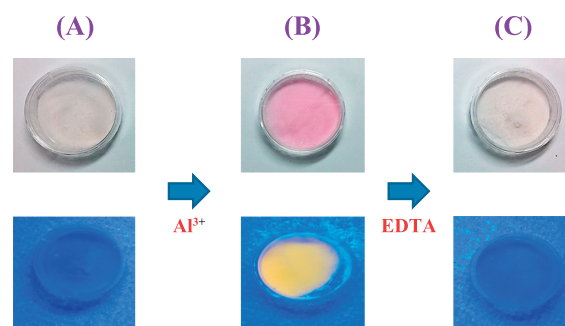


Fig. 4 Photographs of PEGDMA/RB-AC in absence (A), presence (B) of 10 μM of Al^{3+} and reversibility with 10 μM of EDTA (C) detected by naked eye (top) and UV-lamp (bottom).

showed yellow fluorescence under the illumination of UV-light as shown in the **Fig. S7**. Further, the sensing performance was examined by the addition of 1 mL of 10 μM of Al^{3+} in ethanol/DMF (9:1) mixture into the 1.0 g of synthesized PEGDMA/RB-AC particles. Besides that the mixture was stirred for 5 min up to attain the pink solid and filtered through the filter paper. As shown in **Fig. 4**, after the addition of Al^{3+} , the color of the PEGDMA/RB-AC was turned from colorless to pink and it showed yellow emission under illumination of UV light, which is sensible via naked eye. The reversibility of PEGDMA/RB-AC was checked by the addition of 1 mL of 10 μM of EDTA extraction. Upon addition of EDTA in to Al^{3+} bounded PEGDMA/RB-AC, the color of the particle was turned from pink to color less and the yellow fluorescent emission was also turned off (**Fig. 4**). Further, the selectivity of PEGDMA/RB-AC particles towards Al^{3+} in the presence of 10 μM of other competitive metal ions was checked. As depicted in **Fig. 5**, Al^{3+} only changes the color of PEGDMA/RB-AC particles from color less to pink in visible light and yellow fluorescence under UV light whereas other competitive metal ions did not showed any changes. This indicates that the

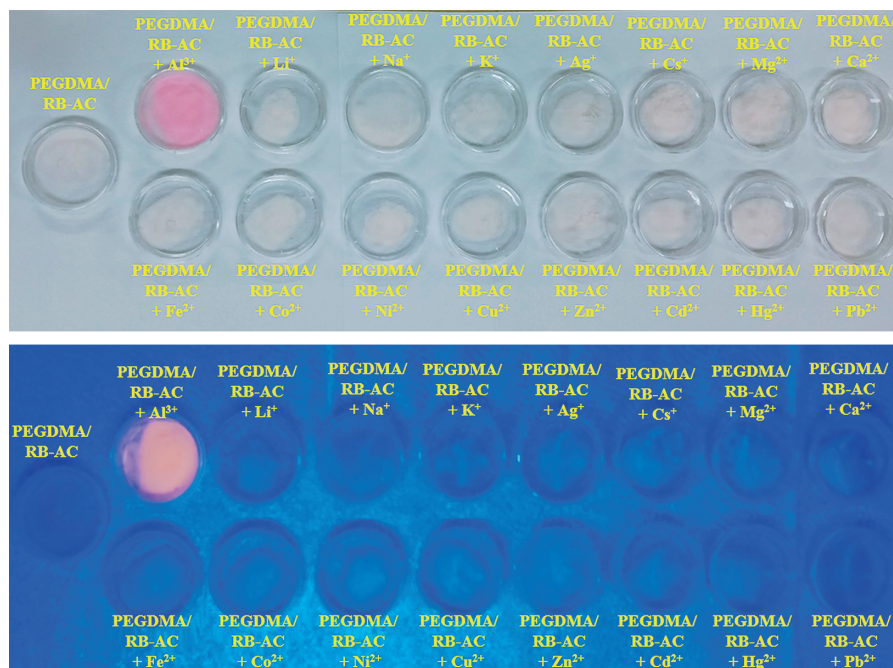


Fig. 5 Photographs of PEGDMA/RB-AC in the presence of 10 μM of various metal ions detected by naked eye (top) and by UV-lamp (bottom).

PEGDMA/RB-AC particles show the fluorescence turn on by sensing of Al^{3+} with good selectivity and reversibility.

3.4. Depicting the sensing property of PEGDMA/RB-AC by confocal laser scanning microscopy (CLSM)

Consequently, it was of great interest to investigate the sensory property by CLSM (Tao et al., 2011). The 1 mL of 1×10^{-6} M Al^{3+} (ethanol/DMF (9:1)) was dropped on the surface of a dry PEGDMA/RB-AC particles and allowed to stand for 1 min, resulting in the immediate adsorption of the Al^{3+} by particles, after drying the particles in an oven at 150 $^{\circ}\text{C}$, the CLSM was performed. As shown in **Fig. 6A**, PEGDMA/RB-AC particles did not show any fluorescence under the selective excitation whereas after the dropping of Al^{3+} (1 mL) in to the PEGDMA/RB-AC particles, a significant increase in the fluorescence was observed from the selective excitation area (**Fig. 6B**).

3.5. Al^{3+} binding on PEGDMA/RB-AC by SEM analysis

The CLSM results confirmed that the sensing property of PEGDMA/RB-AC towards Al^{3+} , to get further insight, SEM analysis was carried out. **Fig. 7** showed the SEM images of prepared PEGDMA polymer encapsulated RB-AC in the absence and presence of Al^{3+} . The morphology of prepared PEGDMA/RB-AC particles is spherical in shape, and was arranged in an orderly

three-dimensional shape and the particle size distribution is given in **Fig. S8**. There is only a little bonding between the particles (**Fig. 7A**). While in the presence of 1×10^{-5} M of Al^{3+} , the PEGDMA/RB-AC particles were aggregated together (**Fig. 7B**). The difference in the surface morphology of these samples may be due to the formation of complex between RB-AC and Al^{3+} followed by ring opening. Energy-dispersive analysis of X-rays (EDAX) was used to analyze the elemental constituents of prepared PEGDMA/RB-AC particles in the presence of Al^{3+} . **Fig. 8** illustrates the EDAX spectra of PEGDMA/RB-AC particles after the sensing of Al^{3+} . The presence of aluminum in elemental analysis confirmed that the Al^{3+} has been entrapped into PEGDMA/RB-AC by formation of complex with RB-AC.

3.6. Mechanism for the sensing of Al^{3+} by PEGDMA/RB-AC

Since the sensing part of PEGDMA/RB-AC is RB-AC, to investigate the recognition of PEGDMA/RB-AC towards Al^{3+} , the stoichiometry and complex formation of RB-AC to Al^{3+} were studied. The stoichiometry of RB-AC to Al^{3+} was calculated by Job's plot analysis and the complex formation was explained by FT-IR binding study. Total concentration of RB-AC and Al^{3+} was kept constant at 10 μM according to the continuous variations changing the mole fraction of RB-AC from 0.1 to 0.9 (**Fig. S9**). The stoichiometry ratio of RB-AC with Al^{3+} was analyzed by absorbance method. The maximum of curve

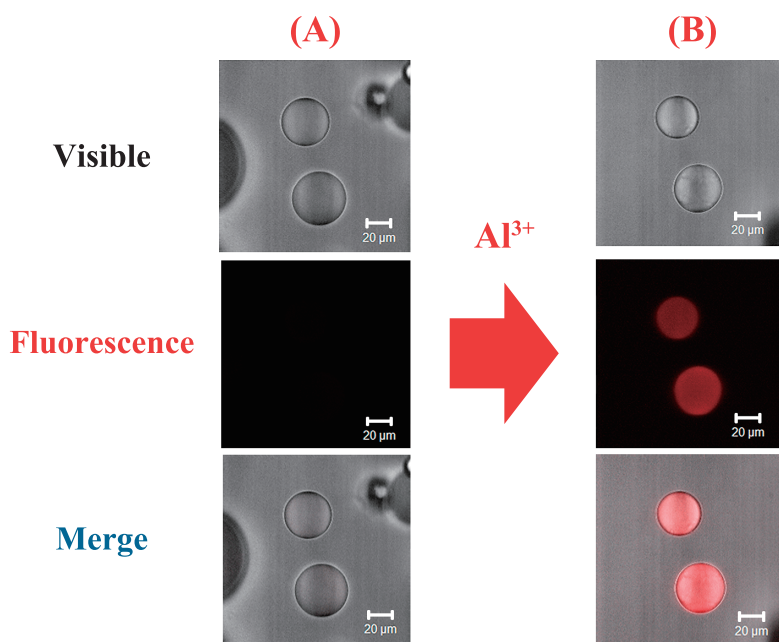


Fig. 6 CLSM images of PEGDMA/RB-AC in absence (A) and presence (B) of Al^{3+} .

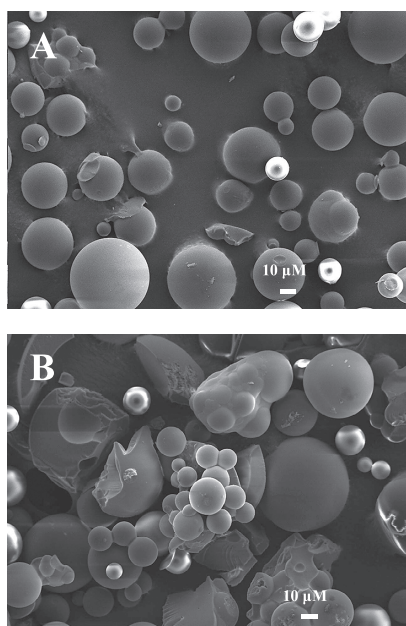


Fig. 7 SEM images of PEGDMA/RB-AC in absence (A) and presence (B) of Al^{3+} .

was showed at 0.5 mole fraction, indicating that the formation of 1:1 complex between RB-AC and Al^{3+} . **Fig. 9** shows the FT-IR spectra of RB-AC before and after binding with Al^{3+} . The FT-IR spectrum of RB-AC alone shows the peaks at 1678, 1610 and 1550 cm^{-1} corresponding to spirolactam amide carbonyl, imine ($\text{C}=\text{N}$) and pyridine ($\text{C}=\text{N}$) stretching vibrations, respectively. While the addition of 1 eq of Al^{3+} , the stretching frequency of these peaks was changed. Upon the addition of 1 eq Al^{3+} the characteristic stretching frequency of spiro-

lactam rings amide carbonyl at 1698 cm^{-1} was completely disappeared and the imine ($\text{C}=\text{N}$) and pyridine ($\text{C}=\text{N}$) stretching vibrations are shifted to 1643 and 1580 cm^{-1} , respectively. Which confirms the Al^{3+} was opened the spirolactam ring, formed the complex with oxygen and imine and pyridine nitrogen. It has been well established that Al^{3+} forms complex with oxygen and nitrogen rich ligands (Dhara et al., 2014; Ghosh et al., 2014). Based on this, we have proposed the complex formation of Al^{3+} with RB-AC (**Scheme 2**).

4. Conclusion

In conclusion, we have developed a novel fluorescent probe β -(2-pyridyl)acrolein-rhodamine B/poly(ethylene glycol) dimethacrylate (PEGDMA/RB-AC). The PEGDMA/RB-AC particles showed good selectivity and sensitivity towards Al^{3+} . Fluorescence enhance mechanism is presumably due to the chelation of Al^{3+} with the oxygen atoms of the amide groups of RB-AC results in the formation of the open-ring form, which leads to the enhancement of fluorescence of PEGDMA/RB-AC particles. The selectivity for Al^{3+} can be attributed to the rigid hydrazone binding site as well as the affinity of the pyridine group toward Al^{3+} .

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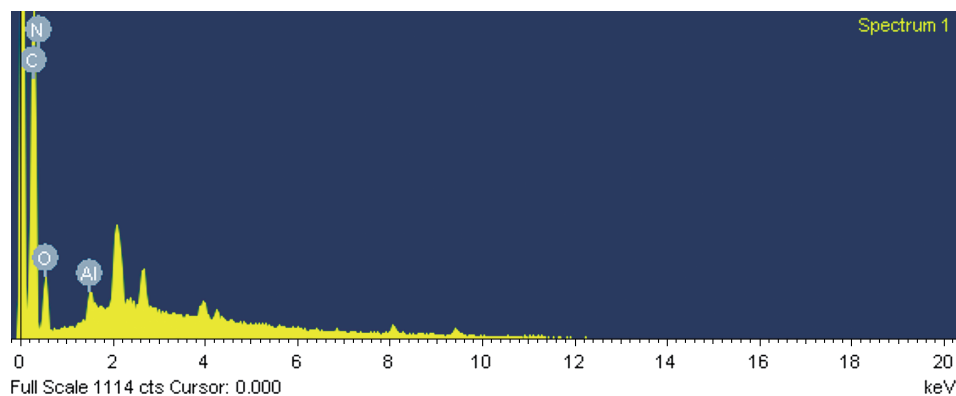


Fig. 8 EDAX spectra of PEGDMA/RB-AC in the presence of Al^{3+} .

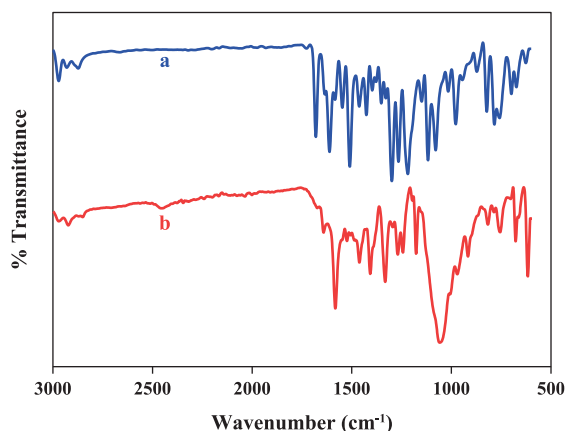
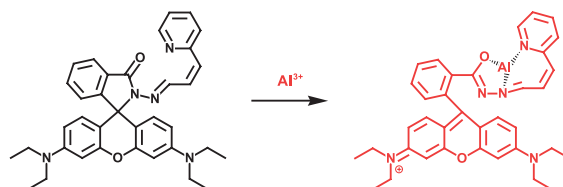


Fig. 9 FT-IR spectra of RB-AC before (a) and after (b) binding with Al^{3+} .



Scheme 2 Plausible binding mode of RB-AC with Al^{3+} .

References

- Akkaya E.U., Squaraine-based long wavelength fluorescent chemosensors for ions, *Chemosensors of Ion and Molecule Recognition*, 492 (1997) 177–188.
- Andersson L.I., Molecular imprinting for drug bioanalysis: A review on the application of imprinted polymers to solid-phase extraction and binding assay, *J. Chromatogr. B*, 739 (2000) 163–173.
- Beaumont P.C., Johnson D.G., Parsons B.J., Photophysical properties of laser dyes: picosecond laser flash photolysis studies of rhodamine 6G, rhodamine B and rhodamine 101, *J. Chem. Soc., Faraday Trans.*, 89 (1993) 4185–4191.
- Chen F., Liu .G., Shi Y., Xi P., Cheng J., Hong J., Shen R., Yao X., Bai D., Zeng Z., A coumarin-derived fluorescent chemosensor for selectively detecting Cu^{2+} : Synthesis, DFT calculations and cell imaging applications, *Talanta*, 124 (2014) 139–145.
- Chen X., Jou M.J., Lee H., Kou S., Lima J., Nam S-W., Park S., Kim K.W., Yoon J., New fluorescent and colorimetric chemosensors bearing rhodamine and binaphthyl groups for the detection of Cu^{2+} , *Sen. Actuators B*, 137 (2009) 597–602.
- Chen X., Pradhan T., Wang F., Kim J.S., Yoon J., Fluorescent chemosensors based on spiroring-opening of xanthenes and related derivatives, *Chem. Rev.*, 112 (2012) 1910–1956.
- Dai H., Xu H., A water-soluble 1,8-naphthalimide-based ‘turn on’ fluorescent chemosensor for selective and sensitive recognition of mercury ion in water, *Bioorg. Med. Chem. Lett.*, 21 (2011) 5141–5144.
- Dhara A., Jana A., Guchhait N., Ghosh P., Kar S.K., Rhodamine-based molecular clips for highly selective recognition of Al^{3+} ions: synthesis, crystal structure and spectroscopic properties, *New. J. Chem.*, 38 (2014) 1627–1634.
- Ghosh K., Majumdar A., Sarkar T., Selective sensing of Al^{3+} by naphthyridine coupled rhodamine chemosensors, *RSC Adv.*, 4 (2014) 23428–23432.
- Haupt K., Mosbach K., Molecularly imprinted polymers and their use in biomimetic sensors, *Chem. Rev.*, 100 (2000) 2495–2504.
- Jeong J.W., Rao B.A., Son Y-A., Rhodamine-chloronicotinaldehyde-based “OFF–ON” chemosensor for the colorimetric and fluorescent determination of Al^{3+} ions, *Sens. Actuator B*, 208 (2015) 75–84.
- Ju H., Lee M.H., Kim J., Kim J.S., Kim J., Rhodamine-based chemosensing monolayers on glass as a facile fluorescent “turn-on” sensing film for selective detection of Pb^{2+} , *Talanta*, 83 (2011) 1359–1363.
- Jung J.H., Lee J.H., Shinkai S., Functionalized magnetic

- nanoparticles as chemosensors and adsorbents for toxic metal ions in environmental and biological fields, *Chem. Soc. Rev.*, 40 (2011) 4464–4474.
- Kim H.N., Lee M.H., Kim H.J., Kim J.S., Yoon J., A new trend in rhodamine-based chemosensors: application of spirolactam ring-opening to sensing ions, *Chem. Soc. Rev.*, 37 (2008) 1465–1472.
- Kim K.B., You D.M., Jeon J.H., Yeon Y.H., Kim J.H., Kim C., A fluorescent and colorimetric chemosensor for selective detection of aluminum in aqueous solution, *Tetrahedron Lett.*, 55 (2014) 1347–1352.
- Krasnaya Zh.A., Burova S.A., Bogdanov., Smirnova Yu.V., Synthesis of δ -Hetaryl- α,α -dicarbonylalkadines and a study of their isomerization, *Chem. Hetrocycl. Compd.*, 33 (1997) 410–422.
- Lee Y.H., Lee M.H., Zhang J.F., Kim J.S., Pyrene excimer-based calix[4]arene FRET chemosensor for mercury(II), *J. Org. Chem.*, 75 (2010) 7159–7165.
- Lee S., Rao B.A., Y-A Son, A highly selective fluorescent chemosensor for Hg^{2+} based on asquaraine-bis(rhodamine-B) derivative: Part II, *Sens. Actuators B.*, 210 (2015) 519–532.
- Li Q., Guo Y., Shao S., A BODIPY based fluorescent chemosensor for Cu(II) ions and homocysteine/cysteine, *Sens. Actuators B.*, 171–172 (2012) 872–877.
- Li X., Husson S.M., Two-dimensional molecular imprinting approach to produce optical biosensor recognition elements, *Langmuir*, 22 (2006) 9658–9663.
- Lohani C.R., Kim J.-M., Chung S.-Y., Yoon J., Lee K.-H., Colorimetric and fluorescent sensing of pyrophosphate in 100 % aqueous solution by a system comprised of rhodamine B compound and Al^{3+} complex, *Analyst*, 135 (2010) 2079–2084.
- So H.-S., Rao B.A., Hwang J., Yesudas K., Son Y.-A., Synthesis of novel squaraine-bis(rhodamine-6G): A fluorescent chemosensor for the selective detection of Hg^{2+} , *Sens. Actuators B*, 202 (2014) 779–787.
- Tao X., Fernandez B., Azucena O., Fu M., Garcia D., Zuo Y., Chen D.C., Kubby J., Adaptive optics confocal microscopy using direct wavefront sensing, *Optics Letters*, 36 (2011) 1062–1064.
- Wang F., Wang L., Chen X., Yoon J., Recent progress in the development of fluorometric and colorimetric chemosensors for detection of cyanide ions, *Chem. Soc. Rev.*, 43 (2014) 4312–4324.
- Wang M., Xu J., Liu X., Wang H., A highly selective pyrene based “off–on” fluorescent chemosensor for cyanide, *New. J. Chem.*, 37 (2013) 3869–3872.
- Weerasinghe A.J., Schmiesing C., Sinn E., Highly sensitive and selective reversible sensor for the detection of Cr^{3+} , *Tetrahedron Lett.*, 50 (2009) 6407–6410.
- Wulff G., Sarhan A., Über die Anwendung von enzymanalog gebauten Polymeren zur Racemattrennung, *Angew. Chem.*, 84 (1972) 364–365.
- Xu Z., Yoon J., Spring D.R., Fluorescent chemosensors for Zn^{2+} , *Chem. Soc. Rev.*, 39 (2010) 1996–2006.
- Yan H., Row K.H., Characteristic and synthetic approach of molecularly imprinted polymer, *Int. J. Mol. Sci.* 7 (2006) 155–178.
- Yang Q.Y., Sun Q., Zhou T.S., Shi G.Y., Jin L.T., Determination of parathion in vegetables by electrochemical sensor based on molecularly imprinted polyethyleneimine/silica gel films, *J. Agric. Food Chem.*, 57 (2009) 6558–6563.
- Zhang J., Yu C., Qian S., Lu G., Chen J., A selective fluorescent chemosensor with 1, 2, 4-triazole as subunit for Cu (II) and its application in imaging Cu (II) in living cells, *Dyes Pigm.*, 92 (2012) 1370–1375.
- Zhang Z., Zheng Y., Hang W., Yan X., Zhao Y., Sensitive and selective off–on rhodamine hydrazide fluorescent chemosensor for hypochlorous acid detection and bioimaging, *Talanta*, 85 (2011) 779–786.
- Zheng H., Yan M., Fan X.-X., Sun D., Yang S.-Y., Yang L.-J., Li J.-D., Jiang Y.-B., A heptamethine cyanine-based colorimetric and ratiometric fluorescent chemosensor for the selective detection of Ag^{+} in an aqueous medium, *Chem. Commun.*, 48 (2012) 2243–2245.
- Zhou Y., Zhang J.F., Juyoung Yoon J., Fluorescence and colorimetric chemosensors for fluoride-ion detection, *Chem. Rev.*, 114 (2014) 5511–5571.

Appendix: Supporting information

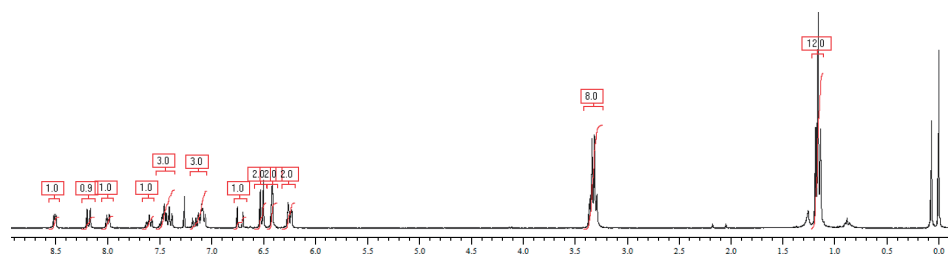


Fig. S1 ^1H NMR spectrum of RB-AC.

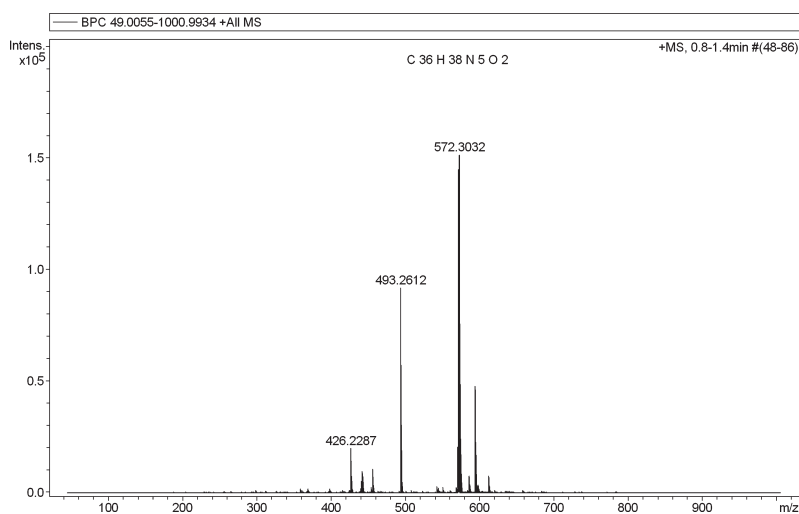


Fig. S2 HR-MS spectrum of RB-AC.

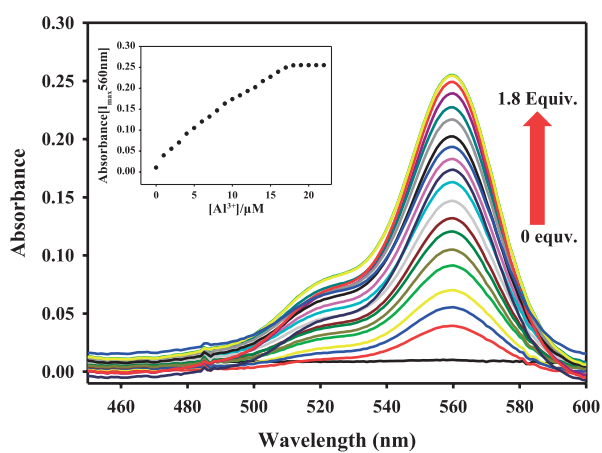


Fig. S3 UV-Vis spectra of 10 μM of RB-AC in ethanol/DMF (9:1) in the presence of different concentrations of Al^{3+} . Inset: Absorbance at 560 nm as a function of the concentration of Al^{3+} .

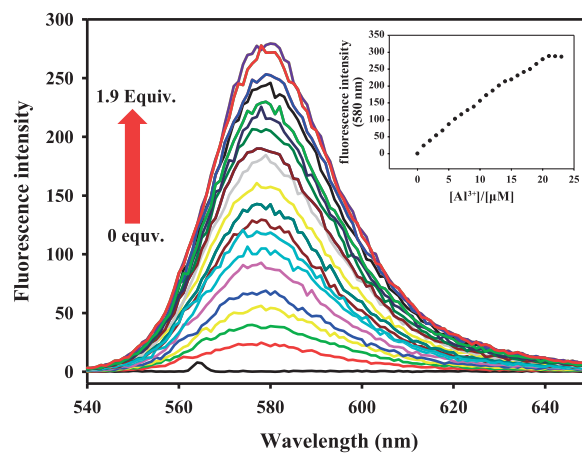
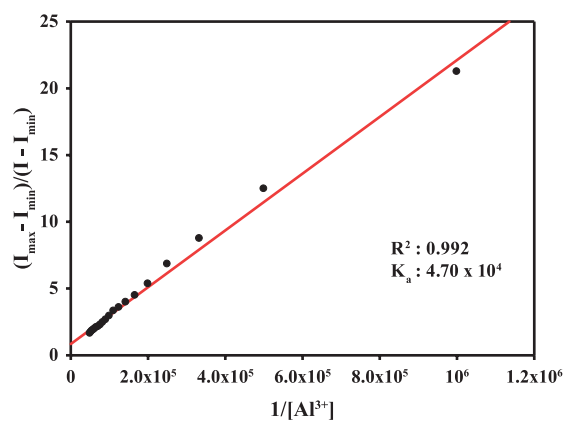


Fig. S4 Fluorescence spectra of 10 μM of RB-AC in ethanol/DMF (9:1) in the presence of different concentrations of Al^{3+} . Inset: Fluorescence at 580 nm as a function of the concentration of Al^{3+} .



$$\frac{1}{I - I_{\max}} = \frac{1}{I_{\max} - I_{\min}} + \frac{1}{K_{[\text{Metal}]}} \frac{1}{I_{\max} - I_{\min}}$$

Fig. S5 Benesi-Hildebrand plot and equation for binding of Al^{3+} .

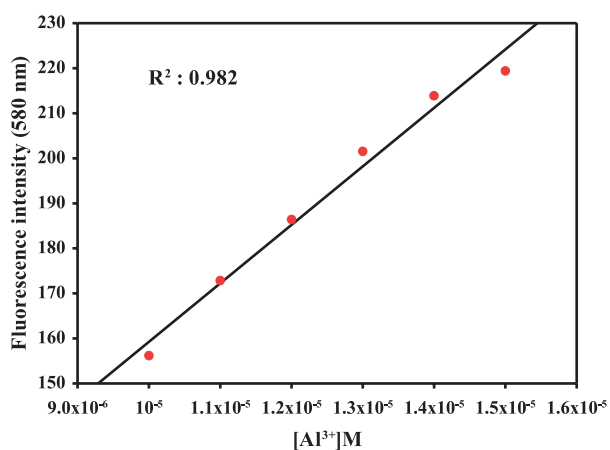


Fig. S6 Calibration plot for fluorescence intensity against concentration of Al^{3+} .

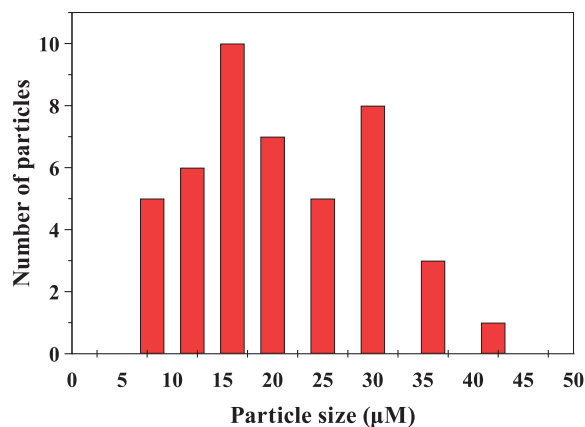


Fig. S8 Size histogram of PEGDMA/RB-AC particles.

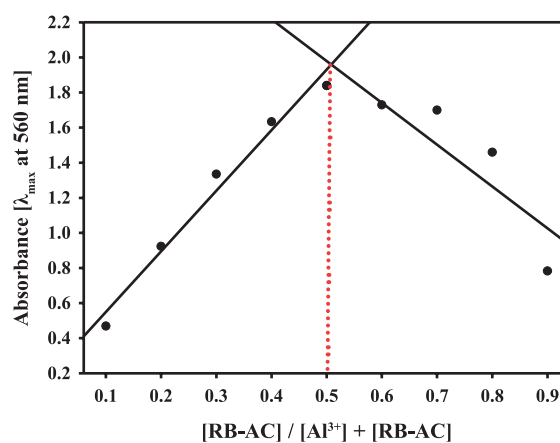


Fig. S9 Job's plot for RB-AC with Al^{3+} ion.

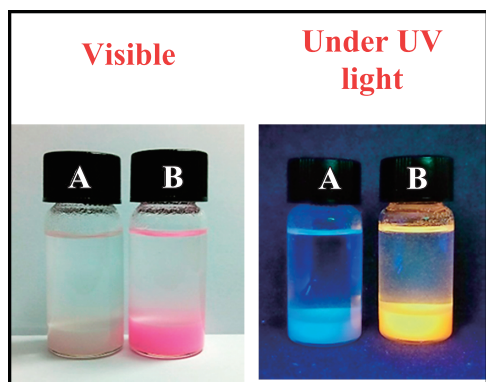
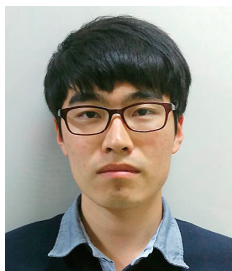


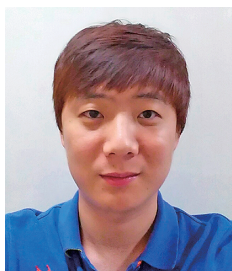
Fig. S7 Photographs of PEGDMA/RB-AC particles in ethanol/DMF mixture (9:1) (A) absence and (B) presence of Al^{3+} .

Author's short biography



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Kyo-Sun Ku received his B.Sc. (Advanced Organic Materials Engineering) in 2015 at Chungnam National University, Daejeon, South Korea, under the supervision of Prof. Dr. Young-A Son. He is currently a master candidate in the Department of Advanced Organic Materials and Textile System Engineering, Chungnam National University. His research interests lie in the synthesis of rhodamine, pyridine derivatives and their sensing applications towards cation and anion.



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