

Synthesis, Photophysical Properties, and Self-Assembly Behavior of Amphiphilic Polyfluorene: Unique Dual Fluorescence and Its Application as a Fluorescent Probe for the Mercury Ion

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Received: July 30, 2010; Revised Manuscript Received: September 30, 2010

Two new fluorene-based copolymers PFOH and PHOH were synthesized through Suzuki-coupling reaction, with *p*-*N,N*-bis-(2-hydroxyethyl)aminophenyl and bis(6'-(diethanolamino)hexyl) as side chains, respectively. They were characterized by ¹H NMR, IR, and gel-permeation chromatography (GPC). PFOH shows blue-green emission in THF, and the long emission band exhibits significant bathochromic shift with the increase in solvent polarity, whereas PHOH exhibits a bright blue emission regardless of the solvent polarity. The fluorescence emission behavior of PFOH is analogous to its corresponding terfluorene TFOH, indicating the existence of the intramolecular through-space charge transfer upon being copolymerized into a polymer. Taking advantage of the unique dual emissions, PFOH displays ratiometric “turn-on” responses for Hg²⁺. In addition, the two new polymers show an amphiphilic feature and can form self-assembled nanostructures in a THF–H₂O system, which has influence on their photophysical properties.

Introduction

Fluorene-based oligomers and polymers have found a rich variety of applications in the fields of optoelectronic materials, such as organic light-emitting diodes, organic field effect transistors, and organic solar cells, etc.^{1–4} Recently, polyfluorenes (PF) have also been used as fluorescent sensory materials. In this regard, several groups have developed a series of water-soluble polyfluorenes for detection of protein, DNA/RNA, and even some biological processes;^{5–10} however, the application of polyfluorenes as chemosensors has been but little reported to date. Furthermore, most of them have involved fluorescence quenching of polymers.^{11–13} Therefore, it will be of significance to design fluorescent chemosensors with a “turn-on” response.^{14–16} On the other hand, the self-assembled structures formed from rod–coil block copolymers have attracted great attention in recent years. If modified with proper hydrophilic groups, oligofluorenes/polyfluorenes can assemble into nanoparticles of various morphologies, with the formed structures showing characteristic optical properties.^{17–20} For example, the rod–coil grafted copolymers containing oligofluorene/polyfluorene backbones and poly(ethylene oxide) side chains can form fluorescent micellar structure in aqueous solution,¹⁸ and amphiphilic terfluorene with *n*-hexyl and hydroxyethoxymethyl side chains can form self-condensed nanoparticles in THF–H₂O mixtures.^{19,20}

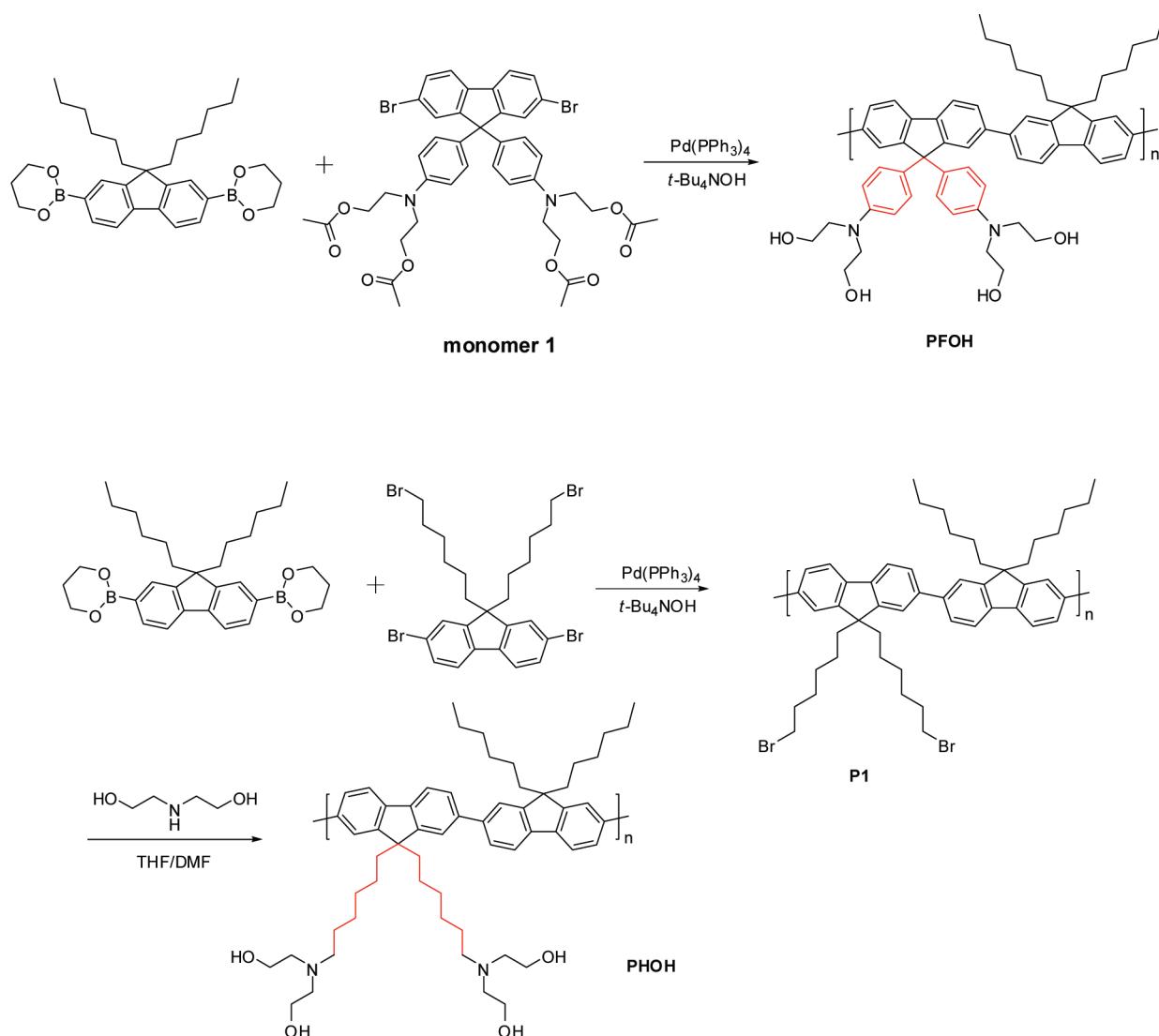
We have recently reported a series of novel terfluorenes exhibiting dual fluorescence emissions in polar solvents.²¹ Combining them with DFT calculations, we have assigned the dual emissions to a $\pi-\pi^*$ transition from the fluorene chain and a new intramolecular through-space charge transfer emission from the pendent aminophenyl group to fluorene chain. We have also substantiated that the pivotal structure responsible for the dual fluorescence emissions is the electron-donating aminophenyl group linked to the C9 position of fluorene. It will be interesting to investigate whether the dual fluorescence emissions

still exist in the corresponding copolymers and how the charge transfer process affects their emissions, as well. In this context, we hereby designed and synthesized a new copolymer, PFOH, with *p*-*N,N*-bis-(2-hydroxyethyl)aminophenyl as pendent groups. For comparison, the copolymer PHOH with *n*-hexyl and bis(6'-(diethanolamino)hexyl) side chains was also synthesized. Their absorption spectra are quite similar, but their emission behaviors have distinct differences due to their structural discrepancy. Because of the hydrophilic hydroxyethyl group and hydrophobic hexyl chain, we expected that both polymers would be amphiphilic; therefore, their self-assembly behaviors as well as the influence on photophysical properties were studied. As an application of the dual fluorescence emissions, the fluorescence response of PFOH toward different metal ions was also investigated.

Experimental Section

General Information. ¹H NMR and ¹³C NMR spectra were recorded on a MECUYRVX300 spectrometer in CDCl₃ or DMSO-*d*₆ using tetramethylsilane as an internal reference. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Carloerba-1106 microanalyzer. The molecular weight of the polymer was determined by an Agilent 1100 GPC using a PLgel 5 mm MIXED-C column and THF as the eluent. The number-average and weight-average molecular weights were estimated by using a calibration curve of polystyrene standards. UV-vis absorption spectra were recorded on a Shimadzu UV-2550 recording spectrophotometer. PL spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. The PL quantum yields were measured from the dilute THF solution of the polymer ($\sim 10^{-6}$ mol/L) by an absolute method using an Edinburgh Instruments (FLS920) integrating sphere excited with a Xe lamp. SEM images were taken by using a field emission scanning electron microscope (FEI Sirion FEG) operated at a voltage of 15 kV. Water was added into PFOH/PHOH in THF solution (at a concentration of 5.0×10^{-6}

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SCHEME 1: Synthesis of PFOH and PHOH

M). After the mixture was allowed to equilibrate over a period, one drop of this mixed solution was transferred onto a quartz substrate.

2,7-Dibromo-9,9'-bis(4-(bis(2-acetoxyethyl)amino)phenyl)-fluorene (**1**) and polymer **P1** were synthesized according to the literature.^{20,22} Other materials were used directly without further purification unless stated otherwise.

Synthesis of PFOH. A mixture of monomer **1** (260 mg, 0.32 mmol), 2,2'-(*9,9*-dihexyl-*9H*-fluorene-2,7-diyl)bis(1,3,2-dioxaborinane) (170 mg, 0.34 mmol), *t*-Bu₄NOH (4.0 mL) and Pd(PPh₃)₄ (10 mg) in 10 mL of THF was stirred at 100 °C for 3 d. After cooling to room temperature, the resulting polymer was purified by precipitating in methanol three times. Yield: 52%. ¹H NMR (300 MHz, DMSO-*d*₆, δ ppm): 8.03 (br), 7.87 (br), 7.71–7.61 (br), 7.05 (br), 6.58 (br), 4.67 (br), 3.48 (br), 1.01 (br), 0.67 (br). FT-IR: 3368 (H—O••H), 2927 (C—H stretching), 1609, 1515, 1457 (aromatic). *M*_n (GPC) = 16 000, PDI = 1.2.

Synthesis of PHOH. Diethanolamine (0.5 mL) was added to a solution of polymer **P1** (200 mg) in a mixture of THF (15 mL) and DMF (15 mL). The mixture was stirred vigorously for 48 h at room temperature. After reaction, the solvent was removed under reduced pressure, and then water was added to get a sage-green solid. Yield: 66%. ¹H NMR (300 MHz, CDCl₃,

δ ppm): 7.82 (br), 7.68 (br), 7.48 (br), 7.37 (br), 3.57 (br), 2.61 (br), 2.49 (br), 2.03 (br), 1.91 (br), 1.25 (br), 1.13 (br), 0.85 (br). *M*_n (GPC) = 7640, PDI = 1.9.

Results and Discussion

Synthesis and Characterization. As depicted in Scheme 1, the copolymer PFOH was prepared by Suzuki polycondensation of monomer **1** and 2,2'-(*9,9*-dihexyl-*9H*-fluorene-2,7-diyl)-bis(1,3,2-dioxaborinane), with a feed ratio of 50:50 mol %, carried out in a mixed solvent of THF and H₂O, with *t*-Bu₄NOH aqueous solution (50%) as base and Pd(PPh₃)₄ as catalyst. PHOH was prepared by postfunctionalization of polymer **P1** with diethanolamine. The number average molecular weight of the two polymers, determined by GPC using THF as eluent and a calibration curve of polystyrene standards, are 16 000 g/mol for PFOH, and 7640 g/mol for PHOH.

The ¹H NMR spectra of monomer **1** and PFOH are shown in Figure 1. For monomer **1**, chemical shifts of *H*_a, *H*_b are ascribed to the protons of pendent phenyl rings at the C9 position of fluorene, and *H*_c and *H*_d are assigned to methene protons of bis(2-acetoxyethyl)amino moieties. These peaks can be seen in the ¹H NMR spectrum of the copolymer PFOH (denoted as *H*_{a'}, *H*_{b'}, *H*_{c'}, and *H*_{d'}). In addition, the methyl proton signals (*H*_e) assigned to the ester groups of monomer **1** completely disappear

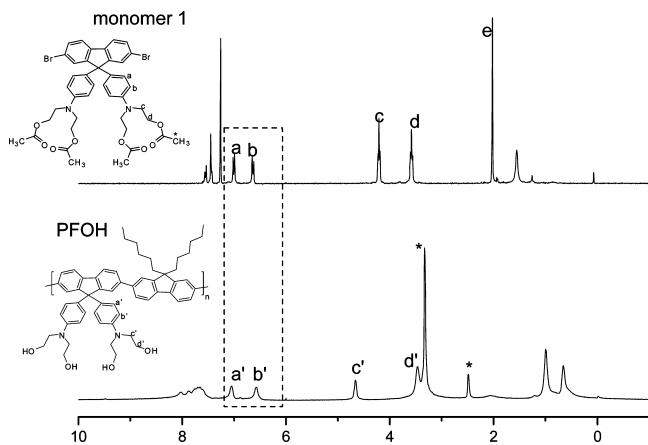


Figure 1. ^1H NMR spectra of monomer **1** and copolymer PFOH.

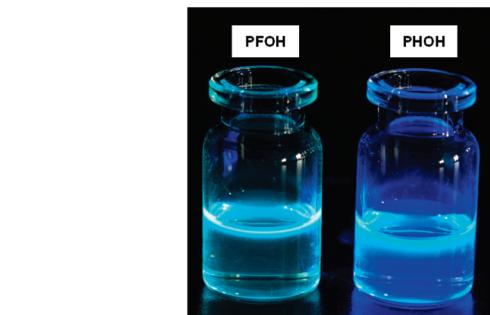
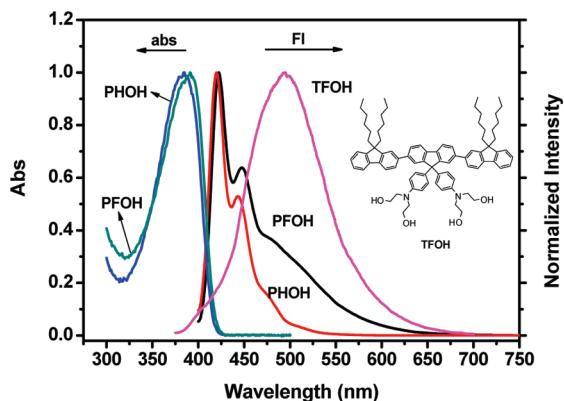


Figure 2. The normalized absorption and fluorescence spectra of PFOH, PHOH, and the terfluorene TFOH in THF. The inset shows the chemical structure of TFOH. Their concentrations are 5×10^{-6} M, with the excitation wavelength of 390 nm for the two polymers, and 350 nm for TFOH, respectively; The photos are taken under a handheld UV (365 nm) lamp.

in the ^1H NMR spectrum of PFOH, indicating that the ester groups undergo hydrolysis upon polymerization. This hydrolysis could also be further confirmed from the FT-IR data. The characteristic peak at 1742 cm^{-1} assigned to the $\text{C}=\text{O}$ stretching band of pendent acetoxyethyl groups for monomer **1** completely disappears in the FT-IR spectrum of the polymer PFOH.

Photophysical Properties. The absorption and emission spectra of the two copolymers in THF solution are shown in Figure 2. Their absorption spectra are quite similar, with the maximum peak at 385 nm, resembling those of the polyfluorenes reported in the literature,^{23,24} whereas their emission behaviors have distinct differences. The emission spectrum of PFOH exhibits a shoulder band at 500 nm, which is responsible for its weak green emission color. In contrast, PHOH shows bright blue emission without green emission bands. Their fluorescence

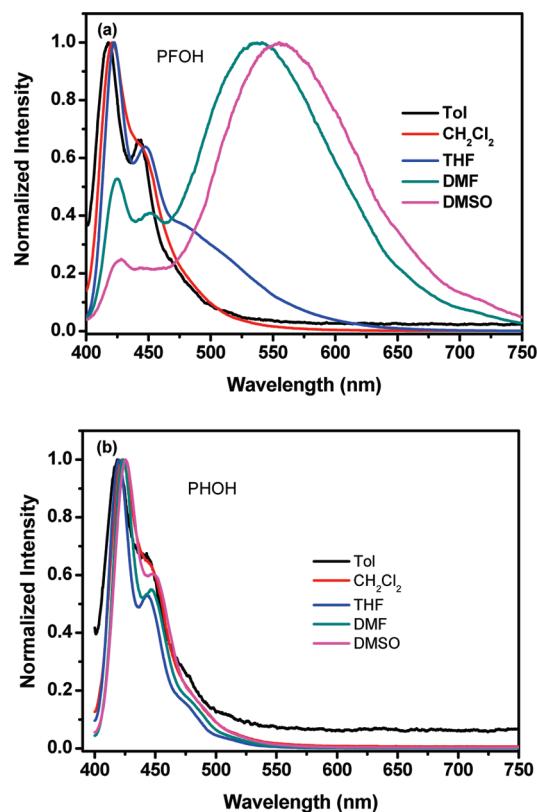


Figure 3. Normalized fluorescence emission spectra of (a) PFOH and (b) PHOH in different solvents. The concentration of the polymers is 5×10^{-6} M with an excitation wavelength of 390 nm.

quantum yields measured in THF solution are 23.6% for PFOH and 77% for PHOH, respectively.

To further study their photoluminescent properties, the emission spectra of the two polymers in different solvents were examined (Figure 3). PFOH exhibits blue-green emission in THF, and the low-energy emission shows notable bathochromic shift with the increasing solvent polarity (from 500 nm in THF to 556 nm in DMSO). PFOH exhibits typical dual emissions in DMF and DMSO, that is, a weak blue emission around 420 nm and a yellow emission band around 550 nm. The emission behavior of PFOH resembles that of its corresponding terfluorene TFOH, indicating that the dual fluorescence emissions of TFOH still exist upon copolymerization into polymers. In contrast, PHOH exhibits a bright blue emission regardless of the solvent polarity, suggesting the absence of intramolecular charge transfer in this polymer.

As has been investigated for the terfluorene TFOH, we also measured the emission spectra of the two copolymers in a THF solution at 77 K and in the film state, respectively (Figure 4). For PFOH, the intensity of the low-energy emission band substantially decreases under these conditions, indicating a suppression of charge transfer process due to the restriction of molecular motions. For PHOH, a slight red shift is observed, most likely due to the molecular aggregation in these cases. These results further confirm the existence of intramolecular charge transfer from pendent aminophenyl group to the fluorene chain in PFOH, although the effect of charge transfer in PFOH is significantly weaker than that in the terfluorene TFOH (Figure 2).

Self-Assembly Behaviors and Effects on the Photophysical Properties. Since the hydroxyethyl groups are hydrophilic, whereas the hexyl chains are hydrophobic, we anticipate that both PFOH and PHOH are amphiphilic; therefore, the self-

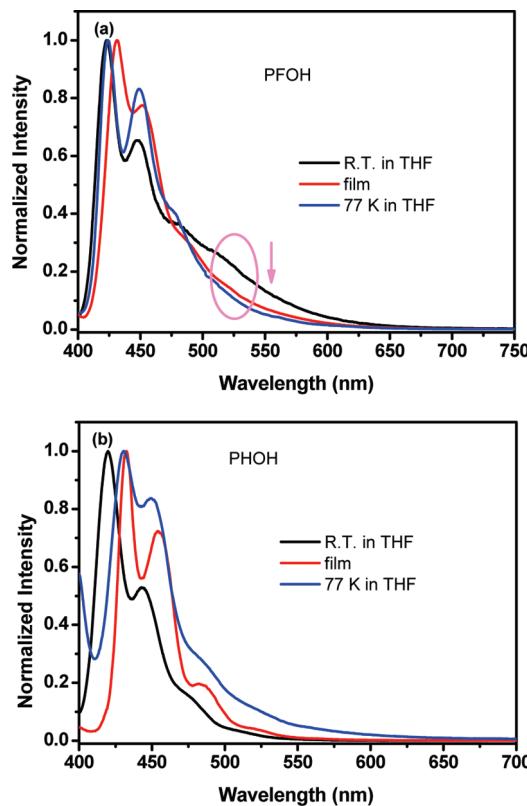


Figure 4. Normalized fluorescence emission of (a) PFOH and (b) PHOH in THF solution at room temperature, at 77 K, and in the film state. The concentration of the solution is 5×10^{-6} M, with an excitation wavelength of 390 nm.

assembly behaviors of the two polymers in a THF–H₂O mixed system and the corresponding photophysical properties were investigated. The two polymers have better solubility in THF than water; thus, they cannot form nanoparticles when the THF/THF + H₂O ratio is higher than ~50%. However, they can form nanoparticles when the THF/THF + H₂O ratio is lower than ~50%. According to the dynamic light scattering (DLS) results, PFOH forms nanoparticles with average diameter of ~106 nm in 1% THF (volume percent, and the same below); as the THF ratio increases to 10%, the average diameter increases to ~213 nm, and with a further increase in the THF ratio but lower than ~50%, the average diameter increases. This possibly results from the different types of nanoparticles due to the different ratios of THF/H₂O.

This phenomenon is also observed in the case of terfluorones.²⁰ The spherical nanoparticles can be clearly seen in the SEM images of PFOH film, which is prepared by a drop-cast method from THF/H₂O mixtures (Figure 5). However, the sizes of nanoparticles evaluated from SEM images are smaller than the results from DLS experiments due to shell shrinkage after being dried in air. PHOH shows DLS results and SEM images similar to those of PFOH.²⁵

The UV-vis absorption and emission spectra of the two polymers in THF and a THF/H₂O mixture are shown in Figure 6. Their absorption spectra do not show much difference when the solvent system changes from THF to THF/H₂O (1:99), apart from the band broadening and a slight red shift. However, their PL spectra display remarkable distinctions (Figure 6). The shoulder at 500 nm for PFOH shows substantial intensity enhancement and a slight red shift (to 515 nm) when the water fraction increases but remains below 50%; upon further increase

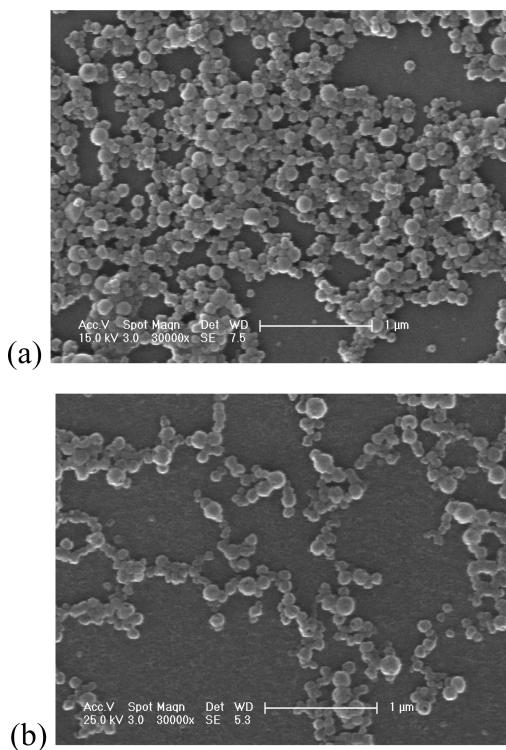


Figure 5. The SEM images of (a) PFOH and (b) PHOH, dropping from a THF/H₂O mixture with 1% THF onto a quartz substrate.

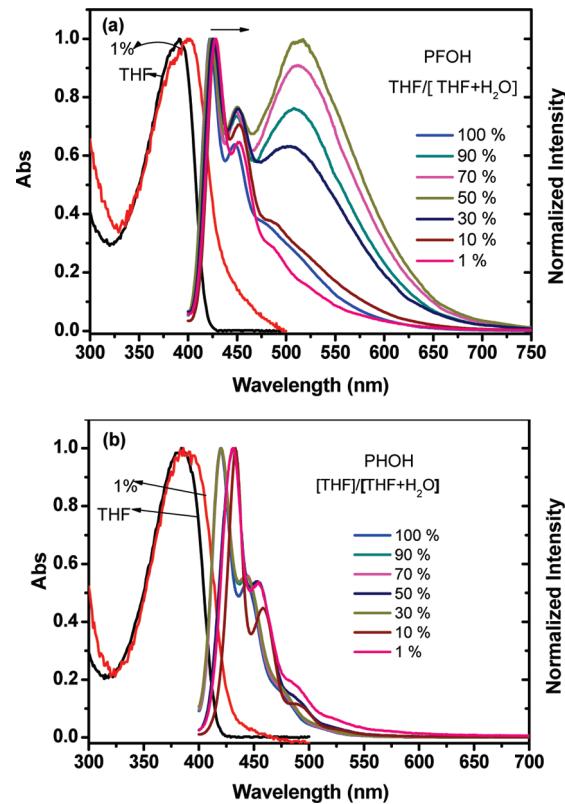


Figure 6. Normalized absorption and fluorescence emission of (a) PFOH and (b) PHOH in THF and THF/H₂O mixtures. The percentage in the figure is the volume fraction of THF. The excitation wavelength is 390 nm.

in the water fraction, the intensity at 515 nm decreases prominently and gradually blue-shifts (from 515 to 483 nm) (Figure 6a).

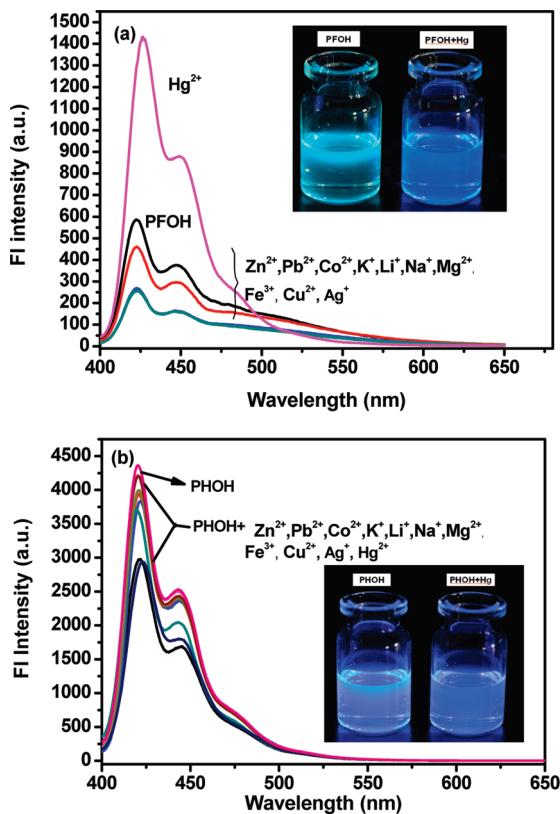


Figure 7. Fluorescence responses of (a) PFOH and (b) PHOH toward different metal ions. Each metal ion is of 20 equiv to the polymer. The polymers are at a concentration of 5×10^{-6} M, with an excitation wavelength of 390 nm. The photos are taken under a hand-held UV (365 nm) lamp as soon as the Hg^{2+} ions were added.

In contrast to this, the emission behaviors of PHOH do not exhibit significant changes with an increase in the water fraction; only a red shift of the maximum emission peaks from 419 to 432 is observed when the water content reaches 99% (Figure 6b). The above fluorescence change of PFOH in THF/H₂O mixtures is similar to that of the terfluorene TFOH and could be interpreted as follows: In the range of a water fraction lower than 50%, the increasing water content increases the polarity of the system, which facilitates the charge transfer process and consequently brings about the intensity enhancement and bathochromic shift of the charge transfer emission. By the time water dominates in the system (over 50%), micellization leads to the formation of nanoparticles, which restricts the molecular motions and inhibits the charge transfer process to some extent, therefore resulting in the decreasing intensity and blue shifts of the charge transfer emission band.

Fluorescence Responses to Hg^{2+} Ion. The structure feature of the polymers with *N,N'*-di-(2-hydroxyethyl)amino as a potential binding group for metal ions prompts us to exploit their application for the detection of metal ions. Figure 7 shows the fluorescence responses of the two polymers (in a concentration of 5×10^{-6} M in THF for each polymer) toward different metal ions in MeOH (Co^{2+} , Mg^{2+} , Zn^{2+} , Fe^{3+} , Cu^{2+} , Pb^{2+} , Hg^{2+} , Ag^+ , Li^+ , Na^+ , and K^+ as their perchlorate salts). For PFOH, among all the metal ions examined, only Hg^{2+} causes a prominent enhancement of blue emission, while the others cause a slight decrease in the emission intensity. In contrast, fluorescence spectra of PHOH have little change in the presence of all the metal ions examined.

The fluorescence titration course of PFOH toward Hg^{2+} is shown in Figure 8. Interestingly, upon addition of Hg^{2+} in an

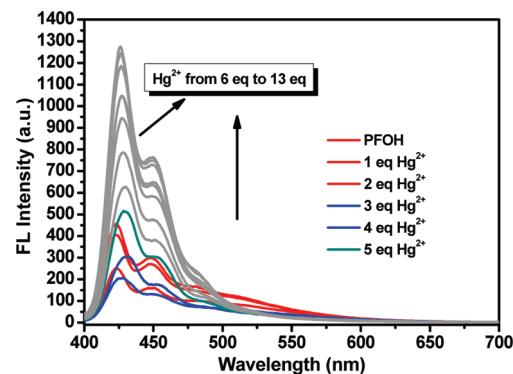


Figure 8. Fluorescence emission changes of PFOH (5×10^{-6} M) upon addition of Hg^{2+} in THF. The excitation wavelength is 390 nm.

concentration of less than 1.0×10^{-6} M, the emission of PFOH at 422 nm is significantly quenched, by more than half (57%). When the concentration of Hg^{2+} reaches 1.5×10^{-5} M, the emission peak of PFOH has a slight red shift from 422 to 430 nm. Upon a further increase in the Hg^{2+} concentration, the blue emission intensity of the polymer is significantly enhanced. Meanwhile, the shoulder peak (assigned to the charge transfer band) around 500 nm gradually decreases during the whole titration process. Finally, a bright blue emission dominates, instead of the original blue-green emission.

This sensory process is different from the case of the corresponding terfluorene TFOH. For the latter, the addition of Hg^{2+} causes a significant enhancement of the blue emission and, meanwhile, a gradual decrease in the green emission. From the titration course, a small amount of Hg^{2+} (a concentration of $<1.0 \times 10^{-6}$ M) results in the emission quench of PFOH at 422 nm by more than half (57%), whereas for TFOH, the same amount of Hg^{2+} causes only a tiny drop in the green emission intensity. Therefore, at the beginning of titration, the copolymer is more sensitive than the terfluorene.

The sensory mechanism of PFOH for Hg^{2+} is related to the dual fluorescence emissions of the polymer. The coordination of Hg^{2+} ions with pendent *N,N'*-di-(2-hydroxyethyl)amino groups greatly weakens the electron-donating ability of nitrogen atoms, and thus, the intramolecular through-space charge transfer process could be suppressed. In consequence, the intensity of green emission resulting from the charge transfer is reduced, and blue emission remarkably increases.

As to the binding mode, there are three possible components of PFOH (depicted as P in the following description) coexisting during the titration courses: P (free polymer), P-1 M (1:1 complex), and P-2 M (1:2 complex). P-1 M and P-2 M both have a smaller band gap compared to the free P and are able to serve as low-energy traps for the whole polymer chain; therefore, an energy transfer between P and P-1M/P-2 M could happen.²⁶ As a result, at the beginning of titration, only a decreased emission intensity of PFOH is observed. Upon continuing addition of Hg^{2+} , P-1 M and P-2 M gradually increase in solution, and the emission spectra have a slight red shift because of the smaller band gap of these species. However, with a further increase in the Hg^{2+} concentration, the blue emission intensity of PFOH enhances dramatically when the P-2 M species are dominant.

The different fluorescent responses of the two polymers to Hg^{2+} further support the assignments of the dual fluorescence emissions of PFOH. Notably, fluorescence quenching is a common phenomenon for conjugated polymer-based sensors, and the emission “turn-on” type probe constructed from conjugated polymers is of practical significance.

Conclusions

In summary, we have synthesized and characterized two new fluorene-based copolymers by Suzuki polycondensation, with *n*-hexyl and *p*-*N,N*-bis-(2-hydroxyethyl)aminophenyl/bis(6'(diethanolamino)hexyl) as side chains, respectively. The photophysical property of PFOH resembles that of its corresponding terfluorene TFOH. The low-energy emission band of PFOH exhibits remarkable bathochromic shift with an increase in the solvent polarity, assigned to the intramolecular charge transfer process from the pendent aminophenyl group to the fluorene chain. By virtue of the dual fluorescence emissions, PFOH can be used as a prominent ratiometric fluorescent probe for Hg^{2+} detection, with the emission color changing from green to bright blue. In sharp contrast, PHOH without aminophenyl pendent groups displays bright blue emission, regardless of the solvent polarity, and no response toward the metal ions examined. The two new polymers exhibit amphiphilicity, and can form self-assembled nanostructures in the THF–H₂O system. All the results demonstrated that the dual fluorescence emissions still exist after terfluorene TFOH is copolymerized into polymer.

Acknowledgment. We are grateful for financial support from the National Natural Science Foundation of China (Nos. 20874077 and 50773057), and the National Basic Research Program of China (973 Program 2009CB623602).

Supporting Information Available: ¹H NMR spectra for monomer 1 and the copolymer PFOH and PHOH. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JP1071567