Articles

Phosphonate-Functionalized Polyfluorene as a Highly Water-Soluble Iron(III) Chemosensor

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ABSTRACT: An anionic, phosphonate-functionalized polyfluorene, i.e., poly(9,9-bis(3′-phosphatepropyl)fluorene-*alt*-1,4-phenylene) sodium salt (**PFPNa**), has been synthesized by copolymerization of phosphonic acid-substituted 2,7-dibromofluorene and phenyldiboronic ester via direct Suzuki polycondensation reaction in DMF/water. Polymer **PFPNa** is highly soluble and emissive in water with a solubility of 60 mg/mL and a photoluminescence quantum yield of 75%. The absorption and fluorescence spectra of **PFPNa** are strongly dependent on pH value owing to the partial protonation of phosphate groups and the aggregation of the polymer chains. In aqueous media polymer **PFPNa** shows high sensitivity and selectivity for Fe^{3+}. A 400-fold fluorescence quenching was achieved upon adding Fe^{3+} into its aqueous solution. Most importantly, ultrathin multilayer films constructed by alternatively depositing polyanionic **PFPNa** and polycationic poly(diallyldimethylamine) via the layer-by-layer (LbL) self-assembling method are stable and highly sensitive to Fe^{3+} with a sensitivity up to 10^{-7} M.

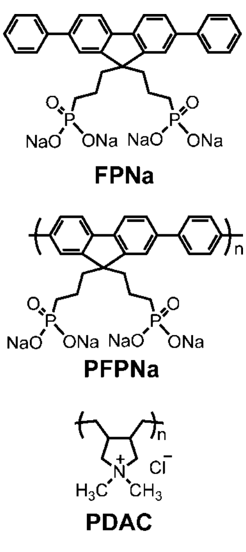
Introduction

Over the past decade conjugated polyelectrolytes (CPEs) have been widely investigated as highly sensitive and selective fluorescent sensors for chemical[1] and biological targets[2] in aqueous solution. Generally, CPEs are conjugated polymers with pendent functionalities capable of ionizing in highly dielectric media.[3] Carboxylate groups,[1d,4] sulfonate groups,[5] phosphonate groups,[6] carbohydrate groups[7] and ammonium groups[2a,8] have been introduced to the pendant chains of poly(phenylene vinylene)s (PPVs),[9] poly(*p*-phenylene)s (PPPs),[10] poly(phenylene ethylene)s (PPEs),[11] polythiophenes (PTs)[12] and polyfluorenes (PFs).[13] However, most reported CPEs exhibit rather poor solubility in water probably due to their low charge densities which compete with the aromatic $\pi-\pi$ stacking of the hydrophobic backbones. As a result, the CPEs usually exhibit low photoluminescence (PL) quantum efficiencies due to the main-chain aggregation, which is detrimental to their sensing application. Moreover, the fluorescence of the CPEs could be quenched by trace of charged molecules (quenchers) via charge transfer or energy transfer.[2a] Although the trapping of the excitons along the CPE backbones produces an amplified sensitivity,[1a,14] the strong Coulombic attractions between the water-soluble CPEs and the oppositely charged quenchers result in a limited selectivity for charged analytes.

Fe^{3+} is an essential trace element that plays significant roles in chemical and biological processes. Fe^{3+} is indispensable for most organisms, and both its deficiency and overload can induce various disorders with iron trafficking, storage, and balance.[15] For example, Fe^{3+} deficiency leads to anemia and excess iron in the body causes liver and kidney damage (hemochromatosis). Thus, there is an urgent need to develop chemical sensors that are capable of detecting Fe^{3+} in environmental and biological samples at a physiological pH value.[16] However, most of them have limitation such as interference from other metal ions, delayed response to Fe^{3+}, and/or low water solubility. Only a few sensors have been reported to selectively detect Fe^{3+} in aqueous solutions.[17]

In our previous work, we reported PFs with diethyl phosphonate groups in the side chains, which are highly soluble in various organic solvents with PL quantum efficiencies as high as 73% in ethanol.[18] The polymers exhibit strong selectivity for Fe^{3+} over a wide variety of other metal ions with amplified and reversible fluorescence quenching in organic solvents. The

Chart 1



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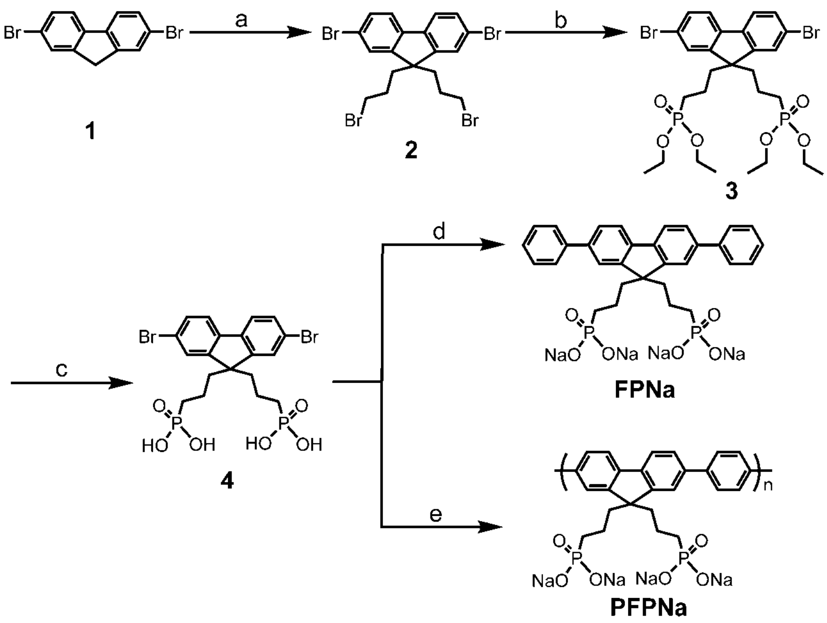
Scheme 1. Synthetic Route of Polymer PFPNa and Model Compound FPNa[a]



[a] Reagents and conditions: (a) 1,3-dibromopropane, NaOH/H_2O, 70 °C, 6 h, 64%; (b) triethylphosphite, 140 °C, 16 h, 96%; (c) bromotrimethylsilane, CH_2Cl_2, room temperature, 4 h; methanol 12 h, 96.8%; (d) phenylboronic acid, $Pd(OAc)_2$, Na_2CO_3, DMF/H_2O, 85 °C, 12 h, 90%; (e) 1,4-phenylenebis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane), $Pd(dppf)Cl_2$, Na_2CO_3, DMF/H_2O, 85 °C, 48 h, 55%.

promising results obtained encouraged us to further develop the corresponding phosphonate-functionalized water-soluble PFs used for the detection of Fe^{3+} ions in aqueous media.

In this contribution, we report the synthesis and properties of a novel anionic, phosphonate-functionalized polyfluorene, poly(9,9-bis(3′-phosphatepropyl)fluorene-*alt*-1,4-phenylene) sodium salt (**PFPNa**) (Chart 1), which contains four negative charges in each repeating unit. The polymer **PFPNa** is found to be highly water-soluble and strongly emissive with a solubility of 60 mg/mL and a PL quantum yield as high as 75%. Meanwhile, the sensing properties of polymer **PFPNa** in both aqueous solution and ultrathin multilayer films were investigated in detail.

Results and Discussion

Synthesis and Structure Characterization. The synthetic procedure for polymer **PFPNa** is shown in Scheme 1. The monomer 2,7-dibromo-9,9-bis(3′-phosphonic acid propyl)fluorene (**4**) was synthesized by treatment of 2,7-dibromo-9,9-bis(3′-diethoxylphosphorylpropyl)-fluorene (**3**)[18] with bromotrimethylsilane and subsequently methanol as a white solid in 96.8% yield. The polymerization of monomer **4** and 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene via Suzuki polycondensation[19] with $Pd(dppf)Cl_2$ as catalyst in *N*,*N*-dimetylformamide (DMF) and Na_2CO_3 aqueous solution yielded the crude polymer **PFPNa**. After purification by dialysis with an 8000−15000 molecular weight cutoff membrane to remove ionic impurities and low molecular weight oligomers, polymer **PFPNa** was obtained as a yellow powder in a good yield of 55%. For comparison, model compound 9,9-bis(3′-phosphatepropyl)-2,7-diphenylfluorene sodium salt (**FPNa**) was synthesized by Suzuki−Miyaura coupling of monomer **4** and phenylboronic acid with $Pd(OAc)_2$ as catalyst in 90% yield.

The structures of polymer **PFPNa** and model compound **FPNa** were verified by ^1H NMR, ^{13}C NMR, FT-IR, and elemental analysis. The molecular weight of polymer **PFPNa** could not be measured by normal gel permeation chromatography (GPC) method due to its ionic characteristic. Light scattering method was also performed to try to measure the molecular weight, and unfortunately, no laser signal could be detected. However, the molecular weight of polymer **PFPNa** should be higher than 15 kDa since the cutoff of the membrane was 8000−15000. Therefore, the average polymerization degree should be over 26. Polymer **PFPNa** and model compound **FPNa** are well soluble in water with a strong sky-blue fluorescence but insoluble in normal organic solvents, such as dimethylsulfoxide (DMSO), DMF and chloroform. Noticeably, the solubility of polymer **PFPNa** in water reaches as high as 60 mg/mL.

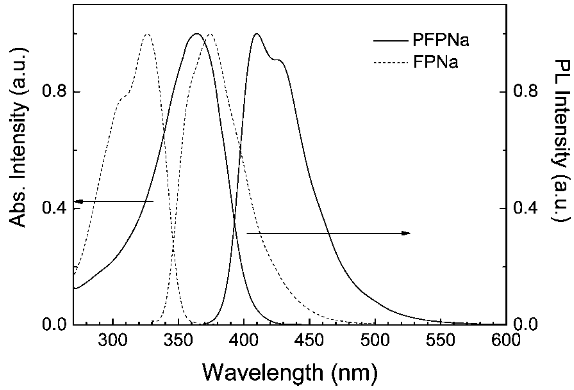


Figure 1. UV−vis absorption and PL spectra of polymer **PFPNa** and model compound **FPNa** in aqueous solutions.

Photophysical Properties. The absorption and PL spectra of polymer **PFPNa** and model compound **FPNa** in deionized water solutions were measured at a concentration of *ca.* 10^{-5} M (repeating unit). As shown in Figure 1, the absorption and PL maxima red shift from 326 and 374 nm of model compound **FPNa** to 364 and 410 nm of polymer **PFPNa**, respectively, due to the increased conjugation of polymer backbone. Furthermore, polymer **PFPNa** exhibits a structured emission with well defined vibronic peaks at 410 and 426 nm, which can be assigned to the 0−0 and 0−1 transitions, respectively. As expected, the spectral features are almost identical to other reported neutral and charged fluorene-*alt*-phenylene copolymers.[2g,8c] Notably, a PL quantum yield as high as 75% for **PFPNa** was measured

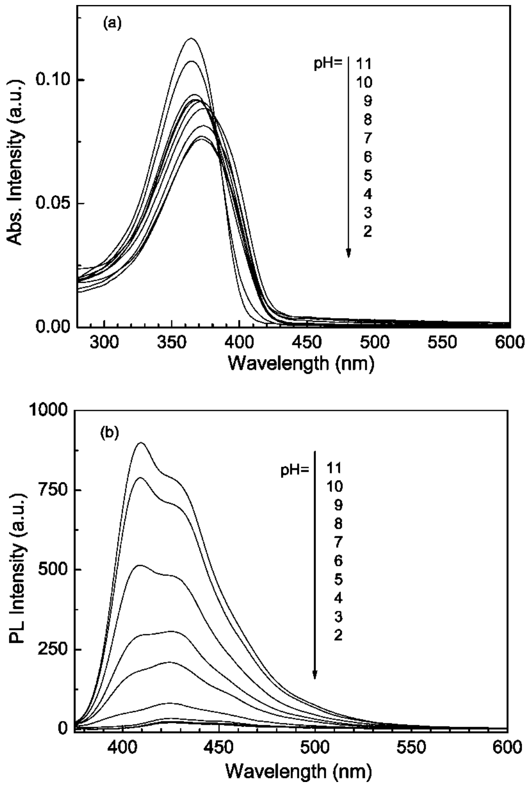


Figure 2. UV−vis absorption (a) and PL (b) spectra of polymer **PFPNa** in aqueous solutions as a function of pH.

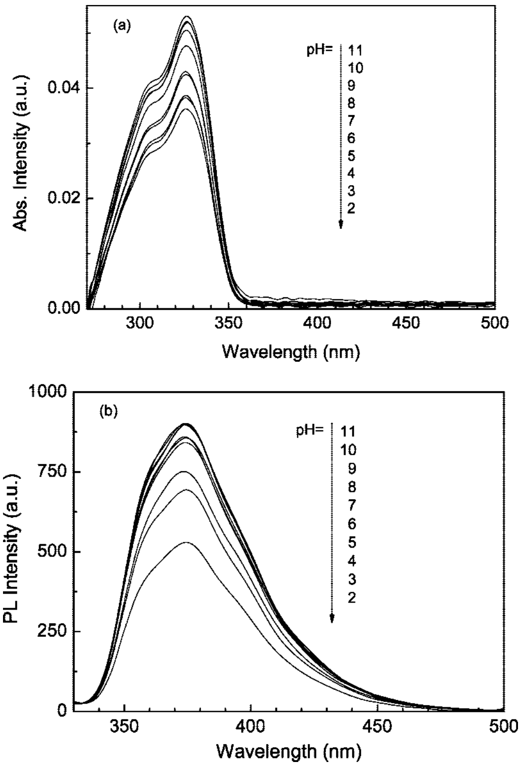


Figure 3. UV−vis absorption (a) and PL (b) spectra of model compound **FPNa** in aqueous solutions as a function of pH.

in aqueous solution (*ca.* 10^{-6} M) with quinine sulfate as a reference.[20] This value is significantly higher than that of previously reported fluorene-based polyelectrolytes,[8c,21] and identical to that of diethyl phosphonate-functionalized PFs in ethanol.[18] We attribute the high PL quantum yield of **PFPNa** to its high anionic density (four negative charges per repeating unit) and appropriate length of the side chains, which may be able to depress the aggregation of conjugated chains.

Similar to other reported CPEs, the absorption and PL spectra of **PFPNa** are pH-sensitive.[3,6a] Figure 2 shows the absorption and PL spectra of **PFPNa** in 5 mM phosphate buffer solutions at pH values ranging from 2 to 11 with an interval of 1. A 6 nm bathochromic shift of the absorption spectra was observed in Figure 2a when pH value decreased from 11 to 8. Since the first (pK_a^1) and second (pK_a^2) acid dissociation constants of organophosphonates (pK_a) are typically 2.5 and 8.2, respectively,[22] the negative charges on the phosphonate side groups in **PFPNa** can be gradually protonated as pH value decreases. Thus, the bathochromic shift is attributed to the partial protonation of the phosphonate groups, which results in an aggregation of polymer chains due to the reduction of the electrostatic repulsion between the phosphate salts.[6a] This aggregation of phosphonate-substituted CPEs was also previously reported by Schanze et al. in a phosphonate functionalized water-soluble PPE-type polymer (**PPE-PO$_3^-$**).[6a] With a further decrease of pH value, the absorption maximum of **PFPNa** was kept identical, but the extinction coefficients decreased gradually. Correspondingly, the PL spectrum of **PFPNa** in aqueous solution is also pH-sensitive. As shown in Figure 2b, the relative intensity of the 0−1 transition peak to the 0−0 transition peak increased with the decrease of pH value followed by a fluorescence quenching, which indicates the aggregation of the polymer chains to some extent. As for the model compound **FPNa**, however, a different response to pH value was observed in Figure 3. For example, no obvious change could be found in PL spectra when pH value decreased from 11 to 8, which shows a weaker fluorescence quenching induced by pH value compared with the polymer **PFPNa**. It also demonstrates that the pH-sensitivity should be molecular weight dependent and here, their relation has not been investigated in detail.

Sensing Properties. The sensing properties of polymer **PFPNa** to different metal ions were characterized in its 1 μM aqueous solutions. Upon addition of excess metal ions (4 μM), i.e., Li^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Cd^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Ag^+, Hg^{2+}, Pb^{2+}, and Al^{3+}, no significant changes of the absorption spectra were observed. However, the extinction coefficient of **PFPNa** decreased obviously upon addition of Fe^{3+}, as shown in Figure 4a. Another subtle feature is that the absorption onset is red-shifted by about 7 nm, indicating that the fluorescence quenching induced by Fe^{3+} occurs mainly via static (associated complex) process[23] owing to the strong association interaction between the analytes, Fe^{3+} ions and the receptors, phosphonate groups.[18] Similarly, the PL spectrum of **PFPNa** is much more sensitive to Fe^{3+} over other metal ions. When 4 μM Fe^{3+} was added into the aqueous solution of **PFPNa**, the PL intensity decreased dramatically with a 400-fold fluorescence quenching (Figure 5). In contrast, the addition of 4 μM Al^{3+} and Pb^{2+} only induced a 14- and 15-fold fluorescence quenching, respectively. These results indicate that polymer **PFPNa** is a highly sensitive and selective chemosensor for Fe^{3+}.

The inset in Figure 4b illustrates the Stern-Volmer plot of polymer **PFPNa** upon addition of Fe^{3+} in the aqueous solution. At low concentration, PL_0/PL increases linearly as the concentration of quencher increases. The Stern-Volmer constant (K_{sv}) is calculated to be 1.84×10^6 M^{-1} according to the equation (1).[24]

$$PL_0/PL = 1 + K_{sv}[\text{quencher}] \tag{1}$$

As the concentration of Fe^{3+} increases to >1 μM, the plot becomes superlinear. Such a superlinear quenching was tentatively attributed to quencher-induced aggregation of conjugated

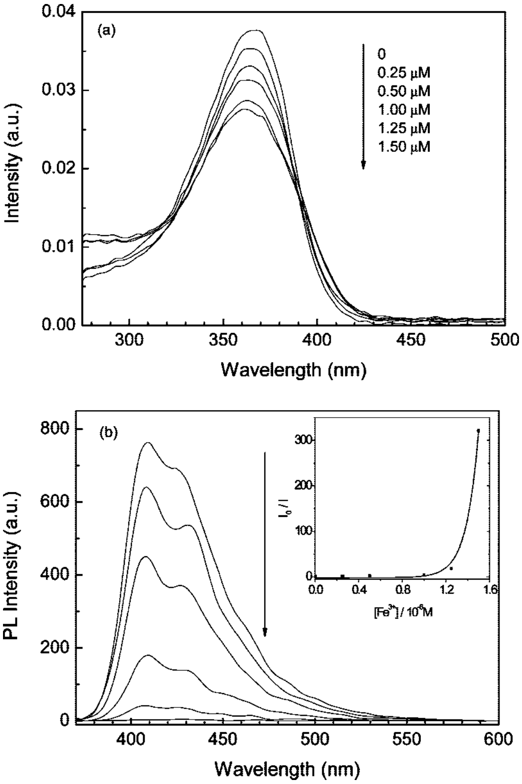


Figure 4. Absorption (a) and PL (b) spectra of polymer **PFPNa** in aqueous solution upon addition of Fe^{3+}.

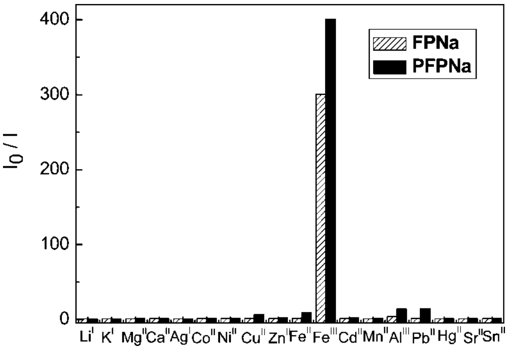


Figure 5. Fluorescence response profiles of model compound **FPNa** and polymer **PFPNa** in aqueous solutions upon addition of different metal ions.

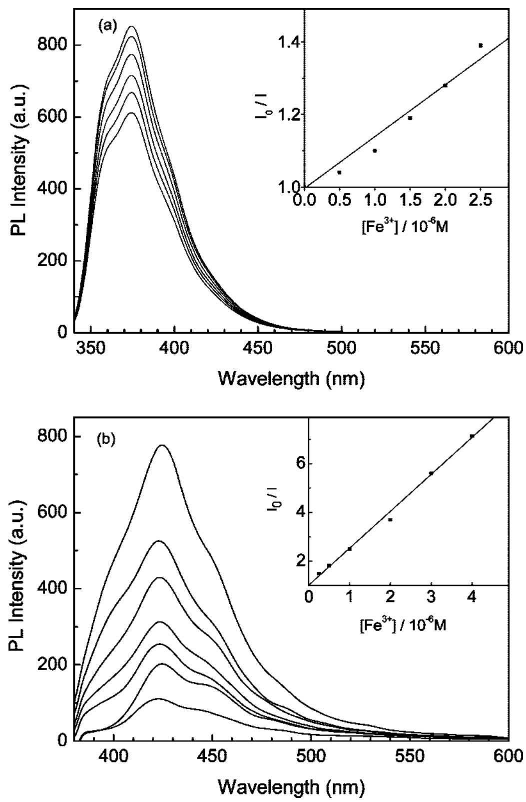


Figure 6. Fluorescence response profiles of **FPNa** (a) and **PFPNa** (b) in buffer solution upon addition of Fe^{3+}. Inset is the Stern–Volmer plot.

polyelectrolytes[1a] on the basis that the 0–1 transition peak of polymer **PFPNa** shows a trend of red shift and the fluorescence intensity decreases simultaneously.

For comparison, the fluorescence response of model compound **FPNa** to different metal ions in aqueous solutions was also studied. Upon addition of excess Fe^{3+} (4 μM) to the water solution of **FPNa** (1 μM), a fluorescence quenching up to 300-fold was observed (Figure 5), which is 3/4 of that of **PFPNa**. Even in an extremely low Fe^{3+} concentration of 0.25 μM, a 10-fold fluorescence quenching could still be achieved. Regarding the origin of the high sensitivity of model compound **FPNa** and the low amplification factor for the conjugated polymer **PFPNa**, the strong association interaction between Fe^{3+} ions and phosphonate groups, as discussed above, should be considered. Although this intense analyte-receptor interaction can enhance the sensitivity for polymer **PFPNa**, the diffusion of Fe^{3+} ions in the aqueous solutions is at the same time limited in fluorescence titration experiments.[23] As a result, the possibility of Fe^{3+} ions simultaneously bound to one same isolated polymer chain or its neighboring chain increases, where the distance between Fe^{3+} ions-occupied receptor sites locates in the exciton diffusion length,[1a] and consequently the amplification effect derived from the conjugated backbone decreases.

To support this hypothesis, the sensing properties of polymer **PFPNa** and model compound **FPNa** in 50 mM Tris–HCl buffer solutions (pH 7.4; Tris = tris(hydroxymethy)aminomethane) were studied at the same time, wherein the association interaction between phosphonate groups and Fe^{3+} could be tuned to facilitate the diffusion of Fe^{3+} with the existence of highly concentrated cations in buffer solutions. Figure 6 shows their fluorescence response profiles upon addition of Fe^{3+}. When excess Fe^{3+} (4 μM) was added into the buffer solution of polymer **PFPNa** (1 μM) and model compound **FPNa** (1 μM), an 86% and 28% fluorescence quenching was observed for polymer **PFPNa** and model compound **FPNa**, respectively. The lower sensitivity compared to that in unbuffered aqueous solution demonstrates the decreased association interaction between phosphonate groups and Fe^{3+} in buffer solutions. As illustrated by the inset in Figure 6, the Stern-Volmer plot for polymer **PFPNa** displays a linear relationship within the quencher concentration range employed. The corresponding K_{sv} value of polymer **PFPNa** was determined to be $1.5 \times 10^6\ M^{-1}$, 1 order of magnitude higher than that of model compound **FPNa** ($1.9 \times 10^5\ M^{-1}$), which is consistent with the signal amplification ability of conjugated polymers due to facile energy migration along the polymer backbones.[1a] Contrary to the observations in aqueous media, the efficient amplification effect as well as the disappearance of superlinear behavior at high quencher concentrations for polymer **PFPNa** may be reasonably ascribed to the suppression of intense analyte-receptor interaction in the presence of concentrated competing cations.

In our previous report,[18] the neutral PFs with phosphonate ester in the side chains are reversible fluorescent chemosensors for Fe^{3+}. In order to verify whether the fluorescence response of **PFPNa** to Fe^{3+} is reversible, 100 μL ammonia aqueous

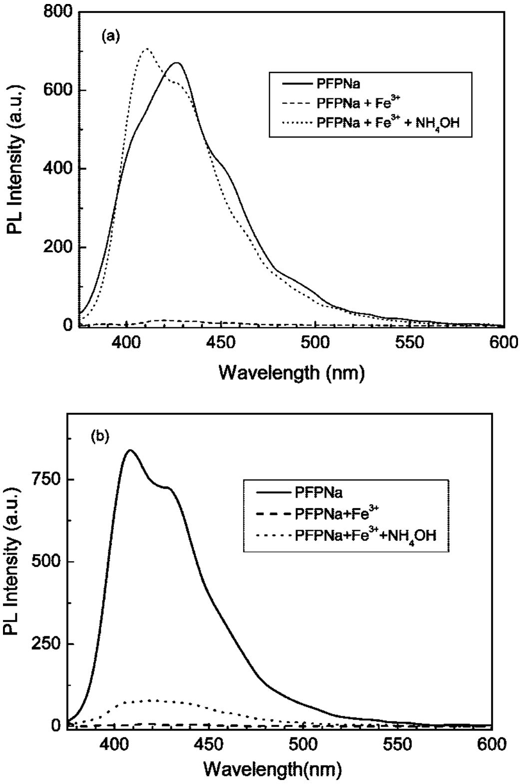


Figure 7. Fluorescence spectra of **PFPNa** in buffer (a) and aqueous solution (b) with or without presence of Fe^{3+} and $NH_3 \cdot H_2O$.

solution (14 M concentration) was added to a 1 μM solution of polymer **PFPNa** in Tris−HCl buffer (50 mM), in which 10 μM Fe^{3+} was added as the fluorescence quencher. As shown in Figure 7a, the fluorescence was nearly recovered to original intensity of that before Fe^{3+} was added accompanied by the increase of the intensity of 0−0 transition peak, indicating a reduced aggregation of polymer chains. In contrast, only 10% of the fluorescence intensity was recovered in unbuffered aqueous solutions of **PFPNa** on the same experimental condition (Figure 7b). The pH values for buffered and unbuffered aqueous solutions varied from 7.4 and 7.2 to 7.4 and 6.6, and then to 9.6 and 11.1, respectively, when Fe^{3+} and $NH_3 \cdot H_2O$ were added in sequence. If only the repulsion effect between the anionic groups induced by the increase of pH values is responsible for the fluorescence reversibility, it could be expected that the fluorescence in unbuffered aqueous solution is easier to be recovered than the buffered solution. Hence, the other factor, such as the interaction between the Fe^{3+} ions and $NH_3 \cdot H_2O$, similar in organic solvent,[18] should be considered. Since it is a competitive process between the interaction of Fe^{3+} ions and $NH_3 \cdot H_2O$ and the interaction of Fe^{3+} ions and phosphonate groups, the stronger association interaction between Fe^{3+} ions and phosphonate groups could lead to the irreversibility of the fluorescence. Therefore, the different PL response to $NH_3 \cdot H_2O$ in buffered and unbuffered aqueous solutions further supports the above-mentioned fact that the strong association interaction between Fe^{3+} ions and phosphonate groups can exist in unbuffered aqueous solution and be weakened by concentrated competing cations in buffered solution.

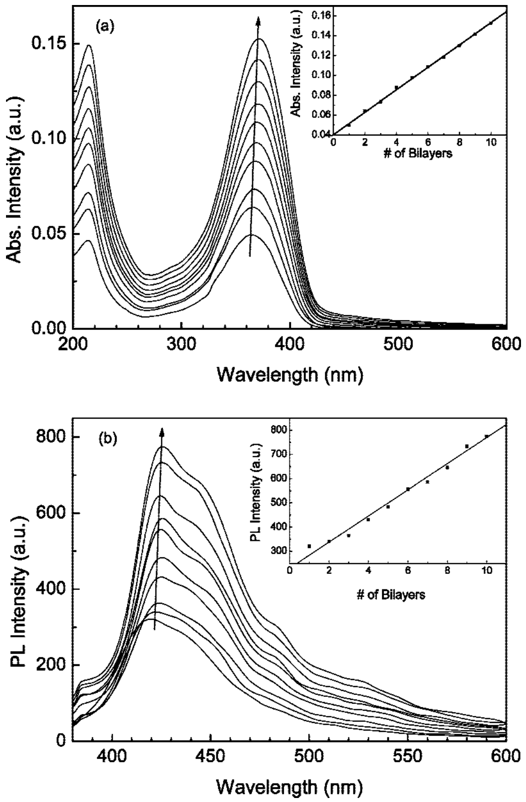


Figure 8. Absorption (a) and fluorescence (b) spectra as a function of number of bilayers deposited for LbL assembled films of **PDAC/PFPNa**. Insets illustrate plots of the absorbance and PL intensity at λ_{max} vs bilayer number.

Most real-time and real-space sensory systems rely on thin film technologies. Up to now, although quite a large amount of sensory materials have been developed to detect analytes in water or organic solvents, few sensitive and selective solid state optical sensors have been realized due to the exciton's diffusion length or stability issue.[1a,2] To make thin-film chemosensors based on **PFPNa**, multilayer thin films on quartz substrates were fabricated by layer-by-layer (LbL) self-assembling technique[25] with **PFPNa** and **PDAC** as the anionic and cationic polyelectrolytes, respectively. The deposition process was monitored by measuring the absorption and PL spectra of the LbL films as a function of deposition layers. As illustrated in Figure 8, both the absorption and PL intensity of the LbL films enhanced with a linear relationship to the bilayer number. Interestingly, the 10-bilayer film demonstrated a bathochromic shift of 6 nm in both absorption and PL spectra compared to those for the single-bilayer film, which is probably due to the aggregation of polymer **PFPNa** formed by electrostatic assembly.[25] The LbL films were stable in aqueous solutions. Even after immersed in aqueous solution for 10 min, no obvious change in the absorption and PL spectrum could be observed compared to the original one, which excluded the influence of water on the PL intensity and the instability of the LbL film. Furthermore, in order to obtain the optimal thickness of the thin film to get the highest sensitivity, the relationship between the bilayer number of the LbL film and the sensitivity was investigated. As can be seen in Figure 9, the sensitivity is almost independent of the bilayer number, indicating that only the surface polymer **PFPNa** layer could interact with Fe^{3+}. Therefore, the 1-bilayer LbL film was used to detect Fe^{3+} in aqueous solution. When immersed into the Fe^{3+} aqueous solution, 0.1 μM Fe^{3+} induced a fluorescence quenching of 22% and 1 μM Fe^{3+} could quench more than 67% of original fluorescence (Figure 10), which implies that the **PDDA-PFPNa** LbL self-assembled film is very sensitivity to Fe^{3+}. The limit of detection reaches 10^{-7} M.

Conclusion

In summary, a novel anionic water-soluble polymer **PFPNa** has been synthesized from neutral phosphonic acid substituted monomer **4** by direct Suzuki-coupling polymerization. The

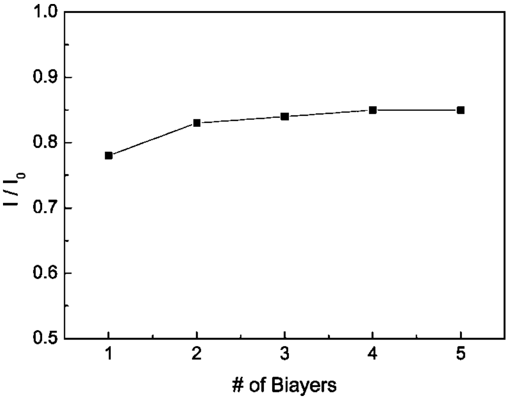


Figure 9. Fluorescence response of **PDAC/PFPNa** film upon addition 0.1 μM Fe^{3+} as a function of bilayers number.

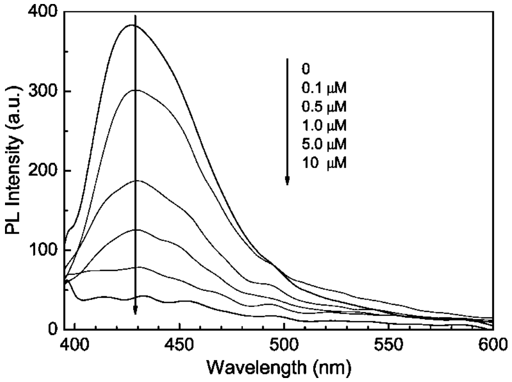


Figure 10. PL spectra of 1-bilayer **PDAC/PFPNa** film upon addition of Fe^{3+}.

obtained polymer is highly soluble in water (60 mg/mL) with a high PL quantum yield of 0.75. The absorption and fluorescence of polymer **PFPNa** demonstrate intense pH-dependence due to its strong aggregation at low pH value. Polymer **PFPNa** is highly sensitive and selective sensory material for Fe^{3+}. A 400-fold fluorescence quenching could be achieved upon adding Fe^{3+} to the aqueous solution of polymer **PFPNa**. The layer-by-layer film assembled from negatively charged polymer **PFPNa** and positively charged polymer **PDAC** is highly sensitive to Fe^{3+} and the detection limit is measured to be 10^{-7} M.

Experimental Section

Measurement and Characterization. ^1H and ^{13}C NMR spectra were recorded on Bruker AV-300 with DMSO-*d6* or D_2O as solvents. The elemental analysis was performed on a Bio-Rad elemental analysis system. IR spectra were obtained on FT-IR Bruker Vertex 70 spectrometer at a nominal resolution of 2 cm^{-1}. The 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. Mass spectroscopy spectrum was recorded on 5975C inert XL MSD gas chromatograph/mass spectrometer (Agilent Technologies Co. Ltd.). The solution pH was measured using a Model 20 pH/conductivity meter (Cole-Parmer Instrument Co.) with combination pH electrode, calibrated with buffers of pH = 4, 7, and 10.

Fluorescence Titration Procedure. Measurements of ultraviolet−visible absorption spectra were carried out on Perkin-Elmer Lambda 35 UV−vis spectrometer, with a scan rate of 500 nm per min. Fluorescence spectra were recorded on a Perkin-Elmer LS 50B luminescence spectrometer with Xenon discharge lamp excitation. A 10 × 10 mm quartz cuvette was used for solution spectra, and emission was collected at 90° relative to the excitation beam. The water was purified with a Millipore filtration system. The solutions of polymer **PFPNa** and model compound **FPNa** were successive diluted to a concentration of 10^{-6} M in water (the concentration of polymers is based on the moles of the repeated unit) or in 50 mM Tris−HCl (pH 7.4; Tris = tris(hydroxymethy)aminomethane) buffer solution. Solutions of cationic perchloride or nitric salts with the concentration of typically 5×10^{-4} M were prepared by successive dilution in water. Fluorescence quenching experiment was carried out by sequentially adding small aliquots of cationic salts stock solutions to 4.00 mL of the polymer solutions by using calibrated microliter pipet. The solutions were vibrated prior to obtaining fluorescence spectra. The pH-dependent experiment was carried out by adding 40 μL of polymer **PFPNa** or model compound **FPNa** (4×10^{-4} M) to 4 mL Na_3PO_4−HCl buffer solution of different pH, then the solutions were vibrated prior to obtaining fluorescence spectra.

Layer-by-Layer Film Fabrication and Sensing Property. The multilayer films were prepared on the surface of round quartz slides with a 0.75 cm radius according to the reported procedure.[6a] The quartz slides were soaked in piranha solution ($H_2SO_4/H_2O_2 = 3/1$) for 12 h, rinsed with water, sonicated with 5 N NaOH for 10 min, and rinsed again with water. Then the quartz slides were soaked sequentially in 1 mM aqueous solutions of polymers **PDAC** and **PFPNa**. Each polymer deposition step in water lasted for 5 min and the films were kept wet during all dipping processes. A Fe^{3+} quenching of the **PDAC/PFPNa** multilayer films was evaluated by measuring the PL spectra of the films. After immersing the films in different concentration Fe^{3+} solution, the slides were rinsed with water, and dried with N_2, and the spectra were obtained immediately.

Material Synthesis. All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to standard procedures. All chemical reactions were carried out under an inert atmosphere. Intermediate 2,7-dibromofluorene, 2,7-dibromo-9,9-bis(3′-bromopropyl)fluorene and 2,7-dibromo-9,9-bis(3′-diethoxylphosphorylpropyl)fluorene were synthesized as previously described.[18]

2,7-Dibromo-9,9-bis(3′-phosphonic acid propyl)fluorene (4). Bromotrimethylsilane(8.5 mL, 80 mmol) was added dropwise to a solution of 2,7-dibromo-9,9-bis(3′-diethoxylphosphorylpropyl)fluorene (3.4 g, 5 mmol) in 50 mL dry CH_2Cl_2 under nitrogen. After the addition, the resulting solution was stirred for 12 h at room temperature. The solvent was removed under vacuum and methanol (50 mL) was added. The resulting solution was stirred for 12 h. Methanol was removed under vacuum, then the crude product was washed with water for three times and filtrated through 0.22 μm cellulose film. Monomer **4** (2.75 g, 96.8%) was obtained as white powder after vacuum at 50 °C for 12 h. ^1H NMR (300 MHz, DMSO-d_6) δ (ppm): 7.81 (d, 2H, $J = 8.1$ Hz), 7.69 (s, 2H), 7.56 (d, 2H, $J = 8.1$ Hz), 2.07 (t, 4H, $J = 7.8$ Hz), 1.28 (m, 4H), 0.66 (m, 4H).^{13}C NMR (75 MHz, DMSO-*d6*) δ (ppm): 152.73, 139.65, 131.16, 127.00, 123.00, 121.94 (C-fluorene ring), 56.35 (C9-fluorene ring), 29.51 ($-CH_2-$), 27.70 ($-CH_2-$), 18.25 ($-CH_2-$). FTIR (ν_{max}, KBr pellet): 2941, 2870, 1462, 1449, 1416, 1058, 1004, 978, 947, 812, 738, 707 cm^{-1}. Anal. Calcd for $C_{19}H_{22}Br_2O_6P_2$: C, 40.11; H, 3.87, Br, 28.34. Found: C, 40.17; H, 3.90; Br, 28.13; GC−MS for $C_{19}H_{22}Br_2O_6P_2$: calculated, 565.93; found, 566.

Poly(9,9-bis(3′-phosphatepropyl)fluorene-*alt*-1,4-phenylene) Sodium Salt (PFPNa). A mixture of monomer **4** (0.568 g, 1 mmol), 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (0.33 g, 1 mmol) and Pd(dppf)Cl_2 (15 mg) was added and degassed for 30 min. Then a solution of 0.2 M aqueous Na_2CO_3 (50 mL) and DMF (20 mL) was added and the reaction mixture was degassed and stirred at 85 °C for 48 h under argon atmosphere. After cooling to room temperature, 200 mL of acetone was poured into the resulting mixture with stirring. A precipitate was collected by filtration, followed by washing with acetone and redissolving in 30 mL of water and the resulting solution was dialyzed against deionized water using an 8000−15000 molecular weight cutoff cellulose for three days. After dialysis, the polymer solution was filtered through a 0.22 μm cellulose membrane, and the product was isolated by evaporation of the water as yellowish powder in 55% yield (0.35 g). ^{1}H NMR (300 MHz, D_2O) δ (ppm): 7.88 (b, 8H), 7.76 (b, 2H), 2.15 (b, 4H), 1.16 (b, 4H), 0.81 (b, 4H). FTIR (ν_{max}, KBr pellet): 3240, 3027, 2942, 2362, 1638, 1520, 1462, 1412, 1222, 1138, 1056, 902, 808, 782, 760, 741, 703, 536, 474 cm^{-1}.

9,9-Bis(3′-phosphatepropyl)-2,7-diphenylfluorene Sodium Salt (FPNa). Monomer **4** (0.568 g, 1 mmol), phenylboronic acid (2.2 mmol 0.268 g) and $Pd(OAc)_2$ (7 mg) was added and degassed for 30 min. A mixture of 0.2 M aqueous Na_2CO_3 solution (20 mL) and DMF (10 mL) was injected via syringe. Then the mixture was degassed and stirred at 80 °C for 12 h. After cooling to room temperature, the resulting mixture was filtrated and the filtrate was poured into 200 mL of acetone. A precipitate was collected by filtration, followed by washing with acetone. Finally the white powder was obtained after dry in vacuum at 50 °C for 24 h with a yield of 90% (0.58 g). ^{1}H NMR (300 MHz, D_2O) δ (ppm): 7.92 (d, 2 H, $J = 7.8$ Hz), 7.85 (s, 2 H), 7.76 (d, 4 H, $J = 7.2$ Hz), 7.69 (d, 2 H, $J = 7.8$ Hz), 7.51 (t, 4 H, $J = 7.8$ Hz), 7.40 (t, 2 H, $J = 7.2$ Hz), 2.20 (t, 4 H, $J = 8.1$ Hz), 1.17 (m, 4 H), 0.84 (m, 4 H). ^{13}C NMR (75 MHz, D_2O), δ (ppm): 152.79, 141.17, 140.42, 140.36, 129.54, 128.04, 127.53, 126.49, 122.55, 120.75, 56.14, 29.42, 27.22, 19.59. FTIR (ν_{max}, KBr pellet): 3303, 3030, 2944, 2616, 1668, 1599, 1465, 1453, 1373, 1221, 1152, 1065, 977, 900, 834, 762, 699 cm^{-1}.

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