

Fluorene-Based Conjugated Polymer with Tethered Thymines: Click Postpolymerization Synthesis and Optical Response to Mercury(II)

Yanli Lei,^{1,2} Fudong Ma,^{1,2} Yong Tian,^{1,2} Qiaoli Niu,³ Hongyu Mi,^{1,2} Ismayil Nurulla,^{1,2} Wei Shi^{1,2}

¹Key Laboratory of Petroleum and Gas Fine Chemicals, Educational Ministry of China, School of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, People's Republic of China

²Key Laboratory of Functional Polymers, Xinjiang University, Urumqi 830046, People's Republic of China

³Institute of Optoelectronic Materials and Technology, South China Normal University, Guangzhou 510631, People's Republic of China

Correspondence to: W. Shi (E-mail: xjuwshi@gmail.com)

ABSTRACT: A kind of fluorene-based conjugated polymer with tethered thymine (T) groups {poly[(9,9-dioctyl)-2,7-fluorene-(9,9-dioctyl)-4-1,2,3-triazol-[5-(hydroxymethyl)tetrahydrofuran-2-yl]-5-methylpyrimidine-2,4(1H,3H)-dione]-2,7-fluorene]-*co*-[(9,9-dioctyl)-2,7-fluorene-4,7-bis(5-thiophen-2-yl)benzo-2,1,3-thiadiazole] (**P-3**)} was successfully synthesized by a Cu(I)-catalyzed click reaction between the acetylene-substituted polymer precursor {poly[(9,9-dioctyl)-2,7-fluorene-(9,9-dioctyl)-4-phenylacetylene fluorene]-*co*-[(9,9-dioctyl)-2,7-fluorene-4,7-bis(5-thiophen-2-yl)benzo-2,1,3-thiadiazole]} and 3'-azido-3'-deoxythymidine. The chemical structures of the intermediates and target polymer were verified by Fourier transform infrared spectroscopy and ¹H-NMR analyses. The specific binding with Hg²⁺ of **P-3** was corroborated by ultraviolet-visible spectroscopy and photoluminescence analyses against other metal ions. The results show that **P-3** possessed selectivity and sensitivity toward Hg²⁺. Around 77% of photoluminescence intensity of **P-3** was quenched when the concentration of Hg²⁺ reached 7.7×10^{-4} M and with a detection limit in the range of about 4.8 μM. A comparison experiment suggested that a synergic effect of the tethered T and S atoms interrelated with Hg²⁺ existed in **P-3**. Most of the fluorescence intensity of **P-3** was recovered upon the addition of iodide anions to the **P-3**/Hg²⁺ complex; this suggested that **P-3** could be used as a potential reversible optical Hg²⁺ probe. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 1763–1772, 2013

KEYWORDS: conjugated polymer; click post-polymerization; fluorene; thymine; Hg²⁺ probe

Received 5 September 2012; accepted 12 November 2012; published online 22 December 2012

DOI: 10.1002/app.38817

INTRODUCTION

Highly toxic mercury ions can cause lethal threats to the environment and to human beings.^{1–4} Its accumulation in organisms cause serious illness, including prenatal brain damage, cognitive problems, motion disorders, and minamata.^{5,6} Thus, it is highly desirable to develop new methods that are sensitive and selective for the detection of Hg²⁺ contamination for the protection of the environment and human health.

Researchers have reported some methods of realizing Hg²⁺ detection by methods such as capillary electrophoresis,⁷ atomic absorption spectroscopy,⁸ cold-vapor atomic fluorescence spectrometry,^{9–11} and gas chromatography.¹² However, many of these methods require complicated, multistep sample preparation or sophisticated instrumentation, and there is still the great challenge of finding methods of providing technically simple Hg²⁺ detection.¹³ Optical probes have been widely developed for detecting analytes because of their high sensitivity, low cost, easy detection, and reusable properties in some cases.^{14–17} Thus,

a series of small molecules,^{18,19} polymers,^{20–22} DNA,^{23,24} and nanomaterials^{25,26} based optical sensors for Hg²⁺ have been successfully synthesized.

Thymine (T), a natural base in DNA, has been demonstrated to be one of the most specific ligands for Hg²⁺; it forms a T–Hg²⁺–T pair with strong affinity and high selectivity.^{27–29} However, most functional T bases are connected to DNA, and they are very expensive and susceptible to the alteration of their surroundings, such as changes in the pH and temperature. So, this is a reasonable way to connect Ts directly with functional compounds to widen their application scope. Some T-substituted materials with optical^{30–32} or electrochemical activity³³ have thus been synthesized, and Hg²⁺ probing has been realized by the detection of the alteration of optical/electrochemical signals.

Among the versatile functional compounds that have sprung up in recent years, conjugated polymers (CPs) are known to provide the advantages of a collective optical response³⁴ and have

been used extensively as chemisensing/biosensing substrates.^{35–38} The sensitivity of CPs in probing applications is thus superior to small molecular derivatives because of their signal-amplification effect.^{39,40} Inspired by this knowledge, some trials have been performed that used CP/T composites for Hg²⁺ detection. Ren and Xu⁴¹ used a combination of oligonucleotides, DNA intercalators, and CP for the turn-on detection of Hg²⁺ by combining the effect of the specific binding between Hg²⁺ and T and the optical amplification properties of CPs. Lee et al.²² took advantage of the interactions among sulfur, Hg²⁺, and T to probe Hg²⁺ with S-containing CPs as optical reporters and bishymines as shackles. To obtain chemically stable CP/T systems, polythiophene and poly(*para*-phenylene)-based CPs with Ts covalently bonded on the side chains have been successfully synthesized by the research groups of Wang et al.⁴² and Li et al.,⁴³ respectively. They found that these T-substituted CPs could specifically detect Hg²⁺, and their optical properties could be recovered to some extent by the addition of stronger Hg²⁺ binding agents. In other words, this type of CP can be used as a reusable Hg²⁺ probe because of its intrinsic chemical stability. Despite these obtained efforts, the design and synthesis of chemically substituted T fluorescent CPs with more versatile chemical structures (and thus with variable optoelectronic properties) via a simple reaction under moderate conditions still need to be explored for further modification of their optical response properties.

Inspired by these findings, in this study, we successfully synthesized a kind of novel fluorescent CP, poly[(9,9-dioctyl)-2,7-fluorene-(9,9-dioctyl-4-1,2,3-triazol-5-(hydroxymethyl)tetrahydrofuran-2-yl)-5-methylpyrimidine-2,4(1H,3H)-dione]-2,7-fluorene]-*co*-[(9,9-dioctyl)-2,7-fluorene-4,7-bis(5-thiophen-2-yl)benzo-2,1,3-thiadiazole] (**P-3**), with a peripheral T substituent and a fluorene backbone via the click postreaction of an alkyne-substituted precursor polymer. Its response to various metal ions was investigated. The results show that this polymer could act as potential probe for Hg²⁺ ions, and the detection limit was about 4.8×10^{-6} M. In this study, we aimed to provide a modified method for the synthesis of T-substituted CPs with controllable optoelectronic properties.

EXPERIMENTAL

Materials

All of the reagents, unless otherwise specified, were purchased from Aldrich, Acros, and TCI Chemical Co. (supplied by the local agents in China) and were used without further purification. Diisopropylamine, toluene, and tetrahydrofuran (THF) were distilled from sodium in the presence of benzophenone and were degassed before use. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene and 4,7-bis(5-bromothiophen-2-yl)benzo-2,1,3-thiadiazole (DBT) were synthesized by a procedure reported previously.⁴⁴

Solutions of Al³⁺, Ba²⁺, Cu²⁺, K⁺, Mg²⁺, Na⁺, Ni²⁺, and Zn²⁺ were prepared from their chloride salts; Hg²⁺ and Pb²⁺ were prepared from their acetate salts; Fe³⁺ and Cd²⁺ were prepared from their sulfate salts; and Ag⁺ were prepared from its nitrate salts. The concentrations of the metal solutions were controlled at 10⁻¹ M in deionized water, and their stocks were subsequently diluted to different concentrations for further use.

Measurements and Characterization

IR spectra were recorded on an Equinox 55 Fourier transform infrared (FTIR) spectrometer (BRUKER OPTICS, Germany) with KBr pellets. ¹H-NMR and ¹³C-NMR spectra were collected on a Varian Inova-400 spectrometer (BRUKER, Germany) operating at 400 MHz (for ¹H-NMR) and 100 MHz (for ¹³C-NMR) in deuterated chloroform or in a THF solution with tetramethylsilane as a reference. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) were determined by an UltiMate3000 instrument (Dionex, United States) in THF with a calibration curve of polystyrene standards. Ultraviolet–visible (UV–vis) absorption spectra were recorded on a Shimadzu UV-2450 UV–vis spectrophotometer (Shimadzu, Japan). Photoluminescence (PL) spectra were recorded on a Hitachi F-4500 spectrophotometer (Hitachi, Japan). Thermogravimetric analysis (TGA) was conducted on a Pyris1 TGA instrument (PerkinElmer, United States) at a heating rate of 10°C/min under nitrogen.

Synthesis

The synthetic route of the target polymer is outlined in Scheme 1. 2,7-Dibromo-4-iodo-9,9-dioctylfluorene (**5**) was prepared and purified via procedures similar to those reported in the literature.^{44–46}

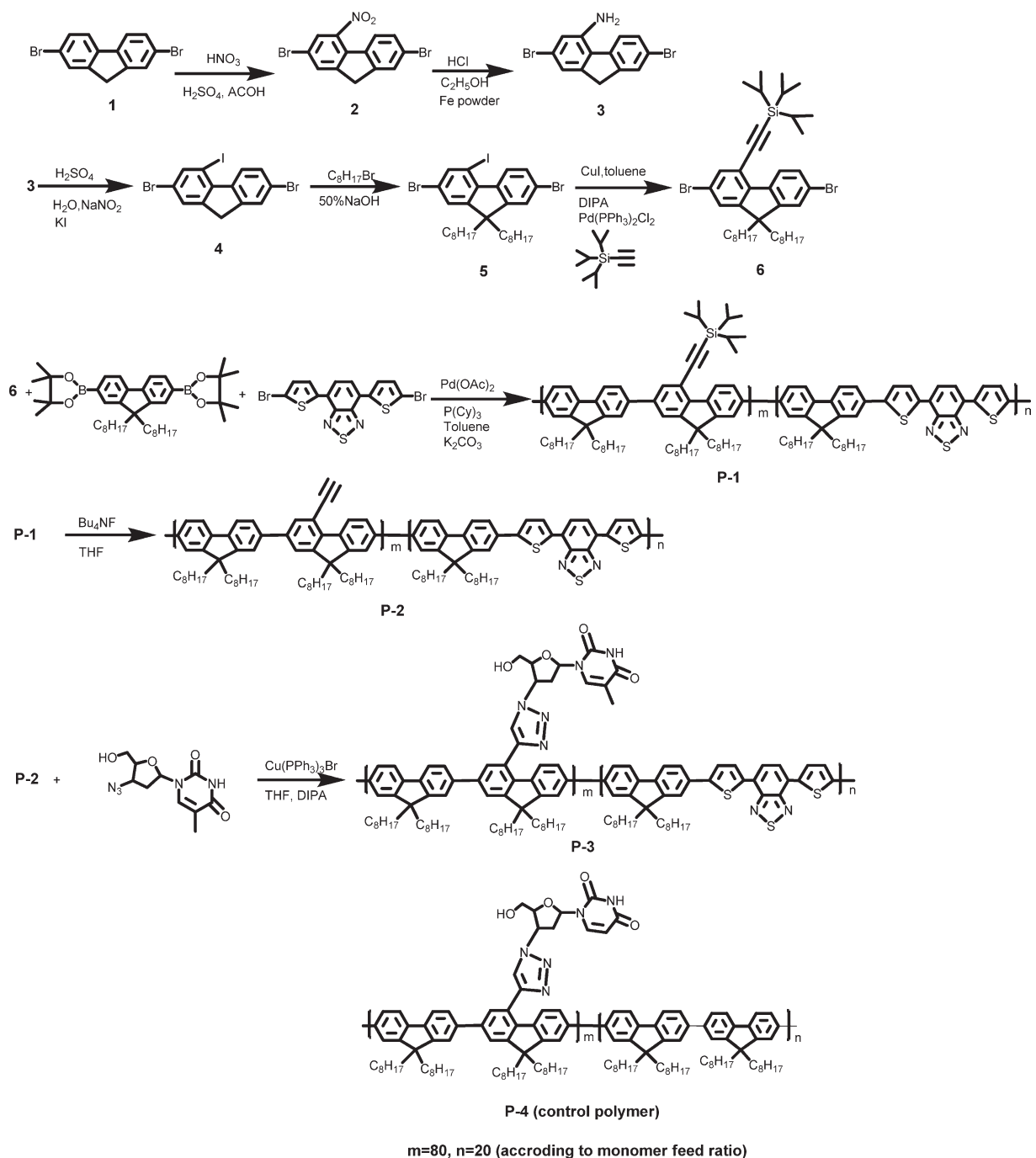
Synthesis of 2,7-Dibromo-4-Triisopropylsilyl-Alkynyl-9,9-Dioctylfluorene (**6**)

5 (0.337 g, 0.500 mmol), Pd(PPh₃)₂Cl₂ (0.017 g, 0.039 mmol), and CuI (0.009 g, 0.047 mmol) were added to a 50-mL, round-bottom flask. After the flask was purged with nitrogen for 5 min, dry toluene (6 mL) and diisopropylamine (3 mL) were added via syringe. The mixture was degassed and stirred for 20 min under nitrogen, and triisopropylsilyl acetylene (0.1014 g, 0.557 mmol) was injected into the flask. The previous mixture was stirred at room temperature overnight. The crude product was purified by column chromatography with petroleum ether as an eluent to give the final product as a white solid (0.2879 g).

Yield: 79.1%. ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 8.47–8.44 (d, $J = 12.4$ Hz, 1H), 7.56–7.55 (s, 1H), 7.46–7.42 (m, 2H), 7.39–7.37 (s, 1H), 1.91–1.87 (m, 4H), 1.25–0.99 (m, 41H), 0.88–0.81 (m, 6H), 0.59–0.57 (m, 4H). ¹³C-NMR (100 MHz, CDCl₃, δ , ppm): 152.80, 138.85, 134.65, 129.90, 126.10, 125.69, 124.05, 121.98, 120.31, 117.99, 104.19, 97.87, 77.17, 55.01, 40.16, 31.72, 29.81, 29.12, 23.53, 22.56, 18.60, 18.52, 14.03, 11.37.

Synthesis of Poly[(9,9-dioctyl)-2,7-fluorene-(9,9-dioctyl-4-triisopropylsilyl alkynyl fluorene)]-*co*-[(9,9-dioctyl)-2,7-fluorene-4,7-bis(5-thiophen-2-yl)benzo-2,1,3-thiadiazole] (**P-1**)

Under nitrogen, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (0.193 g, 0.30 mmol), **6** (0.175 g, 0.24 mmol), and DBT (0.0275 g, 0.06 mmol) were added to degassed toluene (8 mL) and 1.5 mL of a 0.2 M potassium carbonate aqueous solution (1.5 mL). Pd(OAc)₂ (0.003 g, 0.013 mmol) and three drops of Aliquat 336 were added later. The previous mixture was degassed several times, and tricyclohexyl phosphine (0.006 g, 0.021 mmol) was added afterward. The reaction was heated at 90°C for 72 h before it was cooled to room temperature. The crude product was purified by flash column chromatography with toluene as the eluent; then, it was concentrated to a volume of about 3 mL and reprecipitated into methanol



Scheme 1. Synthesis of the monomers and polymers.

(60 mL). The formed precipitate was recovered by filtration. The obtained polymer was further purified by washing with acetone in a Soxhlet apparatus for 24 h to remove oligomers and catalyst residues, and it was vacuum dried after vacuum drying at 50°C overnight (0.161 g).

Yield: 77%. FTIR (KBr, cm^{-1}): 3016, 2926, 2855, 2145 ($\text{C}\equiv\text{C}$), 1618, 1461, 1209, 1040, 1002, 816. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm): 8.79 (m, 0.65 H), 8.19 (m, 0.65 H), 7.98–7.37 (m, 12.25 H), 2.11 (m, 7.2 H), 1.41–0.82 (m, 70.8 H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , δ , ppm): 152.10, 151.82, 140.16, 126.23, 121.46, 120.03,

114.74, 65.88, 57.86, 55.35, 40.38, 37.25, 31.64, 29.87, 29.22, 23.86, 22.74, 18.67, 14.13, 11.48. Gel permeation chromatography (GPC): $M_w = 93,000$, $M_n = 20,380$, and $M_w/M_n = 4.6$.

Synthesis of Poly[(9,9-dioctyl)-2,7-fluorene-(9,9-dioctyl-4-phenylacetylene fluorene)]-co-[(9,9-dioctyl)-2,7-fluorene-4,7-bis(5-thiophen-2-yl)benzo-2,1,3-thiadiazole] (P-2). A solution of P-1 (0.161 g, 0.175 mmol) in anhydrous THF (14.3 mL) was vigorously stirred under a nitrogen atmosphere in a round-bottom flask, and tetrabutyl ammonium fluoride (1M in THF, 0.89 mL, 0.89 mmol) was added to this solution. The mixture

was stirred at room temperature overnight. The crude product was purified by flash column chromatography with toluene as the eluent; it was then concentrated and reprecipitated in methanol. The final product was obtained after vacuum drying at 50°C overnight (0.129 g).

Yield: 95%. FTIR (KBr, cm^{-1}): 3300 ($\equiv\text{C}-\text{H}$), 3016, 2925, 2853, 1622, 1460, 1040, 816. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm): 8.66 (m, 0.55 H), 8.19 (m, 0.55 H), 7.98–7.36 (m, 12.59 H), 3.60–3.58 (m, $\equiv\text{C}-\text{H}$, 0.64 H), 2.11 (m, 7.2 H), 1.26–0.82 (m, 54 H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , δ , ppm): 152.60, 151.85, 146.92, 140.27, 126.41, 121.69, 120.16, 113.30, 65.94, 59.00, 57.91, 55.36, 40.50, 37.24, 31.81, 29.24, 24.18, 22.74, 19.73, 14.13. GPC: $M_w = 186,300$, $M_n = 20,600$, and $M_w/M_n = 9.0$.

Synthesis of P-3. P-2 (0.030 g, 0.0386 mmol) was dissolved in dry THF (15 mL) and diisopropylamine (0.5 mL) under a nitrogen atmosphere. Then, $\text{Cu}(\text{PPh}_3)_3\text{Br}$ (0.005 g, 0.0054 mmol) and 3'-azido-3'-deoxythymidine (0.022 g, 0.08 mmol) were added sequentially. The previous mixture was stirred at 50°C overnight; then, the product was concentrated and reprecipitated in methanol and was vacuum dried at 50°C overnight (0.0310 g).

Yield: 81%. FTIR (KBr, cm^{-1}): 3408 (O—H and N—H), 3065, 2924, 2852, 1887, 1689 (C=O), 1573, 1460, 1374, 1270, 815. $^1\text{H-NMR}$ (400 MHz, THF-d_8 , δ , ppm): 10.40 (m, N—H), 8.38–7.44 (m, Ar H), 6.53 (m), 5.60 (m), 4.66 (m), 4.50 (m), 2.18–0.69 (m, alkyl H). GPC: $M_w = 31,400$, $M_n = 14,100$, and $M_w/M_n = 2.2$.

RESULTS AND DISCUSSION

Synthesis and Characterization

The synthetic route of intermediates and target polymer is shown in Scheme 1.

2,7-Dibromo-4-iodofluorene (**4**) was synthesized from 2,7-dibromofluorene as the starting material by sequential nitrication, ammonification, and iodination at the 4 site.^{45,46} Compound **5** was readily obtained by the alkylation of **4**.⁴⁴ The introduction of triisopropylsilyl acetylene groups in monomer **6** happened exclusively at the iodide site by a Sonogashira reaction because of the much higher reactivity of the iodide site compared to that of the bromo sites. P-1 was successfully synthesized via Suzuki polymerization and deprotected by the disilylation of Bu_4NF in THF at room temperature to give P-2 with a high yield. The T-substituted target polymer, P-3, was synthesized with P-2 and 3'-azido-3'-deoxythymidine as starting materials via a click reaction with $\text{Cu}(\text{PPh}_3)_3\text{Br}$ as the catalyst in THF. The introduction of T groups into optical compounds in previous studies was mainly done by condensation reactions between haloalkane and $\text{T}^{30,31}$ or aminoalkane and carboxylic acid-substituted $\text{T}^{42,43}$ and was limited by relatively low reaction yields and complicated syntheses. The highly efficient Cu(I)-catalyzed click reaction was applied in this study to favor the introduction of Ts under mild conditions and high yield. Both P-1 and P-2 are readily soluble in common organic solvents such as THF, chloroform, and toluene at room temperature, whereas P-3 is just soluble in THF and is almost insoluble in toluene, chloroform, dimethylformamide, and dimethyl

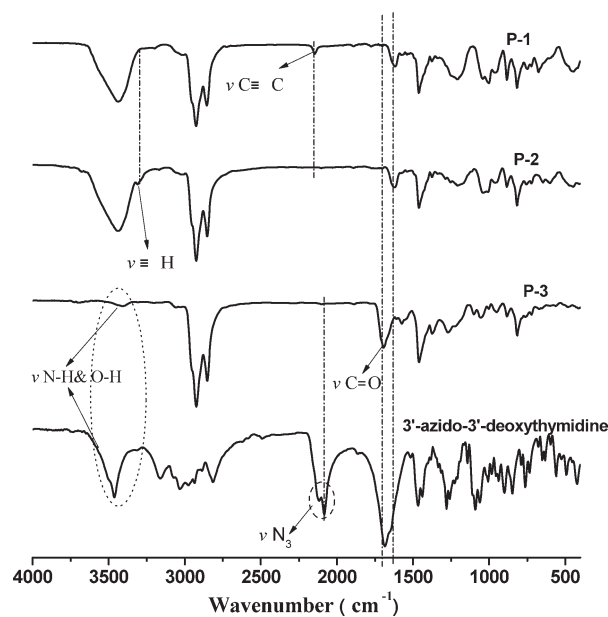


Figure 1. FTIR spectra of P-1, P-2, P-3, and 3'-azido-3'-deoxythymidine.

sulfoxide; this might be due to the complicated influence of its polarity, which is brought about by the substitution of T groups. The M_n values of P-1 and P-2 were measured by means of GPC analysis with THF as the eluent against polystyrene standards; the values were 20,380 and 20,600 with polydispersities of 4.6 and 9.0, respectively, whereas the corresponding M_n value for P-3 ($\sim 14,100$) was smaller than those of P-1 and P-2. This might have been due to P-3's lower solubility in THF compared with those of P-1 and P-2 (presumably brought about by the complicated influence of its polarity after the introduction of T groups).

The chemical structures of P-1, P-2, and P-3 were verified by FTIR and NMR analyses. As shown in Figure 1, clear changes in the FTIR spectra between P-1 and P-2 appeared at about 2145 cm^{-1} and about 3300 cm^{-1} . In the spectrum of P-2, the absorption signal intensity at about 2145 cm^{-1} (corresponding to the $\text{C}\equiv\text{C}$ stretching vibrations) weakened significantly compared to that of P-1, and a new band at about 3300 cm^{-1} appeared exclusively in the spectrum of P-2. This was assigned to the typical stretching absorption signal of $\equiv\text{C}-\text{H}$. This indicated that the disilylation of TIPS (triisopropylsilyl) groups occurred successfully. The $\equiv\text{C}-\text{H}$ stretching vibration in P-2 almost vanished in the spectrum of P-3, and for P-3, new absorption signals appeared at about 3408 and 1689 cm^{-1} ; these might have been typical O—H and N—H and C=O stretching vibrations, respectively, in the tethered T groups. When we made a comparison between the FTIR spectra of the click reaction substrates (3'-azido-3'-deoxythymidine and P-3), we found that the strong absorption signal of the $-\text{N}_3$ group at about 2086 cm^{-1} in 3'-azido-3'-deoxythymidine did not appear in the spectrum of P-3; this illustrated that there was no presence of unreacted 3'-azido-3'-deoxythymidine in P-3 and that the C=O vibration in P-3 should have been attributed to the corresponding covalently bonded product.

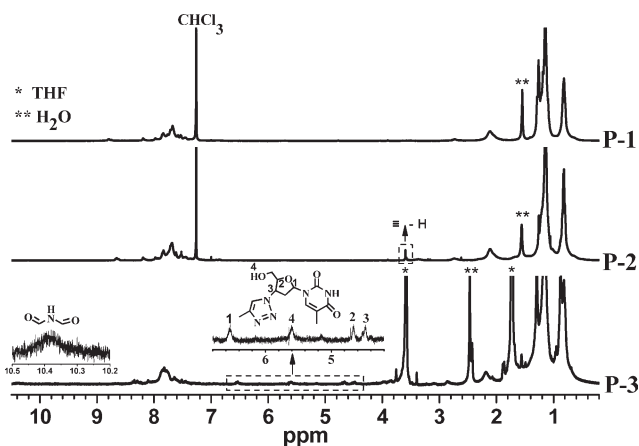


Figure 2. $^1\text{H-NMR}$ spectra of P-1, P-2 (in deuterated chloroform), and P-3 (in deuterated THF).

The $^1\text{H-NMR}$ spectra of the polymers are shown in Figure 2. The $^1\text{H-NMR}$ spectra of P-1 and P-2 were similar to each other as a whole, except that a proton signal at about δ 3.60 ppm appeared exclusively in the spectrum of P-2; this corresponded to the signal of substituted acetylene ($\equiv\text{C-H}$) groups. This result was consistent with the findings of the FTIR analysis; from this, we concluded that the desilylation reaction occurred successfully. From spectrum of P-3 (with THF- d_8 as the solvent), we found that weak characteristic signals of protons on the pendent deoxythymidine groups appeared at about 10.40, 6.53, 5.60, 4.66, and 4.50 ppm (their possible assignment is marked in the inset in Figure 2); this suggested that the T groups were successfully attached onto P-3. The other alkyl and aromatic protons signals were also reasonable and matched their chemical structures.

Thermal Properties

The thermal properties of the polymers were evaluated with TGA (temperature = 25–800°C in nitrogen), and the corresponding results are shown in Figure 3. TGA revealed that the decomposition onsets of P-1 and P-2 appeared at about 400

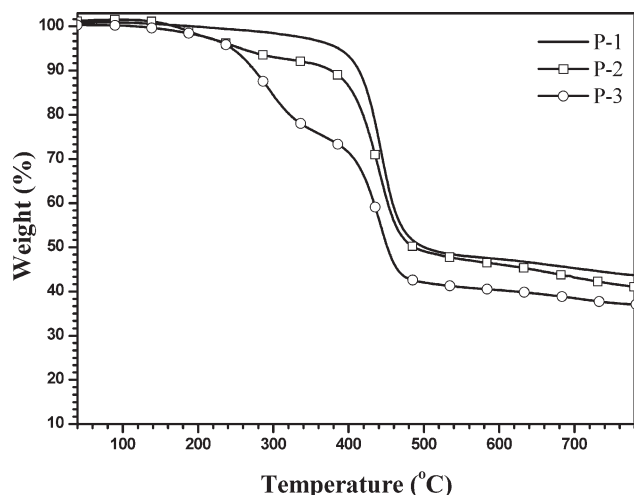


Figure 3. TGA studies of P-1, P-2, and P-3.

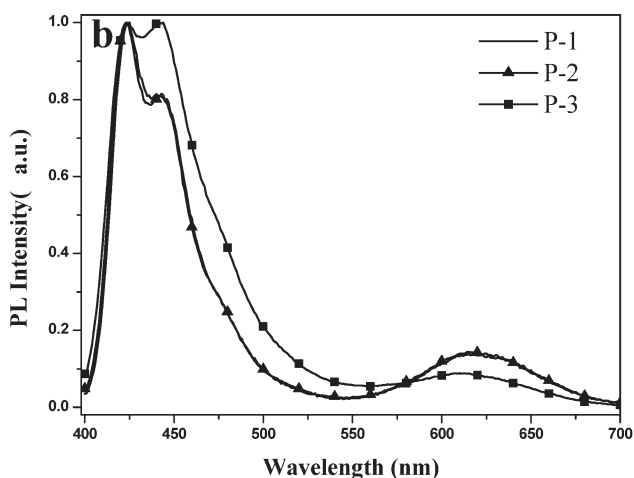
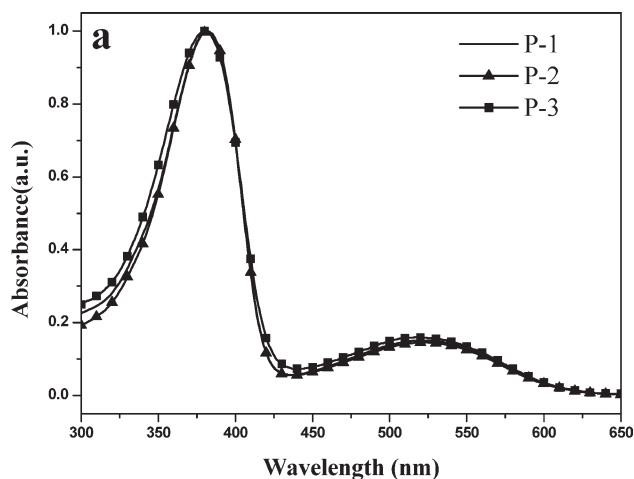


Figure 4. Normalized (a) UV-vis and (b) PL spectra of P-1, P-2, and P-3 in THF ($\sim 3 \times 10^{-5} M$).

and 380°C, respectively; these values may have corresponded to the removal of alkyl side chains. A two-step decomposition (with onset temperatures of about 240 and 380°C, respectively) was found in P-3; this was presumably because of the presence of two groups of leaving units (pendant T and alkyl groups) in P-3.

Optical Properties

The optical properties of the three polymers were measured in THF (with a concentration of $\sim 3 \times 10^{-5} M$). Figure 4(a) shows the UV-vis spectra of these polymers in normalization. As shown in the figure, two absorption bands at about 380 nm and about 520 nm were present for all of these polymers; these bands could be assigned to the absorption of the fluorene and 4,7-bis(thiophen-2-yl)benzo-2,1,3-thiadiazole segments, respectively. The UV-vis spectra of the three polymers highly resembled each other; this might have been due to their identical backbone structures. Their band gaps were not pronouncedly affected by the decoration of the side chains. The PL emission spectra of the polymers are shown in Figure 4(b). The spectra of P-1 and P-2 were almost identical to each other, whereas for P-3, there was a tiny difference from the others. That is, the intensity of the shoulder emission of the

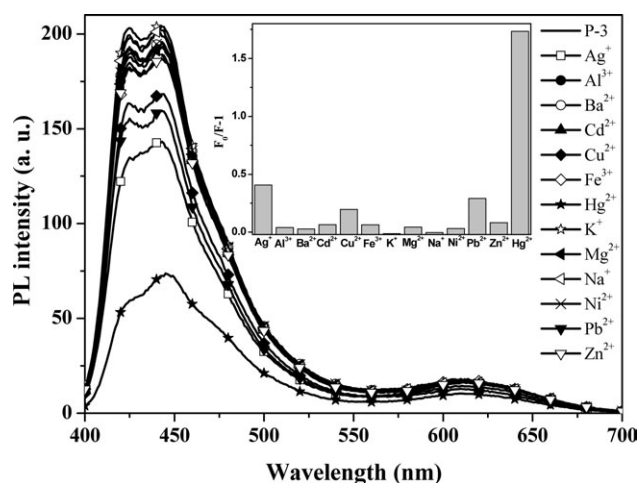


Figure 5. Fluorescence intensity changes of P-3 in THF (concentration $\approx 3 \times 10^{-5}$ M) in the presence of various metal ions (concentration $\approx 8.3 \times 10^{-4}$ M). The inset illustrates the column spectra of P-3's PL intensity alterations toward various metal ions. The excitation wavelength was 380 nm, and the slit width was identical in all cases.

blue-emitting fluorene segment at about 444 nm increased, and the red emission at about 620 nm decreased slightly. The fluorescence quantum yields of P-1, P-2, and P-3 in THF were investigated with 9,10-diphenylanthracene's cyclohexane solution as a standard, and their values were about 0.17, 0.18, and 0.24, respectively.

Investigation of P-3's Probing Properties

As mentioned in the Introduction, a specific binding with Hg^{2+} can be realized by T groups. To verify that such an interrelation also worked in P-3, the metal-ion response of P-3 was investigated in this study. Figure 5 shows the changes in P-3's PL intensity with the presence of different metal ions (the concentrations of P-3 and each ion were controlled at $\sim 3 \times 10^{-5}$ and 3.3×10^{-4} M, respectively, and the PL spectra were recorded 3 min later after the addition of each ion). As shown in Figure 5, compared to the other metal ions, Ag^+ and Hg^{2+} caused more obvious fluorescent quenching.

In view of the previous situation, the question that urgently needed to be solved was whether the distinct detection of Hg^{2+} and Ag^+ could be realized by P-3. The difference between the UV-vis changes in P-3 upon the titration of Hg^{2+} and Ag^+ was thus enlightened to answer the aforementioned question, and the corresponding results are shown in Figure 6. Figure 6(a,b) illustrates the gradual variation of the UV-vis spectra of P-3 with the presence of incremental amounts of Hg^{2+} and Ag^+ , respectively. As shown in Figure 6(a), with the enhancement of the concentration of Hg^{2+} , the UV-vis spectra of P-3 remained approximately unchanged within the low-concentration range, whereas the curves turned up and prominent changes were detected when the concentration of Hg^{2+} exceeded about 1.1×10^{-4} M. However, for Ag^+ [Figure 6(b)], the absorption shape was retained, and a monotonous decrease in the absorption intensity was detected within the titration process. The UV-vis changes in P-3 with the presence of deionized water (80 μL)

were also tested to clarify that alteration of the UV-vis spectra had no connection with the participation of water. The combination of PL and UV-vis analyses indicated different interrelations between P-3 and these two metal ions, and P-3 possessed the capability of discriminating these two ions to some extent.

Detailed fluorescence changes of P-3 with the gradual titration of Hg^{2+} ions in increasing concentrations were also investigated, and the corresponding results are shown in Figure 7. As expected, when the concentration of Hg^{2+} was increased, P-3's PL intensity began to quench continuously [as shown in Figure 7(a,b)]. This might have been to the quenching effect resulting from T-Hg(II)-T (T-Hg-T) base pair induced aggregation between the polymer chains.²⁷⁻³² Around 77% of the intensity of P-3 was quenched when the concentration of Hg^{2+} reached 7.7×10^{-4} M, and the detection limit was in the range of about 4.8×10^{-6} M [based on the 3 sigma (3σ) criteria, the standard deviation (0.013) was obtained by 10 measurements of blank P-3 solutions, and the slope was evaluated by the linear response range from 10 to 50 μM in Figure 7(b)]. Such a detection limit was comparable^{30,31} or slightly better^{22,42} to the corresponding data for the reported T-decorated probes. Although the detection limit obtained in this study was inferior to reported results

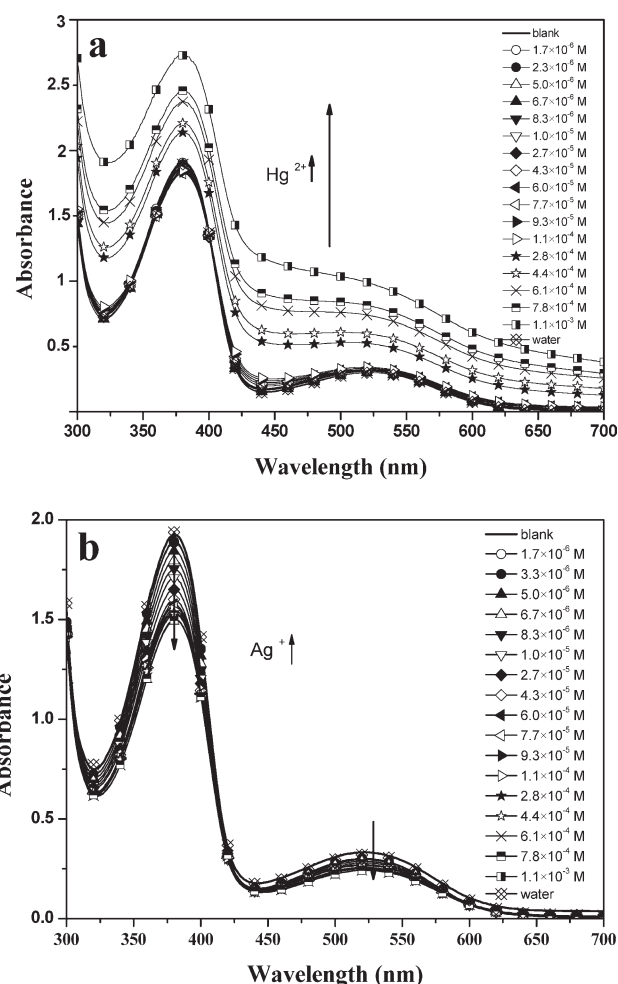


Figure 6. UV-vis spectra of P-3 (concentration $\approx 3 \times 10^{-5}$ M) in the presence of incremental (a) Hg^{2+} and (b) Ag^+ in THF.

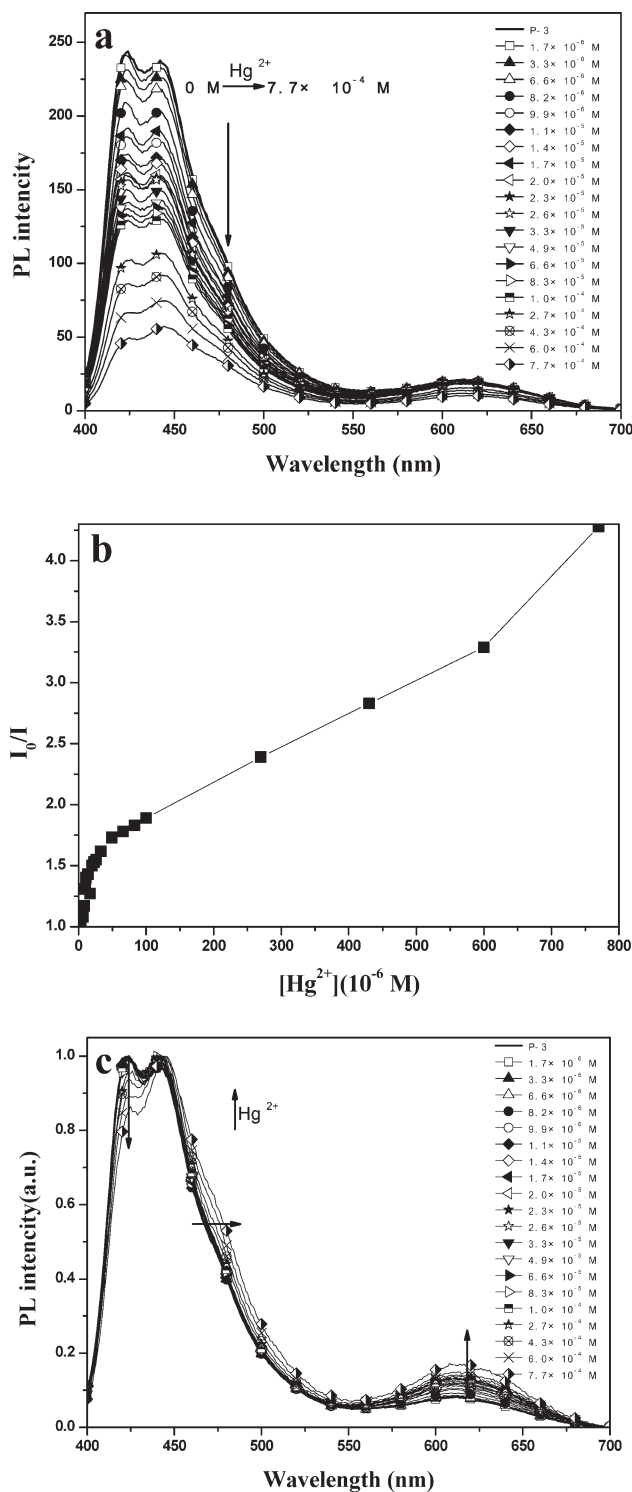


Figure 7. (a) Fluorescence spectra of P-3 in THF ($\sim 3 \times 10^{-5} M$) upon incremental addition of Hg^{2+} (0 to $7.7 \times 10^{-4} M$) in deionized water, (b) corresponding I_0/I values versus Hg^{2+} concentration, and (c) corresponding normalized ones.

about DNA⁴¹ and nanoparticle^{25,26} involved probes, their fluorescence reversibility (discussed later) is a unique property that most existing Hg^{2+} probes from other designs do not possess.

Figure 7(c) shows the normalized fluorescence spectra of P-3 in THF upon the gradual titration of Hg^{2+} . As shown in the figure, with increasing concentration of Hg^{2+} , the relative intensity of the blue emission peak (~ 422 nm) decreased, whereas that of the red emission (~ 620 nm) increased sequentially; this was accompanied by the gradual broadening of the spectral profiles in the wavelength range between 400 and 550 nm; this was another reflection of the previously mentioned T—Hg—T induced aggregation between P-3 chains.

The aforementioned investigations suggested that P-3 could act as potential probe for Hg^{2+} . However, it is well known that the optical properties of a lot of sulfur-containing CPs are affected intrinsically because of the interaction between S atoms and Hg^{2+} .^{20,22,47} S atoms existed in all three of the polymers in this case. So another issue laid before us was whether P-3's optical response to Hg^{2+} was really related to the T groups in the presence of S atoms in its structure. The PL intensity alterations of P-1, P-2, and P-3 against Hg^{2+} were thus investigated with identical experimental conditions (a repetitive experiment on P-3 was conducted once again here with selective concentrations of Hg^{2+}) to obtain some clues for the aforementioned question.

The PL characteristics of the monomer DBT toward incremental Hg^{2+} was detected first to determine whether there was any interaction between DBT and Hg^{2+} ; the results are shown in Figure 8 (the PL spectra within the low-concentration range of Hg^{2+} are not shown here because these alterations were not apparent). We found that the PL intensity of DBT was subsequently quenched by the addition of Hg^{2+} ; this suggested the presence of an interrelation between the S atoms in DBT and Hg^{2+} .

Figure 9(a–c) shows the fluorescence intensity changes of P-1, P-2, and P-3 in THF in the presence of incremental Hg^{2+} ions, respectively. PL intensity quenching was detected for all of these polymers. By careful comparison, we found that the quenching of P-3 was more noticeable compared to the others, especially in the low-concentration range of Hg^{2+} . When the concentration of Hg^{2+} reached $6.67 \times 10^{-5} M$, about 35% of P-3's PL

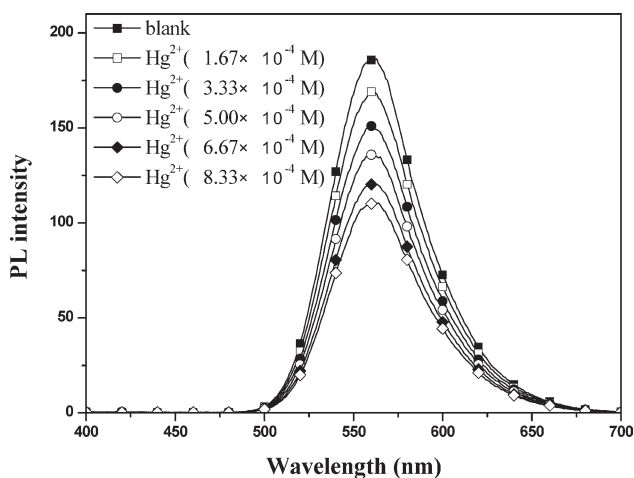


Figure 8. Fluorescence spectra of DBT in THF ($\sim 3 \times 10^{-5} M$) upon incremental addition of Hg^{2+} (0 to $8.33 \times 10^{-4} M$) in deionized water.

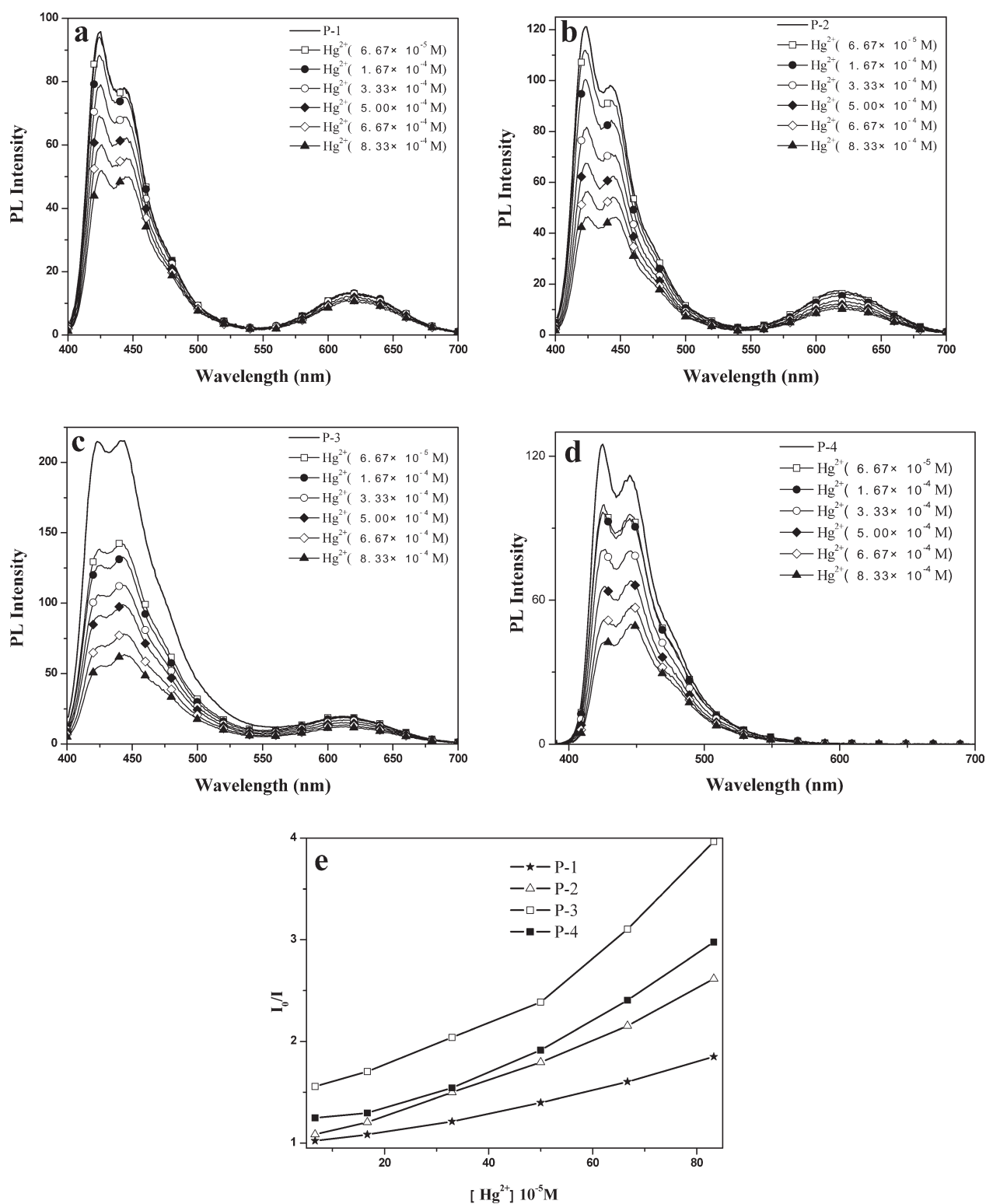


Figure 9. Fluorescence intensity alterations of (a) P-1, (b) P-2, (c) P-3, and (d) P-4 in THF (concentration $\approx 3 \times 10^{-5} \text{ M}$) in the presence of incremental Hg^{2+} ions and (e) corresponding I_0/I values versus Hg^{2+} concentration.

intensity was quenched, and for P-1 and P-2, the quenching degrees were just about 3 and 9%, respectively. We deduced from Figure 9(a-c) that the aggregation in P-3 was more pronounced relative to that of the other polymers because of the

synergic effect of the tethered T and S atoms to interrelate with Hg^{2+} . That is, the Hg^{2+} detection capability of such S-atom-containing polymers was modified by the introduction of T. To find more evidence for the aforementioned synergic effect

between S atoms and T, a control polymer, **P-4** (its chemical structure is shown in Scheme 1), which did not have any benzothiadiazoles but had the same quantity of T units as **P-3**, was synthesized, and its fluorescence response toward Hg^{2+} was investigated under the same conditions as those used for **P-1** to **P-3**. Figure 9(d) shows the fluorescence intensity alterations of **P-4** in THF in the presence of incremental Hg^{2+} ions, and the corresponding I_0/I values versus the Hg^{2+} concentration for **P-1** to **P-4** are shown in Figure 9(e) for direct comparison of their quenching efficiencies. When we made a comparison between the curves of **P-3** and **P-4**, we found that with a given amount of Hg^{2+} , **P-3** displayed more pronounced quenching compared to **P-4**; this supported the previously mentioned hypothesis on the synergic effect between the S atoms and T.

Figure 10 illustrates the interference of other metal ions for **P-3** against Hg^{2+} . From it, we found that the addition of Hg^{2+} caused stronger quenching compared to those only with background metals, and for Ag^+ , an additive effect was detected with the introduction of Hg^{2+} . Because these spectra were recorded in a short time interval without a long-time standing at room temperature (3 min later with the addition of each ion) and with its anti-interference and sensitivity, **P-3** might be act as a potential immediacy optical probe for Hg^{2+} .

As mentioned earlier, reversibility is an advantageous characteristic for such T-decorated Hg^{2+} probes. To determine whether **P-3** was a reversible probe for Hg^{2+} , I^- was added to the **P-3**/ Hg^{2+} system (because of the high interrelation constant between Hg^{2+} and I^- according to a previous report³¹). Hg^{2+} ions should have been extracted from the T– Hg^{2+} –T complexes because of their stronger binding with I^- to release **P-3** and restore its fluorescence. As shown in Figure 11, with the increasing concentration of I^- , **P-3**'s PL intensity recovered continuously, and this was accompanied by the recovery of the spectral profiles (the intensity of the blue emission at ~ 422 nm increased continuously and became stronger than the shoulder emission at ~ 441 nm when $\text{I}^-/\text{Hg}^{2+}$ reached ~ 0.32). This suggested the release of the polymer chains from the

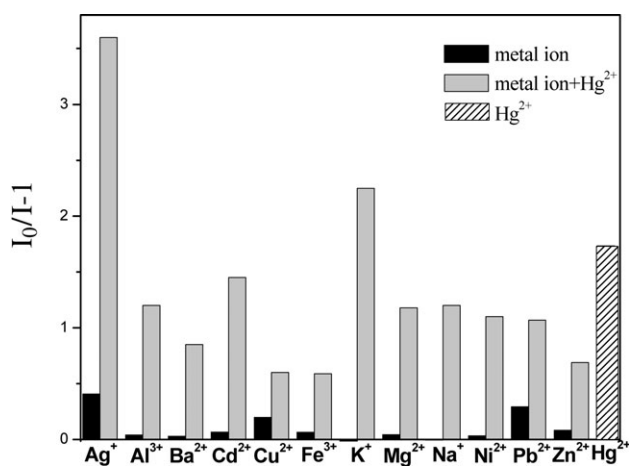


Figure 10. Fluorescence quenching of **P-3** in THF (concentration $\approx 3.0 \times 10^{-5}$ M) in the presence of various background metal ions (concentration = 3.3×10^{-4} M for each ion) and with the sequential addition of Hg^{2+} (3.3×10^{-4} M). The excitation wavelength was 380 nm.

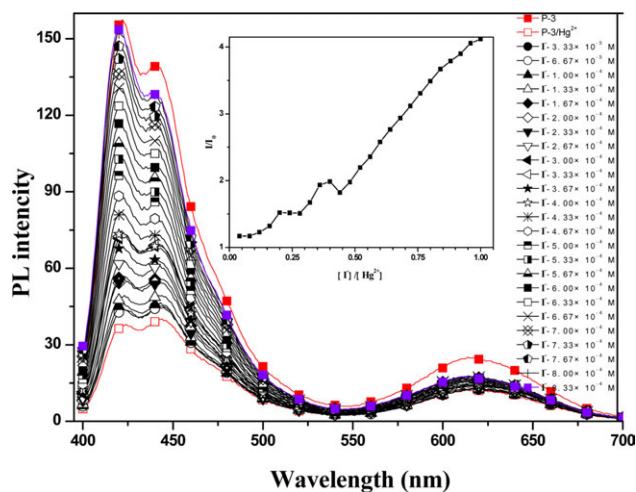


Figure 11. Fluorescence spectra of **P-3**/ Hg^{2+} in THF (concentrations $\approx 3 \times 10^{-5}$ and 8.3×10^{-4} M for **P-3** and Hg^{2+} , respectively) with the sequential addition of I^- ions (from 0 to 8.3×10^{-4} M). The inset is the plot of I/I_0 versus the $\text{I}^-/\text{Hg}^{2+}$ ratio. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

aggregate state. When the concentration of I^- reached about 8.3×10^{-4} M ($\text{I}^-/\text{Hg}^{2+} = 1$), about 91% of the fluorescence intensity of **P-3** was recovered. This suggested that **P-3** could act as a potential reversible optical Hg^{2+} probe. Further work to modify the solubility and optoelectronic and probing properties of this type of Hg^{2+} -sensing polymer by adjustment of its chemical structures and T composition ratios is under way.

CONCLUSIONS

A conjugated fluorene-based fluorescent polymer with tethered T, **P-3**, was successfully prepared via click postpolymerization between an acetylene-containing precursor polymer and an azide-substituted T derivative. The optical properties of the precursor polymers and **P-3** were systematically investigated in this study. By studying the metal-ion response of **P-3**, we found that this polymer could act as potential reversible, anti-interferential, selective, and sensitive Hg^{2+} optical probe in THF solution. Further work to prepare Hg^{2+} fluorescent sensing polymers through the tuning of their chemical structures and T composition ratios for probing in an aqueous environment and with improved sensitivity is under way.

ACKNOWLEDGMENTS

The authors greatly appreciate the financial support from the Natural Science Foundation of Xinjiang Uygur Autonomous Region (project number 2011211A007) and the National Natural Science Foundation of China (project numbers 50903068, 10904042, and 21063013).

REFERENCES

1. Tchounwou, P. B.; Ayensu, W. K.; Ninashvili, N.; Sutton, D. *Environ. Toxicol.* **2003**, *18*, 149.
2. Kuwabara, J. S.; Arai, Y.; Topping, B. R.; Pickering, I. J.; George, G. N. *Environ. Sci. Technol.* **2007**, *41*, 2745.

3. Harris, H. H.; Pickering, I. J.; George, G. N. *Science* **2003**, *301*, 1203.
4. Korbas, M.; Blechinger, S. R.; Krone, P. H.; Pickering, I. J.; George, G. N. *PNAS* **2008**, *105*, 12108.
5. Grandjean, P.; Weihe, P.; White, R. F.; Debes, F. *Environ. Res. Sect. A* **1998**, *77*, 165.
6. Wang, H. H.; Xue, L.; Yu, C. L.; Qian, Y. Y.; Jiang, H. *Dyes Pigments* **2011**, *91*, 350.
7. Li, Y.; Jiang, Y.; Yan, X. P. *Anal. Chem.* **2006**, *78*, 6115.
8. Erxleben, H.; Ruzicka, J. *Anal. Chem.* **2005**, *77*, 5124.
9. Houserová, P.; Matějček, D.; Kubáň, V.; Pavlíčková, J.; Komárek, J. *J. Sep. Sci.* **2006**, *29*, 248.
10. Yu, L. P. *J. Agric. Food. Chem.* **2005**, *53*, 9656.
11. Nguyen, T. H.; Boman, J.; Leermakers, M.; Baeyens, W. *X-Ray Spectrom.* **1998**, *27*, 277.
12. Epov, V. N.; Rodriguez-Gonzalez, P.; Sonke, J. E.; Tessier, E.; Amouroux, D.; Bourgoïn, L. M.; Donard, O. F. X. *Anal. Chem.* **2008**, *80*, 3530.
13. Nolan, E. M.; Lippard, S. J. *Chem. Rev.* **2008**, *108*, 3443.
14. Han, B. Y.; Yuan, J. P.; Wang, E. K. *Anal. Chem.* **2009**, *81*, 5569.
15. Lee, K. H.; Chen, S. J.; Jeng, J. Y.; Cheng, Y. C.; Shiea, J. T.; Chang, H. T. *J. Colloid. Interface Sci.* **2007**, *307*, 340.
16. Ros-Lis, J. V.; García, B.; Jiménez, D.; Martínez-Mañez, R.; Sancenón, F.; Soto, J.; Gonzalvo, F.; Valldecabres, M. C. *J. Am. Chem. Soc.* **2004**, *126*, 4064.
17. Shibata, A.; Furukawa, K.; Abe, H.; Tsuneda, S.; Ito, Y. *Bio-org. Med. Chem. Lett.* **2008**, *18*, 2246.
18. Alfonso, M.; Tárraga, A.; Molina, P. *J. Org. Chem.* **2011**, *76*, 939.
19. Cao, Q. Y.; Lee, M. H.; Zhang, J. F.; Ren, W. X.; Kim, J. S. *Tetrahedron Lett.* **2011**, *52*, 2786.
20. Huang, X. B.; Meng, J.; Dong, Y.; Cheng, Y. X.; Zhu, C. J. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 997.
21. Liu, S. J.; Fang, C.; Zhao, Q.; Fan, Q. L.; Huang, W. *Macromol. Rapid Commun.* **2008**, *29*, 1212.
22. Kwon, N. Y.; Kim, D.; Son, J. H.; Jang, G. S.; Lee, J. H.; Lee, T. S. *Macromol. Rapid Commun.* **2011**, *32*, 1061.
23. Joseph, K. A.; Dave, N.; Liu, J. *Am. Chem. Soc. Appl. Mater. Interfaces* **2011**, *3*, 733.
24. Zhou, Y. Y.; Deng, M. G.; Du, Y. Y.; Yan, S. Y.; Huang, R.; Weng, X. C.; Yang, C. L.; Zhang, X. L.; Zhou, X. A. *Analyst* **2011**, *136*, 955.
25. Li, H. B.; Yan, H. J. *J. Phys. Chem. C* **2009**, *113*, 7526.
26. Ma, C.; Zeng, F.; Huang, L. F.; Wu, S. Z. *J. Phys. Chem. B* **2011**, *115*, 874.
27. Miyake, Y.; Togashi, H.; Tashiro, M.; Yamaguchi, H.; Oda, S.; Kudo, M.; Tanaka, Y.; Kondo, Y.; Sawa, R.; Fujimoto, T.; Machinami, T.; Ono, A. *J. Am. Chem. Soc.* **2006**, *128*, 2172.
28. Tanaka, Y.; Oda, S.; Yamaguchi, H.; Kondo, Y.; Kojima, C.; Ono, A. *J. Am. Chem. Soc.* **2007**, *129*, 244.
29. Torigoe, H.; Ono, A.; Kozasa, T. *Chem. Eur. J.* **2010**, *16*, 13218.
30. Wang, Z.; Zhang, D. Q.; Zhu, D. B. *Anal. Chim. Acta.* **2005**, *549*, 10.
31. Ma, B. L.; Zeng, F.; Zheng, F. Y.; Wu, S. Z. *Chem. Eur. J.* **2011**, *17*, 14844.
32. Liu, X. J.; Qi, C.; Bing, T.; Cheng, X. H.; Shangguan, D. H. *Anal. Chem.* **2009**, *81*, 3699.
33. Zhu, Z. Q.; Su, Y. Y.; Li, J.; Li, D.; Zhang, J.; Song, S. P.; Zhao, Y.; Li, G. X.; Fan, C. H. *Anal. Chem.* **2009**, *81*, 7660.
34. McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.
35. Chen, X. Q.; Zhou, G. D.; Peng, X. J.; Yoon, J. *Chem. Soc. Rev.* **2012**, *41*, 4610.
36. Li, K.; Liu, B. *J. Mater. Chem.* **2012**, *22*, 1257.
37. Liu, X. F.; Fan, Q. L.; Huang, W. *Biosens. Bioelectron.* **2011**, *26*, 2154.
38. Alvarez, A.; Salinas-Castillo, A.; Costa-Fernández, J. M.; Pereira, R.; Sanz-Medel, A. *Trac-Trend. Anal. Chem.* **2011**, *30*, 1513.
39. Thomas, S. W., III; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107*, 1339.
40. He, F.; Tang, Y. L.; Wang, S.; Li, Y. L.; Zhu, D. B. *J. Am. Chem. Soc.* **2005**, *127*, 12343.
41. Ren, X.; Xu, Q. H. *Langmuir* **2009**, *25*, 29.
42. Tang, Y. L.; He, F.; Yu, M. H.; Feng, F. D.; An, L. L.; Sun, H.; Wang, S.; Li, Y. L.; Zhu, D. B. *Macromol. Rapid Commun.* **2006**, *27*, 389.
43. Lv, J.; Ouyang, C. B.; Yin, X. D.; Zheng, H. Y.; Zuo, Z. C.; Xu, J. L.; Liu, H. B.; Li, Y. L. *Macromol. Rapid Commun.* **2008**, *29*, 1588.
44. Yang, R. Q.; Tian, R. Y.; Hou, Q.; Yang, W.; Cao, Y. *Macromolecules* **2003**, *36*, 7453.
45. Price, D. W.; Tour, J. M. *Tetrahedron* **2003**, *59*, 3131.
46. Oldridge, L.; Kastler, M.; Müllen, K. *Chem. Commun.* **2006**, 885.
47. Li, J.; Meng, J.; Huang, X. B.; Cheng, Y. X.; Zhu, C. *J. Polymer* **2010**, *51*, 3425.