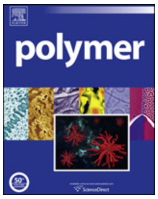
Polymer 50 (2009) 5422–5426

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



New fluorene-based alternating copolymers with pendent *N*,*N*-diethylaniline group: Highly sensitive and selective detection for Hg^{2+} with “Turn-on” fluorescence response

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ARTICLE INFO

Article history:
Received 8 August 2009
Received in revised form
21 September 2009
Accepted 25 September 2009
Available online 1 October 2009

Keywords:
Polyfluorene
Intramolecular charge transfer
Fluorescent chemosensor

ABSTRACT

Two fluorene-based alternating copolymers **P1** and **P2** with the *N*,*N*-diethylaniline pendent group in different contents on the polymer backbone were synthesized through Suzuki Coupling Reaction, and were fully characterized by ^1H NMR, elemental analysis, and gel-permeation chromatography (GPC). Photophysical studies show that changes of the contents of the *N*,*N*-diethylaniline groups have little effect on the ground state electronic structure, but take a significant effect on the excited state. The intensities of green emission band in these polymers changes with the different content of diethylaniline groups, and are supposed to be originated from an intramolecular charge transfer process. Both of the **P1** and **P2** show remarkable fluorescence emission “turn-on” responses exclusively to Hg^{2+}. Moreover, fluorescent titration experiments indicate that the two copolymers have high sensitivity for Hg^{2+}. The coordination between metal ions and N atoms could greatly weaken the electron-donating ability of N atoms, consequently inhibit the intramolecular charge transfer process, leading to fluorescence emission enhancement. As far as we know, this is the first report for detection of Hg^{2+} with “turn-on” output signals based on polyfluorenes.

1. Introduction

Fluorene-based copolymers have attracted increasing attention due to their high photoluminescence efficiency, good charge-carrier mobility, convenient color tunability and favorable thermal stabilities [1]. Although for a long time, they have been mostly applied as luminescent materials in polymeric light emitting diodes (PLEDs) [2], they began to find use as sensing materials both in chemistry and biology in recent years [3]. Compared with small molecules, polymers have many advantages such as high light absorption ability, molecular wire effect, and good film forming property [4]. For example, Zhou et al. synthesized a polyfluorene with grafted imidazole for detecting Cu^{2+} [5]; Wang et al. reported two polyfluorene derivatives with pendent phosphonate groups as highly sensitive and selective sensory units for Fe^{3+} [3a,6]; we have also previously reported a copolyfluorene with aza-15-crown-5 as pendent groups showing high affinity for Cu^{2+} [7]. Whereas, most of the sensors based on polyfluorenes for metal ions detection usually exhibit signal output of fluorescence emission quenching because of their propensities to quench fluorophore emission, which is prone to be disturbed by the environmental disturbances in real analytical systems. The construction of fluorescent chemosensors with emission “turn-on” response based on polyfluorenes is of quite significance.

Mercury as poisonous heavy metal, could easily accumulate in organisms, and cause irreversible damages to central nervous and endocrine system; therefore concerns over the toxic metal has inspired people to develop efficient sensors to monitor it [8]. In recent years, optical chemosensors have been extensively investigated due to their high sensitivity and selectivity, as well as easy to handle property [9]. Most of the reported fluorescent chemosensors for Hg^{2+} are turn-off detection because of its intrinsic property to quench fluorophore emission [10]; thus designing fluorescent chemosensor for Hg^{2+} with turn-on response is still a considerable challenge.

In this article, we designed and synthesized two new fluorene-based alternating copolymers **P1** and **P2** with pendent *N*,*N*-diethylaniline group. We tend to investigate their metal ions sensing abilities, since the complexation with metal ions would weaken the electron-donating ability of N atoms in pendent *N*,*N*-diethylaniline group, and consequently induce fluorescence

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doi:10.1016/j.polymer.2009.09.071

emission changes. The photophysical properties of the copolymers and their fluorescent response for metal ions will be discussed.

2. Experimental section

2.1. General information

The ^{1}H NMR spectra were recorded on a MECUYRVX300 spectrometer in $CDCl_3$ using tetramethylsilane as an internal reference. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Carlorerba-1106 microanalyzer. The molecular weight of the polymer was determined by Agilent 1100 GPC using the column PLgel 5 mm MIXED-C and THF 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 Shimadzu UV-2550 recording spectrophotometer. PL spectra (at room temperature) were recorded on Hitachi F-4500 fluorescence spectrophotometer. The PL quantum yields were measured from the dilute THF solution of the polymer (ca. 10^{-6} mol/L) by an absolute method using the Edinburgh Instruments (FLS920) integrating sphere excited with Xe lamp. The concentrations of the polymers for UV–vis absorption and fluorescence emission measurements, as well as for the fluorescence titration courses are 5×10^{-6} M. The concentration of metal ions used in the detection processes are 5×10^{-3} M in MeOH solution. Fluorescence titration courses were carried out by addition of metal ions dissolved in MeOH into the THF solution of each polymer, and after stirring for seconds, emission spectra were undertaken.

Tetrakis-(triphenylphosphine)palladium, benzen-1,4-bis(boronic acid)-propane-1,3-diol diester were purchased from Acros. Other materials were used directly without further purification unless otherwise stated. The monomer M1 was prepared according to literature procedure [3c].

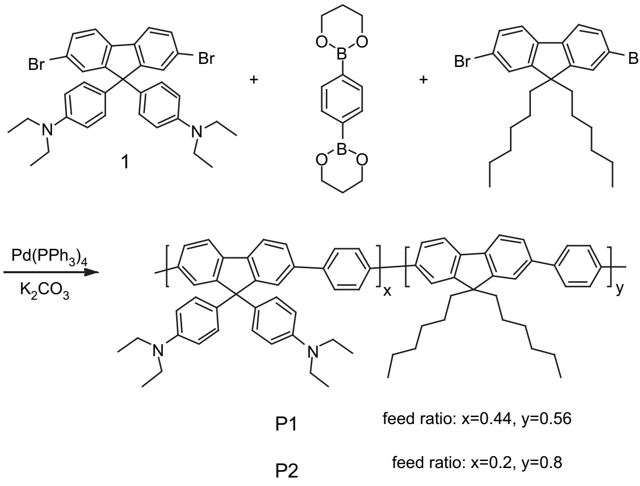
2.2. Synthesis of copolymers

P1: To a solution of monomer M1 (82.9 mg, 0.134 mmol), 2,7-dibromo-9,9-dihexylfluorene (81.7 mg, 0.166 mmol), and benzen-1,4-bis(boronic acid)-propane-1,3-diol diester (73.8 mg, 0.3 mmol), $Pd(PPh_3)_4$ (10 mg) in 6 mL of THF, 2 mL of aqueous potassium carbonate (2.0 M) was added. The above mixture was degassed for several minutes, and then stirred at 85 °C for 3 d. After cooling to room temperature, the resulting polymer was purified by reprecipitating in methanol for three times to afford **P1** as a yellowish slice. Yield: 80 mg, 62%.

^{1}H NMR (300 MHz, $CDCl_3$, δ ppm).: 7.81–7.65 (br), 7.18 (br, 4H), 6.56 (br, 4H), 3.29 (br, 8H), 2.07 (br), 1.58 (br), 1.25 (br), 1.11 (br), 0.77 (br). Anal. Calcd. for $C_{70}H_{76}N_2$: C, 88.93; H, 8.10; N, 2.96. Found: C, 85.92; H, 8,07; N, 2.17. M_n (GPC) = 16 390 g/mol, PDI = 1.37.

P2: To a solution of M1 (100 mg, 0.16 mmol), 2,7-dibromo-9,9-dihexylfluorene (315 mg, 0.64 mmol), and benzen-1,4-bis(boronic acid)-propane-1,3-diol diester (197 mg, 0.8 mmol), $Pd(PPh_3)_4$ (10 mg) in 12 mL of THF and 4 mL of aqueous potassium carbonate (2.0 M) were added. The above mixture was degassed for several minutes, and then stirred at 100 °C for 3d. After cooling to room temperature, the resulting polymer was purified by reprecipitating in methanol for three times to afford **P2** as a yellowish slice. Yield: 280 mg, 81%.

^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.75 (br), 7.67–7.58 (br), 7.12 (br), 6.49 (br), 3.23 (br), 2.01 (br), 1.03 (br), 0.71 (br). Anal. Calcd. for $C_{32.6}H_{37.4}N_{0.4}$: C, 89.99; H, 8.72; N, 1.30. Found: C, 88.95; H, 7.70; N, 1.00. M_n (GPC) = 35 010, PDI = 1.80.



Scheme 1. Synthetic routes for **P1** and **P2**.

3. Results and discussion

3.1. Synthesis and characterization

As depicted in Scheme 1, the copolymers **P1** and **P2** were prepared by Suzuki polycondensation of monomer **1** and 2,7-dibromo-9,9-dihexylfluorene and benzen-1,4-bis(boronic acid)-propane-1,3-diol diester in feed ratios of 22:28:50 and 10:40:50 mol%, respectively. Both copolymers have good solubility in common organic solvents, such as toluene, $CHCl_3$, CH_2Cl_2 and THF. The structures of the polymers were characterized by ^{1}H NMR and elemental analysis. Gel-permeation chromatography (GPC) analysis with polystyrene standards gave number-averaged molecular masses (M_n) of 16 390 g/mol for **P1** and 35 010 g/mol for **P2**, with polydispersities of 1.37 and 1.80, respectively.

3.2. Optical properties

In the UV–vis spectra shown in Fig. 1, the two copolymers exhibit similar properties in THF. The main absorption peaks of **P1** and **P2** are situated at 370 nm, ascribing to the π–π* transition state of the conjugated backbone. Compared to the polyfluorenes that usually show main absorption peak at 390 nm [11], this maximum absorption is relatively blue shifted because the rotation of phenyl

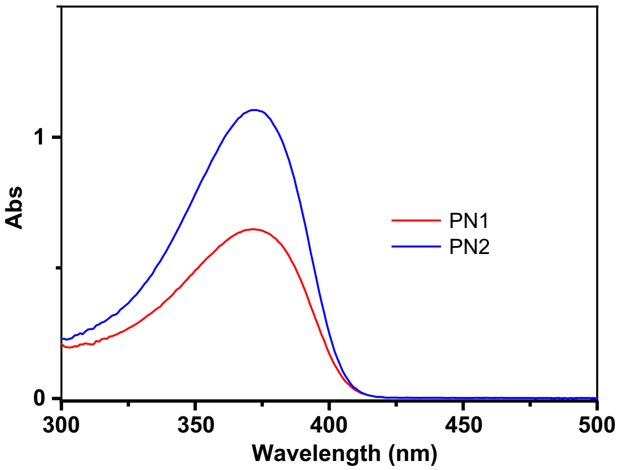


Fig. 1. UV–vis spectra of **P1** and **P2** in THF solution. The concentration is 5 μM for each polymer.

rings in the main chain of **P1** and **P2** reduces the coplanarity of the whole polymer chains. In addition, the absorption spectra of the polymers exhibit little change with the solvent polarity, indicating the absence of charge transfer process in the ground state for the copolymers.

Fig. 2 shows the fluorescence spectra of the two copolymers in THF solution at different concentrations. It is obvious that the emission spectra have two peaks, one centered at ca. 410 nm, another centered at ca. 500 nm. The former could be assigned to the emission of fluorene-based main chain. The long wavelength emission still exists even at very low concentration of 10^{-7} M, implying that it does not come from aggregation. Moreover, the fluorescence emission peaks of the copolymers in films show hypsochromic shift to around 450 nm, therefore, the possibility of long wavelength emission originating from aggregation state can be completely excluded.

To further investigate the origination of green emission bands, we then examine the emission spectra of the copolymers in different solvents. As shown in Fig. 3, the copolymers show strong blue emission in toluene, and the green emission band undergoes significant red shift and intensity enhancement with the increase of solvent polarity from toluene to dichloromethane to tetrahydrofuran. We also note that the emission spectra changes depend on the contents of the diethylaniline groups. For example, in CH_2Cl_2 and THF solution, **P1** shows mainly green emission peaked at 500 nm, with relatively weaker blue emission bands; while **P2** is bluish green emissive with a much weaker green emission band due to its lower contents of diethylaniline moieties. In view of the above phenomena, we could ascribe the green emission bands to be of intramolecular charge transfer nature like our previously reported trifluorene TFOH [12]. When copolymerized into polymers, the molecular motions related to green emission are inhibited to some extent, and thereby, the green emission in these polymers is not as prominent as in the trifluorene.

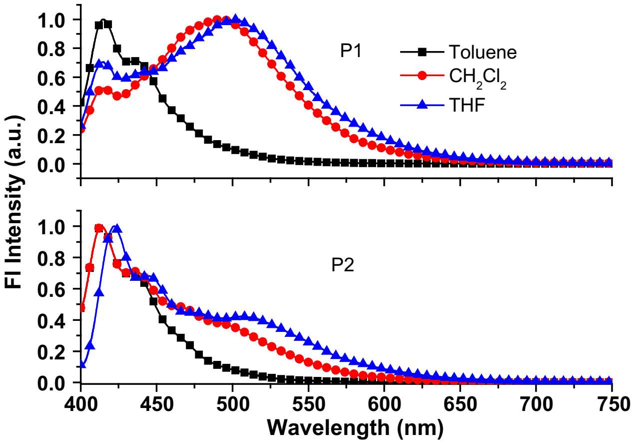


Fig. 3. Fluorescence spectra of **P1** and **P2** in toluene, CH_2Cl_2, and THF, respectively. The concentration is 5 μM for each polymer, and the excitation wavelength for the two polymers is 380 nm.

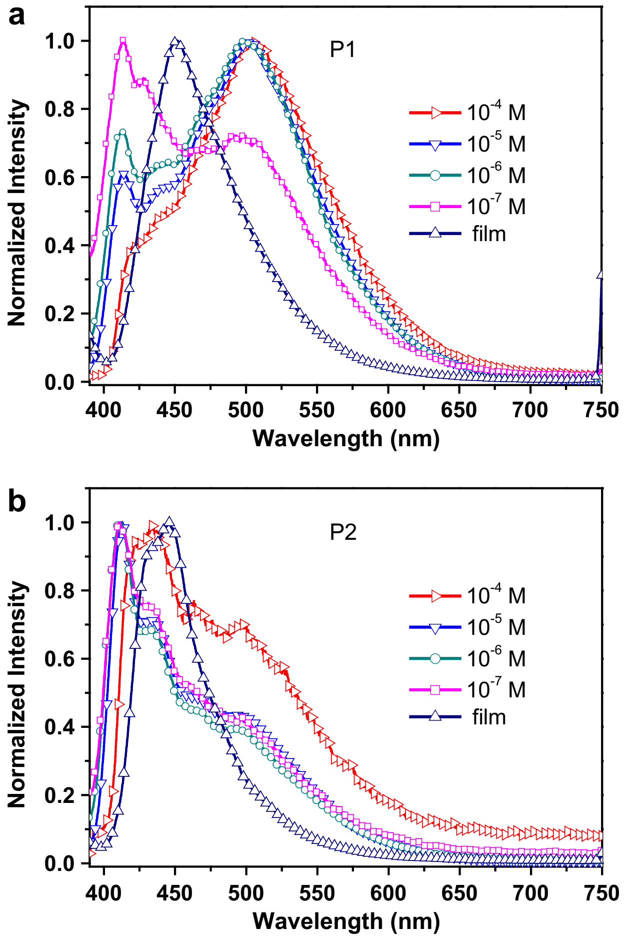


Fig. 2. Normalized fluorescence emission spectra of (a) **P1** and (b) **P2** in THF solution at different concentrations, as well as in films. The excitation wavelength is 380 nm for the two polymers.

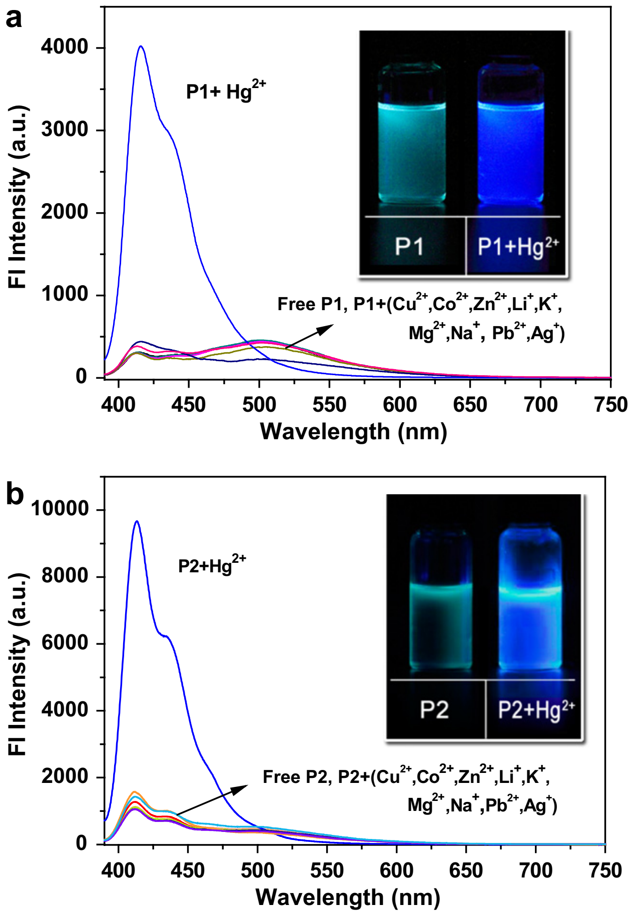


Fig. 4. Fluorescence responses of (a) **P1** and (b) **P2** toward metal ions examined in THF, respectively. The concentration of each polymer is 5 μM, and metal ions added are about 100 μM. The excitation wavelength for **P1** and **P2** is 380 nm.

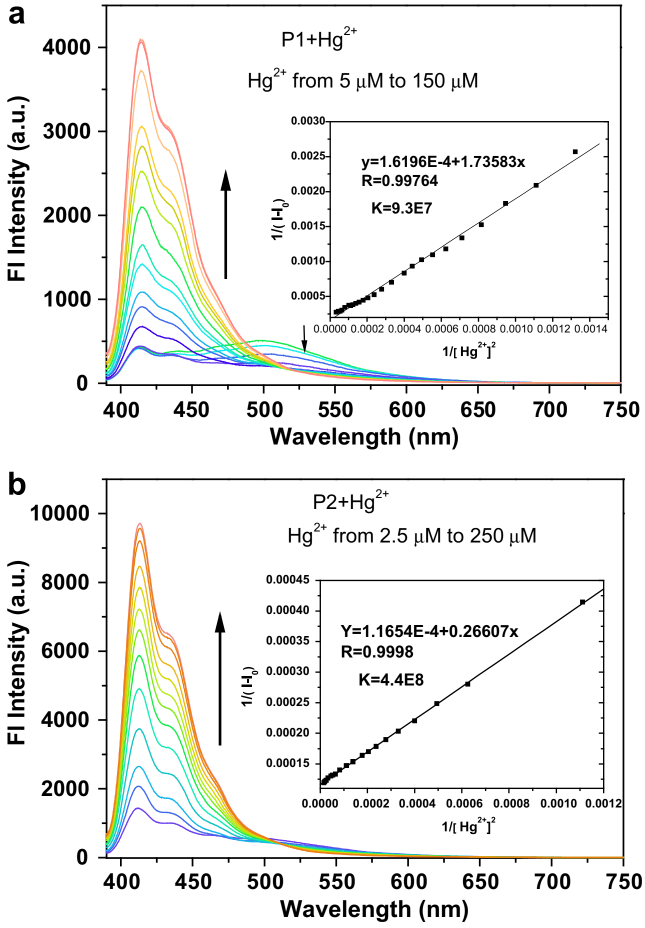


Fig. 5. Fluorescence emission changes of (a) **P1** and (b) **P2** upon addition of Hg^{2+} in THF. The concentration of copolymers is 5 μM, and the excitation wavelength for **P1** and **P2** is 380 nm. (Inset: Benesi–Hildebrand equation linear fitting plots. I_0 is the original emission intensity of the polymer; I is the emission intensity after addition of metal salts).

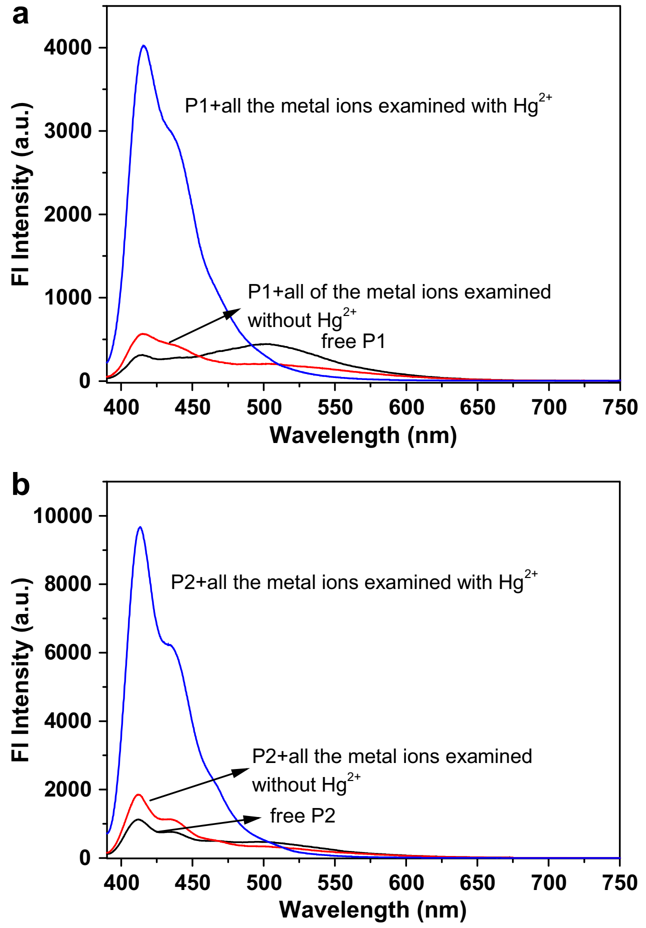


Fig. 6. Fluorescence intensity change of (a) **P1** and (b) **P2** (5 μM, THF solution) upon addition of all the metal ions examined with or without the existence of Hg^{2+} (5 mM). The excitation wavelength is 380 nm for both the two polymers.

3.3. *Fluorescence response to Hg^{2+} ions*

Fluorescent titration experiments were carried out in THF, with all the metal ions in MeOH (Co^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, Hg^{2+}, Li^{+}, Na^{+}, K^{+}, Ag^{+} as their perchlorate salts). Fig. 4 shows the fluorescence response of the two copolymers toward different metal ions in a concentration of 5×10^{-6} M. **P1** and **P2** exhibit a prominent "turn-on" fluorescence emission only with the existence of Hg^{2+}, and the emission color changes remarkably from green to bright blue. The fluorescent quantum yield of **P1** increases from 17.3% to 38.3%, and that of **P2** increases from 25.3% to 56.4% upon addition of 25 equiv of Hg^{2+}. Notably, the fluorescence quantum yield of the polymers decreased from 25.3% (**P2**) to 17.3% (**P1**) with increasing contents of the diethylaniline groups, which is in consistent with the fact that charge transfer process would lead to the increase probability of internal conversion, consequently the decrease of fluorescence quantum yield.

Fluorescence titration results of **P1** and **P2** toward Hg^{2+} are shown in Fig. 5. For **P1**, at the beginning of titration, the green emission intensities gradually decrease and the emission position has a slight red shift when the Hg^{2+} concentration reaches 15 μM. Then the blue emission begins to increase with the sustaining addition of Hg^{2+}, until finally to the equilibrium. While for **P2**, the addition of Hg^{2+} causes gradual increase of the blue emission intensities, without the distinct decrease of green emission. The association constants calculated from Benesi–Hildebrand equation are to be 9.3×10^7 for **P1** (with the correlation coefficient of 0.9976) and 4.4×10^8 for **P2** (with the correlation coefficient of 0.9998), respectively. (The ratio of mercury ion and N atom is supposed to be 1:1.)

The fluorescence responses of **P1** and **P2** to Hg^{2+} during titration might be explained as follows: the coordination of mercury ions with N atoms weakens the electron-donating ability of diethylaniline groups [13], which in consequence causes the decrease of the green emission intensities originating from intramolecular charge transfer process. In view of the fact that the contents of N atoms in **P1** is more than that in **P2**, the decrease of charge transfer emission after coordination with Hg^{2+} is more significant in **P1**. Since the charge transfer process is quite evident in the excited state, the addition of Hg^{2+} mainly affects the electronic properties of excited state.

Although the content of N atoms in **P2** is much less than that in **P1**, the association constants of **P2** for Hg^{2+} is a little higher than that of **P1**. This might be ascribed to the molecular wire effect of conjugated polymers [4]. The whole polymer main chain could be considered as a molecular wire capable of transporting electrical current, and a single analyte binding will produce a resistive element in the wire, and thus the transport of conducting electrons in the whole chain could be reduced. Therefore we can differ that as the content of receptors are much fewer in **P2**, the analyte needed for **P2** is fewer than that for **P1**, and accordingly, the association constant of **P2** is higher.

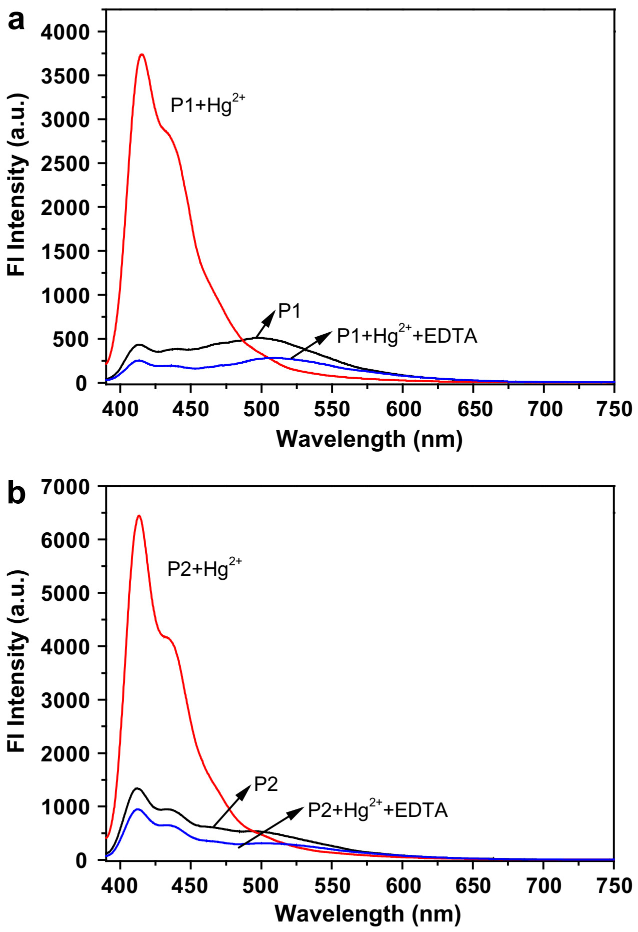


Fig. 7. Fluorescence responses of (a) **P1** (5 μM, THF solution), (b) **P2** (5 μM, THF solution) upon the addition of $Hg(ClO_4)_2$ (50 μL, 5 mM, MeOH solution), followed by the addition of EDTA (5 mM in water).

We also test the interference of other metal ions toward Hg^{2+} detection. From Fig. 6, it is observed that slightly increases of blue emission of **P1** and **P2** were observed as the metal ions (Co^{2+}, Pb^{2+}, Zn^{2+}, Ag^{+}, K^{+}, Cu^{2+}, Mg^{2+}, Na^{+}, and Li^{+}) were added, however prominent increases of blue emission were observed when Hg^{2+} was added to the above solution system. The result indicates that this assay is able to detect Hg^{2+} with the coexistence of other usual transition metal ions, and both of the two copolymers show high selectivity to Hg^{2+}.

The fluorescence responses of **P1** and **P2** toward Hg^{2+} could be restored upon addition of EDTA aqueous solution to the Hg^{2+}–**P1**/**P2** system. As shown in Fig. 7, after adding 50 μL of 5 mM EDTA aqueous solution into the Hg^{2+}–**P1**/**P2** system, the fluorescence emission restored immediately, due to the stronger binding ability between Hg^{2+} and EDTA. Yet the fluorescence intensity of the two polymers could not be fully recovered, probably because of the water added with EDTA that brought about fluorescence quenching of the polymers to some extent. The recovery experiment further confirmed that mercury ions interact with the two polymers through coordination with the pendent diethylaniline groups.

4. Conclusion

In summary, we have synthesized and characterized two novel fluorene-based copolymers with diethylaniline groups as pendent groups. Photophysical studies of the copolymers show that the content of diethylaniline group has negligible effect on their absorption properties, but has obvious impact on the excited state properties. Of all the metal ions screened, both **P1** and **P2** show high sensitivity and selectivity for Hg^{2+}, and the emission color changes remarkably from green/bluish green to strong blue. The detection mechanism is proved to be restraining of the charge transfer processes by coordination of Hg^{2+} and N atoms in the polymers. As a result, the two polymers could be used as efficient Hg^{2+} chemosensors with fluorescence "turn-on" responses. To the best of our knowledge, this is the first report for detection of Hg^{2+} with "turn-on" output signals based on polyfluorenes.

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