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Hydrophobic poly(azomethine-urethane) Film for Detection of Fe^{3+} Ions in Aqueous Media

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Abstract: A new and easy-to-make polymer film sensor was prepared by dip-coating technique and this film used as fluorescent chemosensor for the detection of metal ions in aqueous solution. The proposed film sensor exhibited dual emissions at 540 and 582 nm under a single excitation wavelength. The fluorescence behavior of this film sensor toward metal ions has been investigated using these two wavelengths. The proposed sensor was found to show selectivity and sensitive to Fe^{3+} ion when compared the other metal ions in deionized water with excellent photostability. Detection limit of the polymeric film sensor was calculated as 86.15 and 28.90 µM. The results showed that the sensor can be successfully applied to the determination of Fe^{3+} ions in aqueous media. Contact angle measurement of PAZU film probe was also investigated and the result showed that the proposed film probe has hydrophobic property.

Keywords: Fe (III) sensor; Poly(azomethine-urethane); Chemosensor; Hydrophobic property

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1. Introduction

Over the last few decades, the development of new fluorescent probes for the detection of biologically and environmentally important metal ions has attracted great attention because fluorescent chemosensors have several advantages such as low cost, simplicity, high sensitivity, selectivity, response time, when compared with other optical methods [1-4]. A lot of effort has been devoted to designing and synthesizing of new fluorescent chemosensors for metal ions in the past few years [5-9]. However, most of these studies are stressed on the design of selective and sensitive fluorescent probes used only in solution phase, which is hard to realize repetitive application. In contrast, the investigation of film sensors has been rarely studied [10, 11]. In terms of practicality, fluorescent film sensors offer more favorable properties than a fluorescent probe used only in solution. For instance, film sensors can be used repeatedly, easily be made into devices and have no contamination to analyte solution [12-14].

Iron is one of the most prominent elements in chemicals and biological systems, which performs a vital role in many biochemical processes at the cellular level [15-18]. It is an essential element for the formation of hemoglobin of red blood cells and plays major roles in oxygen transport, DNA and RNA synthesis, short-term oxygen storage, and energy generation [19, 20]. However, the concentration of iron in body has to be efficiently balanced as both its deficiency and overload can induce different disorders. For this reason, the rapid and simple methods for the recognition of trace iron ions in aqueous solutions become very important topics in the analytical, biomedical, and environmental sciences [21-23].

Liu et al. and Liao et al. were reported a series of fluorescence sensor for detection of Fe^{3+} ions based on conjugated polymers containing fluoranthene [24-27]. They were reported in these paper that the detection limit of proposed fluorescence sensors found in the range 1 to 62.5 nM due to strong fluorescent emitter property and synergistic effect of *p*-conjugated electrons of fluoranthene.

In consideration of all the factors above, we proposed a hydrophobic copolymer, poly(azomethine-urethane), as the film sensor for Fe^{3+} in aqueous medium. The polymer was prepared according to the literature [28] and this hydrophobic copolymer designed as fluorescence film probe for the detection of metal ions. It was observed that the film probe is capable of selective complexion with Fe^{3+} which causes great quenching in the fluorescence intensity. Selectivity study of the Fe^{3+}sensor was examined and an admirable selectivity was obtained according to relative intensity change values. The obtained results show that the fluorescence film sensor can be successfully applied to the detection of Fe^{3+} ions.

2. Experimental

2.1 Materials

5-nitro vanillin, 2,4-toluenediisocyanate (TDI), *p*-phenylenediamine, acetic acid, acetonitrile, boric acid, chloroform ($CHCl_3$), dimethylformamide (DMF), ethanol (EtOH), hydrochloric acid (HCl), phosphoric acid, sodium hydroxide (NaOH), tetrahydrofurane (THF), $AlCl_3$, $Ba(NO_3)_2$, $Cd(CH_3COO)_2.2H_2O$, $Co(CH_3COO)_2.4H_2O$, $Cu(CH_3COO)_2.H_2O$, $Fe(NO_3)_3$, $HgCl_2$, $Mn(CH_3COO)_2.H_2O$, $Mg(SO_4).7H_2O$, $Ni(CH_3COO)_2.4H_2O$, $Pb(CH_3COO)_2.3H_2O$, $SnCl_2.6H_2O$ and $Zn(CH_3COO)_2.2H_2O$ were supplied from Merck Chemical Co. (Germany) and all reagents and chemicals used as received.

2.2. Synthesis of poly(azomethine-urethane) (PAZU)

PAZU [4-((E)-((4-((E)-(3, 4-dimethoxy-5-nitrobenzylidene) amino) phenyl) imino) methyl)-2-methoxy-6-nitrophenyl (3-acetamido-4-methylphenyl) carbamate] was synthesized via step-polymerization reaction in our previous paper [28]. Synthesis procedure of the employed polymer is shown in Fig. 1. ^1H-NMR (400 MHz, DMSO-d_6, δ ppm): 9.80 (urethane $–N\underline{H}$), 8.62 (imine $–N=C\underline{H}$), between 7.03 and 8.36 (Ar-$C\underline{H}$), 3.91 (methoxy, $–OC\underline{H}_3$) and 2.17 ppm (-$C\underline{H}_3$); ^{13}C-NMR (100.6 MHz, DMSO-d_6, δ ppm): 160.3 (imine, $–N=\underline{C}H$), 152.4 (urethane $–\underline{C}=O$), 143.8 (-$\underline{C}$-NO_2), between 111.8 and 150.0 (Ar-$\underline{C}H$), 56.4 (methoxy, -$O\underline{C}H_3$) and 17.0 ppm (-$\underline{C}H_3$).

The infrared spectra of Fe^{3+}, PAZU and PAZU-Fe complex were obtained by Perkin Elmer FT-IR Spectrum one using universal ATR sampling accessory (4000–650 cm^{-1}) in DMF solution. ^1H and ^{13}C-NMR spectra (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) were recorded in deuterated DMSO-d_6 at 25 °C. Tetramethylsilane (TMS) was used as internal standard. The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) were determined by size exclusion chromatography (SEC) techniques of Shimadzu Co. For SEC investigations a SGX (100 Å and 7 nm diameter loading material) 3.3 mm i.d. x 300 mm column, DMF/Methanol (v/v; 4/1, 0.4 mL min^{-1}) as solvent, polystyrene standards were used. A refractive index detector (RID) were used to analyze the products at 55°C. The M_n, M_w and PDI values of PAZU were 12500, 19800 g mol^{-1} and 1.58, respectively. The polymerization yield of PAZU was found as 46%. This could be probably substituents effect. As shown in Scheme 1, the obtained polymer has composed of hydroxyl (-OH), methoxy (-OCH_3) and nitro (-NO_2) as substituents group. Moreover, polyurethane formation reaction occurs between diisocyanates and polyol and this reaction starts by nucleophilic attack of hydroxyl group to the unpaired electron couples of diisocyanates [28]. The steric effect of these -OCH_3 and nitro -NO_2 groups could effected this nucleophilic attack and decrease the polymerization yield.

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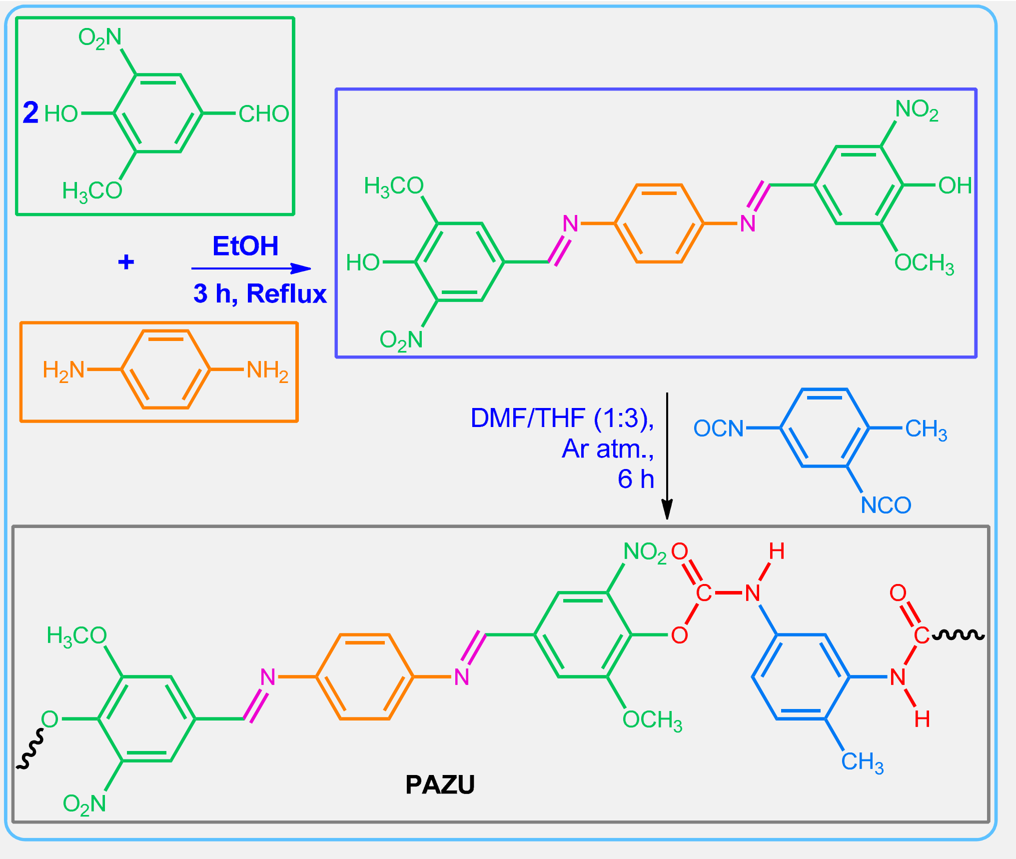

Scheme 1. Synthesis of poly(azomethine-urethane).

2.3. Preparation of PAZU Film

Polymer film was prepared using transparent polyester plate. Firstly, polyester plate was cleaned in MeOH, MeCN and deionized water at room temperature and dried at 100 °C in vacuum oven. Then, this cleaned plate was used as substrate to coating polymer film. Secondly, a polyepoxide layer was coated on polyester plate from its chloroform solution by dip-coating technique and polyepoxide layer coated plate was dried at room temperature overnight in desiccator. These coating processes were carried out due to compensate for weak adherence of polymer onto polyester plate. Finally, polymer (50 mM solution in DMF) was coated on polyepoxide coated plate by dip-coating technique with a withdraw rate 100 mm min^{-1} and polymer film was dried at room temperature overnight in desiccators (Fig. 1).

Figure 1 here

2.4. Preparation of Buffer Solution

Britton-Robinson (B-R) buffer solution was prepared by mixing acetic, boric and phosphoric acid at different pH. Concentration of these acids was adjusted as 0.040 M and this buffer solution adjusted to desired pH with 0.20 M NaOH or 0.20 M HCl.

2.5. Preparation of Stock Solution

1.0 mM stock solution of Fe^{3+} was prepared in 50 mL deionized water using its chloride salt. The stock solutions of the other metal ions (1.0 mM) such as Al^{3+}, Ba^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, Mn^{2+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, $Sn^{2+}$and Zn^{2+} were prepared in 50 mL deionized water using certain amount of metal salts and these prepared stock solutions were also used in all measurements.

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2.6. UV-Vis Measurements

UV-Vis absorption spectra of PAZU film was recorded using Perkin-Elmer Lambda 25 UV-Vis spectrophotometer in the presence of different molarity Fe^{3+} ions at room temperature in the range 250 to 800 nm.

2.7. Fluorescence Measurements

All fluorescence measurements were carried out using Shimadzu Perkin-Elmer LS 55 fluorescence spectrometer in the range 200 to 800 nm equipped with 300 Watt Xenon arc lamp. Excitation and emission spectra of PAZU film were obtained due to determine the optimal emission and excitation wavelengths and Stokes Shift value in deionized water. Also, transition metal ions effect on PAZU film was investigated by monitoring the fluorescence spectral behavior upon addition of several metal ions such as Al^{3+}, Ba^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, Mn^{2+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, $Sn^{2+}$and Zn^{2+} (1.0 mM) in deionized water. Concentration effect of Fe^{3+} ion on polymer film was determined using a series of different concentrated metal solutions (in the range 1.0 to 8.0 mM) in deionized water solution. Excitation wavelength was set at 400 nm and slit width adjusted as 5 nm in the mentioned experiments.

2.8. Detection of Quantum Yield

Fluorescence quantum yield measurements were carried out using Fluorescein in 0.1 M concentrated aqueous EtOH solution due to understand its fluorescence behavior. Moreover, fluorescence quantum yield (Φ_f) was calculated by comparative methods as in the literature [29] and Fluorescein solution in ethanol used as standard solution in this calculation.

2.9. Contact Angle Measurements

The equilibrium (θ_e) contact angle's (CA's) of PAZU under air using water as liquid were determined using KSV Attension Theta Lite Optical Tensiometer. For θ_e measurement, 6 µL droplet volume was used and the needle was removed from droplet during this measurement.

2.10. Optical Microscopy Measurements

To investigate the surface topography of PAZU film, optical microscopy Nikon Optical microscopy Nikon LV150ND metal microscope was used at different magnification.

3. Results and Discussion

Schiff base was synthesized using 5-nitro vanillin and *p*-phenylenediamine via condensation reaction and this preformed Schiff base was converted to poly(azomethine-urethane) derivative using 2,4-toluenediisocyanate as co-monomer. Additionally, hydrophobic poly(azomethine-urethane) film was easily prepared by dip-coating technique.

3.1. Photoluminescence Behavior of PAZU Film

To determine excitation and emission spectral data of polymer film, fluorescence spectra of this film was measured in deionized water and the obtained spectral data listed in Table 1. As shown in Table 1, PAZU has two emission wavelengths at 540 and 582 nm. Also, Stokes shift values ($\Delta\lambda_{ST}$) of film probe were calculated as 140 and 182 nm at mentioned wavelengths, respectively. These calculated $\Delta\lambda_{ST}$ showed that the designed film chemosensor has large Stokes shift. Larger Stokes shift values result in very low background signals. Because of this property, poly(azomethine-urethane) can be employed as a fluorescence sensor [30]. Additionally, quantum yield (Φ_f) of the polymer film is found to be 2% when excited at 400 nm.

Table 1 here

3.2. Metal Ions-Sensing Properties of PAZU Film

To determine the suitability of the polymeric film probe for metal ions, the fluorescence behavior of the film probe was investigated due to selective recognition of the target ion from competitive systems is an essential parameter. For these reason, to investigate the ability of recognition of the PAZU film sensor for metal ions the fluorescent spectral changes were monitored in the presence of a wide range of metal cations (1.0 mM) including Al^{3+}, Ba^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+}, Mn^{2+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, $Sn^{2+}$and Zn^{2+} in deionized water (Fig. 2). Emission intensities of PAZU film were measured as 209 and 278 a.u. for 540 and 582 nm. As shown in Fig. 2, upon addition of 3 mL metal ion solution (1.0 mM), emission spectrum of PAZU film showed an increasing response at 540 nm in the presence of Al^{3+} (218 a.u.), Ba^{2+}(223 a.u.), Cd^{2+}(227 a.u.), Co^{2+}(219 a.u.), Cu^{2+}(220 a.u.), Hg^{2+}(222 a.u.), Mg^{2+}(230 a.u.), Mn^{2+}(224 a.u.), Ni^{2+} (217 a.u.) and Zn^{2+} (216 a.u.) while a decreasing response in the presence of Fe^{3+}(195 a.u.), $^{Pb2+}$ (208 a.u.) and Sn^{2+}(207 a.u.). This tendency could be probably the strong interaction between PAZU fluorescent film probe and Fe^{3+}, Pb^{2+} or Sn^{2+} at the mentioned wavelength.

Additionally, the emission peak of PAZU film probe was decreased in the presence of Fe^{3+} (246 a.u.) whereas the emission peak of this probe was increased when added Al^{3+} (299 a.u.), Ba^{2+}(320 a.u.), Cd^{2+}(2330 a.u.), Co^{2+}(296 a.u.), Cu^{2+}(295 a.u.), Hg^{2+}(292 a.u.), Mg^{2+}(309 a.u.), Mn^{2+}(308 a.u.), Ni^{2+} (280 a.u.), Pb^{2+} (283 a.u.), Sn^{2+}(290 a.u.) and Zn^{2+} (305 a.u.) at 582 nm. These results indicate that PAZU could be used as selective and sensitive Fe^{3+} sensor in aqueous solution at mentioned wavelength.

Figure 2 here

3.3. UV-vis Absorption Property of PAZU Film

UV-vis absorption property of PAZU film was studied in the range 1 mM to 62.5 μM Fe^{3+} ion concentrations (Fig. 3) and the different molarity effect on absorbance also investigated. UV-vis spectra indicated that PAZU film probe was showed only one absorbance band at 344 nm. As shown in Fig. 3, the absorption maximum of PAZU is observed at 344 nm. The measured absorbance values indicated that the absorbance value of PAZU film probe was decreased when Fe^{3+} ion concentration continuously increased in the range 1 mM to 62.5 μM.

Figure 3 here

3.4. Fe^{3+} Ion Concentration Effect on PAZU Film

To find out Fe^{3+} ion concentration effect on PAZU film, fluorescence properties of this film probe were measured in the presence of different Fe^{3+} ions concentration (Fig. 4). As seen Fig. 4, the fluorescence intensity of the film probe at both 540 and 582 nm was found decreased gradually with the increasing of the concentration of Fe^{3+} ion from 1.0 to 8.0 mM.

Figure 4 here

3.5. Determination of Limit of Detection (LOD)

To determine slope, regression equations and coefficients of the fluorescent film probe, calibration curves of PAZU (at 540 and 582 nm) were obtained using fluorescence measurements. The obtained curves were given in Fig. 5a and b. Also, the obtained equations from these calibration curves were given in Eqs. 1 and 2, respectively.

$$F_o - F = 10726[Fe^{3+}] + 4.15 \qquad \text{(at 540 nm)} \qquad (1)$$

$$F_o - F = 25287[Fe^{3+}] + 56.60 \qquad \text{(at 582 nm)} \qquad (2)$$

where F is the emission intensity of tested metal ion and F_o is the emission intensity of metal-free PAZU film.

As shown in these results, a good linearity relationship against fluorescence intensity versus Fe^{3+} concentration was obtained with the regression coefficients R_1= 0.991 and R_2= 0.990 for Eqs. 1 and 2, respectively. These results showed that the proposed fluorescent film probe has potential prospects as a selective detector of Fe^{3+}ion in aqueous environment.

Additionally, limit of detection (LOD) of the fluorescent chemosensor film was determined using fluorescence titration method. To determine standard deviation (σbi), the emission spectra of PAZU fluorescent film without metal ions were measured 10 times in deionized water and the standard deviation of blank measurements was found to be 0.924 and 0.731 for PAZU (540 and 582 nm). LOD value of PAZU film was calculated as in the literature (Eq. 3) [31].

$$\mathrm{LOD} = \frac{3\sigma bi}{m} \qquad (3)$$

where σbi is the standard deviation of blank measurements and m is the slope the obtained from Fig. 5a and b. Also, limit of detection of this fluorescent film probe was calculated as 86.15 and 28.90 µM for PAZU (540 and 582 nm).

Figure 5 here

3.6. Interference Study

To determine possible interference or anti-interference effect of other metal ions (Al^{3+}, Ba^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+}, Mn^{2+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, $Sn^{2+}$and Zn^{2+}) on Fe^{3+} complexion with the proposed fluorescent film probe, competition experiments were carried out in the presence of Fe^{3+} ion (1.0 mM) mixed with various metal ions (at the same concentration) at 540 and 582 nm (Fig. 6). As shown in Fig. 6, Fe^{3+} ion was the lowest relative emission intensity and the other tested metal ions were not induced significant fluorescence change except Fe^{3+} ions at mentioned wavelengths.

Figure 6 here

3.7. Quenching Ion Effect on PAZU Film

Quenching ion effect on the proposed sensor was investigated at 540 and 582 nm using polymeric film, 0.1 M Fe^{3+} ion in deionized water and 1 mg different metal ion such as Pb^{2+}, Sn^{2+}, Zn^{2+}, Ni^{2+}, Al^{3+}, Co^{2+}, Cu^{2+}, Hg^{2+}, Ba^{2+}, Mn^{2+}, Cd^{2+} or Mg^{2+} as shown in Fig. 7. As can be seen in Fig. 7, the presence of some transitional metal ions such as Pb^{2+}, Sn^{2+}, Zn^{2+}, Ni^{2+}, Al^{3+}, Co^{2+}, Cu^{2+}, Hg^{2+}, Ba^{2+}, Mn^{2+}, Cd^{2+} or Mg^{2+}caused only slight changes in the emission spectra of the proposed film sensor.

Figure 7 here

3.8. pH Effect on PAZU Film

The pH value has great parameter for the detection procedure of chemosensor. To find out the convenient pH condition of PAZU–Fe^{3+}complex, the effect of pH on the emission intensity of PAZU film probe was investigated in the presence of 1.0 mM Fe^{3+} solution and the range of pH from 2.0 to 12.0 using Britton-Robinson (B-R) buffer solutions. The emission intensity was seen to change depending on pH values. The results were also shown in Fig. 8. As seen in Fig. 8, the fluorescence intensity of PAZU film probe was stable in the range pH from 2.0 to 12.0 and the emission intensity of the complex between PAZU and Fe^{3+} reached to the maximum a pH range of 6.0–8.0. These results indicated that Fe^{3+} could be clearly detected by the fluorescence spectra measurement using PAZU over the environmentally relevant pH range (pH 7.0–8.0).

Figure 8 here

3.9. Binding Model between Polymeric Film Probe and Fe^{3+}

To determine binding model between polymeric film probe and Fe^{3+} ions, the optimized structure, molecular orbital and Huckel charge density of PAZU were calculated using Huckel calculation method [9, 30]. Also, the optimized 3D structure and molecular orbital charge density of PAZU were shown in Fig. 9. As can be seen in molecular orbital charge density of PAZU, imine group (-NH=CH) has higher molecular orbital charge density than urethane (-NH-CO-O), methoxy (-$\underline{O}CH_3$) and nitro groups (-$\underline{N}O_2$) in the structure of polymeric film probe (Fig. 9).

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According to the Huckel charge density of PAZU, imine (-N=CH), urethane (-NH-CO-O) and nitro (-NO_2) nitrogen atoms have -0.05, 0.28 and 1.28 Huckel charge density, respectively. Additionally, urethane (-NH-CO-O), carbonyl (-NH-CO-O), methoxy (-OCH_3) and nitro (-NO_2) oxygen atoms have -0.22, -0.80, -0.27 and -0.78 Huckel charge density, respectively. These results showed that urethane carbonyl (-0.80) and nitro oxygen atoms (-0.78) have lower Huckel charge density than the other atoms.

As a result, the imine group has the highest molecular orbital charge density and urethane carbonyl and nitro oxygen atoms have the lowest Huckel charge density. According to these explanations, the possible complexation between PAZU and Fe^{3+} ion could be mainly carried out with imine nitrogen atoms, carbonyl and nitro oxygen atoms (Fig. 9c).

Figure 9 here

Moreover, to detection binding mode of PAZU with Fe^{3+} ion FT-IR spectra of Fe^{3+} ion, PAZU and PAZU-Fe complex measured in DMF solution (Fig. 10). According to Fig. 10, characteristic urethane –NH and –C=O stretch vibrations of PAZU were observed at 3256 and 1675 cm^{-1}, respectively. Also, imine (-N=CH) and nitro (-NO_2) stretch vibrations were observed at 1640 and 1210 cm^{-1}, respectively. In the FT-IR spectra of PAZU-Fe complex, these urethane –NH (3398 cm^{-1}), imine (-N=CH, 1655 cm^{-1}) and nitro (-NO_2) (1260 cm^{-1}) stretch vibrations were shifted 142, 15 and 50 cm^{-1} lower frequency, respectively, due to the coordination of these stretch vibrations with Fe^{3+} ion [32].

Insert Fig. 10 here

3.10. The Photostability Property of PAZU Film

The photostability of PAZU film was tested in deionized water under a xenon arc lamp. The xenon arc lamp–based photostability test of the film probe was performed with a steady-state spectrofluorometer in the mode of Time-Based Measurements. The laser light intensity of xenon arc lamp was 100 mW/cm^2 in these measurements. The film probe was excited at 400 nm, and the data was acquired at 582 nm after 1800 sec of monitoring. The acquired data for PAZU were shown in Fig. 11. The fluorescence initial intensity (%) of the sensor did not change over the 1800-sec period. The results showed that the complex formed between PAZU and Fe^{3+} was stable and that no reaction took place within the first 1800-sec.

Figure 11

3.11. Contact Angle Measurement of PAZU Film

Contact angle of materials has been widely used to measure the wettability of polymer surfaces that reflect the polarity and the chemical composition of surfaces. Water equilibrium (θ_e) contact angle (CA) of PAZU film probe was determined and presented in Fig. 12a. The CA of PAZU film was determined as 84±1°, and the film has hydrophobic property. This result may come from the hydrophobic groups such as phenyl, methyl and –CH in the polymer, which decrease the polarity of the surface [33].

Figure 12

3.12. Optical Microscopy Measurement

Surface topography of PAZU fluorescent film was investigated using Nikon LV150ND Metal Microscope and optical microscope image of the polymer film was given in Fig. 12b at 500x magnification. As shown in Fig. 12b, the surface of PAZU polymer film probe seems to be smooth and dense with uniform dispersion

4. Conclusions

A new film chemosensor based on poly(azomethine-urethane) was easily fabricated by dip-coating technique and used as fluorescence probe. The photophysical properties of the fluorescent film sensor were investigated using fluorescence and UV-Vis spectroscopy techniques. Fluorescent measurements indicated that this sensor is useful as sensitive and selective fluorescent sensor for the detection of Fe^{3+} ion. The polymeric film appears to be particularly attractive owing to its simplicity and applicability for aqueous samples and the practicality in visual sensing of Fe^{3+} ions. The photostability of film sensor was determined using the fluorescence lifetime data and found to be quite high. Additionally, contact angle of film probe was also measured as 84 ± 1^o and this result showed that polymeric film probe has hydrophobic characteristic. Hydrophobic groups such as phenyl, methyl and -CH in the polymer chain endow the film sensor not only high affinity toward Fe^{3+} ions but also increase the sensitivity toward these metal ions in the form of inorganic salts.

Compliance with ethical standards

Conflict of interest

The authors declare that they have no conflict of interest.

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Captions of Figures

Fig. 1. Preparation of polymeric film probe.

Fig. 2. Fluorescence spectra of PAZU film in presence of different metal ions (1000 μM) at room temperature in deionized water. (Top to bottom at **540 nm**: Mg^{2+}, Cd^{2+}, Mn^{2+}, Ba^{2+}, Hg^{2+}, Cu^{2+}, Co^{2+}, Al^{3+}, Ni^{2+}, Zn^{2+}, host, Pb^{2+}, Sn^{2+}, Fe^{3+}; **582 nm:** Cd^{2+}, Ba^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Al^{3+}, Co^{2+}, Cu^{2+}, Hg^{2+}, Sn^{2+}, Pb^{2+}, Ni^{2+}, host, Fe^{3+}, $\lambda_{Ex.}$= 400 nm, Slit: Ex: 5 nm, Em: 5 nm).

Fig. 3. UV-vis spectra of PAZU film in the presence of different molarity Fe^{3+}

Fig. 4. Fluorescence emission spectra of PAZU film in the presence of different molarity Fe^{3+} ion.

Fig. 5. A plot of the relationship between Fe^{3+} concentration and relative emission intensities at 540 (a), 582 nm (b) for fluorescence measurements and at 344 nm.

Fig. 6. Interference effect on polymer film in the presence of different metal ions (0.1 M) at 540 and 582 nm.

Fig. 7. Quenching ion effect on polymer film probe at 540 (a) and 582 nm (b).

Fig. 8. pH effect on PAZU film in the presence of Fe^{3+}.

Fig. 9. 3D optimized structure of PAZU (a) molecular orbital charge density of polymer (b) (blue: carbon, green: oxygen, orange: nitrogen atoms and hydrogen atoms are not shown), and the proposed binding mode of poly(azomethine-urethane) and Fe^{3+} ions.

Fig. 10. IR spectra of Fe^{3+}, PAZU and PAZU-Fe complex in solution.

Fig. 11. The photostability curve of PAZU film with Fe^{3+} ion complex in deionized water.

Fig. 12. The equilibrium contact angle droplet (a) and optical microscopy image (b) of PAZU at 500x magnification.

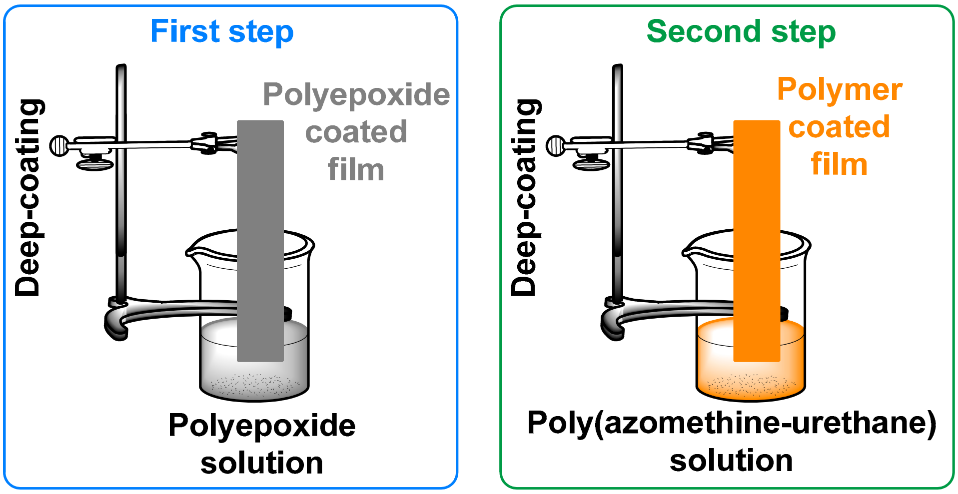

First step
Deep-coating
Polyepoxide coated film
Polyepoxide solution
Second step
Deep-coating
Polymer coated film
Poly(azomethine-urethane) solution

Fig. 1.

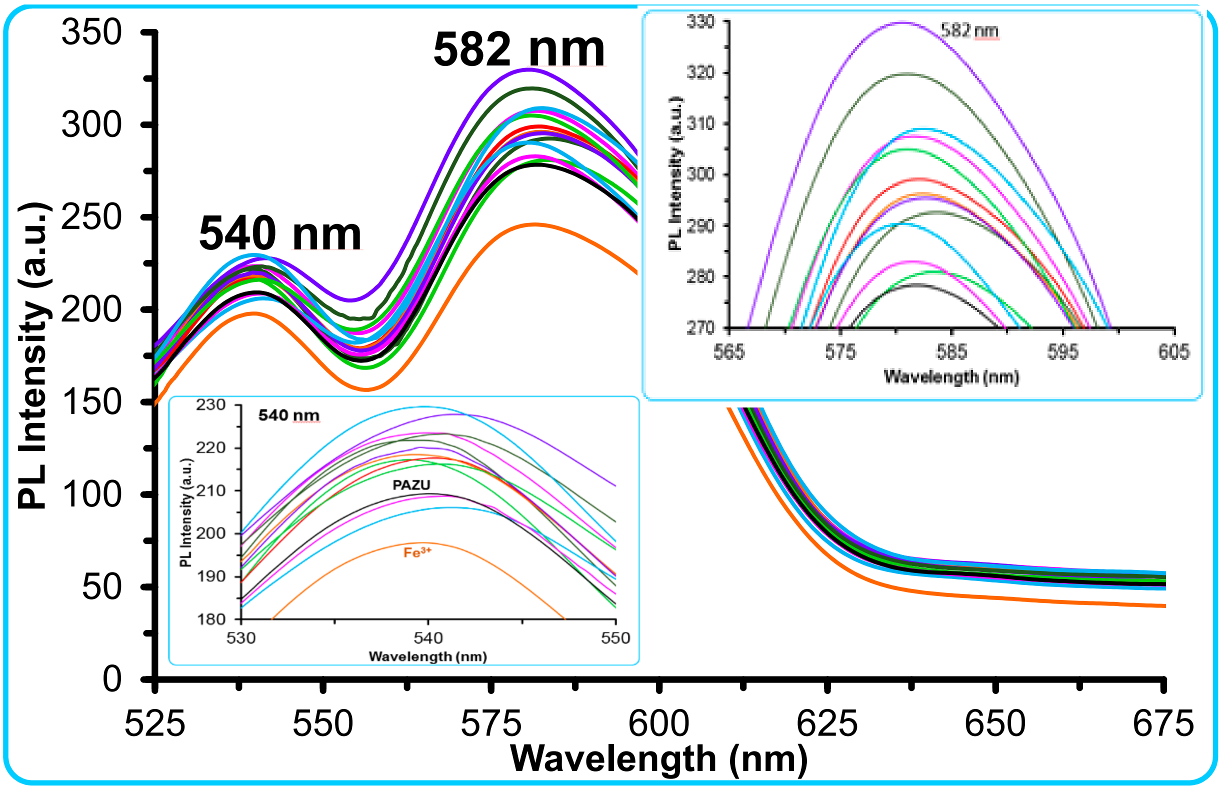

PL Intensity (a.u.)
Wavelength (nm)
582 nm
540 nm
0
50
100
150
200
250
300
350
525
550
575
600
625
650
675
582 nm
PL Intensity (a.u.)
Wavelength (nm)
270
280
290
300
310
320
330
565
575
585
595
605
540 nm
PAZU
Fe³⁺
PL Intensity (a.u.)
Wavelength (nm)
180
190
200
210
220
230
530
540
550

Fig. 2.

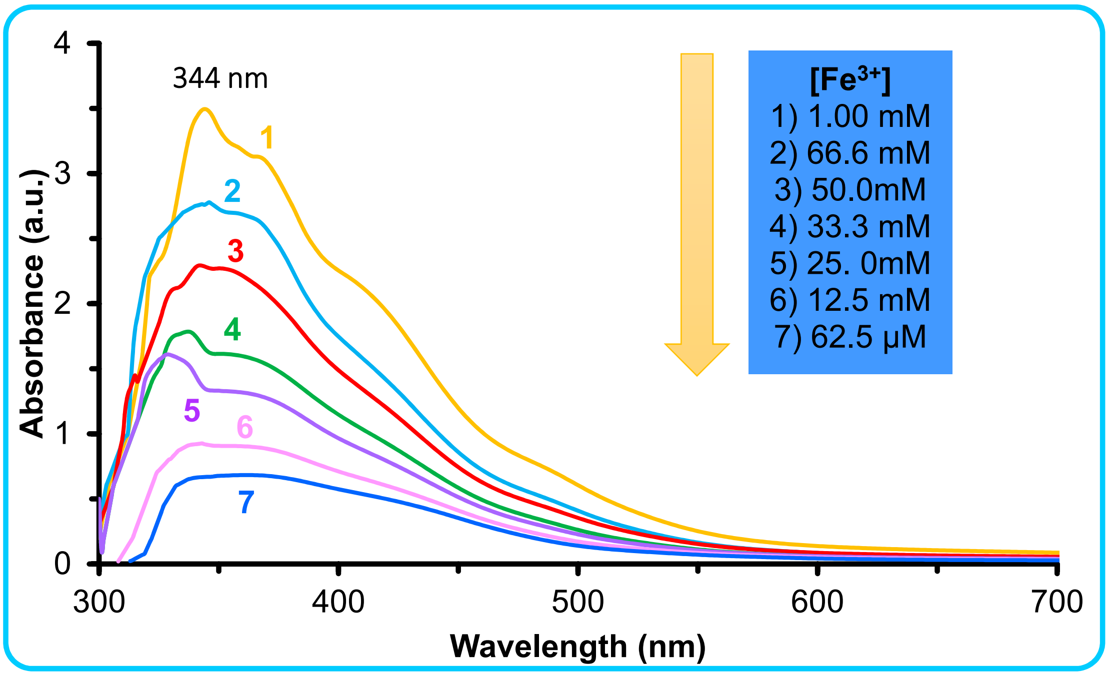

Absorbance (a.u.)
0
1
2
3
4
344 nm
1
2
3
4
5
6
7
300
400
500
600
700
Wavelength (nm)
[Fe^{3+}]
1) 1.00 mM
2) 66.6 mM
3) 50.0mM
4) 33.3 mM
5) 25. 0mM
6) 12.5 mM
7) 62.5 μM

Fig. 3.

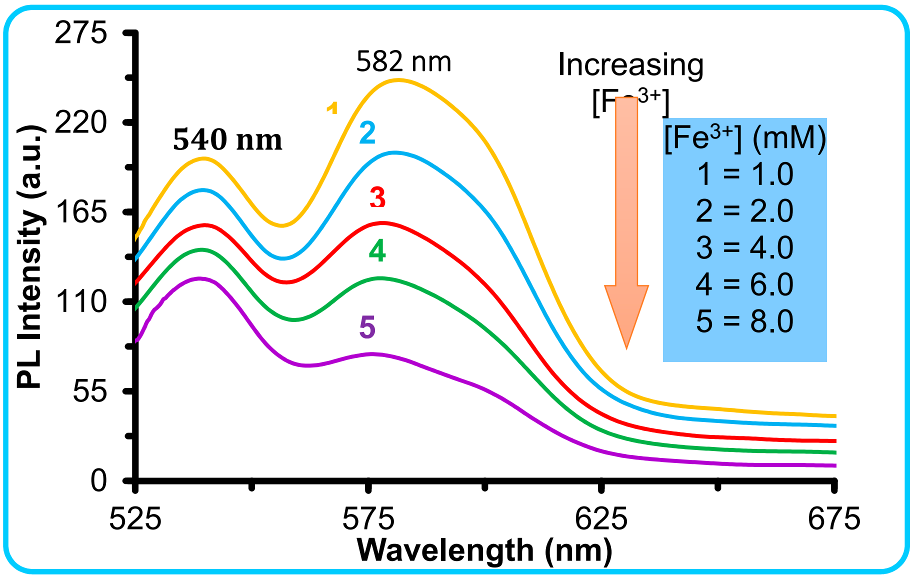
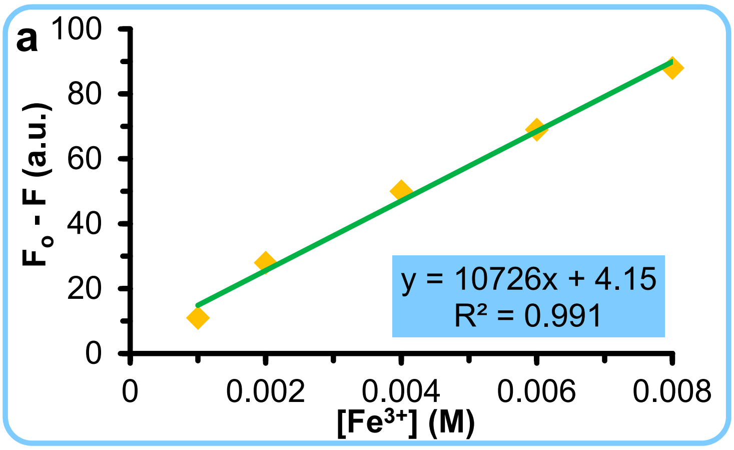

PL Intensity (a.u.)
0
55
110
165
220
275
540 nm
582 nm
1
2
3
4
5
Increasing
[Fe^{3+}]
[Fe^{3+}] (mM)
1 = 1.0
2 = 2.0
3 = 4.0
4 = 6.0
5 = 8.0
525
575
625
675
Wavelength (nm)

Fig. 4.

doi:10.20944/preprints201704.0058.v1



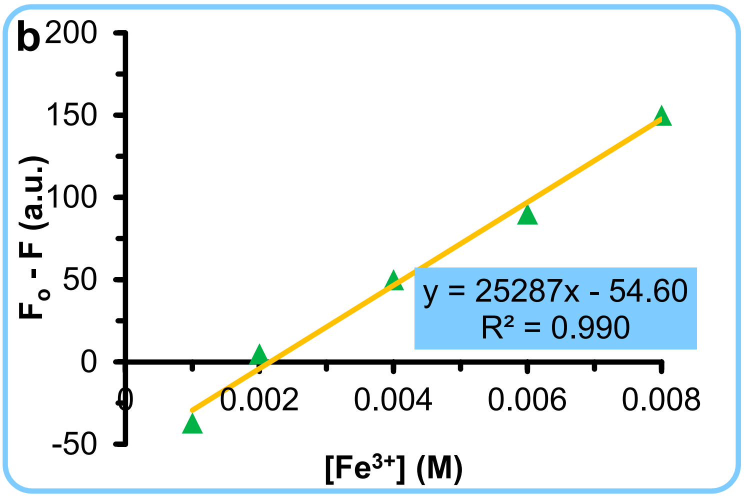


Fig. 5.

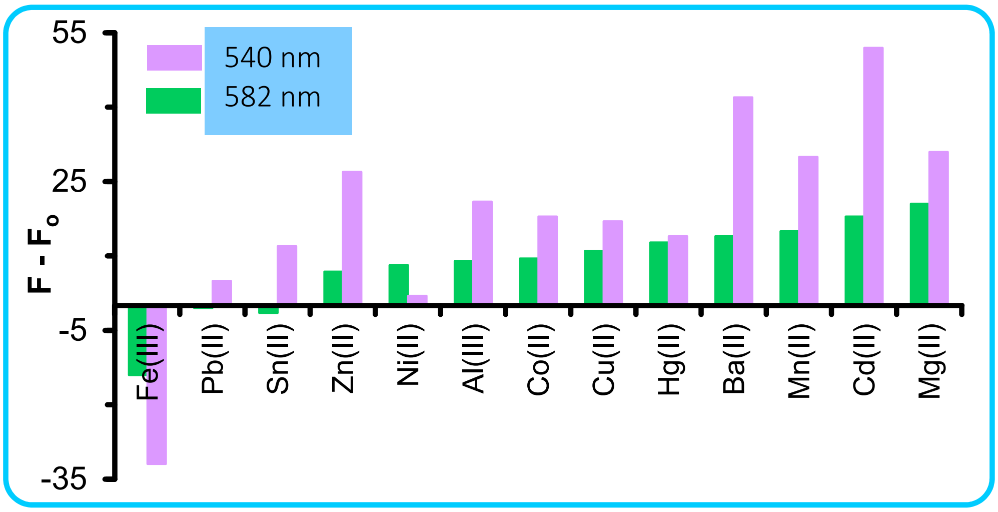


Fig. 6.

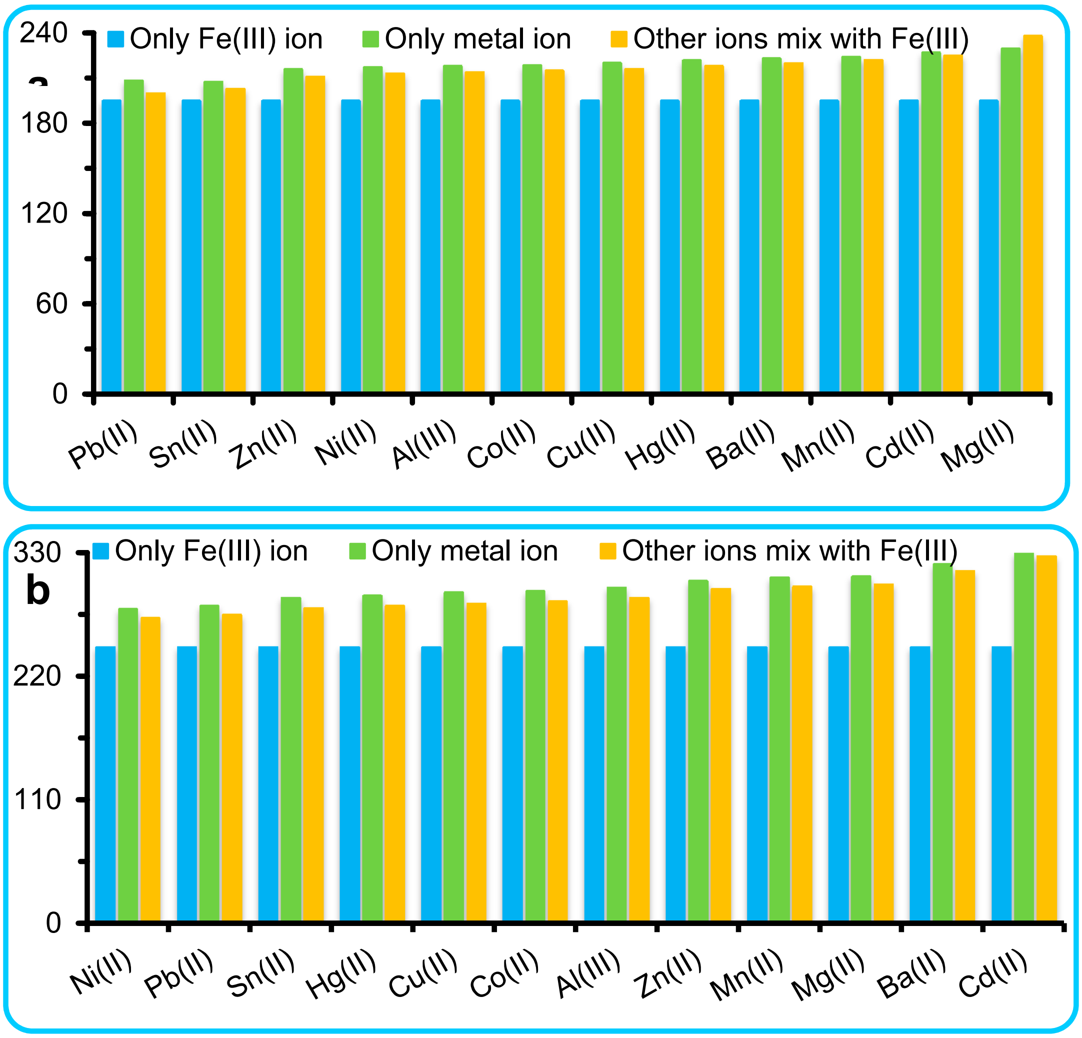

a
Only Fe(III) ion
Only metal ion
Other ions mix with Fe(III)
240
180
120
60
0
Pb(II)
Sn(II)
Zn(II)
Ni(II)
Al(III)
Co(II)
Cu(II)
Hg(II)
Ba(II)
Mn(II)
Cd(II)
Mg(II)
b
Only Fe(III) ion
Only metal ion
Other ions mix with Fe(III)
330
220
110
0
Ni(II)
Pb(II)
Sn(II)
Hg(II)
Cu(II)
Co(II)
Al(III)
Zn(II)
Mn(II)
Mg(II)
Ba(II)
Cd(II)

Fig. 7.

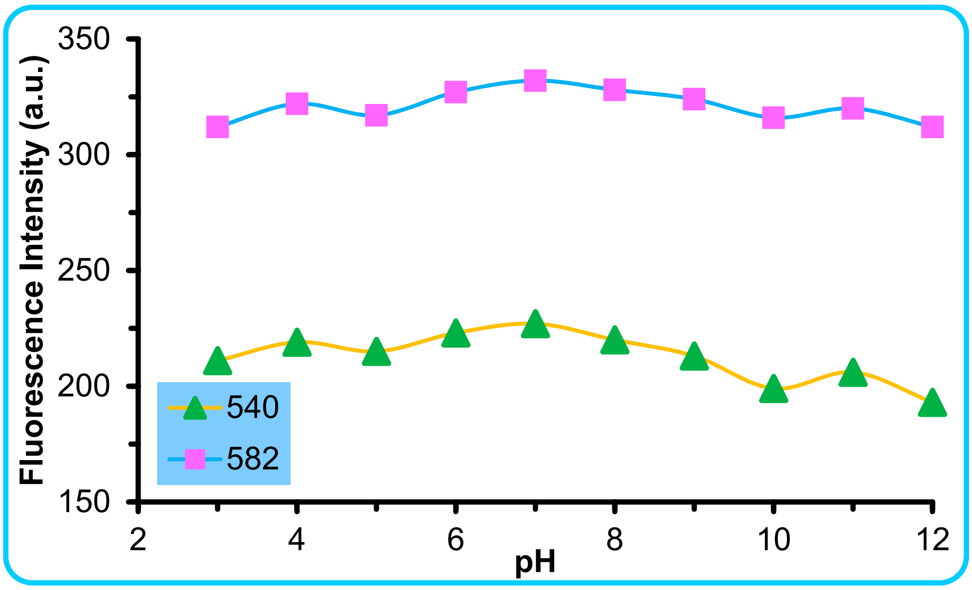

Fluorescence Intensity (a.u.)
350
300
250
200
150
2
4
6
8
10
12
pH
540
582

Fig. 8.

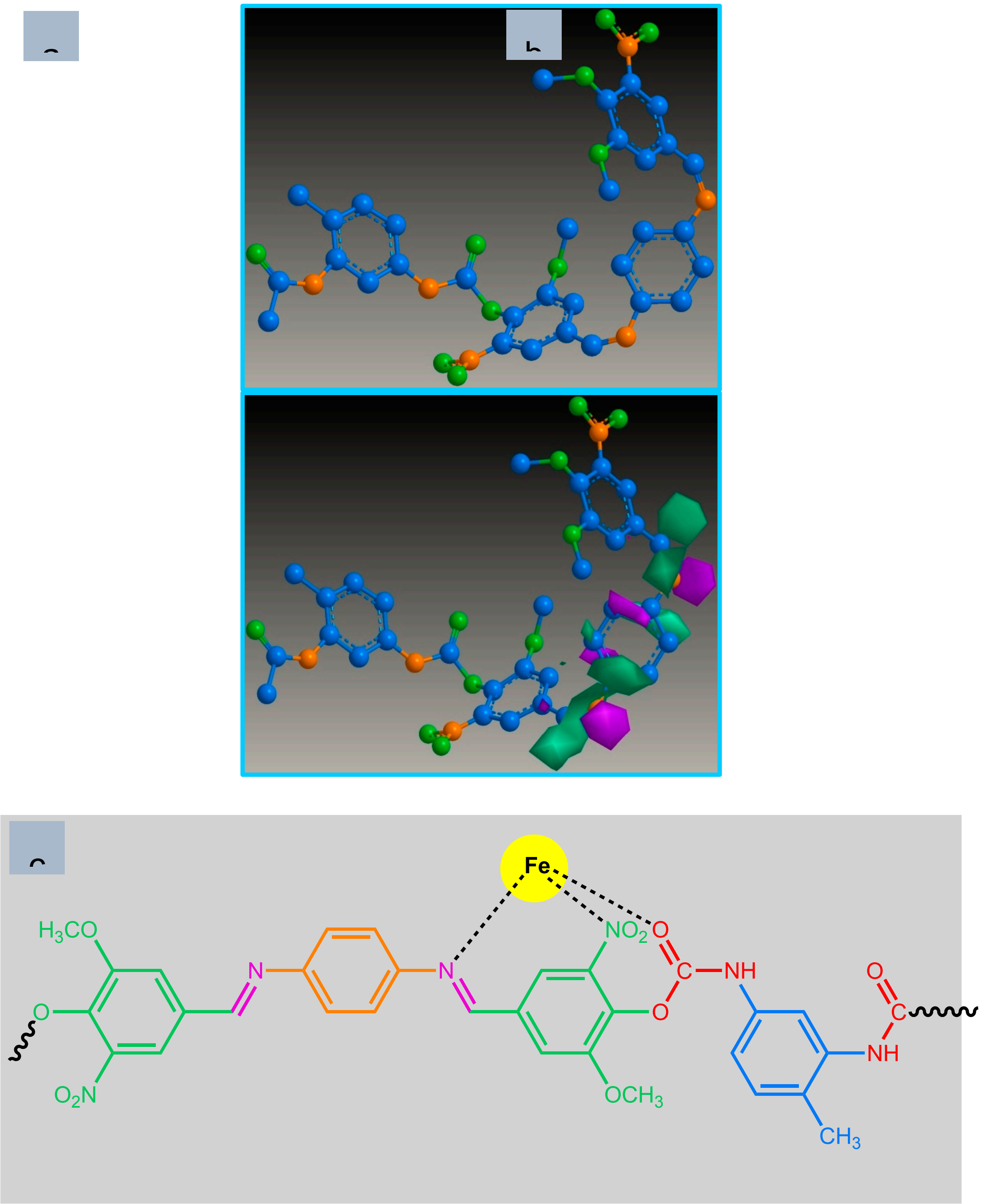


Fig. 9.

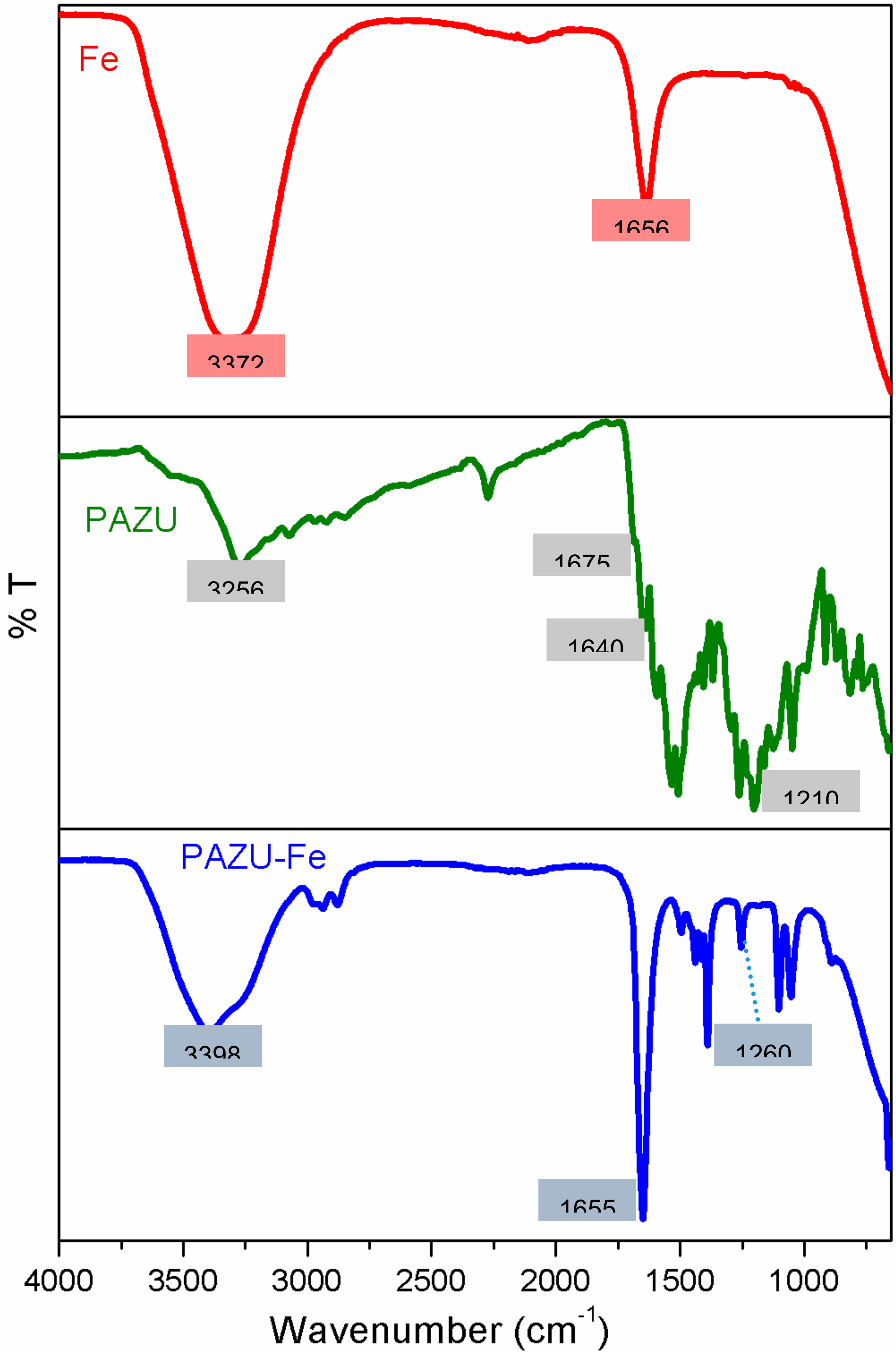

Fe
3372
1656
PAZU
3256
1675
1640
1210
PAZU-Fe
3398
1260
1655
% T
4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm^{-1})

Fig. 10.

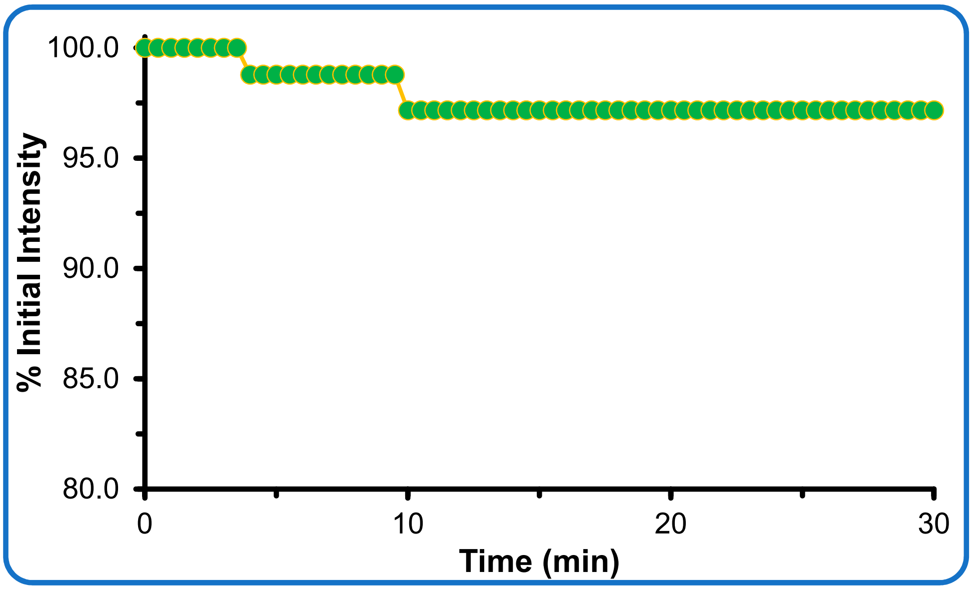

100.0
95.0
90.0
85.0
80.0
% Initial Intensity
0
10
20
30
Time (min)

Fig. 11.

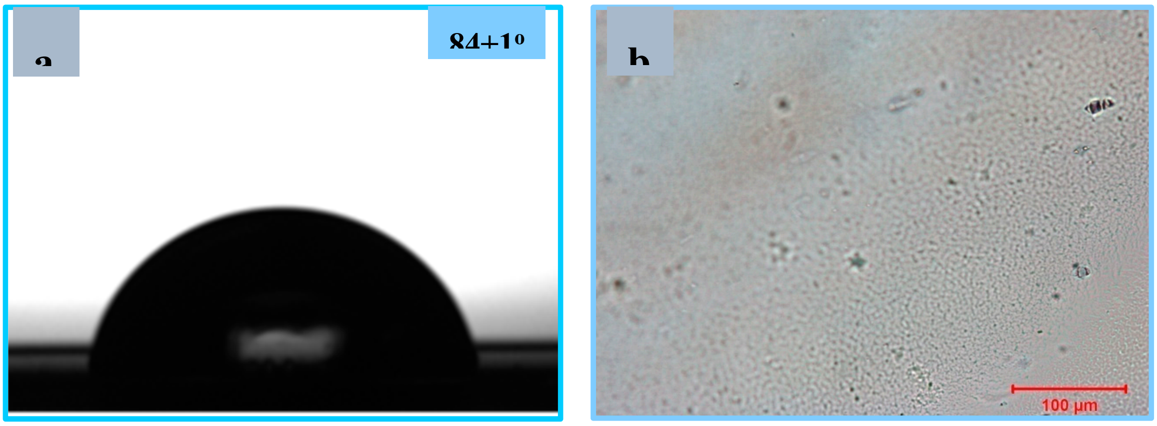

a
84±1°
b
100 µm

Fig. 12.

Table 1

Fluorescence measurement data of PAZU film in deionized water.

$^{a}\lambda_{max(Ex.)}$ nm	$^{b}\lambda_{max(Em.)1}$ nm	$^{b}\lambda_{max(Em.)2}$ nm	$^{c}I_{Ex.}$	$^{d}I_{Em.1}$	$^{d}I_{Em.2}$	$^{e}\Delta\lambda_{ST1}$	$^{e}\Delta\lambda_{ST2}$
400	540	582	311	209	278	140	182

[a] Maximum excitation wavelength

[b] Maximum emission wavelength

[c] Maximum excitation intensity

[d] Maximum emission intensity

[e] Stokes Shift value: [$\lambda_{max\ (Em.)}$- $\lambda_{max\ (Ex.)}$]