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RESEARCH ARTICLE

Hyperbranched polyyne containing naphthalimide moiety as a fluorescent chemosensor for mercury ion

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The development of multidimentional conjugated polymers as fluorescent sensor has been extremely attractive for detecting toxic ion in trace level. In this paper, a new hyperbranched polyyne with polytris(4-ethynylphenyl) amine (PTEPA) as the core, benzoyl thiourea-naphthalimide (NAP) as Hg (II) detected unit was designed and synthesized. The addition of Hg (II) ion transforms the thiourea unit of the chemodosimeter under THF conditions into an imidazoline moiety that is a much less electron-donating group, and hence results in a reduction in electron delocalization within the fluorophore. The emission maximum exhibits blue-shift and increase of fluorescent intensity. To confirm selectivity of the sensor towards mercury ions, it was also titrated with other divalent metal ions. No significant change was observed in the fluorescence spectra.

Keywords polytris(4-ethynylphenyl)amines, naphthalimide, fluorescent sensor, mercury ion

1 Introduction

There is a growing interest in the design and development of chemical sensors for mercury ions because of their inherent toxic effect on human health and on environment [1–5]. The Environmental Protection Agency (EPA) standard for the maximum allowable level of inorganic Hg^{2+} in drinking water is 2 ppb [6]. Concentrated mercury poses serious problems to human health since bioaccumulation of mercury within the brain and kidneys ultimately leads to neurological diseases [7]. An ideal probe should thus display a very low detection limit but retain its selectivity towards Hg^{2+}. Fluorescent molecular sensing, which translates molecular recognition into tangible fluorescence signals, has attracted much attention in this field. Many fluorescent chemosensors for Hg^{2+} based on small molecules have been reported to date [8–15]. Recently, Tang et al. demonstrated the use of fluorescent sensors for toxic mercury detection in cells under EPA levels [16]. Although some small molecular chemosensors for Hg (II) have been reported, many of these systems exhibit features limiting their practical use, such as poor solubility in water [17] and/or cross-sensitivity toward other metal ions [18,19]. Therefore, the development of new and practical assays for Hg(II) remains a challenge.

One potential approach is the use of conjugated polymers (CPs) that provide high sensitivity for the detection of metal ions because their optical properties exhibit high luminescence characteristics and electrical conductivity. An additional advantage of using polymers as sensor materials emerges from their internal properties, i.e., the conjugated polymer backbone allows efficient electron delocalization and exciton migration over large distances and thereby creates amplified sensory responses compared to small-molecule-based sensors [20]. It is well known that the backbone of these conjugated polymers consists of a large number of chromic repeat units. The electronic structure of acetylenic polymers coordinates the action of a large number of absorbing units. Several kinds of polymers have been successfully used for sensing ions and biological species, including poly(phenylene)s [21], poly(p-phenyleneethynylene)s [22,23], poly(p-phenylenevinylene)s [24], polythiophenes [25,26], and polyfluorenes [27–29] with receptor groups, for example, crown ethers, pyridine derivatives, and ionic groups in the side chain or main chain [30–32]. Acetylenic polymers have light harvesting properties that can be used in the function of very sensitive optical sensors in conjunction with reporter fluorophores attached to high-specificity probes. However, all these linear polymers often exhibit large persistent lengths in solution and can present the exciton with a one-dimensional diffusional conduit. The hyperbranched polymers provide an excellent alternative with the additional advantage of being easily synthesized in one or two reactions while showing comparable properties [33]. Compared to linear conjugated polymers, the incorporation of hyperbranched structure is advantageous because its multidimentional diffusional conduit can provide greater number of possible exciton migration pathways [34].

In 2005, our group reported a small molecular ratiometric sensor for mercury ion based on benzoyl thiourea, in which the sensory process was achieved by taking advantage of the known Hg(II)-induced transformation of thiourea moieties into guanidine derivatives [35]. In this paper, a new hyperbranched polyyne, with polytris(4-ethynylphenyl)amine (***hb*PTEPA**) as the core and benzoyl thiourea-naphthalimide (**NAP**) as Hg (II) detected unit (Scheme 1), was designed and

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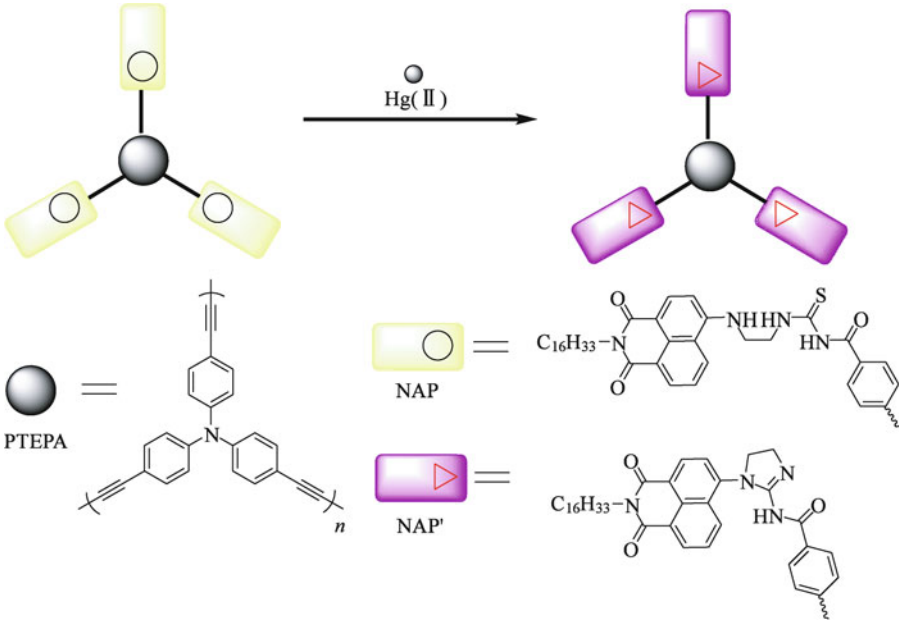


Scheme 1 Description of ***hb*PTEPA-NAP** working with Hg^{2+} ion.

synthesized in order to amplify the fluorescent signal change in Hg^{2+} addition process. The ***hb*PTEPA** was constructed by Glaser-Hay oxidative coupling reaction [36]. Moreover, the ***hb*PTEPA-NAP** was synthesized through sonogashire reaction between the ***hb*PTEPA** and **NAP** moieties. Fluorescent titration was used to confirm the sensitivity and selectivity of the sensor towards mercury ion.

2 Experiments

2.1 General

Tetrahydrofuran (THF) was pre-dried over 4Å molecular sieves and distilled under argon atmosphere from sodium benzophenone ketyl immediately before use. Triethylamine was distillated under normal pressure and dried over calcium hydride. All other chemicals were purchased from Aldrich and used as received without further purification. FT-IR spectra were recorded on a Nicolet Magna-IR550 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-500 spectrometer using chloroform-*d* as solvent and tetramethylsilane (δ = 0) as internal references. The UV/Vis spectra were recorded on a Varian-Cary 500 spectrophotometer with 2 nm of resolution at room temperature. Molecular weights and polydispersity indices of the polymers were estimated in THF by a Waters Associated Gel Permeation Chromatograph (GPC) system. A set of monodisperse polystyrene standards covering the molecular weight range of 10^3~10^7 were used for the molecular weight calibration. The fluorescence spectra were taken on a Varian-Cary fluorescence spectrophotometer. The polymerization reactions and manipulation for ***hb*PTEPA** were carried out in air. A typical experimental procedure for ***hb*PTEPA** will be introduced later [36].

2.2 Monomer synthesis

2.2.1 Preparation of 4-bromo-N-cetanylnaphthalimide (2)

Chemicals were added into a 100-mL two-necked round-bottom flask, including 4.11 g (14.8 mmol) of 4-bromo-1,8-naphthalic anhydride, 4.10 g (19.7 mmol) of cetylamine, and 50 mL glacial acetic acid. The solution was refluxed and stirred for 4 h and then cooled to room temperature. Then, 150 mL water was added into the system under mild stirring. Crude product was recrystallized from 25 mL ethanol, and pure product was obtained as white power after suction filtration and vacuum drying. Yield: 6.9 g (13.8 mmol, 93%).

^{1}H-NMR ($CDCl_3$), δ : 8.59 (d, 1H, J = 7.2 Hz), 8.57 (d, 1H, J = 8.0 Hz), 8.42 (d, 1H, J = 8.0 Hz), 8.05 (d, 1H, J = 8.0 Hz), 7.86 (t, 1H, J = 8.0 Hz), 4.17 (t, 2H, J = 7.6 Hz), 1.71 (m, 2H), 1.32 – 1.42 (m, 26H), 0.8 (t, 3H, J = 7.2 Hz).

2.2.2 Preparation of 4-amidoethynlimine-N-cetanylnaphthalimide (3)

3.195 g (6.8 mmol) of 4-bromo-N-cetanylnaphthalimide (**2**) and 40 mL methyl glycol were added into a 100-mL two-necked round-bottom flask. The solution was refluxed and stirred while the anhydrous ethylenediamine was added as

solvent into the flask. The reaction lasted 5 h, and then the system was pulled into 150 mL water. Crude product obtained by suction filtration was recrystallized from 20 mL ethanol. The pure product was obtained as pale yellow power. Yield: 62%, 2.96 g (6.2 mmol).

^{1}H-NMR ($CDCl_3$), δ : 8.588 (d, 1H, J = 7.2 Hz), 8.465 (d, 1H, J = 8.4 Hz), 8.193 (d, 1H, J = 8.4 Hz), 7.625 (t, 1H, J = 8.0 Hz), 6.713 (d, 1H, J = 8.4 Hz), 6.192 (w, 1H), 4.161 (t, 2H, J = 7.6 Hz), 4.429 (t, 2H, J = 4.4 Hz), 3.195 (t, 2H, J = 5.6 Hz), 1.988 (s, 1H), 1.429 (m, 2H), 1.268 (m, 26H), 0.893 (t, 3H, J = 7.2 Hz).

2.2.3 Preparation of monomer 1

1.0 g (4.13 mmol) 4-bromobenzoyl isothiocyanic ester dissolved in 20 mL flash acetone was added into a 50-mL round-bottom flask. Then 0.5 g (1.12 mmol) of 4-amidoethynlimine-N-cetanylnaphthalimide (**3**) was added for three times while the system was under stirring and refluxing. Reaction lasted for 3 h. The filter mass was purified on a silica gel chromatography column using DCM as eluent. The removal of the eluents yielded 0.40 g (0.56 mmol) of yellow powder. Yield: 50%.

^{1}H-NMR ($CDCl_3$), δ : 9.15 – 9.06 (w, 1H), 8.55 (d, 1H, J = 8.0 Hz), 8.30 (d, 1H, J = 8.0 Hz), 7.77 – 7.57 (m, 5H), 7.27 (s, 1H), 6.71 (d, 1H, J = 8.4 Hz), 6.60 (s, 1H), 4.168 (t, 2H, J = 7.6 Hz), 3.441 (q, 2H, J = 6.4 Hz), 3.201 (t, 2H, J = 5.2 Hz), 1.738 (m, 2H), 1.271 (m, 26H), 0.897 (t, 3H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$), δ : 182.88, 166.83, 165.36, 164.84, 150.14, 134.98, 133.30, 131.83, 130.79, 130.42, 129.91, 129.63, 127.75, 125.63, 123.76, 121.09, 111.62, 104.41, 46.04, 44.47, 40.96, 32.61, 30.38, 30.34, 30.28, 30.13, 30.04, 28.91, 27.91, 23.36, 14.80.

2.3 Polymerization

2.3.1 Preparation of hbPTEPA

2 mg (0.02 mmol) of CuCl, 8 mg (0.07 mmol) of TMEDA, and 4 mL of o-DCB were added into a 10-mL Schlenk tube with side arm. The mixture was stirred under 50°C, while 253.6 mg (0.8 mmol) of 4,4′,4″-triacetylenetyl triphenylamine dissolved in 1 mL of o-DCB was added into the tube. The reaction continued for 15 min. Then the mixture was added dropwise to 300 mL methanol through a cotton filter under stirring. The precipitate was allowed to stand overnight and then filtered with Gooch crucible. The polymer was washed with methanol and dried in a vacuum oven to a constant weight. White power was obtained. Yield: 50.2 mg (19.8%).

^{1}H-NMR ($CDCl_3$), δ : 7.3 – 7.5 (Ar – H), 6.9 – 7.1 (Ar – H), 3.1 (≡CH). ^{13}C-NMR ($CDCl_3$), δ : 147.33, 147.13, 146.95, 146.8, 146.63, 133.74, 133.45, 133.4, 125.01, 124.49, 124.21, 124.07, 123.77, 123.44, 117.46, 117.16, 116.75, 116.4, 116.06, 83.32, 83.27, 81.73, 81.64, 81.58, 77.25, 77.12, 74.25, 74.11, 73.95.

2.3.2 Preparation of hbPTEPA-NAP

The polymerization reactions and manipulation for ***hb*PTEPA-NAP** were carried out in argon. A typical experimental procedure for ***hb*PTEPA-NAP** is summarized later.

We added 5 mg (0.05 mmol) of CuCl, 10 mg (0.014 mmol) of $Pd(PPh_3)_2Cl_2$, and 40 mg ***hb*PTEPA** dissolved in 2 mL of THF/Et_3N into a 50-mL Schlenk tube, which was washed by argon three times. Then 80 mg (1.12 mmol) monomer **1** dissolved in 2 mL of THF/Et_3N was injected slowly in the tube under room temperature. The mixture was heat up to 50°C and reacted for 24 h. Then the mixture was poured into 300 mL methanol with one drop of 37% HCl. The crude product was dissolved in 2 mL THF and refiltered by methanol through a cotton filter under stirring. The precipitate was allowed to stand overnight and then filtered with Gooch crucible. The polymer was washed with methanol and dried in a vacuum oven to a constant weight. Yield: 28 mg (23.3%).

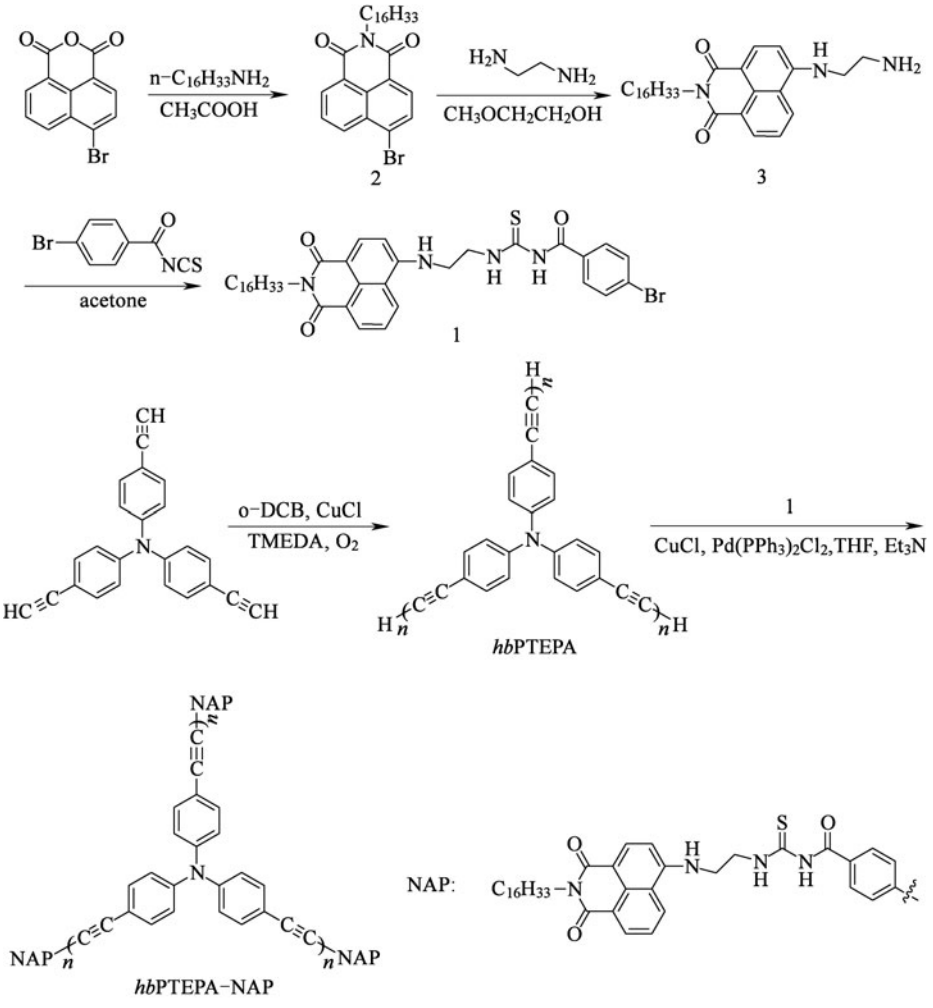
^{1}H-NMR ($CDCl_3$), δ : 9.05 – 7.90 (w), 7.79 – 6.42 (w), 4.48 – 3.30 (w), 2.03 – 0.34(w). ^{13}C-NMR ($CDCl_3$), δ: 164.76, 128.41, 126.12, 64.06, 30.81, 28.22, 27.71, 24.94, 21.62, 13.06.

3 Results and discussion

3.1 Synthetic routine

The synthetic route to ***hb*PTEPA-NAP** containing the polytris (4-ethynylphenyl)amine (***hb*PTEPA**) and benzoyl thiourea-naphthalimide (**NAP**) unit is depicted in Scheme 2. The important monomer **1** was synthesized by the reaction of 4-amidoethynlimine-N-cetanylnaphthalimide (**3**) with 4-bromobenzoyl isothiocyanic ester. Such addition could offer an acceptor reacting with the mercury ion when the naphthalimide group was attached to ***hb*PTEPA**. All the reactions went smoothly and monomer **1** was isolated in medium yields (50%). All the intermediates and monomer **1** were characterized by standard spectroscopic methods, from which satisfactory analysis data were obtained (see Experimental Section for details).

CuCl and TMEDA were useful catalysts for coupling reaction among all sorts of mon-, di-, or tri-acetylnyl compounds under air atmosphere; we thus tried to polymerize 4,4′,4″-triacetylenetyl triphenylamine. By stirring an o-DCB



Scheme 2 The synthesis routine of ***hb*PTEPA-NAP**.

solution of catalysts under 50°C and then injecting the monomer solution into the catalysts system, the polymerization yields a viscosity solution after 15 min. It means that the reaction produces a polymer with a molecular weight of 31,000 (M_w) and a yield of 19.8% after precipitation in a methanol. ***hb*PTEPA** was completely soluble in common organic solvents.

As $Pd(PPh_3)_2Cl_2$ is a well-known catalyst for the sonogashira coupling reaction, we tried to end our ***hb*PTEPA** with monomer **1**. By stirring a THF/Et_3N solution of ***hb*PTEPA** at room temperature with a catalytic amount of $Pd(PPh_3)_2Cl_2$ and then injecting monomer **1** dissolved in 1mL THF/Et_3N and heated up to 50°C, a viscosity solution was obtained after 24 h. The reaction generated a polymer with a molecular weight of 43,000 (M_w) with a yield of 23.3% after precipitation in a methanol. ***hb*PTEPA-NAP** was completely soluble in common organic solvents.

3.2 Structural characterization

The purified polymerization product gives satisfactory spectroscopic data corresponding to its expected molecular structure (see Experimental Section for details).

The IR spectrum of ***hb*PTEPA-NAP** is illustrated in Figure 1. The spectra of monomer **1** and ***hb*PTEPA** are also presented in the same figure for comparison. The ***hb*PTEPA** shows a strong, sharp peak at 3288 cm^{-1} due to ≡C-H stretching vibrations. This peak, however, completely disappeared in the spectrum of ***hb*PTEPA-NAP**, suggesting that the terminal alkyne belonged to ***hb*PTEPA** has been completely consumed by the sonogashira coupling reaction. The ***hb*PTEPA** shows a strong and sharp peak at 2125 cm^{-1} due to C≡C stretching vibrations and the monomer **1** shows strong peaks at 1690 cm^{-1} and 1653 cm^{-1} due to C = O contained in acidamide, respectively. These peaks both

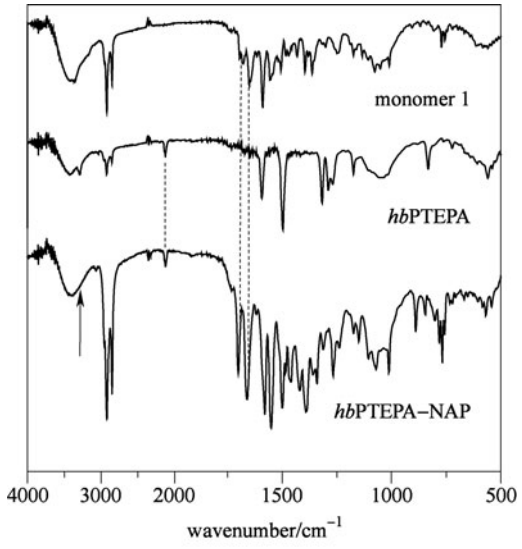


Figure 1 The IR spectra of monomer **1**, ***hb*PTEPA**, and ***hb*PTEPA-NAP**.

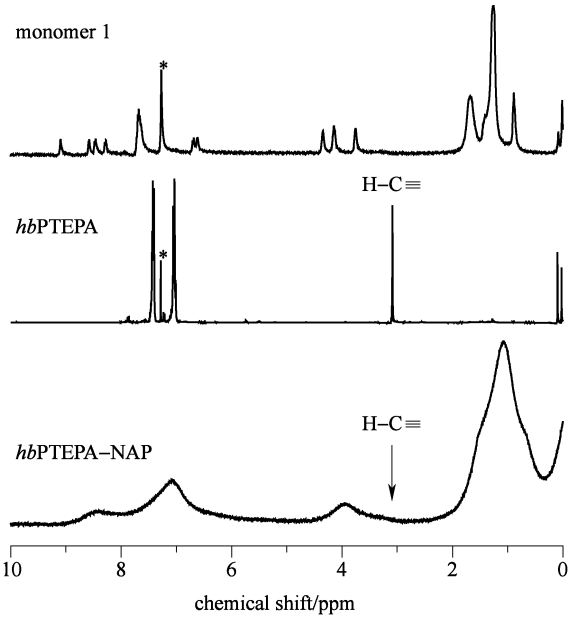


Figure 2 The NMR spectra of monomer **1**, ***hb*PTEPA**, and ***hb*PTEPA-NAP**.

appeared in the spectrum of ***hb*PTEPA-NAP**, suggesting that the product successful couples monomer **1** and ***hb*PTEPA**.

Besides IR, NMR spectroscopy is also a powerful tool to elucidate the molecular structures of materials. Figure 2 shows the ^{1}H NMR spectra of monomer **1**, ***hb*PTEPA**, and ***hb*PTEPA-NAP** in chloroform-*d*. The characteristic peaks of monomer **1** at δ of 8.57, 8.44, 8.23, 7.65, 6.69, and 6.62 ppm and δ of 4.33, 4.14, and 3.75 ppm are due to the resonance of protons on aromatic rings and methylene groups linked up with nitrogen atom of imide and oxygen atom of ester, respectively. The characteristic peaks of ***hb*PTEPA** at δ of 7.43 and 7.07 ppm and δ of 3.06 ppm are due to the resonance of protons on aromatic rings and acetylene groups, respectively. However, the ^{1}H NMR spectrum of polymer ***hb*PTEPA-NAP** displays apparent changes, i.e., the peaks of polymer are broader than those of monomer **1** and ***hb*PTEPA**. Moreover, no peak in the acetylene absorption region (δ 3.06 ppm) was observed in the polymer spectra.

3.3 Optical properties

The UV-Vis absorption spectra of monomer **1**, **NAP′**, ***hb*PTEPA**, and ***hb*PTEPA-NAP** in THF at dilute concentration are shown in Figure 3(a). In the UV-Vis spectra, monomer **1** and ***hb*PTEPA** show typical naphthalimide and polytriphenylamine absorption peaks at 432 and 380 nm with high coefficients, respectively. ***hb*PTEPA-NAP** matches the obtained profile by the summation of the spectra of component units ***hb*PTEPA** and monomer **1** within experimental error, suggesting that there is no significant electronic interaction between ***hb*PTEPA** backbone and monomer **1** in the ground state. Figure 3(b) shows the fluorescence spectra of monomer **1**, **NAP′**, ***hb*PTEPA**, and ***hb*PTEPA-NAP** in THF, in which monomer **1** and ***hb*PTEPA** show intense fluorescent maxima at 497 and 437 nm, respectively. Moreover, ***hb*PTEPA-NAP** has emission spectra with characteristic features of the naphthalimide and polytris(4-ethynylphenyl) amine unit. The fluorescence quantum yield of the ***hb*PTEPA-NAP** is 0.33 versus for that of monomer **1**.

As shown in Figure 3, the 425 nm band of monomer **1** in the THF solution decreases in absorption spectra with the addition of Hg (II), and a new band at ~356 nm forms. The addition of Hg (II) ion transforms the thiourea unit of the chemodosimeter under THF conditions into an imidazoline moiety, which is much less an electron-donating group. It results in a reduction in electron delocalization within the fluorophore. The absorption maximum exhibits blue-shift. At the same time, the emission maximum also shows blue-shift, in which the result of different excitation spectra between monitoring at monomer **1** with or without Hg(II) led us to conclude that dual fluorescence originated from different precursors, namely, the unreacted monomer **1** and product **NAP′**, respectively.

3.4 Sensing properties

Polytris(4-ethynylphenyl)amine (***hb*PTEPA**) was used as a light harvesting unit in the energy-transfer experiments. The absorption spectrum of the **NAP** (acceptor) overlaps with the emission of ***hb*PTEPA** (donor) and thus satisfies the conditions for efficient fluorescence resonance energy transfer

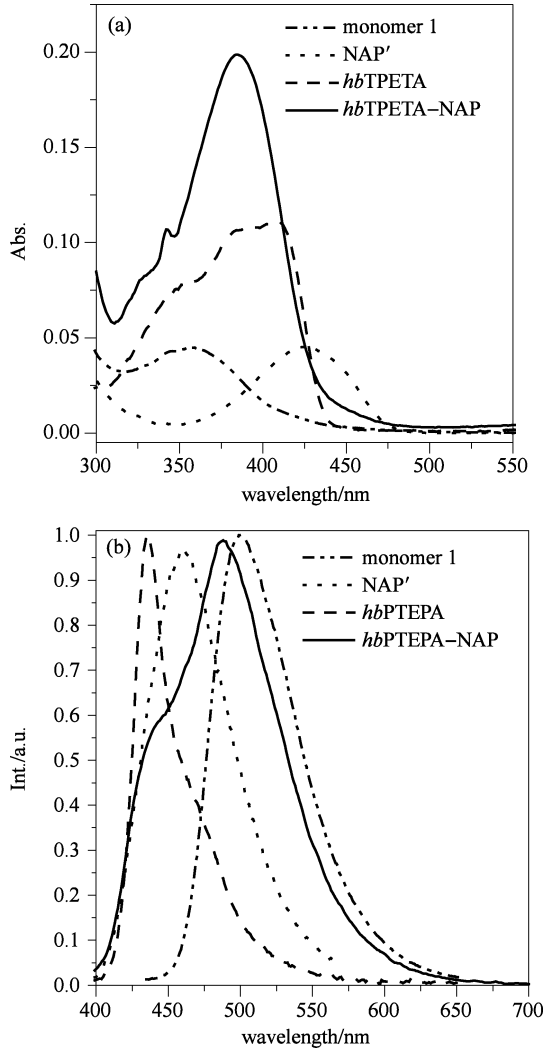


Figure 3 The (a) absorption and (b) emission spectra of monomer **1**, **NAP′**, ***hb*PTEPA**, and ***hb*PTEPA-NAP** in THF. ((a) $c = 1\times10^{-5}$ mol·L^{-1}; (b) $c = 1\times10^{-5}$ mol·L^{-1}, $\lambda_{ex\ NAP}$: 435 nm, $\lambda_{ex\ NAP'}$: 290 nm, $\lambda_{ex\ hbPTEPA}$: 425 nm, $\lambda_{ex\ hbPTEPA\text{-}NAP}$: 380 nm.)

(FRET). These features allow for simple evaluation of the FRET efficiencies between ***hb*PTEPA** and **NAP** (Figure 4). When mercury ion was added into the system, desulfurization between **NAP** and mercury ion occurs, but there is weak energy transfer in polymer sensor with the blue-shift in absorption spectrum of **NAP** moiety.

Stock solutions (0.01 mol·L^{-1}) of the metal acetic salts were prepared in deionized water. Stock solution of ***hb*PTEPA-NAP** was prepared in THF. For all fluorescent tests, excitation wavelength was 380 nm with excitation and emission slit widths of 5 and 3 nm, respectively. The sensing properties of ***hb*PTEPA-NAP** to different metal ions were characterized in 1×10^{-5} mol·L^{-1} of THF solutions.

Figure 5 displays the absorption and emission spectra of ***hb*PTEPA-NAP** with the addition of mercury ion. The

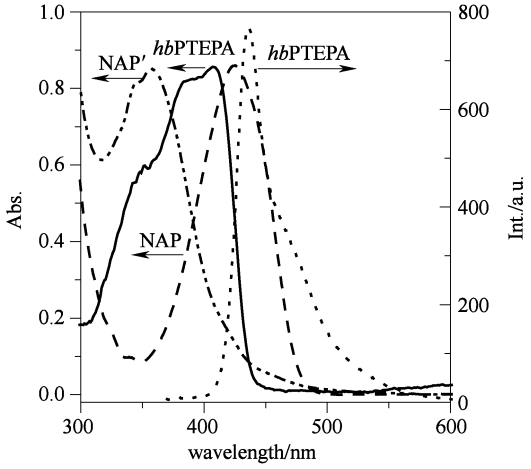


Figure 4 The absorption spectrum of ***hb*PTEPA** (solid), the emission spectrum of ***hb*PTEPA** (dot), the absorption spectrum of **NAP** (dash), and the absorption spectrum of **NAP'** (dash dot dot).

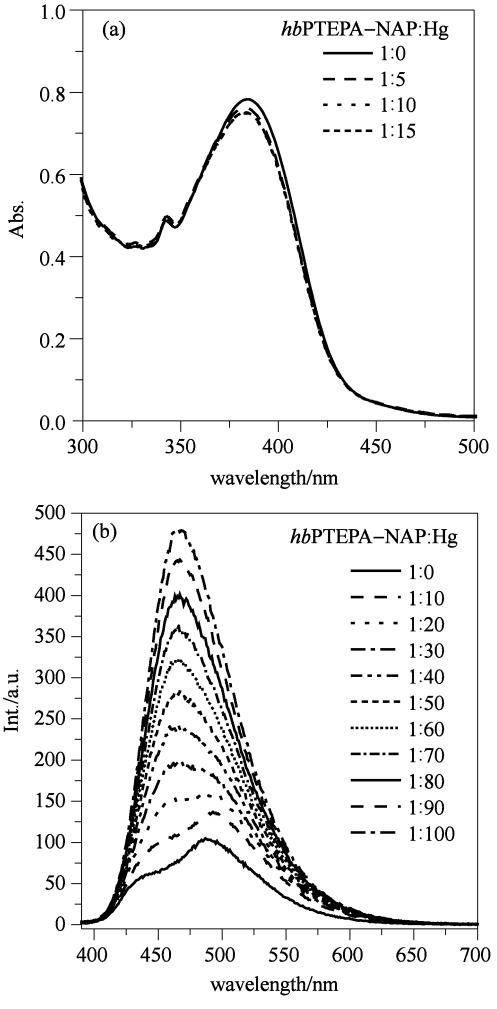


Figure 5 The (a) absorption and (b) emission spectra of ***hb*PTEPA-NAP** with the mercury ion titration. ($c = 1\times10^{-5}$ mol·L^{-1}, (b) excitation at 380 nm)

absorption spectra of ***hb*PTEPA-NAP** (10 μmol·L^{-1}) in THF exhibited a very weak band at 435 nm, which belonged to the **NAP** group of ***hb*PTEPA-NAP**. The main absorption band at 380 nm was ascribed to the ***hb*PTEPA**. As shown in Figure 5(a), no major changes was observed for ***hb*PTEPA-NAP** with 15 eq. of Hg^{2+}. In Figure 5(b), ***hb*PTEPA-NAP** exhibits weak fluorescence at 490 nm and 437 nm (shoulder) in THF solution without mercury ion. With the addition of mercury salt, an emission band emerged at approximately 465 nm, which can be assigned to a mercury-triggered intramolecular cyclization of thioureas attached the naphthalimide group [35]. The titration curve shows a steady and smooth increase until a plateau was reached with 100 eq. mercury ion addition.

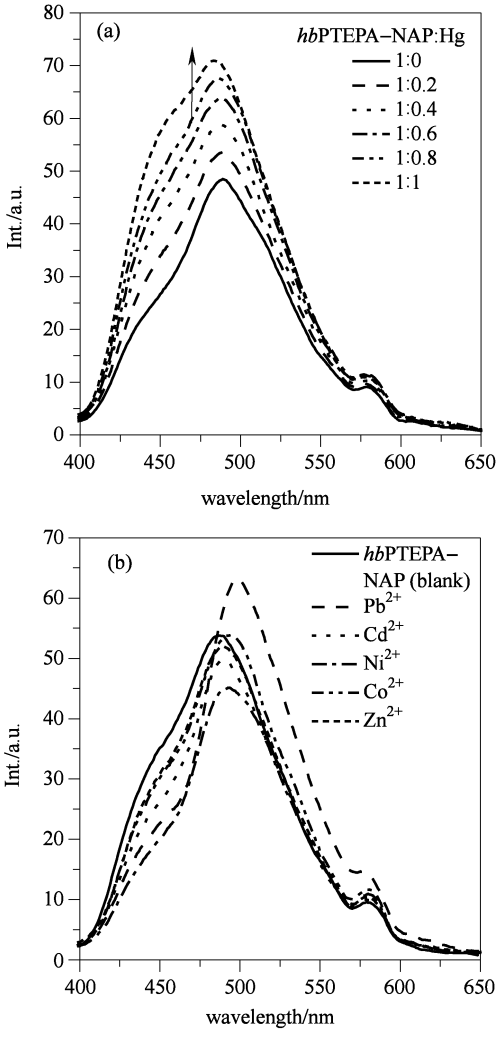


Figure 6 The fluorescent spectra of ***hb*PTEPA-NAP** added by (a) mercury and (b) other ions ((a) c(***hb*PTEPA-NAP**) = 1×10^{-5} mol·L^{-1}, (b) c(***hb*PTEPA-NAP**) = 1×10^{-5} mol·L^{-1}, $c(M^{2+}) = 1\times10^{-4}$ mol·L^{-1}). Excitation at 290 nm.

The fluorescence enhancement effects of various metal ions on ***hb*PTEPA-NAP** in THF solution were also investigated (excitation at 290 nm). As illustrated in Figure 6, when other ions were added into the system, no significant spectral change of ***hb*PTEPA-NAP** was observed in the presence of many divalent metal ions, such as Cd^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+}. However, Pb^{2+} gives intensity enhancement and red-shift to 498 nm, which also can be easily distinguished from mercury ion.

4 Conclusion

The synthesis and fluorescent properties of a new hyperbranched polytris(4-ethynyl-phenyl)amine (***hb*PTEPA**)-based chemosensor ***hb*PTEPA-NAP** containing benzoyl thiourea-naphthalimide (**NAP**) moiety, which functions as Hg^{2+}-induced FRET from the ***hb*PTEPA** (donor) to **NAP** (acceptor), are described. The addition of Hg (II) ion transforms the thiourea unit of the chemodosimeter under THF conditions into an imidazoline moiety that is a much less electron-donating group. It results in a reduction in electron delocalization within the fluorophore. The emission maximum exhibits blue-shift and increase of fluorescent intensity. Other divalent metal ions, such as Cd^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+}, were found to hardly induce any variation in fluorescence spectra. This naphthalimide side-chain polytris (4-ethynylphenyl)amines ***hb*PTEPA** shows the promise sensor for the selective detection of Hg (II) ion in the presence of other metal ion.

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