

Phosphonate-Functionalized Polyfluorene Film Sensors for Sensitive Detection of Iron(III) in both Organic and Aqueous Media

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ABSTRACT: A novel conjugated polymer (CP) based thin film sensor toward Fe^{3+} was prepared by covalent immobilization of a phosphonate-functionalized polyfluorene on glass surface. Contact angle, XPS and steady-state fluorescence measurements proved that the polyfluorene was successfully chemically conjugated on the substrate surface. Like the organic solution and spin-casting film of this polyfluorene, the fluorescence of the immobilized film can be selectively quenched by Fe^{3+} in both organic and aqueous solutions. Limit of detection of this film sensor for Fe^{3+} could be down to 8.4 ppb in THF solution and 0.14 ppm in aqueous solution, which were among the best results for Fe^{3+} sensing by fluorescence film sensors reported so far. Compared with the fluorescence quenching properties of the same polyfluorene in THF solution and in spin-casting film, both quenching constant and detection limit of the immobilized film were improved by 1 order of magnitude, which demonstrated the advantage of the immobilized film fluorescence sensor. In addition, the sensing process is reversible in both organic and aqueous solutions.

Introduction

Fluorescent chemosensors for spying on molecular recognition events are particularly attractive for their advantages, such as intrinsic sensitivity ease of detection, low cost, and rapid implementation.¹ They have been widely utilized for the detection of various analytes, such as cations,² anions,³ and organic analytes.⁴ However, most of the researches on fluorescent sensor are focused on the design of selective receptors and fluorophores used in organic or aqueous solutions. From the viewpoint of practicability, fluorescent sensors in thin film are more applicable than fluorescent sensors in solution phase,^{5–7} because film sensors can be easily integrated into real sensor devices. Unfortunately, only few fluorescent sensors in thin films can preserve their selectivity, sensitivity and stability in solutions.⁸ Taking the detection of metal ions for example, the solution approach usually shows higher sensitivity compared with the fluorescent film sensors.^{7,9}

As fluorescent sensing materials, conjugated polymers (CPs) are considered to be one of the most promising candidates for fluorescent chemosensors due to the signal amplification effect¹⁰ and the versatility in molecular designs.¹¹ Moreover, CPs have good processability and they can easily fabricate the spin-casting film used for actual sensing device implementation. It is believed that more efficient exciton transport of CPs in solid-state than that in dilute solution because the exciton migration occurs as a three-dimensional process by both inter- and intramolecular pathways.¹² The interesting examples for CPs spin-casting films sensors are the application of them for sensing explosive vapors^{13–15} and gas-phase molecules.¹⁶ Despite benefits for actual application, the sensing utility of CP films is also limited by some adverse factors. For instance, compact π -stacking of polymer chains and steric hindrance in solid-state may weaken the interaction between the receptors and analytes, even to decrease the sensitivity. Moreover, the poor stability of physically absorbed CP films can

hardly avoid the leakage of the polymers. Concomitantly, it is difficult to realize the quantitative analysis of species in solution because the target systems are likely to be contaminated.

Self-assembled monolayers (SAMs) methodologies^{17–20} can be conveniently used to produce the covalent immobilized thin film with chemical functionality on different substrate surface. On the basis of this methodology, a series of glass-confined sensing systems are developed and have successfully been demonstrated that the molecules²¹ and ions²² recognition process is feasible at the film–solution interface in aqueous and organic solutions. In terms of fluorescent film sensors, SAMs of fluorescent molecules supported by glass substrates^{5,21c–f,22b–f} is highly desirable for practical application because of the high stability of sensor elements, no contamination to the target systems, as well as fast and reversible response besides the intrinsic advantages of fluorescent chemosensors. In addition, glass substrate does not quench fluorescence, which is suitable for fluorescent detection.⁸ Nevertheless, the lack of strong metal-ion binding sites and the limited number of receptors inherent to a planar glass surface leads to low selectivity and sensitivity. From this point of view, combination of the advantages of covalent immobilization and conjugated polymers may be a promising strategy to realize high sensitivity and high selectivity for thin film sensors.^{23,24} Meanwhile, this strategy will be able to overcome the drawbacks of spin-casting film as sensing materials. Only very few works have been reported about conjugated polymers immobilized on the glass surface used for fluorescent analysis of metal ions.²⁵ However, their metal ions sensing properties are still rather poor compared with the corresponding conjugated polymer solutions.

We have previously reported the preparation and properties of polyfluorenes with phosphonate ester²⁶ and phosphonate sodium salt²⁷ in the side chains. An interesting feature of these polymers is the highly selective and sensitive fluorescence quenching by Fe^{3+} in solutions. As a key role in many biochemical processes at the cellular level, only few selective fluorescent sensors^{28,29} and

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optical sensor films³⁰ for Fe³⁺ have been reported. Therefore, it is attractive to apply our polyfluorene to fabricate Fe³⁺ film fluorescent sensors. In this contribution, we designed and prepared novel immobilized fluorescent films based on the phosphonate-functionalized polyfluorenes on the glass substrate surfaces. It was demonstrated that the stable CP-based film can detect Fe³⁺ with high sensitivity, selectivity and reversible response in both organic and aqueous solution. We also compared the sensing properties of the immobilized film with those of the same polymer solution and spin-casting film, which further proved the advantage of the fluorescent CP immobilized film sensors.

Experimental Section

Material. All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to standard procedures. Monomer 2,7-dibromo-9,9-bis(3'-diethoxyphosphorylpropyl)fluorene²⁶ and 1,4-benzenediboronic acid propanediol ester³¹ were synthesized as previously described.

Measurement and Characterization. ¹H NMR spectra were recorded on Bruker AV-300 with CDCl₃ as solvents. IR spectra were obtained on FT-IR Bruker Vertex 70 spectrometer at a nominal resolution of 2 cm⁻¹. The power samples were prepared by adding model compound and polymer into KBr and the mixture was ground to a fine power and pressed to form disk. X-ray photoelectron spectra (XPS) were obtained on a Thermo Electron ESCALAB 250 spectrometer equipped with a monochromatic Al X-ray source (1486.6 eV). Contact angles of the films were measured by drop shape analysis (Kruss, Germany) at ambient temperature. UV-visible absorption measurements were carried out on Perkin-Elmer Lambda 35 UV-vis spectrometer, with a scan rate of 500 nm/min.

Fluorescence Titration Procedure. Fluorescence emission spectra were recorded on a Perkin-Elmer LS 50B luminescence spectrometer with Xenon discharge lamp excitation. Various solution spectra, solid-state films spectra, and fluorescence quenching experiments were measured by the method reported in the literature.^{21e,26,32} Solutions of cationic perchlorate salts or cationic nitrate salts with the concentration of typically 5 × 10⁻⁴ M were prepared by successive dilution. Fluorescence quenching experiment of the film was carried out by sequentially adding small aliquots of cationic salts stock solutions to 3.00 mL of the testing solution. The solid-state films were placed in a quartz cuvette, which allowed the recording of fluorescence spectra with the films exposed to the testing solutions. The individual fluorescence values given in the text are the average of three measurements.

Synthesis of Poly(9,9-bis(3'-diethoxyphosphatopropyl)fluorene-*alt*-1,4-phenylene) End-Capped with Aldehyde (PFPEt). A mixture of 2, 7-dibromo-9,9-bis(3'-diethoxyphosphorylpropyl)fluorene (0.68 g, 1 mmol), 1,4-benzenediboronic acid propanediol ester (0.246 g, 1 mmol), 4-bromobenzaldehyde (5.5 mg, 0.03 mmol), and Pd(PPh₃)₄ (2.3 mg) was added and degassed for 30 min. Then a solution of 0.2 M aqueous K₂CO₃ (4 mL) and toluene (12 mL) was added and the reaction mixture was degassed and stirred at 90 °C for 48 h under argon atmosphere. After cooling to room temperature, the resulting mixture was diluted in dichloromethane. The solution was washed with brine and deionized water, respectively, and then dried with anhydrous Na₂SO₄. After removal of the solvent, the residue was redissolved with a minimum amount of dichloromethane and precipitated in hexane. The resulting polymers were obtained after drying in vacuum with a yield of 64%. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.78 (br, 6H, Ar-H), 7.66 (br, 4H, Ar-H), 3.91 (m, 8H, -O-CH₂-), 2.26 (br, 4H, -CH₂-), 1.57 (br, 4H, -CH₂-), 1.14 (br, 16H, -CH₃, -CH₂-). IR (KBr, cm⁻¹): 2979, 2930, 2871, 1698, 1603, 1520, 1463, 1391, 1242, 1100, 1027, 958, 814, 782.

Substrate Preparation. All glass wafers (0.8 cm × 3.7 cm) used to prepare the layers were cleaned by sonicating for 2 min in

deionized water, dichloromethane, and acetone, respectively. After cleaning, the substrates were immersed into piranha solution (concentrated H₂SO₄ and 33% aqueous H₂O₂ in a 3:1 (v:v) ratio) [Caution! piranha is a very strong oxidant and reacts violently with many organic materials] at 80 °C for 60 min, and then rinsed with a copious amount of doubly distilled water. Blow the wafers dry with high-pure nitrogen. The wafers treated in this way are rich in hydroxyls at the oxide surface and suitable for the silanization process.

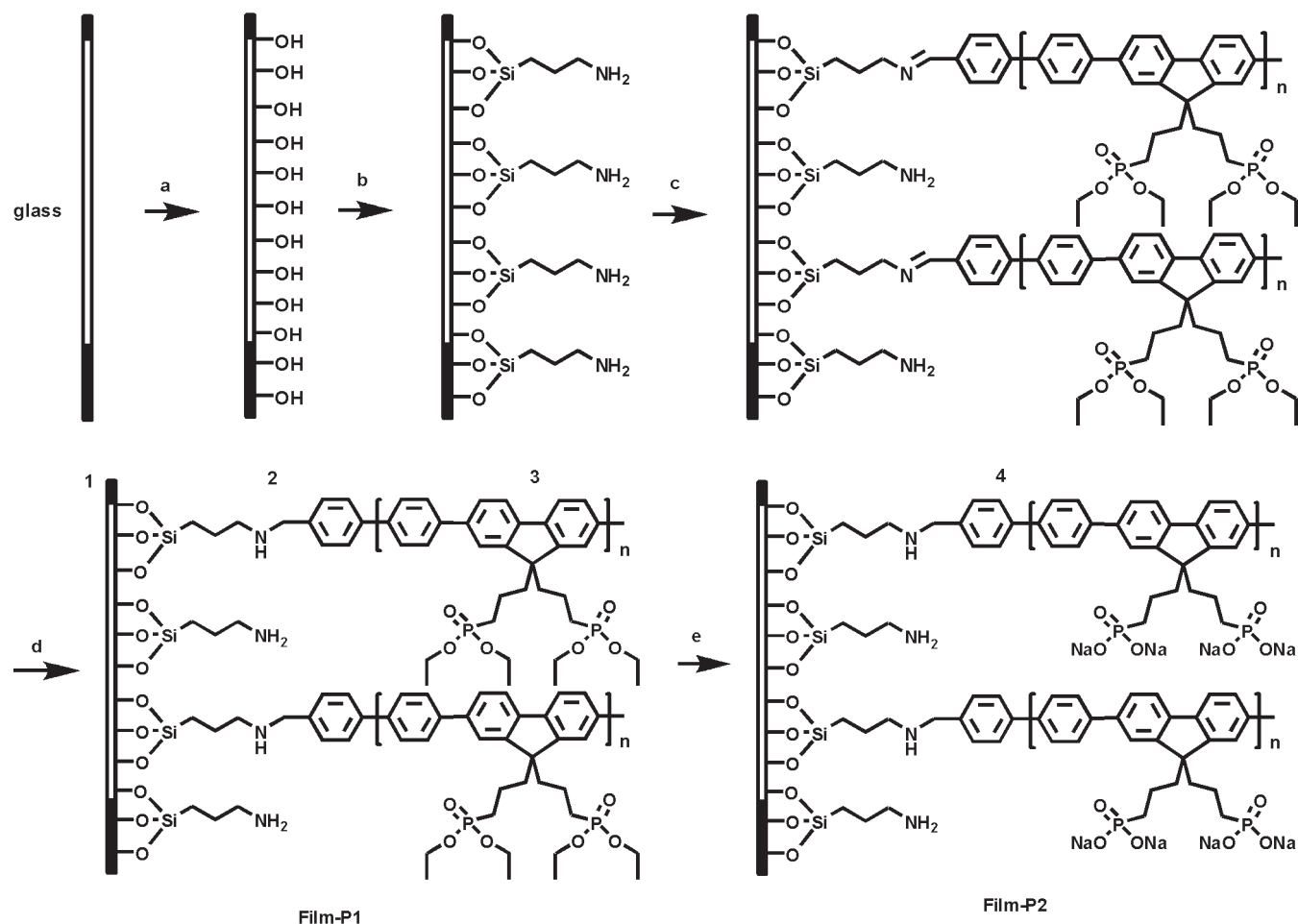
Aminosilylation. Under argon atmosphere, the freshly cleaned substrates were immersed into anhydrous toluene solution (40 mL) containing (3-aminopropyl) triethoxysilane (0.4 mL) for 24 h at room temperature. After the substrates were taken from the solution, it was rinsed with anhydrous toluene at once. After taking out of the solution, they were heated to 110 °C for 1 h under reduced pressure and then rinsed with toluene and methanol several times. Finally, the wafers were blown dry with nitrogen. The samples were stored in a desiccator under a vacuum if not used immediately.

Chemical Coupling of Poly(9,9-bis(3'-diethoxyphosphatopropyl)fluorene-*alt*-1,4-phenylene) End-Capped with Aldehyde (PFPEt) Surface (Film-P1). The APTES-modified wafers were placed into a solution of PFPEt (60 mg) in THF (30 mL). No more than four pieces of the substrates were placed in a flask to avoid the physical overlap among the substrates. To solution, ice acetic acid (0.02 mL), and Linde 4-Å molecular sieve (*ca.* 1 g) was added. The solution was refluxed for 12 h under argon atmosphere to generate corresponding Schiff's base. The glass wafers were washed by THF, and then put into a 1:1 (v:v) mixture of THF/methanol. After cooling to 0 °C, NaBH₄ was added to the solution for several times within 1 h. The reacting solution was stirred for another 3 h at room temperature. The wafers were rinsed with the doubly distilled water, and extracted with CH₂Cl₂ in a Soxhlet extractor for 24 h to remove the unreacted polymer.

Formation of Poly(9,9-bis(3'-phosphatopropyl)fluorene-*alt*-1,4-phenylene) Sodium Salt (PFPPNa) Surface (Film-P2). A reactor containing wafers modified by the phosphonate ester-functionalized polyfluorenes was evacuated, and argon is allowed to fill reactor. Subsequently, anhydrous dichloromethane (20 mL) and bromotrimethylsilane (0.2 mL) were added via syringe and stirred at room temperature for 8 h. The reaction was quenched by adding 40 mL of methanol. The glass wafers were taken out of the reactor and washed with dichloromethane and deionized water. The wafers were immersed into a mixture of methanol and 0.2 M Na₂CO₃ aqueous solution, and the solution was stirred for 6 h at room temperature. After hydrolyzing, the wafers were rinsed copiously with doubly distilled water. Finally, the wafers were blown dry with nitrogen. The synthesis of PFPEt and fabrication of Film-P1 and Film-P2 are shown in Scheme 1 and Scheme S1.

Results and Discussion

Materials Preparation and Characterization. The synthetic procedure for polymer PFPEt is shown in Scheme S1 in the Supporting Information. The polymerization of 2,7-dibromo-9,9-bis(3'-diethoxyphosphorylpropyl)fluorene and 1,4-benzenediboronic acid propanediol ester via Suzuki polycondensation with Pd(PPh₃)₄ as catalyst in toluene and K₂CO₃ aqueous solution yielded polyfluorenes with phosphonate ester in the side chains. Then 3 mol % 4-bromobenzaldehyde was used as an end-capped reagent in order to prepare the polymer with aldehyde-functionalized end group. The structure of the resulting polymer was verified by ¹H NMR and FT-IR, which indicated that the phosphonate ester groups on the polymeric side chains were not hydrolyzed under the conditions of polymerization. At the same time, the chemical shift of ¹H NMR at δ = 10.09 and the IR absorption peak of 1698 cm⁻¹ shows that aldehyde group was introduced into

Scheme 1. Fabricated Process of the Films of Phosphonate Ester and Phosphonate–Sodium Salt Functionalized Polyfluorenes on Glass Surface^a

^a Reagents and conditions: (a) $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$, 90 °C, 1 h. (b) (3-aminopropyl) triethoxysilane (APTES), toluene, room temperature, 24 h. (c) **PFPEt**, THF, HOAc, 4A molecular sieve, reflux, 12 h. (d) NaBH_4 , THF/methanol, 0 °C. (e) bromotrimethylsilane, CH_2Cl_2 , room temperature, methanol, 0.2 M $\text{Na}_2\text{CO}_3(\text{aq})$, room temperature.

the polymer. Because of strong absorption of the polymers on the column fillers possibly induced by the high polarity of the phosphonate ester, the molecular weight of **PFPEt** could not be measured by normal gel permeation chromatography (GPC) method. However, the molecular weight of **PFPEt** calculated by integrated area ratio between hydrogen atoms of aldehyde and alkyl through ^1H NMR was estimated to be 19 kD.

Film-P1 and **Film-P2** on a glass surface were prepared as depicted in Scheme 1. A film of (3-aminopropyl)triethoxysilane was attached to the substrate in the first step. Aminosilylated-surface could react with aldehyde of **PFPEt** to form a film of phosphonate ester-functionalized polyfluorenes linked by imine. In order to enhance the stability of the film, the imine group was further reduced by NaBH_4 to form stable single bonds between carbon and nitrogen. It is confirmed that polymer **PFPEt** was chemically immobilized onto the glass surface because of observation of strong fluorescence after rinsing with a lot of doubly distilled water and extracting with CH_2Cl_2 in a Soxhlet extractor for more than 24 h. **Film-P2** was prepared by reaction of **Film-P1** with bromotrimethylsilane in dry dichloromethane, following hydrolysis by methanol and Na_2CO_3 aqueous solution.

The new films were characterized by combination of XPS, contact angles and UV–vis spectra measurements. Comparing X-ray photoelectron spectra of the glass plates of various surface structures, it is observed that the spectrum of the

Table 1. Static Contact Angles (θ) for Glass Surfaces of Various Structures

glass plates ^a	2	3	Film-P1	Film-P2
contact angles (deg)	11.0 ± 2.0	72.6 ± 1.7	88.3 ± 4.8	68.9 ± 3.4

^a 2, 3, **Film-P1**, and **Film-P2** represent the same meaning as those shown in Scheme 1.

APTES-modified wafer exhibited peaks of N 1s (400.9 eV) and the intensity of peaks C 1s (284.6 eV) were dramatically increased (Figure S1a, Supporting Information). After immobilization of polymer on the surface, the peaks of P 2p (133.2 eV) appeared, indicating successful binding of polymers (Figure S1b, Supporting Information). The intensities of peak C 1s and P 2p were rather stable even after hydrolyzation of phosphonate ester under the condition of acid bromotrimethylsilane and basic aqueous sodium carbonate, which also confirmed that CP-based films were robust after imines had been reduced and the polymer was immobilized on the glass surface with stable chemical bonds.

Aqueous contact angles measurements can also reveal the changes of structures of the glass surfaces (Table 1). Hydroxyl-activated surface was an almost completely hydrophilic surface with a very low static contact angle of $11.0^\circ \pm 2.0^\circ$. The substrate surface covered with APTES will change to be a hydrophobic surface, and the contact angle dramatically increased to $72.6^\circ \pm 1.7^\circ$. Comparing with the APTES-modified surface, the contact angle of **Film-P1** further increased to $88.3^\circ \pm 4.8^\circ$ due to the introduction of a large amount of

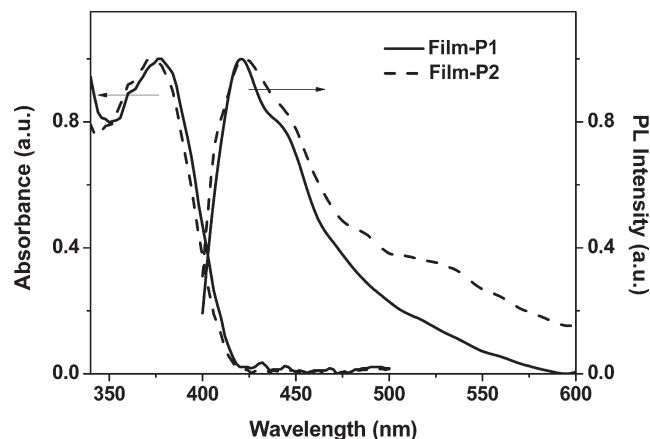


Figure 1. UV-vis absorption and PL spectra of **Film-P1** and **Film-P2** in dry-state.

hydrophobic conjugated aromatic backbones and alkyl side chains to the film during the polymer immobilization process. After hydrolyzation of phosphonate ester, formation of conjugated polyelectrolyte on the surface enhanced the surface hydrophilicity, and the contact angle of **Film-P2** decreased to $68.9^\circ \pm 3.4^\circ$. It is clear that the change of the contact angle was always consistent with the change of the surface structure.

Photophysical Properties. Photophysical properties of **Film-P1** and **Film-P2** films were characterized by absorption and emission spectra (Figure 1). Absorption and emission maxima of **Film-P1** and **Film-P2** in the dry state peaked at 376, 421 nm and 372, 422 nm, respectively. Their optical properties are very similar to those of the same polymers in solution states, which confirm that the immobilization does not change their optical behaviors as conjugated polymers. In the wet state, a small change in the PL spectra of the films in the different solvents was observed (Figure S3, Supporting Information). The PL spectra maximum of **Film-P1** in water peaked at 421 nm, while blue shifts of emission were observed in organic solvents. The PL peaks were at 417, 412, and 411 nm in methanol, tetrahydrofuran, and dichloromethane, respectively. Likewise, the PL spectra of **Film-P2** peaked at 414 nm in dichloromethane, 415 nm in tetrahydrofuran, 418 nm in methanol, and 420 nm in H_2O . These spectral shifts in different solvents may be related to the different polymer chain conformations (extended or coiled) and the different interaction of phosphonate groups with solvent molecules as we suggested previously.²⁶

The stabilities of the CP immobilized films were tested by monitoring the fluorescence emissions of the films and the solutions. After immersing the films in the THF and aqueous solution at room temperature for several hours, the fluorescence signals hardly changed (Figure S4, Supporting Information). Furthermore, by monitoring the fluorescent intensity of the solutions, no leakage of the polymers was found after removal of the slide from the spectrofluorometer cuvette. No fluorescent signal can be observed in the solutions, even after sonication. The robust structure and stable optical readout ensure that the CP immobilized films can be used for detection of analytes in solution.

Sensing Properties. As expected, the fluorescence emission of the immobilized films is very sensitive to the presence of Fe^{3+} ion. When exposing the film in THF solution and in aqueous solution containing $5 \mu M$ Fe^{3+} ion, the fluorescence quenching was observed. The fluorescence intensities of the film decreased rapidly within 1 min (Figure S5, Supporting Information) and finally reached a stable value. It took about 30 min in THF solution and 6 min in aqueous solution

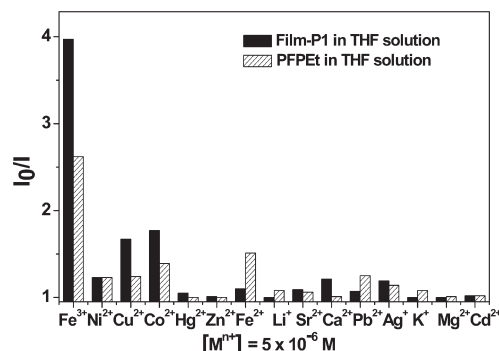


Figure 2. Fluorescence response profiles of **Film-P1** in THF solutions and the polymer **PFPEt** solution upon addition of different metal ions of $5 \mu M$.

to reach equilibrium. It was also found that the fluorescence signal could reach stable within 3 min after sonicating for about 10 s. Consequently, we could get the stable fluorescence signal in a short time.

The fluorescence responses of **Film-P1** were also studied after immersing in THF solutions of $5 \mu M$ other metal ions, such as Ni^{2+} , Cu^{2+} , Co^{2+} , Co^{2+} , Hg^{2+} , Zn^{2+} , Fe^{2+} , Li^+ , Sr^{2+} , Ca^{2+} , Pb^{2+} , Ag^+ , K^+ , Mg^{2+} , and Cd^{2+} . After sonicating for 10 s and incubating for 3 min, the fluorescence intensities at 412 nm were recorded. Generally, molecular interactions on a surface often exhibit conspicuous difference from those in solution.⁶ Therefore, the control tests were carried out in the **PFPEt**–THF solution with various metal ion concentrations in order to compare the selectivity of the film with that of polymer solution. Among all the metal ions studied, Fe^{3+} ion has the most significant quenching effect on the fluorescence intensities of both the film and the polymer solution (Figure 2). In the presence of $5 \mu M$ of Fe^{3+} , the fluorescence of **PFPEt** solution was quenched for 2.6-fold; while a 4.0-fold fluorescence quenching of **Film-P1** was observed, which demonstrated that **Film-P1** was more efficient than the **PFPEt** solution. Although Cu^{2+} and Co^{2+} ions quenched fluorescent emission of the film 1.6- and 1.7-fold, respectively, the fluorescence quenching effect of Fe^{3+} was still almost two and a half times higher than that of Co^{2+} and Cu^{2+} . It was obvious that this thin film can still selectively coordinate Fe^{3+} over the other metal ions as its polymer solution.

We further tested the sensitivity of **Film-P1** for Fe^{3+} in THF solution. The intensity of the fluorescence emission at 412 nm was highly sensitive to Fe^{3+} ion and decreased as the concentration of Fe^{3+} ion increased (Figure 3). To evaluate the sensitivity of this sensing system, we determined the Stern–Volmer quenching constant K_{sv} which was given by the Stern–Volmer equation,³³ $I_0/I = 1 + K_{sv}[Q]$. At low concentration, I_0/I increased linearly as the concentration of quencher increase. On the basis of the correlation curve, a linear range of the plot was from 1.5×10^{-7} to 1×10^{-6} M and the K_{sv} was calculated to be $1.33 \times 10^6 M^{-1}$ (Figure S6, Supporting Information). Therefore, a quantitative analysis of Fe^{3+} ion at the low concentration was achievable. The limit of detection was as low as 1.5×10^{-7} M or 8.4 ppb, which was among the best results for Fe^{3+} sensing by fluorescence film sensors reported so far. Fluorescent intensity of **Film-P1** was completely quenched by the addition of Fe^{3+} of $20 \mu M$. The K_{sv} of polymer solution was $1.14 \times 10^5 M^{-1}$ and the detection limit was 1.0×10^{-6} M, which were 1 order of magnitude lower than those of the film (Figure S7, Supporting Information). The higher sensitivity of **Film-P1** may be attributed to the further enhancement of the amplified

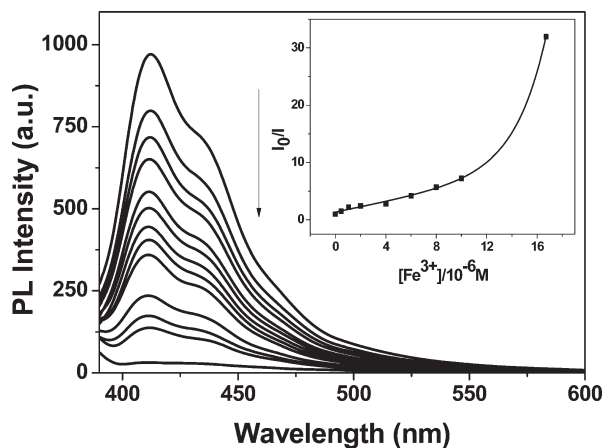


Figure 3. Fluorescence response of **Film-P1** in THF solution upon addition of Fe^{3+} . Inset of the graph illustrates the plot of I_0/I against varying Fe^{3+} concentrations.

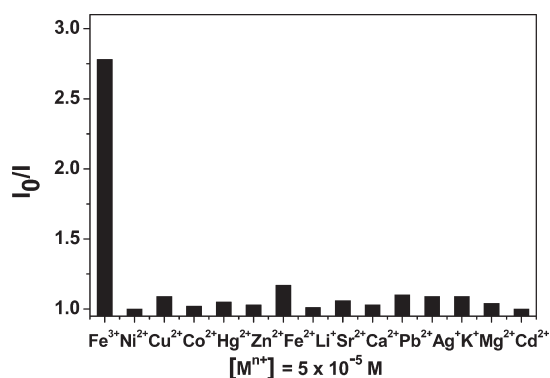


Figure 4. Fluorescence response profiles of **Film-P1** in aqueous solutions upon addition of different metal ions of 50 μM .

fluorescence quenching of CPs in the solid-state. All these findings confirmed that the new CP immobilized film could be used as a thin film fluorescence sensor for the highly selective and sensitive detection of Fe^{3+} in organic solution.

The fluorescence responses of this film with the different metal ions in aqueous solutions were also studied. After sonication and incubation with 50 μM of various ions aqueous solution, we found the Fe^{3+} ion was also the strongest quencher for **Film-P1** (Figure 4). The emission of the film was quenched 2.8-fold by Fe^{3+} ion and less than 1.2-fold by the other metal ions. The quenching effect in aqueous solution was lower than that (4.0-fold by 5 μM Fe^{3+}) in organic solution, which is also observed by others in covalent assembled film sensors.^{21b} Anyway, this new film can also selectively sense Fe^{3+} over the other metal ions in aqueous solution.

Like the case in THF solution, the fluorescence intensities decreased when the concentration of Fe^{3+} increased in aqueous solution (Figure 5a). Good linear correlation was found over the concentration range from 2.5×10^{-6} to 2×10^{-5} M (Figure S8a). From the plot for the linear region, the quenching constant K_{sv} was calculated to be $6.02 \times 10^4 \text{ M}^{-1}$. The detection limit of Fe^{3+} was determined to be 2.5×10^{-6} M, or 0.14 ppm, which was also a rare example of film-based sensors for Fe^{3+} in aqueous solution.^{21b} However, both the quenching constant and the detection limit in aqueous solution are lower than those in THF solution, which may be due to the different conformation of the immobilized polymers in THF solution (the extended conformation in good solvent)

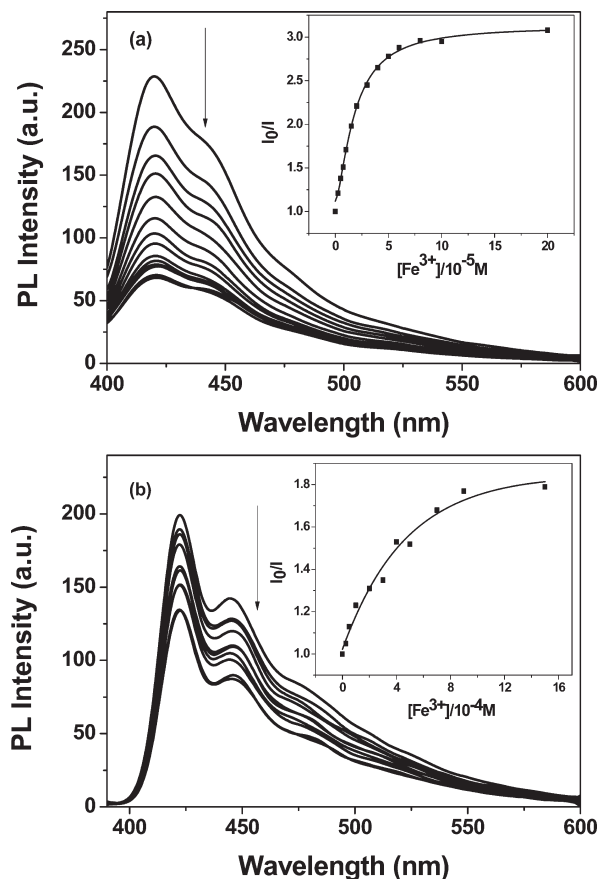


Figure 5. Fluorescence intensities of (a) **Film-P1** and (b) **PFPET** spin-casting film in aqueous solution changed with the different concentrations of Fe^{3+} . Inset illustrates plot of I_0/I against varying Fe^{3+} concentrations.

and in aqueous solution (the coiled conformation in poor solvent). A control experiment was done for the **PFPET** spin-casting film in the aqueous solution. The quenching effect of Fe^{3+} ion on the fluorescence of the spin-casting film was much lower than that of **Film-P1** (Figure 5b, Figure S8b). According to the plot of linear part, the value of K_{sv} was determined to be $2.34 \times 10^3 \text{ M}^{-1}$, 1 order of magnitude lower than that of **Film-P1**. The detection limit was only 2.5×10^{-5} M, which is similar as the fluorescent film sensors for Fe^{3+} by other group.³⁰ Addition of even 10 mM Fe^{3+} could only induce a 2.2-fold fluorescence quenching. The sharp contrast indicated that sensing performance of the CP immobilized film was superior to the spin-casting film. In addition, the spinning-casting films can hardly be used in THF solution. As realizing the detection of Fe^{3+} in both organic and aqueous solutions, this new CP-based film will provide more space for practical sensor applications.

We also checked the sensing ability of the film of conjugated polyelectrolyte **PFPNa** toward Fe^{3+} ion. Unfortunately, the immobilization of conjugated polyelectrolyte on the glass surface did not improve the sensitivity for Fe^{3+} in aqueous solution at all (Figure S9). According to the linear part of I_0/I plot, the value K_{sv} of **Film-P2** was calculated to be only $3.25 \times 10^4 \text{ M}^{-1}$. The low sensitivity may be attributed to the extremely strong interaction of Fe^{3+} ions with phosphonate salts, which restrict their access to the interior of the films.

One advantage of the films chemosensors was their reversible response. To evaluate the reversible sensing ability of **Film-P1** for Fe^{3+} , we monitored the corresponding changes

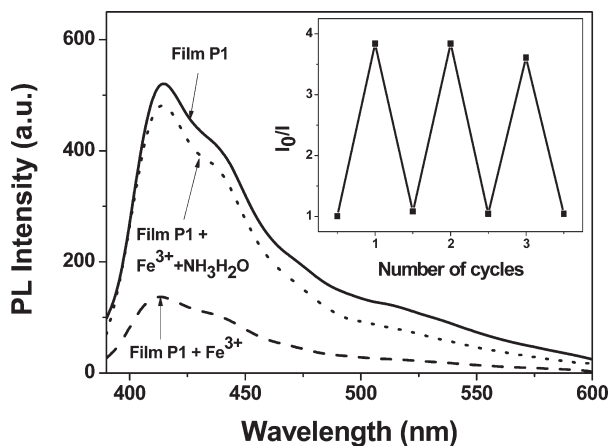


Figure 6. Fluorescence reversibility of **Film-P1**. Inset illustrates plot of I_0/I against the number of cycles of alternately exposing the film to THF solution of Fe^{3+} ion of $5 \mu\text{M}$ and ammonia THF solution.

of its fluorescence intensity when alternately immersing the film into a THF solution of $5 \mu\text{M}$ Fe^{3+} ion and a THF solution containing dilute ammonia. Unsurprisingly, the emission of **Film-P1** quenched by Fe^{3+} was almost fully restored and the process could be repeated for at least three times (Figure 6). In the same way, the fluorescence emission of **Film-P2** could also be restored by using ammonia aqueous solution.

Conclusion

In summary, we have prepared the covalent immobilized fluorescent films based on the phosphonate-functionalized polyfluorenes on the glass surface. Contact angle, XPS, and steady-state fluorescence measurements demonstrated that the polyfluorenes was stably immobilized on the glass surface. The robust films have excellent selectivity toward Fe^{3+} ion over other common metal ions in both organic and aqueous solutions. For **Film-P1**, the detection limits for Fe^{3+} could be down to 8.4 ppb in THF solution and 0.14 ppm in aqueous solution. To the best of our knowledge, these detection limits were among the best results for the fluorescence film-based Fe^{3+} sensors. Compared with the detection limits of the polymer THF solution (56 ppb) and the spin-casting film in aqueous solution (1.4 ppm), a decrease of 1 order of magnitude was observed for **Film-P1**. The quenching constants of the immobilized film in THF solution and in aqueous solution were determined to be $1.33 \times 10^6 \text{ M}^{-1}$ and $6.02 \times 10^4 \text{ M}^{-1}$, respectively, which also were far superior to those of the polymer solution ($1.14 \times 10^5 \text{ M}^{-1}$) and the spin-casting film ($2.34 \times 10^3 \text{ M}^{-1}$). In addition, **Film-P2** of conjugated polyelectrolyte was also prepared by the chemical method without improvement in the sensing properties. Anyway, the highly selective fluorescent quenching at low ion concentration and the reversible response suggest that the immobilized **Film-P1** is promising to make real sensor devices for Fe^{3+} with high performance.

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Supporting Information Available: Scheme showing the details of the synthesis and figures showing XPS, absorption, and PL spectra of the polymer **PFPEt** in solution and in spin-casting film, PL spectra in different solvents, stabilities, and the time-dependent Fe^{3+} -response of the immobilized films, the linear regions of the polymer **PFPEt** solution and **Film-P1** and **PFPEt**

spin-casting film in aqueous solution, and fluorescence titration of **Film-P2** in aqueous solution. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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