

Hybrid polymeric chemosensor bearing rhodamine derivative prepared by sol-gel technique for selective detection of Fe³⁺ ion

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ABSTRACT

To develop a reusable and selective colorimetric chemosensor for visual detection of ferric ion, a new rhodamine-based chelator (RB-UTES) was prepared. The structural constitution and sensing property of RB-UTES were examined. The chelator was sensitive and selective for recognition of ferric ion and could be covalently attached to poly(vinyl alcohol) through siloxane linkage formed by the sol-gel reaction. The physicochemical properties and sensing behavior of the functional chemosensor films were investigated. By simply soaking in aqueous media, the free-standing sensor film exhibited high selectivity and sensitivity to ferric ion and permitted the convenient detection by naked eye with prominent development of pink color throughout the film. The sensor film could return to its original color by washing with 0.1 M ethylenediamine allowing repeated cycles of detection. The combination of its analytical performance, simplicity of operation as well as reusability made this functional sensor promising for the use in aqueous solutions and real samples.

1. Introduction

The development of new colorimetric chemosensors for visual detection of heavy metal ions has attracted considerable attention due to their important roles in biological systems and extreme impacts on the environment. Among the transition metal ions, iron is an essential component in several biochemical processes, for example, in cellular metabolism and transportation of oxygen. Estimates of the minimum dietary intake for iron depend on age, gender, activity, physiological status, and iron bioavailability. Overdose or deficiency of iron results in serious abnormal functions of body system and induces a variety of diseases, such as cancer, anemia, Parkinson and Alzheimer [1,2]. Therefore, investigations have been devoted to selective and effective monitoring of iron content in water and environmental system.

Instrumental analytical methods including atomic absorption spectroscopy (AAs), inductively coupled plasma mass spectrometry (ICPMS) and electrochemical analysis have been developed for the analysis and detection of metal ions, however, these complicated techniques require expensive instruments, sample pretreatment and also specially trained operators. Comparing with the sophisticated instrumentation, colorimetric assays using specific chemosensors have been proven to be the promising alternatives to due to their simplicity, low cost, real-time

monitoring, easy detection by naked eye, high sensitivity and selectivity [3–7].

Rhodamine dye and its derivatives have drawn great interest over the last two decades owing to their particular structural properties and excellent spectroscopic properties [8–10]. The selective ring-opening reaction of rhodamine B derivative for heavy metal ion in water has been reported by Dujols et al. since 1997 [11]. Cyclic lactam structures of rhodamine derivatives are colorless, whereas the ring opening upon binding with specific metal ions results in unique color changes. The utilization of these compounds as molecular chemosensors dissolved in aqueous and organic media has been extensively investigated [12–16]. One drawback of these designed molecular sensors arises from the difference in solubility between the sensor and the target analyte. Furthermore, the separation of used sensor requires further treatment, as a result, they are only suitable for single use. In order to overcome these inconveniences, optical polymeric chemosensors fabricated by incorporation of specific molecular sensors into functional polymers have been designed and investigated [17–19]. The covalent bonding between the sensor molecule and the crosslinked polymer provides stability to solvents and improves environmental stability. The obtained solid-state sensors possess favorable properties for detection of metal ions, as the on-site and naked eye detection can be performed with

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simplicity, high efficiency, and reusability [19–23].

Poly(vinyl alcohol), PVOH, is one of the intensively used polymers due to its good chemical stability, processability, and biocompatibility. However, PVOH exhibits dissolution behavior and poor stability in aqueous solution. Chemical crosslinking is generally used to enhance its water resistance and mechanical properties [24]. The sol-gel reaction is an alternative route for the preparation of hybrid inorganic-crosslinked polymeric materials. The process provides advantages of mild condition, simplicity and a wide range of possibility to control properties of the materials by altering organic-inorganic ratio and various reaction parameters. The final product of three-dimensional network containing siloxane linkage can be fabricated by covalent coupling between the organic polymer molecule and the inorganic compound through hydrolysis and condensation reactions [25–29]. The obtained hybrid materials have attracted considerable interests because they exhibit a unique combination of both organic and inorganic components. PVOH containing numerous hydroxyl functional groups can be designed and hybridized by the sol-gel technique to fabricate hybrid materials for a wide variety of applications [29–31].

In this study, we report a reusable polymeric chemosensor film containing rhodamine derivative for colorimetric detection of ferric ion. Firstly, a rhodamine B derivative, RB-UTES, was prepared and characterized by FTIR and NMR spectroscopy. The sensing and optical properties of RB-UTES as a specific chelator for Fe^{3+} ion were evaluated in terms of selectivity and competition by UV–vis spectroscopy and naked eye detection. Then, RB-UTES component with efficient sensor features was attached to PVOH network by the sol-gel method to obtain a novel hybrid chemosensor film. This free-standing film exhibited a unique color change upon binding with Fe^{3+} ion and could be conveniently used in environmental field as a naked eye indicator. The preparation, characterization, sensing performance and reusability of the fabricated hybrid PVOH chemosensor were discussed in detail.

2. Experimental

2.1. Materials

All reagents were purchased from commercial suppliers and used as received. AR grade reagents for synthesis were obtained from Merck, including rhodamine B (RB), ethylene diamine, triethyl amine,

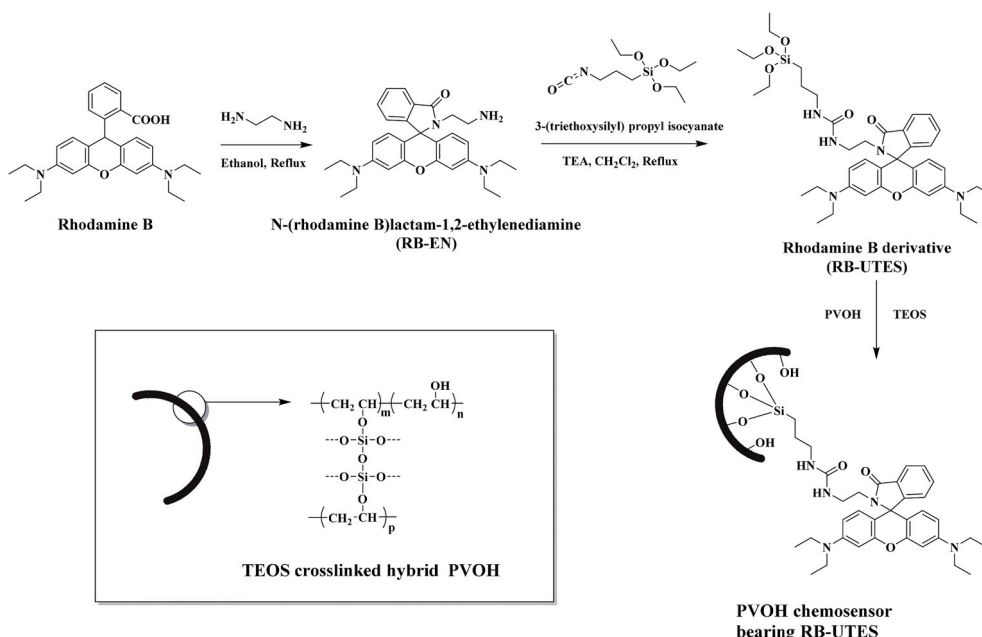
tetraethyl orthosilicate (TEOS) and poly(vinyl alcohol) (PVOH): 98% hydrolysis, MW 89,000–98,000. Triethoxysilyl propylisocyanate (ICPTES), a silane coupling agent, was from Tokyo Chemistry Industry. Organic solvents, triethyl amine (TEA), dimethyl sulfoxide (DMSO), dichloromethane, ethanol (EtOH) and acetone, were supplied by QReC. The salts used for preparation of metal ion stock solutions were NaCl, KCl, AgCl, MnCl_2 , MgCl_2 , NiCl_2 , CaCl_2 , CuCl_2 , ZnCl_2 , PbCl_2 , HgCl_2 , CrCl_3 , AlCl_3 and FeCl_3 .

2.2. Synthesis of rhodamine derivative (RB-UTES)

The rhodamine derivative, RB-UTES, was prepared by a two-step procedure as shown in Scheme 1. Firstly, RB (1.0 mmol) in absolute ethanol (5.0 mL) and ethylene diamine (0.5 mL) were charged into a round-bottomed flask and refluxed for 6 h under nitrogen atmosphere. The solvent was removed by evaporation and the obtained solid was purified by silica-gel column chromatography using CH_2Cl_2 :EtOH (95:5/v:v) as a solvent to afford pale pink solid of *N*-(rhodamine B) lactam-1,2-ethylenediamine (RB-EN). Next, RB-UTES was obtained by condensation of RB-EN and ICPTES. A mixture of RB-EN (1.0 mmol), ICPTES (1.0 mmol), TEA (2.0 mmol) and dried CH_2Cl_2 (5.0 mL) was refluxed under nitrogen atmosphere for 24 h. The organic solvent was removed and the crude product was purified by silica-gel column chromatography using CH_2Cl_2 :EtOH (95:5/v:v) as an eluent to give pale yellow solid (RB-UTES) with 93% yield.

2.3. Synthesis of hybrid poly(vinyl alcohol) chemosensor bearing RB-UTES

Firstly, the optimization of sol-gel process was carried out by varying the ratio between polymeric component and metal-organic alkoxide. The three-dimensional network films containing siloxane linkage were fabricated. Then, the hybrid PVOH films bearing various contents of RB-UTES ligand were prepared by the optimized reaction using components listed in Table 1. A solution of PVOH was prepared in DMSO, followed by a dropwise addition of distilled water and EtOH. After 30 min stirring, a desired amount of TEOS was slowly charged into the mixture, followed by an addition of RB-UTES solution in DMSO (0.5 mL). The mixture was kept under magnetic stirring for 12 h. The obtained homogeneous solution was cast on plastic molds and heated in a hot air



Scheme 1. Synthesis of rhodamine derivatives and hybrid chemosensor film.

Table 1

Notation and composition of different silica-PVOH hybrid films.

Sample code	PVOH (g)	DMSO (mL)	Sol-gel component			RB-UTES (g)
			TEOS (μL)	EtOH (mL)	H ₂ O (mL)	
PV	1.5	20.0	–	–	–	–
PV-1TE	1.5	20.0	15	0.3	0.5	–
PV-3TE	1.5	20.0	45	0.9	1.5	–
PV-5TE	1.5	20.0	75	1.5	2.5	–
PV-3TE-S10	1.5	20.0	45	0.9	1.5	0.10
PV-3TE-S15	1.5	20.0	45	0.9	1.5	0.15
PV-3TE-S20	1.5	20.0	45	0.9	1.5	0.20

oven at 80 °C for 24 h. The obtained hybrid chemosensor films (PV-TE-S) were stored in a desiccator until further use.

2.4. Characterization

¹H NMR spectra were recorded on a 400 MHz NMR spectrometer (Bruker, Advance Ultrashield). ATR-FTIR spectra were collected by a PerkinElmer Frontier instrument. UV-vis absorption spectra were obtained using Shimadzu UV-2600 spectrophotometer. Thermogravimetric analysis was tested on a Mettler Toledo TGA/SDTA 851 instrument.

3. Results and discussion

3.1. Synthesis and characterization of rhodamine B derivative (RB-UTES)

Firstly, the spirolactam-rhodamine B was synthesized via amidation between carboxylic acid group of RB and ethylene diamine, yielding RB-EN as pale pink solid with 98% yield. Next, rhodamine B derivative containing ethoxysilyl groups (RB-UTES) was obtained through the condensation reaction between an isocyanate group of ICPTES and an amine functionality of RB-EN. The pale-yellow product was obtained with a relatively good yield (93%). The overall synthesis route is shown in Scheme 1.

The molecular functionalities of RB-EN and RB-UTES were confirmed by ATR-FTIR (Fig. 1(a)). Comparing the spectrum of starting material, RB, with those of RB-EN and RB-UTES, it was observed that the strong carbonyl vibration band at 1590 cm⁻¹ of RB disappeared after amidation. The new characteristic peaks of RB-EN at 800, 1620, 1690 and 2970 cm⁻¹ that belonged to N–H out of plane bending, N–H bending of primary amine, C=O stretching of lactam and C–H stretching of methylene group appeared as an evidence of success in preparing the rhodamine B spirolactam product [16,19]. The spectrum of RB-UTES shows absorption bands around 1684, 1616, 1218, 1080 and 956 cm⁻¹ which can be attributed to the C=O stretching, N–H bending, C–O stretching, Si–O asymmetric vibration and Si–O symmetric vibration. The band ranging from 3200 to 3500 cm⁻¹ can be assigned to the silanol group (Si–OH) and the absorbed water on the surface [32,33]. The structures of RB-EN and RB-UTES were also confirmed by ¹H NMR and ¹³C NMR spectra. The results are shown in supplementary data (Figs. S1–S3), respectively. The characteristic signal corresponding to urea linkage was observed in the spectrum of RB-UTES confirming that RB-EN successfully reacted with ICPTES and RB-UTES ligand was produced.

3.2. Sensing properties of RB-UTES

3.2.1. Selectivity of RB-UTES

The selectivity of RB-UTES toward various cations, Na⁺, K⁺, Ag⁺,

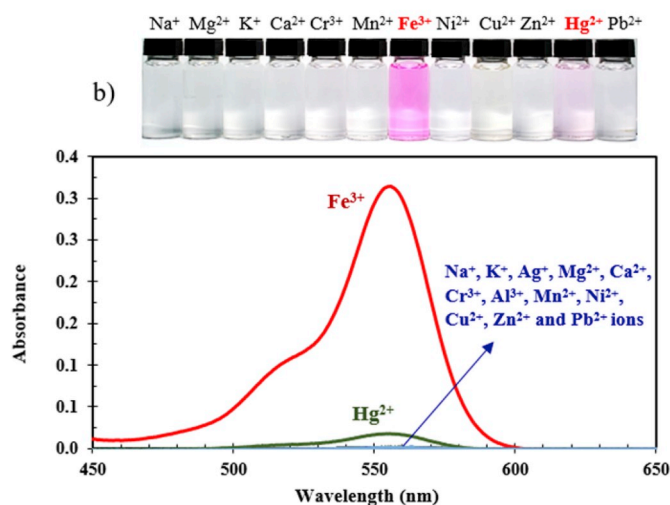
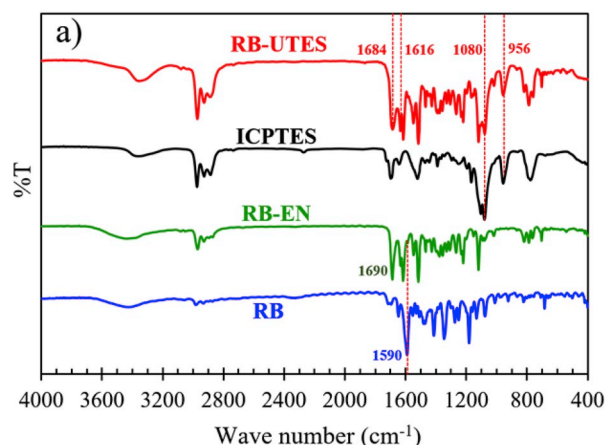


Fig. 1. (a) ATR-FTIR spectra of ICPTES, rhodamine B and its derivatives, (b) color change under natural light and UV-vis spectra of RB-UTES in the presence of various cations. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Mg²⁺, Ca²⁺, Mn²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Hg²⁺, Cr³⁺, Al³⁺ and Fe³⁺ ions was investigated by naked eye and UV-vis absorption. To obtain a complex solution of RB-UTES-metal ion, 1 mL of each metal solution (1 × 10⁻³ M) in acetone:H₂O (95:5/v:v) was added to a volumetric flask (10 mL) containing RB-UTES solution in acetone (1 mL, 1 × 10⁻⁴ M) and the final volume was adjusted with acetone:H₂O (95:5/v:v). The free RB-UTES in acetone was colorless as it was in a ring-closed form. A distinct color change of RB-UTES solution from colorless to pink was observed by naked eye with the addition of Fe³⁺ ion while a change with much less intensity was seen with the addition of Hg²⁺ ion. Other metal ions did not give rise to a color change. Corresponding results were shown in UV-vis absorption spectra (Fig. 1(b)). Only Fe³⁺ ion induced strong absorbance near 556 nm. The solution containing Hg²⁺ and RB-UTES exhibited a weak response, while other ions did not promote signal. This observation confirmed the formation of ring-opened RB-UTES as a result of the selectivity of the RB-UTES ligand toward Fe³⁺ ion.

In order to gain more insight into the sensing properties of RB-UTES, competitive experiments were performed by mixing RB-UTES solution with 10 equivalents of Fe³⁺ ion, then the obtained RB-UTES-Fe³⁺ complex was treated with 10 equivalents of a competitive ion of interest (Na⁺, K⁺, Mg²⁺, Ca²⁺, Cr³⁺, Mn²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Hg²⁺ and Pb²⁺). As shown in Fig. 2, Hg²⁺ ion showed a weak disturbance effect on absorbance of detection at 556 nm, whereas other coexisting ions exhibited negligible interference with the detection of Fe³⁺ ion in acetone:H₂O (95:5/v:v). This result confirmed that RB-UTES could be used as a

potential selective chemosensor for monitoring of Fe^{3+} ion over various metal ions.

3.2.2. Effect of pH

To investigate the effect of pH on sensing behavior of RB-UTES and find a pH range suitable for further investigation, the UV–vis spectra of RB-UTES in acetone:H₂O (95:5/v:v) were obtained by acid-base titration. The absorbance responses at 556 nm in different pH surroundings were recorded and shown in Fig. 3(a). It was clear that the free RB-UTES ligand did not produce distinct absorbance characteristic in the pH range of 4.5–7.5. Below pH 4.5 the sensing increased along with an obvious color change of solution which was attributed to the ring-opening of spiro lactam structure (Fig. 3(b)) [1,34]. Therefore, subsequent investigations on metal ion detection ability of RB-UTES were done in a controlled environment with pH value higher than 4.5.

3.2.3. Response time

To evaluate the respond time of RB-UTES toward Fe^{3+} ion, a mixed solution of acetone:H₂O (95:5/v:v) containing RB-UTES (1×10^{-4} M) and Fe^{3+} ion (1×10^{-3} M) was prepared and monitored the changes in UV–vis absorption spectra with time. It can be seen from Fig. 3(c and d) that the absorbance intensity at 556 nm increased with time and reached equilibrium after 120 min. Therefore, further investigation on sensing of RB-UTES was performed using a duration of 120 min chelation time to allow a stable signal.

3.2.4. Effect of ion concentration

In order to explore the possible application of RB-UTES as a colorimetric chemosensor for Fe^{3+} ion, the absorption titration experiment was carried out in acetone:H₂O (95:5/v:v) solution. The digital photo of RB-UTES- Fe^{3+} solutions taken under normal light shows that the color intensity of complex sensor significantly enhanced with increasing concentration of Fe^{3+} ion (Fig. 4(a)). The detection limit observed by naked eye was approximately 20 μM . From the UV–vis spectra in visible region, it was proven that RB-UTES sensor exhibited very good sensitivity toward Fe^{3+} ion, Fig. 4(b). The maximum absorbance intensity centered at 556 nm was 0.28 with an approximate linear respond in the range of 0–100 μM , Fig. 4(c).

3.2.5. Binding stoichiometry of RB-UTES and Fe^{3+} ion

The stoichiometric binding ratio between RB-UTES and Fe^{3+} ion was also studied by the method of continuous variation, Job's method [35, 36]. As shown in Fig. 5(a), the Job's plot was established using changes of absorbance intensity at 556 nm as a function of molar fraction of Fe^{3+} ion in a solution of Fe^{3+} and RB-UTES. The maximum absorption intensity appeared at 0.5 mol fraction indicated the stoichiometric formation of a 1:1 complex between Fe^{3+} ion and RB-UTES. Accordingly, the complex structure was proposed in Fig. 5(b). The suggested mechanism based on the switch off/on of the spirocyclic structure upon coordination with Fe^{3+} ion. The selectivity was probably due to the cooperation of several combined factors, such as the proper coordination structure and the suitable radius and charge density of the ion. The opening of the spiro lactam ring upon coordination with Fe^{3+} ion could be due to the binding sites from the oxygen atom of amide carbonyl and the two nitrogen atoms of urea [34]. The supporting mechanisms corresponding to our work have been reported [4,6,12,15].

According to all findings, RB-UTES, the molecular chemosensor synthesized in this work, exhibited pronounced selectivity and sensitivity as a naked eye colorimetric sensor for detection of Fe^{3+} ion. However, one limitation for the sensor application arises from the difference in solubility between the ions and the molecular sensor. Fe^{3+} ion is usually found in an aqueous medium, in which the sensor cannot be directly dissolved. In order to deal with this drawback, several researches have been reported attempting to attach the molecular sensors into polymeric substrates [37,38]. The fabricated polymer based sensors exhibited outstanding sensitivity inherited from the ligand molecules and could be repeated used as potential probes for detection of metal ions. In this study, a reusable RB-UTES-containing hybrid poly(vinyl alcohol) sensor was prepared and investigated.

3.3. Synthesis and characterization of hybrid PVOH films (PV-TE)

In order to optimize the synthesis composition, three hybrid PVOH samples containing different degree of siloxane linkage were fabricated by the sol-gel process using starting components given in Table 1. Two reactions proceeding in the process were hydrolysis and condensation [27].

Hydrolysis:

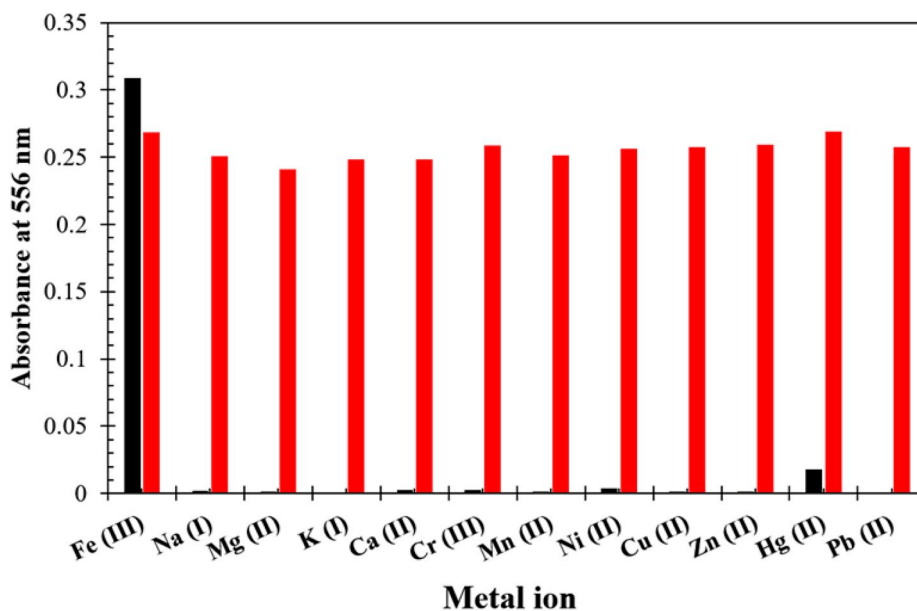


Fig. 2. Competitive profiles of coexisting metal ions with Fe^{3+} ion toward RB-UTES. The absorbance of RB-UTES in the presence of different metal ions (black bars) and in the presence of Fe^{3+} ion and different metal ions (red bars). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

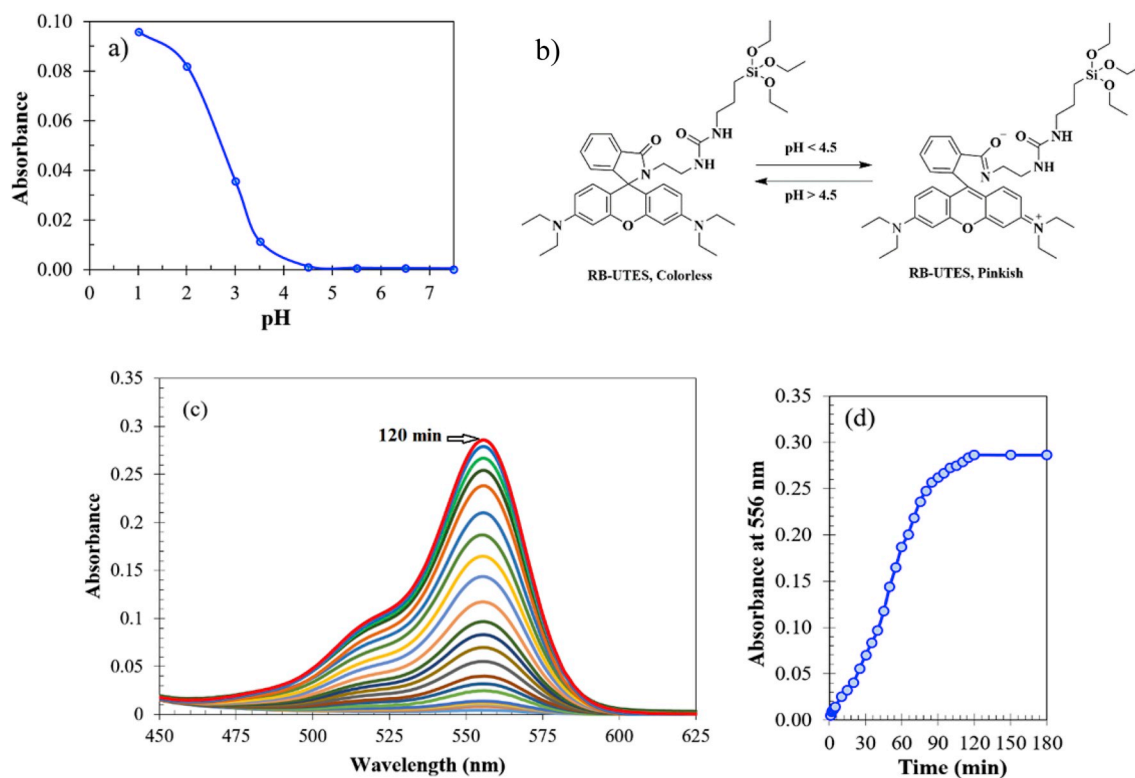


Fig. 3. (a) absorbance intensity at 556 nm of RB-UTES under different pH conditions, (b) the proposed sensing mechanism of RB-UTES under pH change, (c) UV-vis absorption spectra of RB-UTES upon addition of 10 equiv. Fe³⁺ ion at different periods of chelation time and (d) a plot of absorbance intensity at 556 nm over a period of 120 min.

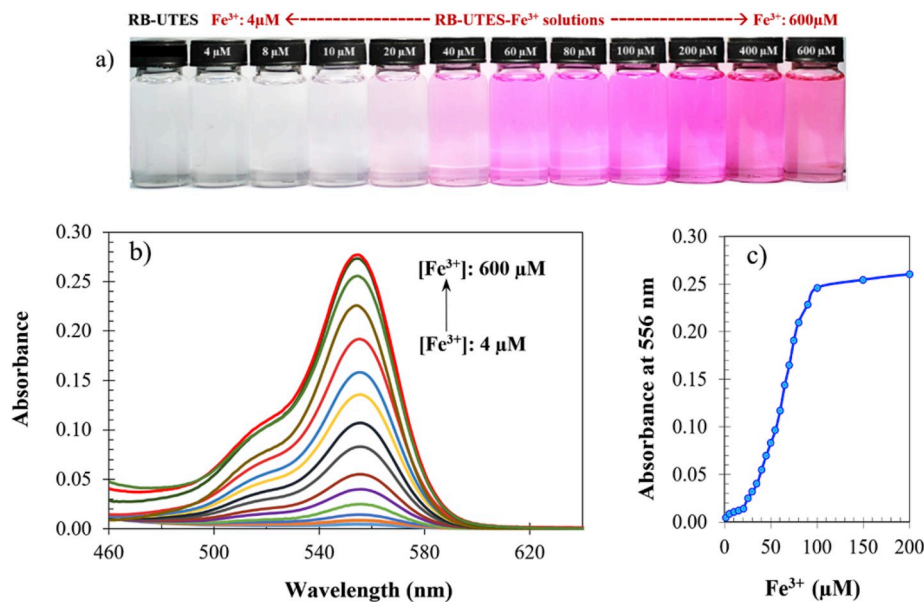
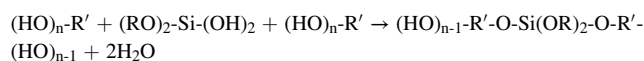
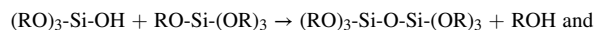
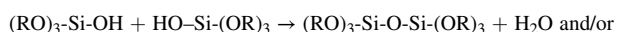


Fig. 4. Response of RB-UTES towards various Fe³⁺ solutions: (a) color change under normal light, (b) UV-vis spectra of the complex and (c) a plot between the maximum absorbance at 556 nm and the concentration of Fe³⁺ ion. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Polycondensation:



R' = PVOH backbone

With an addition of TEOS into the PVOH solution, the ethoxysilane

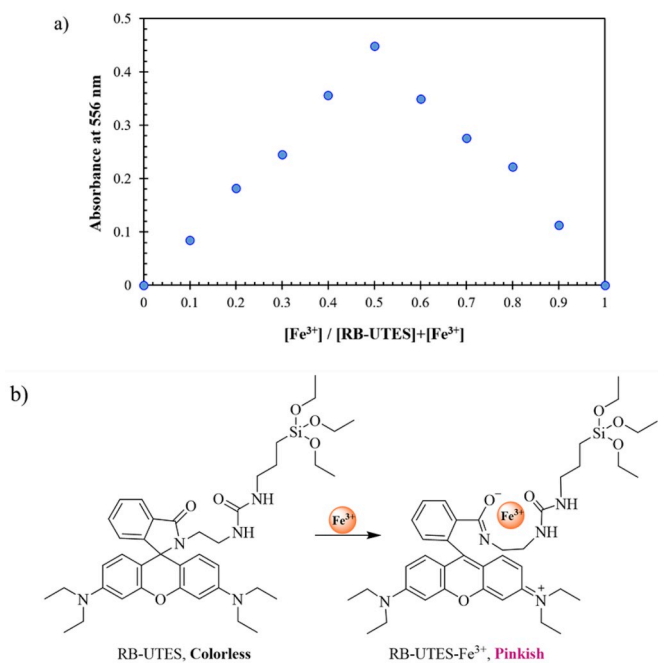


Fig. 5. (a) Job's plot of 1:1 binding stoichiometry between RB-UTES ligand and Fe³⁺ ion and (b) a proposed binding mechanism of RB-UTES toward Fe³⁺ ion.

groups of TEOS would hydrolyze forming -Si-OH pendants. Then, polycondensation occurred between the hydrolyzed pendant and -OH group of PVOH yielding the -Si-O-Si- linkage between polymer chains. Using this hybridization procedure, the PVOH-silica hybrid films were fabricated. The choice of PVOH as a polymeric substrate was due to its advantages of good solubility, excellent film forming ability, durability and its abundant hydroxyl pendant groups that could enable the coupling with ethoxysilyl groups of RB-UTES and TEOS via hydrolysis and polycondensation.

The PVOH and hybrid PVOH films were examined by ATR-FTIR and

the spectra are given in Fig. 6(a). The main adsorption bands of PVOH at 3340, 2950, 1420 and 1100 cm⁻¹ could be assigned to the O-H stretching of intramolecular and intermolecular hydrogen bonded hydroxyl groups, C-H stretching, -CH₂- scissoring and C-O stretching, respectively. The formation of siloxane linkage from polycondensation was observed from the hybrid PV-3TE film. The shift of O-H stretching band could be attributed to the uncondensed silanols (Si-OH) formed during the hydrolysis of alkoxy silane. The peaks at 1080, 850 and 470 cm⁻¹ attributed to the overlapped bands of asymmetric Si-O-Si with Si-O-C stretching, symmetric stretching and symmetric bending of the Si-O-Si, respectively [39,40]. The hybrid chemosensor film was also investigated by SEM-EDX and the obtained micrographs are displayed in supplementary data, (Fig. S5). The morphological structure and elemental composition confirmed the hybridization between the organic-inorganic components with no appearance of phase separation.

Thermal stability of the hybrid PV-TE films compared with the PV was evaluated by TGA. As shown in the thermograms, Fig. 6(b), all samples revealed a similar pattern of residual weight variation with temperature. The first step of minor weight loss (below 150 °C) was attributed to moisture and small molecules, while the following steps of loss were due to the breakdown of side chain and degradation of PVOH backbone structure. The decomposition profiles of hybrid PV-TE films were gradually shifted to higher temperature in accordance with the increasing TEOS composition. Comparing with PV film, the enhanced weight residues in hybrid PV-TE samples were also observed. These findings could confirm the formation of linkage between the organic polymer and the inorganic phase by sol-gel hybridization.

Water absorption behavior of the fabricated hybrid films was investigated as it is one of the prime parameters for the application. An adequate water absorption is required for the diffusion of target ions towards chelating sites of a chemosensor film. An optimized degree of crosslinking enables controlling of the equilibrium swelling state of a polymer network. A highly crosslinked structure exhibits a smaller swelling degree and a slower solute diffusion rate due to smaller mesh size. The swelling profiles in Fig. 6(c) showed that the non-hybridized PV and PV-1TE slowly dissolved into the medium after reaching maximum extent of swelling. Among all fabricated samples, the PV-3TE was a better choice for sensor development, as the film possessed

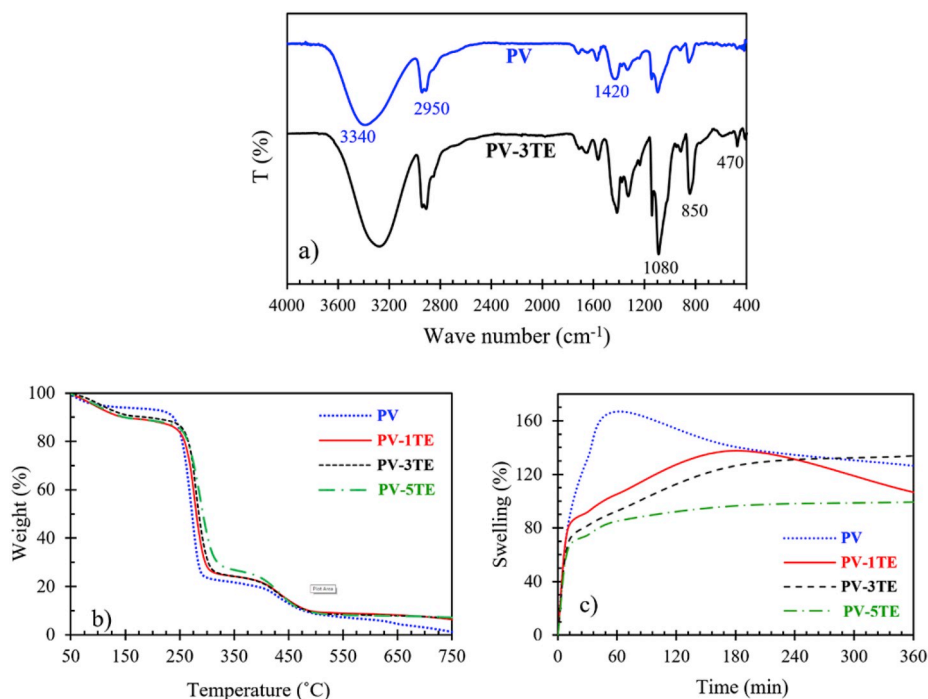


Fig. 6. Characterization of PVOH and hybrid PVOH films: (a) FTIR, (b) TGA and (c) swelling profiles.

initially rapid water uptake as well as dimensional stability in its swollen state.

3.4. Synthesis and characterization of hybrid PVOH chemosensor (PV-3TE-S)

The preparation route of hybrid PVOH chemosensor containing RB-UTES is shown in Scheme 1. The covalent attachment occurred through the coupling of ethoxysilane groups in RB-UTES and TEOS with the hydroxyl pendants in PVOH during the sol-gel process. ATR-FTIR spectra of the hybrid films before and after binding with RB-UTES ligand were obtained and shown in supplementary data, Fig. S4. The fabricated PV-3TE-S20 chemosensor film exhibits characteristic bands of both hybrid PV-TE and RB-UTES, suggesting that the ligand was successfully attached to the polymer film.

3.5. Sensing properties of hybrid PVOH chemosensor (PV-3TE-S)

The obtained chemosensor films, PV-3TE-S10, PV-3TE-S15 and PV-3TE-S20, bearing different contents of RB-UTES with approximate dimensions of $20 \times 30 \times 0.5$ mm were used for the investigation on Fe^{3+} ion sensing in 0.3 ppm aqueous medium (The concentration of Fe^{3+} ion reported in WHO guideline for drinking-water quality). The films were immersed in Fe^{3+} solution and examined for the changes in absorbance at different time intervals (0, 30, 60, 90 and 120 min) by a solid-state UV-vis spectrophotometer. As shown in Fig. 7, the hybrid chemosensor films gave different degrees of response towards Fe^{3+} ion at 565 nm. Among the three samples, PV-3TE-S15 exhibited the most distinct sensitivity with less time to reach optimum absorption intensity. Excess amount of RB-UTES in the sol-gel reaction mixture of PV-3TE-S20 resulted in a lessened response signal towards Fe^{3+} ion and lowering the sensing property of the chemosensor. In its hydrolyzed form, the excess RB-UTES ligand could covalently combine with the reactive TEOS instead of attaching onto the polymeric substrate. In this condition, the fabricated hybrid chemosensor network probably contained low content of the sensor molecule binding to its structure. After casting of the reaction mixture, the forming RB-UTES-TEOS compound that did not

chemically link with the chemosensor film would be readily leached out into solution where the hybrid film was tested for its sensing property. As a result, the response signal towards Fe^{3+} ion of the PV-3TE-S20 chemosensor film prepared with excess amount of RB-UTES was lower than that of the PV-3TE-S15.

The sensing property of hybrid chemosensor films was further investigated using Fe^{3+} solutions with different concentrations (0.3, 3 and 30 ppm). The UV-vis absorption spectra of chemosensor films after 120 min immersion in Fe^{3+} solutions are depicted in Fig. 8(a-c). The exposure of chemosensor films to high ion concentration induced strong change in absorption intensity as a result of ring opening spirolactam structure in RB-UTES attached to the polymeric chemosensor. This was accompanied with an obvious color change of the sensor from yellowish to pink. Among the three samples of chemosensor, the strongest absorbance signal was detected from PV-3TE-S15. The colorimetric change of this chemosensor was further examined by soaking the film in various Fe^{3+} aqueous solutions (0.3, 0.6, 1, 5, 10, 20 and 30 ppm) and the results are displayed in Fig. 8(d). The color change was readily noticeable and enhanced with increasing ion concentration.

The reusability of PV-3TE-S15 was evaluated for 5 cycles by alternating exposure of the film in 3 ppm aqueous solution of Fe^{3+} ion and 0.1 M aqueous solution of ethylene diamine. We found that the pink color upon the recognition of Fe^{3+} ion was turned off by treating with ethylene diamine. This could be explained by the complexation ability of ethylene diamine with Fe^{3+} ion which was superior to that of the chemosensor film. Fig. 9(a) reveals a slight decrease in absorbance intensity of the solid films at 565 nm after consecutive uses. The recovery of signal after five cycles of detection was more than 90%, as the absorbance values of 0.29 and 0.26 were observed at the first and the fifth cycles, respectively. Based on these sensing experimental results, it was revealed that the hybrid chemosensor film possessed a strong potential as a selective optical sensor for Fe^{3+} ion in an aqueous environment.

The utilization of PV-3TE-S15 film as a simple naked-eye sensor for recognition of Fe^{3+} ion was also performed in real samples, tap water and commercial drink water, containing various contents of diverse ions. These aqueous samples were used as solvents for preparation of 30 ppm Fe^{3+} solution. After exposing the sensor with the prepared metal

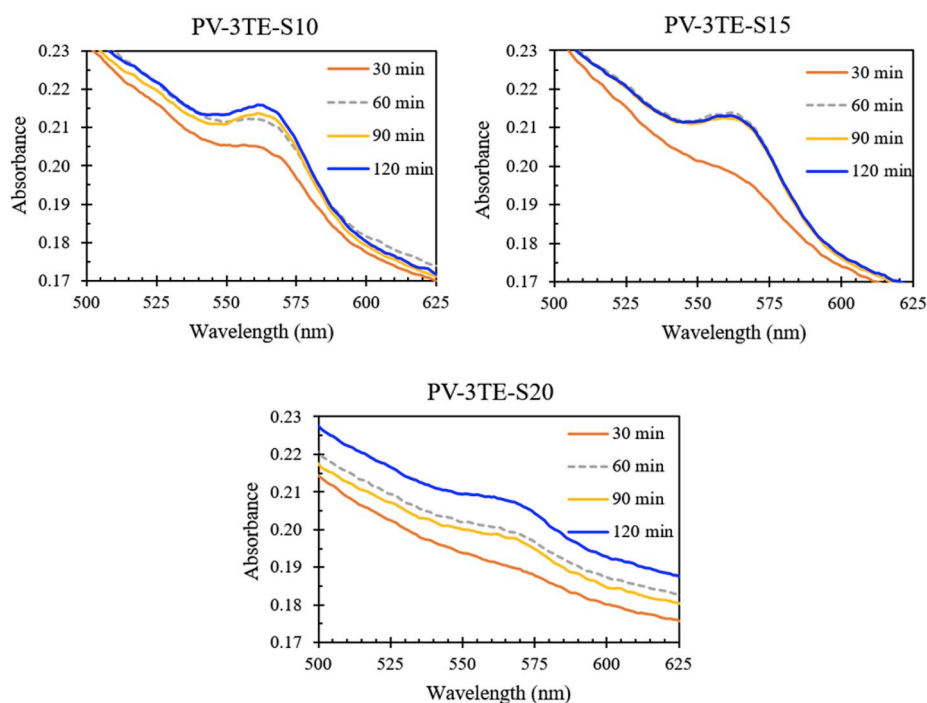


Fig. 7. Solid-state UV-vis absorption spectra of hybrid chemosensor films (PV-3TE-S10, PV-3TE-S15 and PV-3TE-S20) as a function of contact time in 0.3 ppm Fe^{3+} solution.

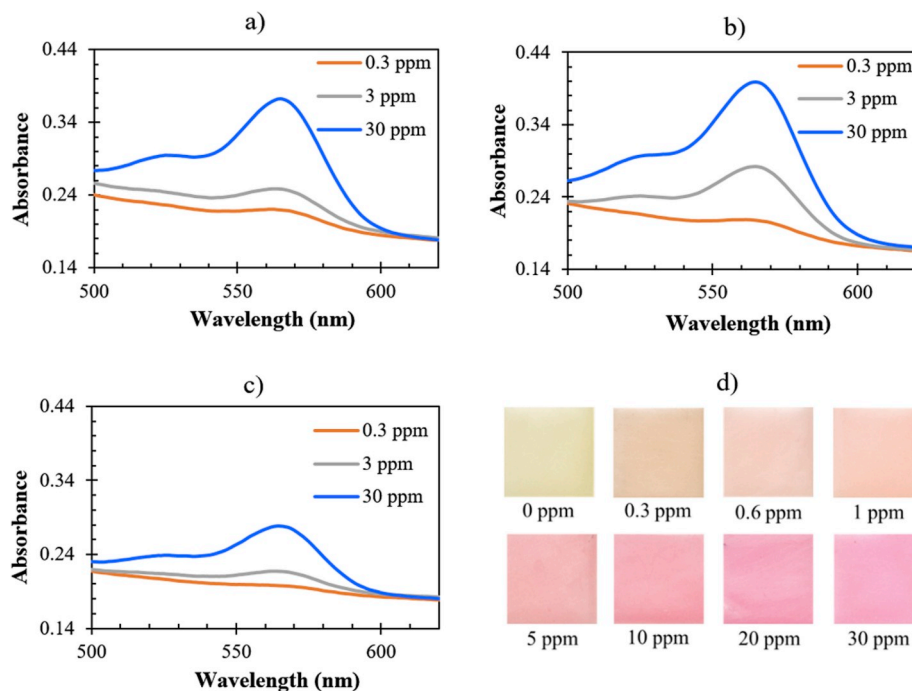


Fig. 8. Solid-state UV-vis absorption spectra of hybrid chemosensor films as a function of Fe^{3+} concentration at 120 min contact time: (a) PV-3TE-S10, (b) PV-3TE-S15 and (c) PV-3TE-S20, and (d) color changes of PV-3TE-S15 films under normal light observed after 60 min immersion in various Fe^{3+} aqueous solutions. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

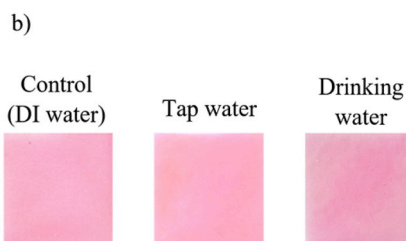
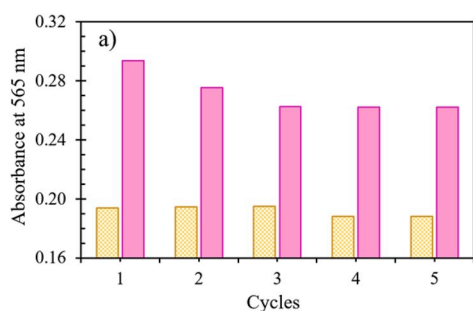


Fig. 9. (a) Changes in absorbance intensity of PV-3TE-S15 upon five cycles of Fe^{3+} ion detection. Dotted yellow bars represent signals of the original sensor film (1st cycle) and the films after treatment with ethylene diamine (2nd-5th cycles). Pink bars indicate the signals after exposure to Fe^{3+} aqueous solution. (b) Photographs of the sensor taken under ambient light after Fe^{3+} ion detection in real sample systems. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

solution, changes in color of the films were monitored and the results are shown in Fig. 9(b). The results revealed that the respond of PV-3TE-S15 sensor film was not affected by the presence of individual contaminating ions in real samples.

4. Conclusions

A new hybrid PVOH film bearing rhodamine derivative ligand was designed, prepared and used as a naked eye colorimetric sensor for detection of Fe^{3+} ion in aqueous systems. The synthesized RB-UTES ligand exhibited excellent selectivity and sensitivity toward Fe^{3+} ion over a wide range of metal ions by an emerging UV-vis absorption peak at 556 nm and an obvious visible change of the solution color to pink. Then, this molecular chemosensor was covalently coupled to the crosslinked PVOH films by a sol-gel process. The fabricated hybrid organic-inorganic chemosensor films were characterized by FT-IR, TGA and swelling test. According to Job's plot experiment, the proposed sensing mechanism was described by 1:1 binding stoichiometry. The Fe^{3+} ion sensing of the hybrid chemosensor was reversible and the chemosensor could be reused for several times without significant signal reducing. Overall, the hybrid PVOH sensor exhibited promising potential for many practical applications such as chemical and environmental

analysis where detection of Fe^{3+} ion is demanded.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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