

A Quinoline carboxamide based Fluorescent Probe's Efficient Recognition of Aluminium Ion and its Application for Real Time Monitoring

*Corresponding author

Young-A Son
(yason@cnu.ac.kr)

Ramalingam Manivannan, Jiwon Ryu and Young-A Son*

Department of Advanced Organic Materials Engineering, Chungnam National University,
Daejeon, Korea

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Abstract A novel binding site for metal ion made by designing molecule with tetrazolo quinoline with hydrazine carboxamide (TQC) and the designed molecule successfully synthesized. The probe works by selectively detecting Al^{3+} ion via both fluorimetric and colorimetric approach. The probe's effectiveness towards aluminium ion detection is highly sensitive and selective with no substantial interference with other competing ions. The added Al^{3+} ion to TQC fetched a rapid change of visual color to yellow from colorless, also the response of fluorescence turn-on. The fluorescence turn-on and color change visibly by the probe TQC with Al^{3+} ion credited to the ICT phenomenon (intramolecular charge-transfer transition). The likely interaction of the probe with aluminium ion has also been there predicted from ESI-MS spectral analysis results. The usefulness of the probe confirmed by practical utility by making a test kit to monitor Al^{3+} ion in water which showed a naked eye detection by notable color change.

Keywords *quinoline-carboxamide, aluminium ion, fluorescence, test strip, colorimetric, selective*

1. Introduction

Al^{3+} is the richest element in the world, representing around 8% of the overall rock crystal^{1,2}, and is extensively used. WHO stated that the normal consumption of Al^{3+} by human being is about 3-10 mg^{3,4}. Too much consumption of Al^{3+} causes anemia and bone softening by the preoccupation of iron in blood and calcium in the bowel, respectively. Besides, a superfluous amount of Al^{3+} suspected in associated with Parkinson's and Alzheimer's diseases. An extreme quantity of Al^{3+} consequences in with the central nervous system destruction⁵⁻⁸. Harmfulness of aluminium ion happens to owe its high electrical charge, atomic size, and it inhibits reasonably elements Fe^{3+} , Ca^{2+} , and Mg^{2+} , which are vital⁹. Pollution is caused by Aluminum either by natural and fabricated causes. Comprising foodstuff-packing material, medical waste, cookery containers, deodorizer, acid rain, and wagon portions, etc. Because of its intense use in daily life activities

gains a more chance of entering water bodies and resulting in transferring the aluminium entry via the food chain and causes intolerable problem to the environment¹⁰⁻¹⁴. The recognition and regulation of Al^{3+} is therefore necessary.

In comparison with other analytical methods, spectrofluorometric methods have a great interest because of their operational easiness, promptness, high sensitivity, and practical monitoring. Currently, the development of chemosensors, which use the electron/energy transmission mechanism between the donor and acceptor in the sensor, has great advantages in applications of cell imaging and live organisms¹⁵⁻¹⁸. Numerous reported approaches existing such as excited-state intramolecular proton transmission (ESIPT), photo-prompted electron/energy transmission, intramolecular charge transmission (ICT), excimer/excimer formation, metal-ligand charge transmission (MLCT), through bond energy transmission (TBET), and fluorescence resonance energy transmission (FRET)¹⁹⁻²⁸. Among these mechanisms, FRET and

TBET have fascinated courtesy because of the prospective uses of such methods in bioimaging. In the FRET probes, energy transmission (ET) occurred through space. However, FRET has several restrictions, including spectral overlay in the middle of acceptor unit absorption and donor unit emission, and the efficiency of FRET rest on the space among the energy acceptor and energy donor. Meanwhile, in the ICT case, the donor unit and acceptor unit fluorophore directly linked through conjugation between donor and acceptor. The monitoring of Al^{3+} for practical use is the requirement for accepting the mechanism of aluminum-induced sicknesses containing Alzheimer's syndrome and Parkinson's diseases. Therefore, the development of an Al^{3+} sensor more suitable for in vivo monitoring is very important. In recent times, we have established many probes towards metal ions and successfully applied them for practical applications²⁹⁻³¹.

In continuing those attempts, in this present endeavor, we designed and synthesized a probe (TQC), which has more nitrogen and oxygen atoms to bind with Al^{3+} ions. Besides, Al^{3+} was monitored using strips and accordingly be able to fetch prominent color changes that is visualized.

2. Experimental

2.1 Chemicals and apparatus

Compounds aimed at the preparation of TQC, solvents, and cations (chloride salts), used for complete tests acquired in Sigma Aldrich, Tokyo chemical industries(Japan), used without any refinement. Distilled water is used for complete experiments. Proton and carbon-NMR of TQC measured and confirmed on a Bruker 600 instrument. Mass analysis is done in JMS 700 JEOL spectrometer. Fluorescence and UV-Visible data were obtained in a Varian Cary Eclipse spectrophotometer and Agilent 8453 instrument respectively. Slit widths for excitation/emission kept constant of 3 nm throughout the experiment.

2.2 TQC Synthesis processes

2.2.1 Tetrazolo[1,5-a]quinoline-4-carbaldehyde

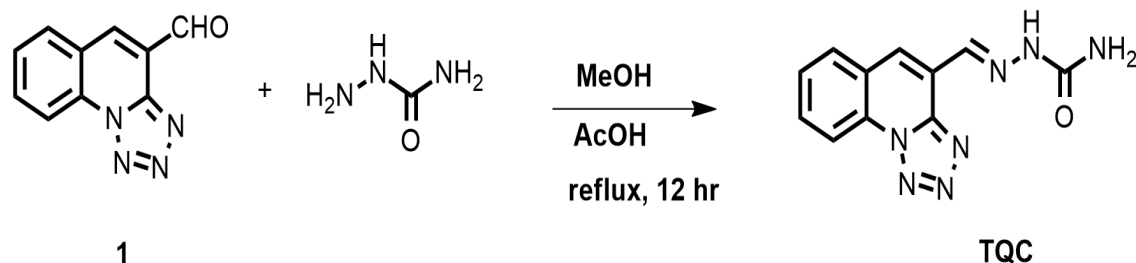
Tetrazolo[1,5-a]quinoline-4-carbaldehyde (1) has been prepared following reported procedure³².

2.2.2 (E)-2-(tetrazolo[1,5-a]quinolin-4-ylmethylene)hydrazinecarboxamide (TQC)

Tetrazolo[1,5-a]quinoline-4-carbaldehyde (1g, 5.05 mmol) in 20 mL of methyl alcohol solution was added hydrazinecarboxamide (0.38g, 5.05 mmol). To the stirred reaction, 2-3 drops of acetic acid were added, the reaction mixture was further stirred under a nitrogen atmosphere with heating at 80 °C for 24 h. Once the reaction is completed, it was cooled to ambient temperature. Added ethyl acetate to it and extracted from water. The filtrate was concentrated in a vacuum to get the crude product, and then it was purified using column chromatography with hexane/ethyl acetate as eluent to obtain pure title compound TQC. ¹H-NMR (DMSO-*d*₆, 600 MHz), δ (ppm): 6.795 (s, 2H), 7.835-7.862 (m, 1H), 7.966-7.994 (m, 1H), 8.183-8.195 (d, 1H, J=7.2 Hz), 8.425 (s, 1H), 8.628-8.642 (d, 1H, J=8.4 Hz), 8.861 (s, 1H). ¹³C NMR (DMSO-*d*₆, 150 MHz), δ (ppm): 116.76, 120.64, 124.54, 128.58, 130.10, 131.84, 132.00, 146.66, 156.92. ESI-MS (m/z): found 254.3 (M-H⁺). calcd. 255.1.

2.3 Aluminium ion sensing experiment method

For UV-Vis titration, experiment a stock solution of 1×10^{-5} M concentration of the probe TQC and 1×10^{-5} M aluminium ion also prepared individually. From the stock solution 2.5 ml of probe solution taken and 0.1 - 1 ml (10 reading) of aluminium ion added to each fresh 2.5 mL of stock solution and measured UV-Vis spectra. Similarly for fluorescence measurement same concentration but for each addition 0.2×10^{-5} M (5 readings) added to the probe solution and measured fluorescence.



Scheme 1. Synthesis of probe TQC.



Figure 1. Color changes of TQC with various cations (10 μM) in normal light.

2.4 Preparation of test kit

The probe solution prepared (1×10^{-4} M) in $\text{H}_2\text{O}:\text{DMSO}$ (8:2 v/v) and the filter paper cut into pieces and dipped in the probe solution and dried in air. After drying, the filter paper dipped in 1×10^{-5} M aluminium ion in water and monitored the changes.

3. Results and Discussion

The probe TQC preparation synthetic route is given below (Scheme 1), with this well-planned structure, we checked the TQC ability to sense Al^{3+} ions by the ICT mechanism.

3.1 Colorimetric response of probe

The naked eye recognition of metal be present inspected by means of probe TQC towards various cations (chloride salts) like Na^+ , Li^+ , Cs^+ , K^+ , Ag^+ , Ca^{2+} , Mg^{2+} , Co^{2+} , Fe^{2+} , Cu^{2+} , Ni^{2+} , Cd^{2+} , Al^{3+} , Zn^{2+} , Pb^{2+} and Hg^{2+}) in $\text{DMSO}:\text{H}_2\text{O}$ (2:8) ratio solution ($\text{pH}=7$). The recognizing ability of the probe through a colorimetric approach is distinct where the differences achieved in the sensing development effortlessly observed. As depicted in Figure 1, the TQC solution turned to bright yellow from colorless with the presence of Al^{3+} . Meanwhile, the other aforementioned cations did not yield any substantial color variations. The observed effects displayed TQC is exceptionally sensitive and selective towards aluminium ion over other cations tested.

3.2 UV-Vis absorption response

Visual detection experiment effects got for the probe towards aluminium ion additionally established through UV-Visible spectroscopic method. Sensing ability of TQC towards various cations like Na^+ , Li^+ , Cs^+ , K^+ , Ag^+ , Ca^{2+} , Mg^{2+} , Co^{2+} , Fe^{2+} , Cu^{2+} , Ni^{2+} , Cd^{2+} , Al^{3+} , Zn^{2+} , Pb^{2+} and Hg^{2+}) in $\text{DMSO}:\text{H}_2\text{O}$ (2:8) ratio solution. As shown in Figure 2, the electronic spectrum of TQC in $\text{DMSO}:\text{H}_2\text{O}$ (2:8) ratio solution exhibits no peaks at

wavelengths around 400 nm. Besides, there are no significant peaks above 400 nm, suggesting that the probe TQC retains the colorless form in the solution. However, the added Al^{3+} ions to a probe solution, the peak intensities at 400 nm range enhanced with concomitant enhancement of bright yellow color in the solution. The appearance of a fresh peak at 405 nm is owing to the formation of ICT in the probe TQC. Other above-mentioned cations, did not exhibit any substantial absorption and color variations of the probe TQC. The binding ability of TQC towards Al^{3+} was investigated by an absorption titration experiment. Upon adding of the gradual amount of Al^{3+} to a TQC in $\text{DMSO}:\text{H}_2\text{O}$ (2:8) ratio solution, the new peak at 405 nm was steadily enhanced and is shown in Figure 3. The new peak at 405 nm appeared in the UV-Vis titration experiment attributes to the formation of the complex between Al^{3+} and TQC. An intramolecular charge-transfer transition (ICT) phenomenon between the probe and Al^{3+} ion confirmed by the new peak appearance in the spectra with the added aluminium

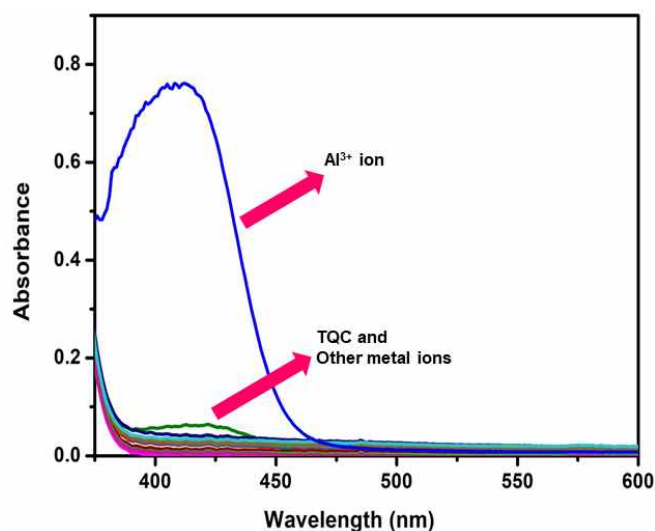


Figure 2. Electronic spectral changes of TQC in presence of different cations (10 μM).

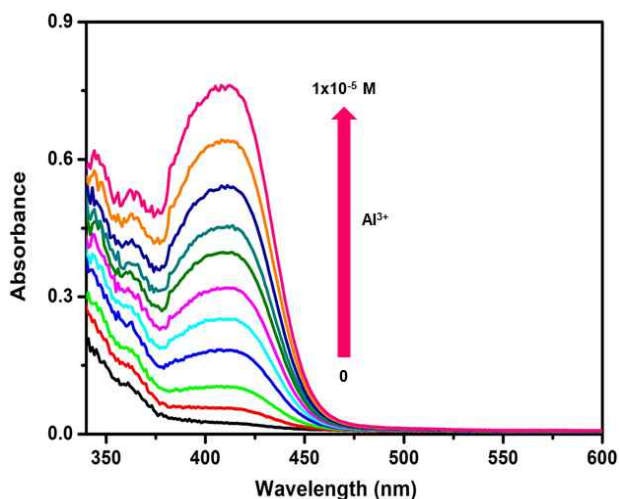


Figure 3. Electronic spectral changes of TQC [1×10^{-5} M] in DMSO:H₂O (2:8) ratio solution with added Al³⁺ ion [0- 1×10^{-5} M].

ion. To quantify the stoichiometric ratio between TQC and Al³⁺, a Job plot measurement was employed (Figure 4), and the molar fraction of $[Al^{3+}]/[TQC+Al^{3+}]$ was found to be 0.5, which indicates that the coordination ratio between TQC and Al³⁺ is approximately 1:1^{33,34}. Besides, the mass spectral data delivered added proof for the 1:1 compound of TQC-Al³⁺ ion.

3.3 Fluorometric study of probe TQC

An approach to determine the associations of probe TQC and Al³⁺ ion, fluorescence response monitored. The experiment was carried out to gain better insight into the sensing of TQC for Al³⁺, a fluorescence titration experiment was employed. With the gradual amounts of Al³⁺ addition to TQC, the new peak gradually grew at 452 nm (exciting at 350 nm). The fluorescence spectrum of TQC in DMSO:H₂O (2:8) ratio solution, the emission behavior of TQC performance checked towards sensing aluminium ion. By adding an increase in the concentration of Al³⁺, ion new peak developed at 452 nm gradually enhanced and the results obtained is shown in Figure 5. The data obtained from the fluorescence spectra, the binding constant can be calculated using the equation (1)³⁴ given below and was found as 1.45×10^5 M⁻¹ for the probe TQC-Al³⁺ complex and the plot found to be linear with $R^2 = 0.988$.

$$(F_x - F_0)/(F_x - F_0) = 1/K[Al^{3+}] \quad (1)$$

where,

F_x: The fluorescence intensities of the probe at a concentration

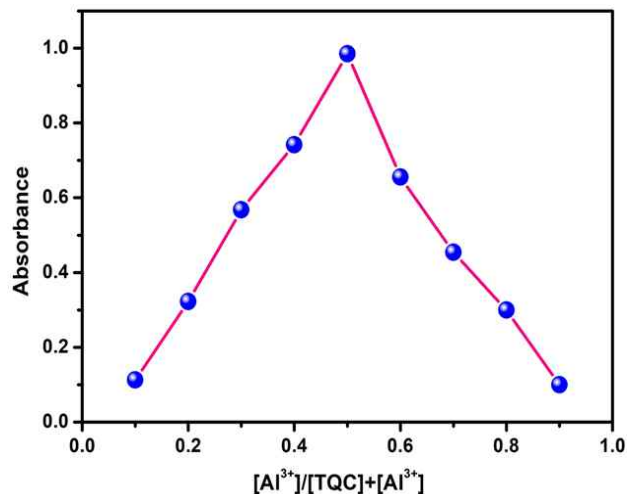


Figure 4. Job's plot of TQC with Al³⁺ ion.

for complete interaction of aluminium ion

F₀: The fluorescence intensities of the probe in the absence of aluminium ion

F_x: The fluorescence intensities of the probe at a given concentration of aluminium ion

K: The binding constant

3.4 Effect of pH in sensing TQC with Al³⁺

In this work the probe TQC sensing ability of aluminium ion in suitable pH determined by visual detection experiment. pH

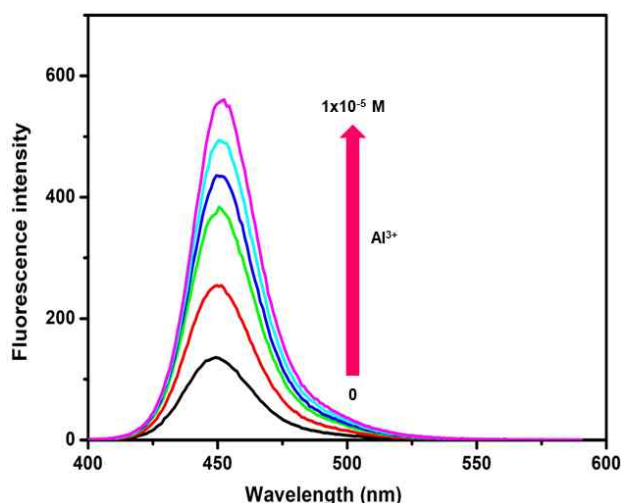


Figure 5. Fluorescence changes of TQC [1×10^{-5} M] in DMSO:H₂O (2:8) ratio solution with the increasing addition Al³⁺ ion [0- 1×10^{-5} M].



Figure 6. Effect of pH and color changes of TQC with and without Al^{3+} in normal light.

effect did to validate the practical utility of probe TQC as it plays a crucial role in determining target cation in bio-systems. TQC sample dissolved in different pH solution from 2-10 pH and shown in Figure 6 (top) the probe color at 8-10 pH changed to yellow this may be attributed to the deprotonation of NH group in the molecule TQC. With the added aluminium ion ($10 \mu\text{M}$) to the corresponding pH solution of TQC no noticeable color change appeared in pH 2 to 6 and 8 to 10 whereas a clear visible bright yellow color appeared in pH 7 of TQC solution the changes observed are shown in Figure 6 (bottom). Therefore the probe is suitable to detect aluminium ions in biological samples and water sources.

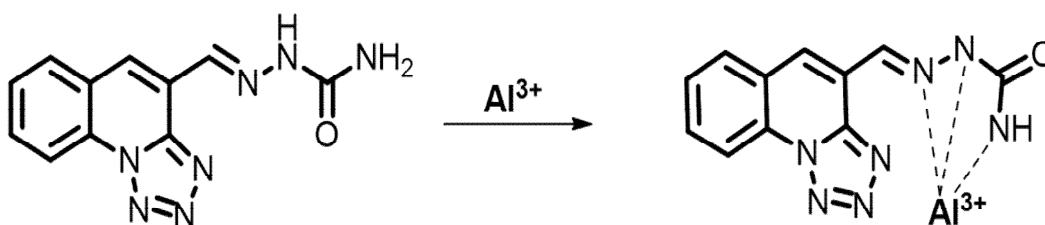
3.5 Study of binding mechanism

To know the proper sites of binding of TQC towards Al^{3+} , an ESI-mass study was done in methanol solvent. 1:1 ratio TQC

and Al^{3+} ion mixed and made a homogeneous mixture in methanol. The added Al^{3+} to the probe gives instant color to yellow from colorless. The interaction expected between Al^{3+} ion with TQC's -NH, imine N, and $-\text{NH}_2$ as illustrated in Scheme 2. An ESI-mass study done in methanol solvent observed a mass peak at 281.1 m/z for TQC- Al^{3+} established nicely as of our prediction. The ESI-mass results reveal that there is a chance of two nitrogen's from -NH, $-\text{NH}_2$ and the imine nitrogen participate in the co-ordination of aluminium ions and the result obtained is shown in Figure 7.

3.6 Practical application

Real-time recognizing properties of the probe TQC in water for the identifying of Al^{3+} ion. Test kit made using filter paper by dip-coating process. Probe solution prepared $\text{H}_2\text{O}:\text{DMSO}$ (8:2 v/v) and filter paper dipped in it and dried in air. The strip



Scheme 2. Probable binding mechanism for TQC with Al^{3+} .

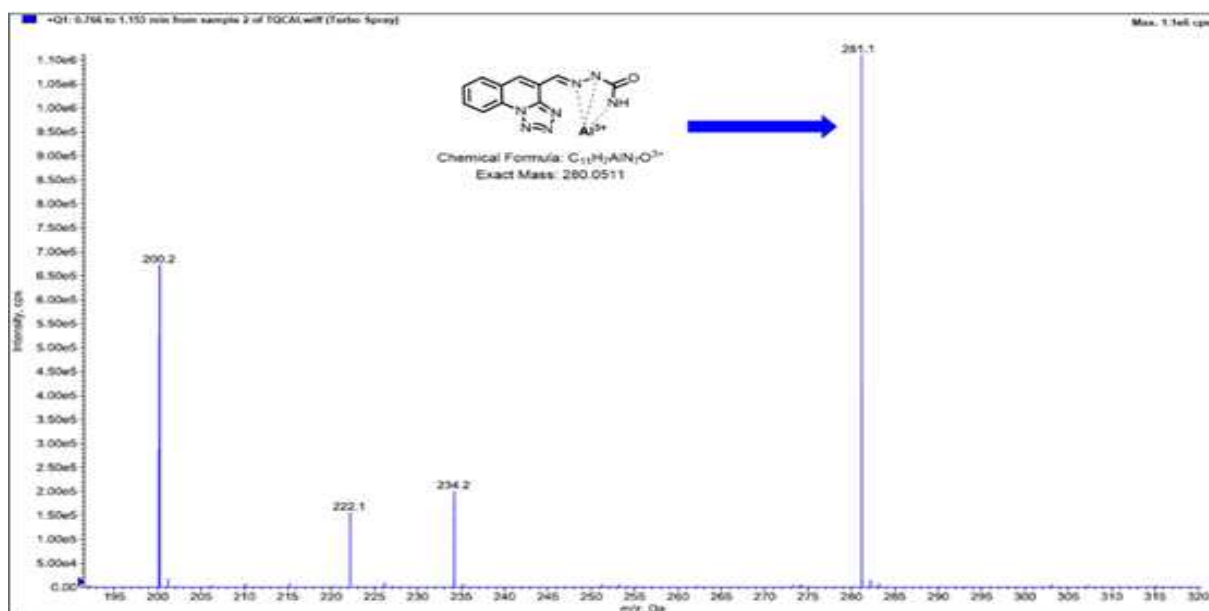


Figure 7. ESI-MS spectra of TQC-Al³⁺ complexes.

exhibited a bright yellow color from colorless after dipping in solution contains Al³⁺, the changes in test strip is seen clearly by the naked eye. Thus, probe TQC fit to be a powerful tool for Al³⁺ detection in daylight in the naked eye (Figure 8).

4. Conclusion

In summary, the synthesized new tetrazolo quinoline moiety fused with hydrazinecarboxamide TQC probe selectively senses

Al³⁺ via the ICT mechanism. The probe's effectiveness towards aluminium ion detection is highly sensitive and selective with no substantial interference with other competing ions. As well, TQC showed a kind of "OFF-ON" signal in the Colorimetric as well as the Fluorometric approach. Jobs plot discloses 1:1 binding stoichiometry between the probe and metal ion. The likely interaction of the probe with aluminium ion was also predicted from ESI-MS spectral analysis results. Additionally, a test kit made using TQC by dip-coating process to monitor the Al³⁺ ions for real-time detection in daylight in the naked eye with a visual color change in the strip.

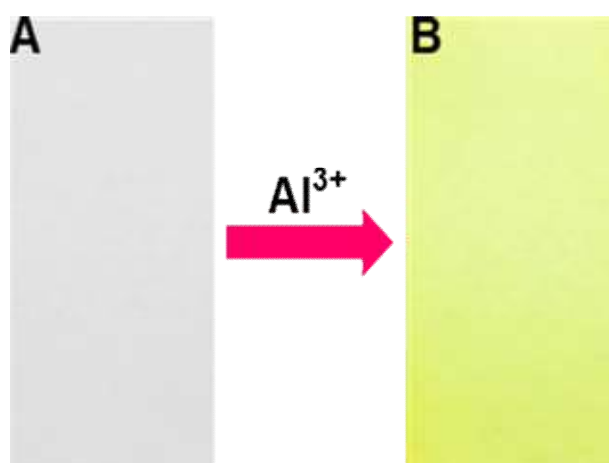


Figure 8. Color change of test strips of (A) only TQC and (B) with Al³⁺ ion in normal light.

Acknowledgements

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Authors

Ramalingam Manivannan Chungnam National University
Department of Advanced Organic Materials Engineering Student

Jiwon Ryu Chungnam National University
Department of Advanced Organic Materials Engineering Student

Young-A Son Chungnam National University
Department of Advanced Organic Materials Engineering Professor