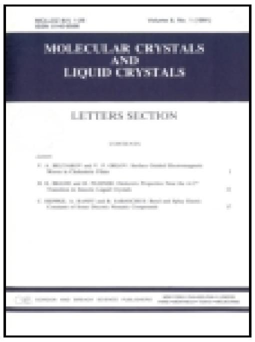

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Synthesis of Rhodamine-based Chemosensor and Determination of Spectral Properties

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A rhodamine-based fluorescent chemosensor (Rh6G-2HC) was synthesized easily by a one-step condensation reaction. The structure was characterized using NMR, MS and EA spectroscopies. As soon as Cu^{2+} *was added into the chemosensor solution, a color change from colorless to pink color was observed, and a considerable change in the absorption and fluorescence spectra. However, no spectral changes were indicated for other heavy metals such as* Ag^{+}, Zn^{2+}, Cd^{2+}, *and* $Co^{2+.}$ *In order to provide a more detailed metal sensing performance, the optical and structural properties for the* Cu^{2+} *sensing effect were investigated using UV-Vis, fluorescence and H-NMR spectroscopies.*

Keywords Rhodamine; chemosensor; fluorescence; energy transfer; Bing site; optical determination

Introduction

In recent years, highly sensitive and selective chemosensors have attracted considerable attention and displayed remarkable potential in various fields such as biological, environmental, nerve gas sensor or molecular device [1, 2].

Cu^{2+} is an essential trace element existing at low levels in cells, tissues and biological systems. However, copper can cause disorders associated with neurodegenerative diseases such as Alzheimer's, Wilson's, Menke's, Parkinson's disease [3]. Thus, fluorescence chemosensors detecting the copper ion have been extensively explored owing to this significance. Until recently, a number of the chemosensors for Cu^{2+} detection had been developed and the selectivity and efficiency should be continuously improved. Due to the paramagnetic effect of copper ions, some chemosensors often undergo fluorescence quenching upon binding of Cu^{2+} [4, 5].

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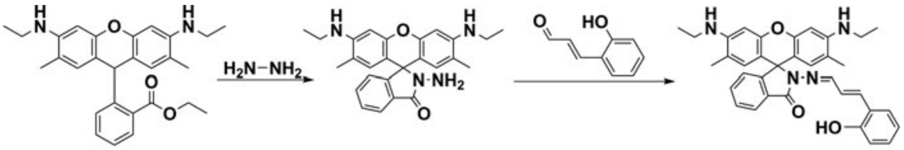

Scheme 1. Synthesis of a novel chemosensor (Rh6G-2HC) based on rhodamine 6G.

Rhodamine derivatives as a chomosensor sensing and detecting metal cation drew attention in the field of organic sensors by the outstanding advantages of their photophysical properties, such as long wavelength absorption and emission, high quantum yield, and large extinction coefficient [6]. The reaction mechanism between these rhodamine based fluorescent chemosensors having a spirolactam ring and metal cation is based on the structural change of the spirocyclic form [7]. Without cations, these chemosensors exist in a ring-closed form (colorless, non-fluorescent). The ring-opening effect by addition of metal cation was caused with a strong fluorescence emission change. Well-known by their specific spectroscopic properties, rhodamine derivatives are excellent candidates for the design of sensors to detect a variety of metal cations [8].

In this paper, a novel rhodamine derivative (Rh6G-2HC) was synthesized containing a 2-hydroxy cinnamaldehyde moiety. The structure of Rh6G-2HC was characterized using H-NMR, MS, and EA, and its optical properties were measured using UV-Visible and fluorescence spectroscopies.

Experimental

All solvents were technical grade unless otherwise specified and were used as obtained. Distilled water was used for all experiments. All inorganic materials (Sigma-Aldrich), namely, $Cu(NO_2)_2$, $Cd(NO_2)_2$, $Co(NO_2)_2$, $Ca(NO_2)_2$, $LiNO_2$, KNO_2, $AgNO_2$, $Ni(NO_2)_2$, and $Zn(NO_2)_2$, were used as obtained without modification. All reactions were monitored by performing thin-layer chromatography (TLC). Merck silica gel sheets (silica gel 60 F254) were used for the diagnostic TLC. Mass spectrometric analyses were performed on a mass spectrometer. Nuclear magnetic resonance spectra (1H-NMR) were collected on Bruker DPX-300 and Bruker AMX-500 FT-NMR spectrometers at 500 MHz and 700 MHz, respectively. All absorption spectra were recorded with a SHIMADZU-UV-3101PC UV–Vis-NIR-Scanning spectrophotometer. All fluorescence measurements were carried out on a PERKIN ELMER luminescence spectrometer.

Measurement of Absorption and Fluorescence Spectra

To measure the optical properties of the chemosensors, all chemosensor solutions were prepared with concentrations of 1.0×10^{-4} M in acetonitrile. After the addition of various metal ions (1.0×10^{-3} M) to the probe solutions, the UV-vis absorption and fluorescence emission were measured.

Measurement of Job's Plot

To determine the stoichiometric properties associated with each metal complex, a series of synthetic chemosensor/metal complexes were examined. For this purpose, equimolar solutions of probes and various metal cations were mixed in different volume ratios (0:10, 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1, 10:0). The resulting solutions were characterized at maximum absorption.

Measurements of ^{1}H-NMR Spectra Change by Variation of Amount for Cu^{2+}

In order to identify the metal binding position, when Cu^{2+} of various concentrations were added in Rh6G-2HC solution in CD_3CN, the change of ^{1}H-NMR spectrum was determined.

Synthesis

Synthesis of Rh6G-hydrazide. To a dissolved solution of rhodamine 6G (2.4 g, 5.01 mmol) in absolute ethanol (60 mL), hydrazine monohydrate (6.40 ml, 131.66 mmol) was added dropwise at room temperature for 40 min, after which the reaction mixture was refluxed for 24 h. Once the reflux was complete, the mixture was cooled, filtered, and washed with ethanol. Subsequent drying under reduced pressure yielded Rh6G-hydrazide (1.84 g, 85%) as a pink solid. This material was used in the next reaction without purification.

^{1}H-NMR (500 MHz, DMSO-d_6) δ 1.18–1.21(t, 6H), 1.85(6H, s), 3.03–3.13(q, 4H), 4.19(2H, s), 4.96–4.98(2H, t), 6.08(2H, s), 6.90(2H, s), 6.90–6.93 (1H, m), 7.43–7.47(2H, m), 7.73–7.76(1H, m).

$$\mathrm{EI-MS}: m/z = 428$$

Synthesis of Rh6G-2HC. Rh6G-hydrazide (0.2 g, 0.47 mmol) was dissolved in 10 ml of chloroform, and then 2-hydroxy cinnamaldehyde (0.08 g, 0.56 mmol) was added. It was then refluxed for 8 h, the reaction mixture was cooled to room temperature, filtered, and washed with chloroform. The crude product was stirred in acetone and filtered twice to yield Rh6G-2HC (0.1 g, 38.3%) as a colorless solid.

^{1}H-NMR (500 MHz, DMSO-d_6) δ 1.18–1.20(6H, t), 1.84(6H, s), 3.09–3.15(4H, m), 5.03(2H, s), 4.96–4.98(2H, t), 6.15(2H, s), 6.30(2H, s), 6.70–6.75 (2H, m), 6.80–6.82(1H, d), 6.88–6.91(1H, d), 6.93–6.95(1H, d), 7.06–7.09(1H, t), 7.43–7.45(1H, dd), 7.48–7.54(2H, m), 7.83–7.85(1H, d), 8.48–8.50(1H, d), 10.01(1H, s).

EI-MS: $m/z = 558$; HR-MS(EI) calcd for $C_{35}H_{34}N_4O_3$[M^+]558.2631, found 558.2635

EA(elemental analysis) : calcd for $C_{35}H_{34}N_4O_3$ C : 75.25; H : 6.13; N : 10.03, found C : 73.08; H : 6.06; N : 9.85

Results and Discussion

No obvious absorbance and fluorescence emission of Rh6G-2HC in acetonitrile solution was observed. However, after addition of a variety of metal cations to the solution of the chemosensor, the absorbance and fluorescence band at nearby 550 nm for Cu^{2+} over other metal cation appeared to increase of intensity, which is attributed to opening of the spirolactam ring in the rhodamine moiety by Cu^{2+}. Weak spectral changes after the addition of metal cations such as Ag^+, Ca^{2+}, Cd^{2+}, Co^{2+}, K^+, Ni^{2+}, Li^{2+}, and Zn^{2+} were indicated under identical conditions (Figs 1a and 1b).

However, the spectral changes were negligible. In addition, a color change from colorless to a purple color with increasing intensity could be easily observed (Fig. 2). UV-Vis and fluorescence results suggest that Rh6G-2HC is suitable for selective and sensitive detection towards Cu^{2+} over others cations.

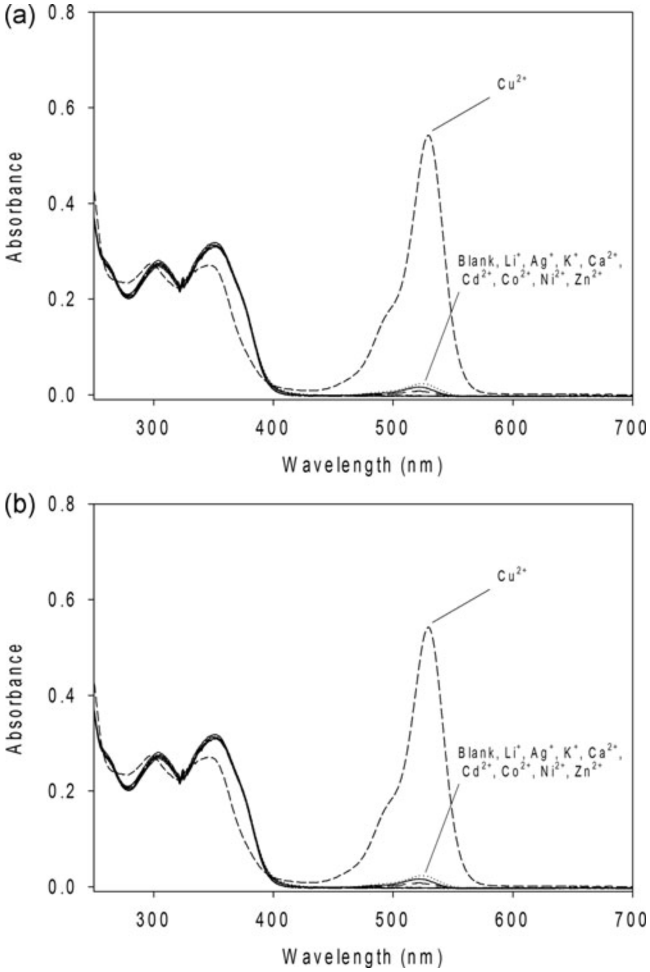

Figure 1. Absorption (a) and fluorescence (b) spectra of Rh6G-2HC solution in the presence of a variety of metal cations.

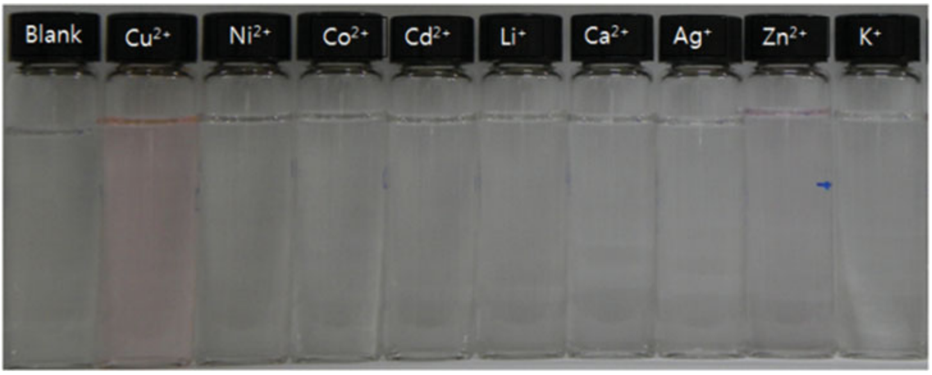

Figure 2. Photograph of Rh6G-2HC after addition of various metal cations in acetonitrile solution.

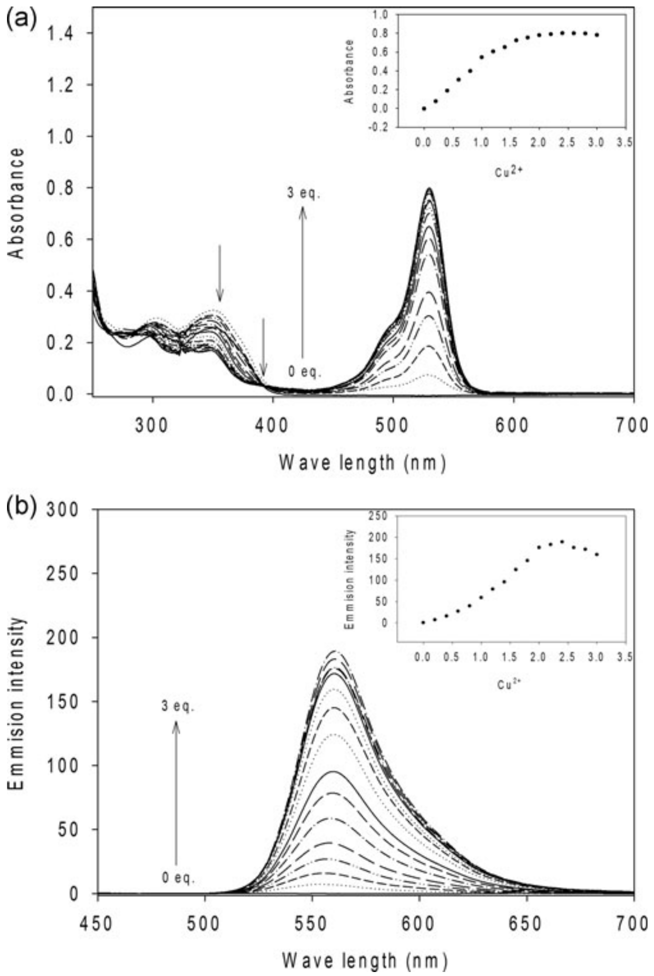

Figure 3. UV-Visible (a), and fluorescence (b) spectral changes of Rh6G-2HC in accordance with increasing amounts of Cu^{2+} in acetonitrile solution. Inset; the plot of the absorbance and fluorescence in the presence of different concentrations of Cu^{2+}.

In order to investigate the spectral change with concentration of Cu^{2+} [9, 10], titration experiments for Cu^{2+} were carried out. As shown in Fig. 3a, when a Cu^{2+} to sensor solution at 3 equivalents was prepared, the original absorption peak of Rh6G-2HC at 385 nm disappeared and the appearance of a new band and an isosbestic point at 528 and 391 nm was indicated with an increase in the concentration of Cu^{2+}. Furthermore, the intensity was gradually enhanced up to 2 equivalents and then reached equilibrium. While the fluorescence titration was similar to the results of the absorption titration, the intensity was decreased gradually after Cu^{2+} at 2 equivalents was added (Fig. 3b). On the basis of the titration experiments, the appearance of the isosbestic point and intensity increase according to amount of Cu^{2+} showed that Rh6G-2HC forms a particular complex in accordance with the presence or absence of Cu^{2+} [11].

The selectivity of the chemosensor is the important parameter to determine performance as a chemsensor. Therefore, detection performance in accordance with coexisting metal

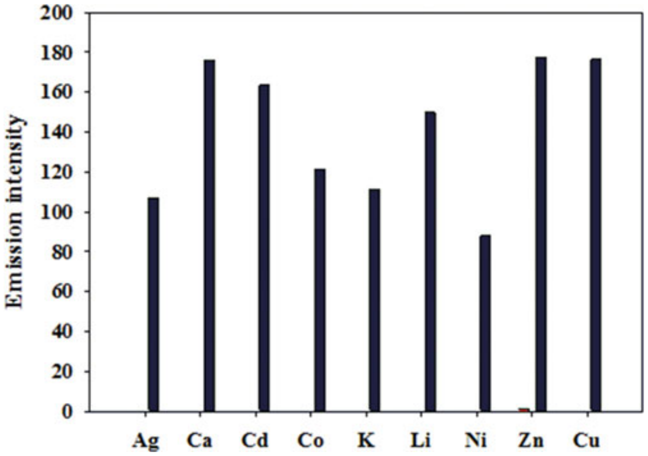

Figure 4. Comparison of fluorescence intensity changes of Rh6G-2HC when both metal cations coexisted.

cations was investigated [12]. As shown Fig. 4, when compared with a standard without other metal ions besides Cu^{2+}, no variation of the intensity ratio of metal ions such as Ca^{2+}, Cd^{2+}, Zn^{2+}, and Li^{+} was found. However, the remaining ions were decreased by about 25%. These results show that metal ions such as Ag^{+}, K^{+}, and Ni^{2+} disrupt the binding reaction of the chemosensor to Cu^{2+}. Job's plot method in order to determine the binding ratio of chemosensor for Cu^{2+} was utilized. The binding stoichiometry of Rh6G-2HC-Cu^{2+} revealed formation of a complex with a 1 : 1 stoichiometry (as shown in Fig. 5) [13, 14].

A change in the 1H-NMR spectra for the Rh6G-2HC + Cu^{2+} complex in CD_3CN solution was observed in accordance with variation of Cu^{2+} concentration. The complex demonstrated its specific structural changes by interaction with Cu^{2+}. All of the proton peaks of the chemosensor were broadened as displayed in Fig. 6 after addition of Cu^{2+}. The proton peaks of the hydrogen atom in the hydroxyl group of the cinnamaldehyde moiety and the

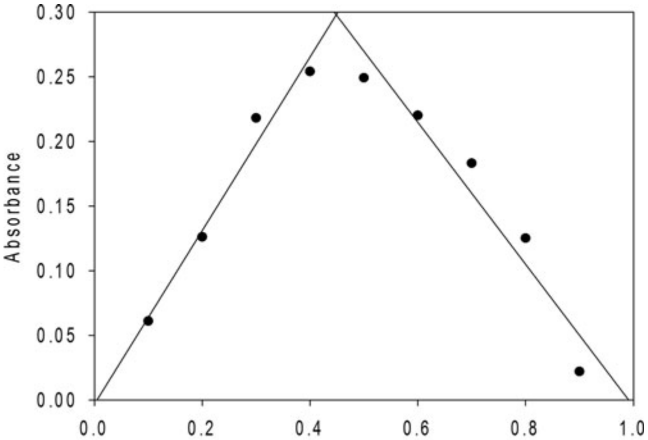

Figure 5. Job's plot method in order to determine the stoichiometry of Rh6G-2HC and Cu^{2+}.

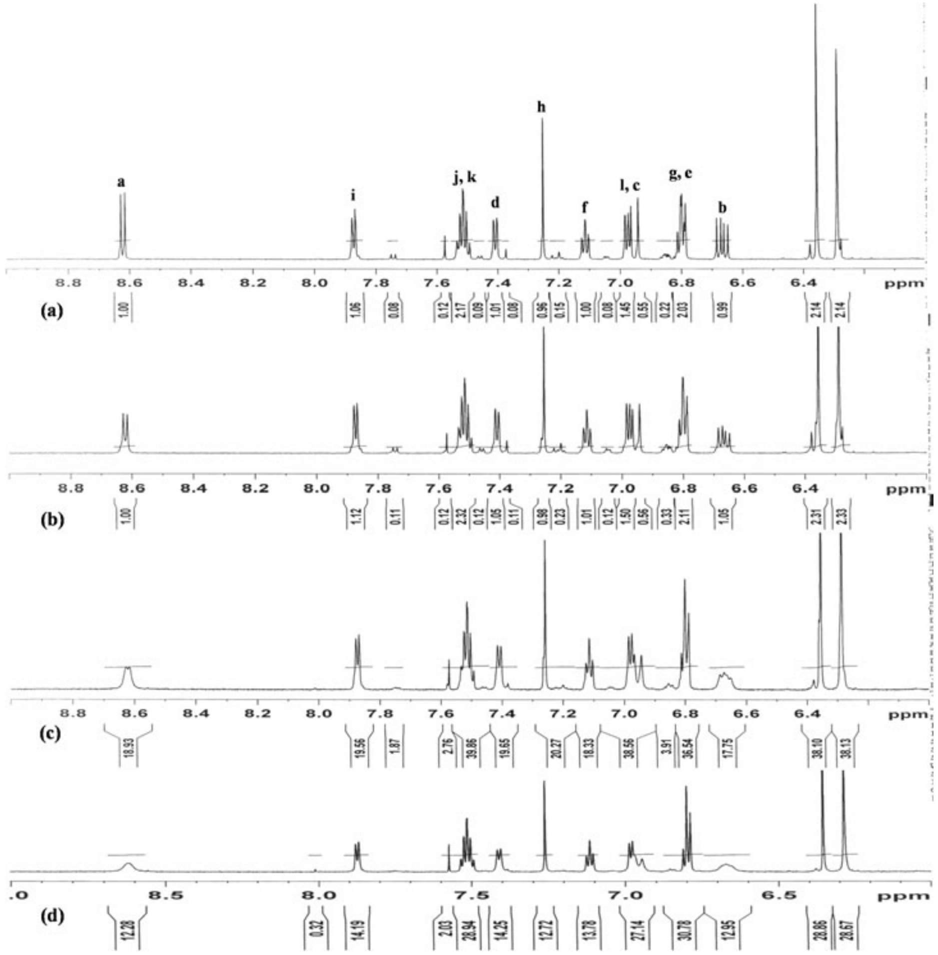

Figure 6. ^{1}H NMR spectra of Rh6G-2HC with Cu^{2+} in CD_3CN. Rh6G-2HC only (a), Rh6G-2HC + 0.2 equivalent of Cu^{2+} (b), Rh6G-2HC + 0.5 equivalent of Cu^{2+} (c), and Rh6G-2HC + 1.0 equivalent of Cu^{2+} (d).

hydrogen atom in the vinyl group of the cinnamaldehyde moiety were especially changed and more so than the others. Therefore, formation of the binding reaction of Rh6G-2HC to Cu^{2+} was considered to be created at the space between the phenol in the rhodamine moiety and the hydroxyl group in the cinnamaldehyde moiety. On the other hand, the Cu^{2+} + sensor complex is likely to chelate via the carbonyl O atom of the rhodamine moiety and phenol H atom of the cinnamaldehyde moiety [3, 11, 15]. Moreover, as shown in Fig. 6, using Job's plot data and ^{1}H-NMR spectra, the combined structural shape of Rh6G-2HC to Cu^{2+} could be predicted.

In order to apply to a practical application, a portable test kit for detecting Cu^{2+} was prepared by immersing filter papers into the solution of Rh6G-2HC and then drying in the air. The prepared test kit was utilized to sense various cations. The obvious color change for the Cu^{2+} solution was the only one observed, while any change for the other metal ions solutions was not observed (as shown in Fig. 7). Therefore, Rh6G-2HC is a useful probe as the simple detection kit for Cu^{2+}.

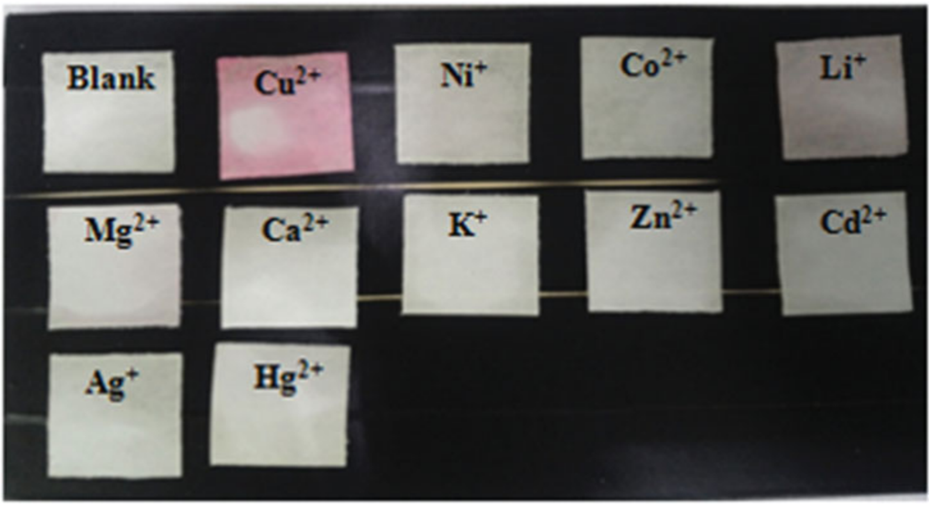

Figure 7. Photographs of the test kit for detecting Cu^{2+}.

Conclusions

A novel fluorescence chemosensor Rh6G-2HC was designed and synthesized. The sensor was able to sensitively and selectively sense Cu^{2+} over other cations. Considerable fluorescence and absorption enhancements after addition of Cu^{2+} were indicated. Also, an explicit color change was easily observed by the naked eye. The binding mode of this chemosensor with Cu^{2+} revealed a 1 : 1 ratio using the Job's plot method. Furthermore, information for the binding location of between the chemosensor and Cu^{2+} was obtained through ^{1}H-NMR spectra and metal complexation. This was predicted to be formed by reaction with Cu^{2+} between carbonyl O and hydroxyl OH. Also, performance as a portable detection kit for Cu^{2+} was demonstrated.

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