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Thiazole-Containing Conjugated Polymer as a Visual and Fluorometric Sensor for Iodide and Mercury

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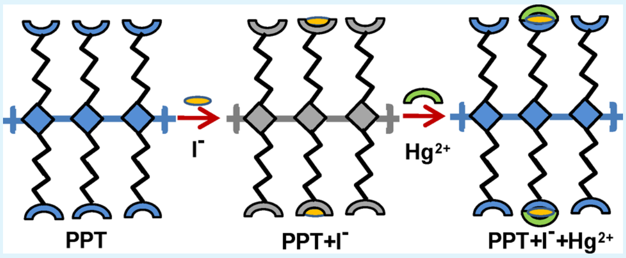
Supporting Information



ABSTRACT: A neutral conjugated polymer poly-*p*-phenylene (PPP) derivative, poly(1,4-bis-(8-(4-phenylthiazole-2-thiol)-octyloxy)-benzene) (PPT), was prepared using a simple and economical method of oxidative polymerization reaction. This newly synthesized polymer PPT was characterized by means of Fourier transform infrared spectroscopy (FT-IR), ^{1}H nuclear magnetic resonance (^{1}H NMR), ultraviolet−visible (UV-Vis), and fluorescence spectroscopy. PPT displays fluorescence "turn-off/turn-on" characteristics and colorimetric responses to I^- and Hg^{2+}. The UV-Vis and fluorescence spectra of the PPT showed a significant shift in λ_{max} via the addition of iodides and mercury. A colorless PPT solution turns to deep yellow in the presence of iodide salts, which subsequently becomes colorless again on addition of Hg^{2+} salts that could be easily detected visually by the naked eye. The Stern−Volmer constant (K_{sv}) value obtained for the detection of iodide is 0.13×10^5 M^{-1}, confirming very high sensitivity of this polymer for iodide salts. The detection limit of Hg^{2+} salt using the PPT polymer was found to be 2.1 nM in water. The detection of both iodide and mercury was also possible in solid state by using a membrane film prepared by mixing 1% PPT in polystyrene. This membrane changes color in the presence of iodide as well as mercury salts. These results confirm that the PPT polymer can be applied for the colorimetric as well as fluorometric sensing of I^- and Hg^{2+} ions in a competent environment in solution, as well as in the solid state, using a membrane film rapidly.

KEYWORDS: *chemosensors, iodide, mercury, fluorometric, colorimetric, conjugated polymer*

INTRODUCTION

Iodine is an indispensable element in human life and plays a key role in several biological activities, such as neurological and thyroid functions.[1−3] However, excessive application of I^- ions and iodine has caused serious environmental pollution and physical diseases.[4] Because of its larger size and weaker basicity than other halides, the binding capacities of the I^- ion with receptors are the weakest, compared to halogen ions, with the following binding order:[5−9]

$$F^- > Cl^- > Br^- > I^-$$

Therefore, it remains a challenge to design chemo sensors that can bind iodide selectively.

Conjugated polymers (CPs) with extended π-electron system and receptors in the side chain or main chain have been widely used as organic light-emitting diodes (OLEDs),[10−12] thin-film transistors, chemical sensors,[13,14] and in various photonic and electronic devices.[15,16] The high sensitivity of CPs toward a range of analytes is believed to be due to the molecular wire effect and has been well-explored. Fluorescence is the most common and highly sensitive optical transduction method to observe analyte binding events that usually produces an enhancement, reduction, or wavelength shift in the emission and can be employed to generate a functional sensor.[17] CPs with receptors affixed to the backbone present a simple and consistent approach to selectivity via changes in absorption and emission spectra.[18−23] These CPs comprise poly(*p*-phenylene)s, poly(*p*-phenylene vinylene)s, polyfluorenes with receptor groups on the side chain or main chain have been successfully used for sensing ions and biological species. Many supramolecular systems capable of recognizing and sensing halides and several other negatively charged species have been developed and studied extensively.[24] However, very few examples using CPs for sensing iodide ions have been reported.[25,26]

According to the survey from the World Health Organization (WHO), iodide deficiency still causes serious public health problems in many countries.[27,28] As a strong nucleophilic reagent, I^- ions are also commonly employed in many important organic reactions. Therefore, it is desirable to detect I^- ions rapidly with high sensitivity and selectivity in either aqueous or nonaqueous media. Among the range of biologically important anions, iodide is of particular interest, because of its essential role for thyroid gland function. In addition, elemental iodine is used in synthesizing several organic chemicals, in manufacturing dyes, in medicine (its radioactive isotope), in analytical chemistry and in several other applications.

Among toxic metals, mercury poisoning remains one of the foremost threat to human health and it has caused serious

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environmental and health problems.[29−31] Severe damages on human central nervous system and endocrine system due to mercury ingestion have been reported.[32−35] Many reports have focused on colorimetric and/or fluorescence[36−44] chemo sensors in the hope of developing new mercury sensors but many of these suffer from competing metal ions, slow response times, etc.[45] Few polymer-based chemo sensors for detection of mercury have been reported.[46−55] In all types of detection platforms, it is stressed to selectively detect mercury in the presence of other environmental metals. Although many sensors showing the "turn-off" response due to the quenching nature of Hg^{2+} have been reported,[56−60] the development of "turn-on" Hg^{2+} sensors of high sensitivity/selectivity still remains a challenging task.

Herein, we report the synthesis and characterization of a new conjugated poly-*p*-phenylene derivative strapped with 4-phenylthiazole-2-thiol, which can optically and visually detect the presence of iodide and mercury over a wide range of other competent ions in an aqueous medium.

EXPERIMENTAL SECTION

Materials and Measurements. All reagents and solvents were purchased from commercial sources and were of reagent grade. Ultraviolet−visible light (UV-Vis) and photoluminescence (PL) spectra were recorded on a Perkin−Elmer Model Lambda-25 spectrophotometer and a Varian Cary Eclipse spectrophotometer, respectively. Tetrahydrofuran (THF) was purified by distillation over sodium under a nitrogen atmosphere. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained with a Varian-AS400 NMR spectrometer. GPC was recorded with a Waters-2414 instrument (polystyrene calibration). Polystyrene (PS) used for film studies was obtained from Total Petrochemicals, USA and had the following specifications: grade 500b general-purpose PS, M_w = 215 010; density = 1.04 g/cm^3; MFI = 14 g/10 min at 200 °C and 5 kg load.

Synthesis of Monomer. Synthesis of 1,4-bis-(8-bromooctyloxy)-benzene was carried out using a previously established procedure from the literature.[61−63]

Synthesis of Poly(1,4-bis-(8-bromo-octyloxy)-benzene) (PPB). Polymer was prepared by methods reported earlier.[64,65] The synthesis of PPB was performed as follows. In a 100 mL three-necked round-bottom flask equipped with a nitrogen inlet, anhydrous ferric chloride (0.74 g, 4.57 mmol) was dissolved in 10 mL of nitrobenzene. 1,4-Bis-(8-bromo-octyloxy)-benzene (1.0 g, 2.03 mmol) dissolved in 10 mL of nitrobenzene was added to the flask using a syringe. The reaction mixture was stirred at room temperature for 36 h, followed by precipitation from methanol. This was stirred for 1 h, centrifuged, and washed repeatedly with methanol. The resulting polymer was dried under reduced pressure to obtain 0.74 g (70% yield) as a light brown powder.

^1H NMR (400 MHz, $CDCl_3$): δ ppm, 7.07(s), 3.91(m), 3.36(m) 1.80(m), 1.67(m), 1.37(m), 1.2(m). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm, 150.2, 115.1, 67.8, 40.1, 33.6, 33.1, 28.9, 28.0, 27.8, 27.2, 26.3. M_w = 3.52×10^4, PDI = 1.9 (GPC in THF, polystyrene standard).

Synthesis of PPT. PPB (0.20 g. 0.41 mmol) and 4-phenyl thiazole-2-thiol (0.32g, 1.6 mmol) were dissolved in dry THF (5 mL) in the presence of K_2CO_3 (4 equiv). The reaction mixture was kept for reflux under stirring for 12 h. The mixture was then filtered to remove the unreacted base and poured into 50 mL of cold methanol (MeOH), followed by stirring for 1 h to obtain a yellow precipitate. The obtained solid was dissolved in THF and reprecipitated in methanol (100 mL); the precipitant then was collected, washed with acetone, and dried in a vacuum desiccator to obtain 210 mg (72% yield).

^1H NMR ($CDCl_3$, δ, ppm): 7.80(s), 7.31(m), 7.28(m), 7.20(m), 7.01(s), 3.87(m), 3.07(m), 1.76(m), 1.63(m), 1.55(m), 1.25(m).

FT-IR (KBr, cm^{-1}): 2930.43, 2853.65, 1467.86, 1261.23, 1099.46, 1027.72, 802.32.

Optical Measurements. The absorption measurements and fluorescence titrations of the polymer PPT with different anions and metal cations in water solution were run by directly adding small aliquots (typically 5 μL) to 3 mL of the 4:1 THF/water solution containing 6.6×10^{-6} M PPT in a quartz cuvette (1 cm × 1 cm). After being mixed thoroughly the absorption or fluorescence spectra were recorded at room temperature.

PPT Film Preparation. Ninety nine milligrams (99 mg) of blending polymer (polystyrene in this experiment) and 1 mg conjugated polymer were taken in a glass vial and dissolved in 2 mL of THF by sonication for 2 h to make a homogeneous mixture. The clear solution was spread onto a smooth glass plate and allowed to dry at room temperature in open air. As the film dried, it was carefully peeled from the glass plate, cut in rectangular shapes, and used for sensor application experiments.

Sensor Experiment Method. The rectangular film was placed on a small glass plate and kept in a beaker filled with distilled water. Under UV light, the film showed bright blue fluorescence. Dilute I^- and Hg^{2+} solutions were prepared and added to the beaker (dropwise) and the fluorescence of the film was observed under UV-lamp illumination.

RESULTS AND DISCUSSION

Synthesis of Poly(1,4-bis-(8-(4-phenylthiazole-2-thiol)-octyloxy)-benzene) (PPT) and Evaluating the Sensing Properties. The synthesis of PPT presented in Scheme 1 involves mainly room-temperature reaction steps without requiring costly metal catalysts/phase-transfer catalysts, while still employing very easy and mild reaction conditions. The 4-phenylthiazole-2-thiol moiety was introduced onto the side chain of CP by substituting the terminal Br atoms of the alkyl chains to obtain the desired PPT polymer using a post-polymerization functionalization method in 72% yield. The molecular weight of the polymer before functionalization was reported to be M_w = 3.52×10^4, PDI = 1.9 (GPC in THF, polystyrene standard).[66] The thiazole ring is one of the important classes of sulfur-containing heterocyclic compounds among the many present in living organisms.[67] Phenyl and substituted phenylthiazoles are common features of a wide range of biologically active natural products. As they possess several vital biological functions and

Scheme 1. Synthesis of Poly(1,4-bis-(8-(4-phenylthiazole-2-thiol)-octyloxy)-benzene: (a) K_2CO_3, dry acetone, 1,8-dibromooctane, 50 °C; (b) $FeCl_3$, nitrobenzene, RT; and (c) K_2CO_3, 4-phenylthiazole-2-thiol, THF, Reflux, 12 h

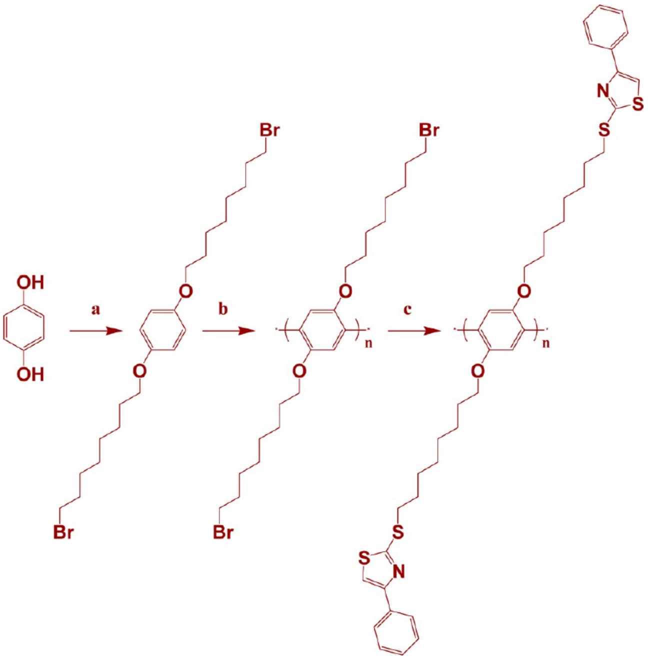

Figure 1. Color of the PPT solution in a 4:1 THF/water solution under (a) ultraviolet (UV) light and (b) the naked eye.

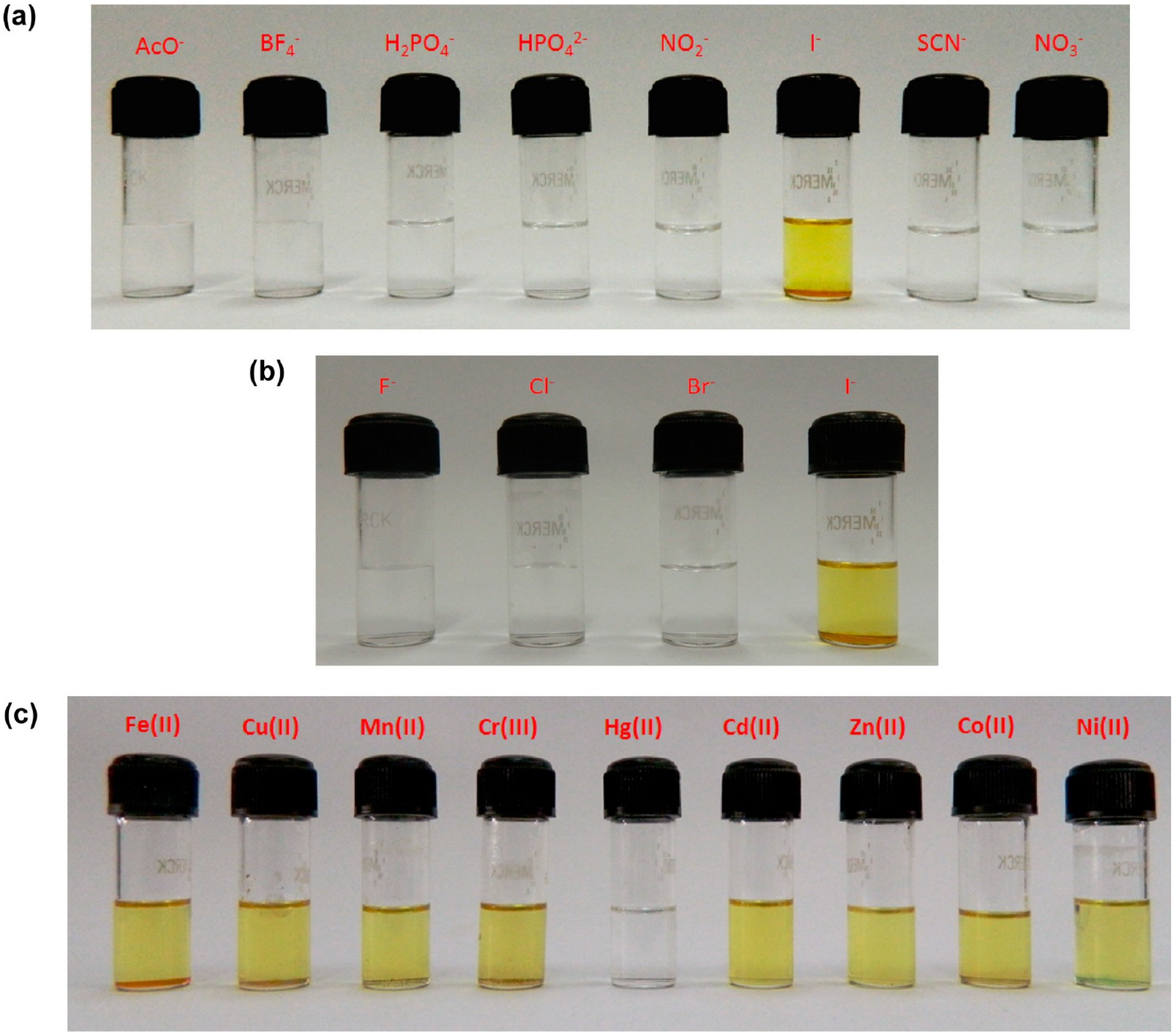

Figure 2. Color changes of PPT solution in a 4:1 THF/water solution upon the addition of (a) anions and (b) halides; in both panels a and b, the concentration of PPT and salt concentrations are 6.6×10^{-6} M and 3.3×10^{-4} M, respectively. (c) Color changes of PPT$-$I$^-$ solution in a 4:1 THF/water solution upon the addition of metal salts in water; in panel c, the concentration of metal salts is 5×10^{-5} M.

properties, thiazole derivatives are regarded as the main tools in pharmaceutical research.[68−71]

CPs of the type PPT display strong blue luminescence that can be visualized in diluted organic solvents. PPT shows absorption maximum at 335 nm and an emission maximum at 402 nm. The fluorescence quenching experiments of polymer PPT by the I$^-$ anion was investigated in a preliminary visual experiment, where the disappearance of the blue luminescence in the presence of the

I^- anion and, again, the reappearance in the presence of mercury salts was very clear (see Figure 1a). The initial colorless solution of the polymer PPT also changes to a yellow color upon the addition of iodide salts, which subsequently becomes colorless again on the addition of dilute mercury salts solution (see Figure 1b). Upon the addition of iodides, with increasing time, the intensity of the yellow color increases, whereas, upon the addition of mercury salts in the same solution, the yellow color starts to disappear. The polymer PPT showed no significant change in color upon the addition of anions other than iodide (see Figures 2a and 2b) and cations other than mercury (see Figure 2c). The sensing properties of PPT were studied in a THF/water (4:1) solution using aliquots of aqueous solution of tetrabutylammonium salts of anions and the perchlorate metal salts. Interestingly, the polymer PPT detects only iodides among common anions such as fluorides, chlorides, bromides, nitrate, nitrite, thiocyanate, hydrogen phosphate, dihydrogen phosphate, acetate, tetrafluoroborate, etc. The nature of counter cations such as tetrabutylammonium, potassium, etc. does not influence the color change while performing the detection experiments. The effect of pH on PPT solution was also studied. It was observed that pH of the detection solution does not affect the detection ability of PPT and the fluorescence of PPT is retained from pH 5.5 to basic pH. The quenching mechanism can be explained by charge transfer complex via "heavy-atom" interaction between the ground state of the polymer PPT and the inorganic anion (iodide) that leads to an enhancement of the spin-orbit coupling.[72−74] Here, the "heavy-atom" effect probably occurs due to the formation of a weak charge-transfer complex between the thiazole moieties of PPT and the I^- anions,[75] leading to the quenching of the luminescence of PPT.

The decrease in fluorescence intensity was investigated by adding successive aliquots of aqueous stock solutions of I^- anions (TBAI) to the solution of PPT (6.6×10^{-6} M) in a 4:1 THF/water solution (see Figure 3). A similar experiment was also repeated with KI and is presented in Figure S1 in the Supporting Information, to verify the counter cation effect. PL quenching of PPT was >96% at a concentration of 1.67×10^{-4} M. PL titration of PPT was performed with several different anions, as depicted in Figure 3. Except with I^-, the intensity of PPT was indistinctly affected upon the addition of anions such as F^-, Cl^-, Br^-, NO^{2-}, CH_3COO^-, HPO_4^{2-}, H_2PO^{4-}, BF^{4-}, and SCN^- (see Figure 4). The efficiency of quenching was studied by plotting a Stern−Volmer plot[76,77] (I_0/I vs [Q], where I_0 is the initial fluorescence intensity of PPT and I is the fluorescence intensity of PPT after the addition of a given concentration of quencher [Q], where [Q] = I^- ion concentration) to obtain a Stern−Volmer constant (K_{sv}). The K_{sv} value calculated from the plot was found to be $0.13 \times 10^5\ M^{-1}$. The fluorescence quantum yield of polymer PPT was found to be 0.24, which decreases rapidly to 0.0095 with the addition of iodide (see the Supporting Information).

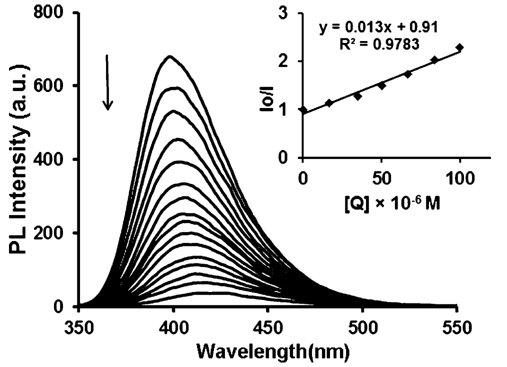

Figure 3. PL spectra of PPT in a 4:1 THF/water solution with increasing concentration of I^-. Inset shows a Stern−Volmer plot of PPT upon the addition of I^- in aqueous medium. Concentration of PPT inside the cuvette was 6.6×10^{-6} M (4:1, THF:water). PL quenching of PPT was >96% at a concentration of 1.67×10^{-4} M of I^- in water.

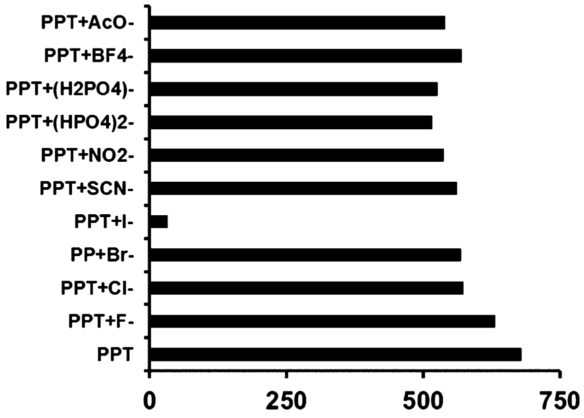

Figure 4. Bar diagram depicting effect of various anions on the fluorescence intensity of PPT. PL titration of different anions (3.3×10^{-4} M) was performed with PPT (6.6×10^{-6} M) in a 4:1 THF/water solution at room temperature.

Titration of I^- ions with PPT was also monitored via UV-vis spectroscopy. The absorption maxima of PPT showed a significant 26-nm red shift (see Figure 5) upon titration with tetrabutylammonium iodide salts. A similar UV-Vis study of the PPT polymer was done with KI to investigate if there is any role of the counter cation on the UV-Vis spectra, but no noticeable change was observed (see Figure S2 in the Supporting Information). The red shift in the absorption and emission maxima can be explained through charge transfer via the heavy-atom effect between the polymer PPT and the I^- anions, as discussed earlier.[26,72−75] In addition, a new peak was observed developing at 295 nm upon the continuous addition of I^- anions, which may be due to the interaction of the thiazole moiety with iodide.

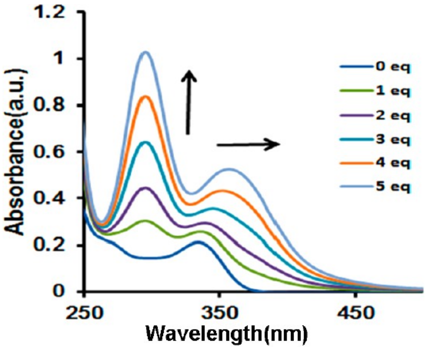

Figure 5. UV-Vis titration spectra of PPT in a 4:1 THF/water solution with increasing concentration of I^- (TBAI) solution in water.

From the above results, it could be concluded that, in this sensory system, the thiazole groups in PPT serve as coordination sites for I^- and facilitates very high fluorescence quenching of >96%. To the best of our knowledge, fluorescence quenching of neutral PPT-type thiazole containing CPs in an aqueous-based

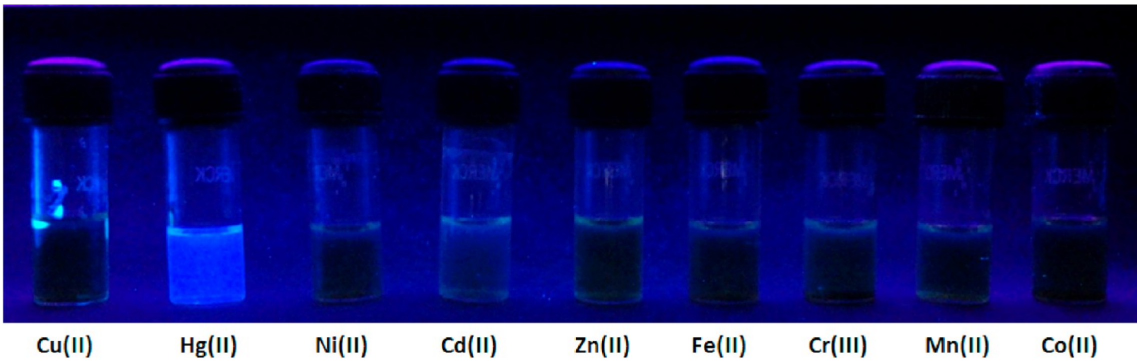

Figure 6. Color changes of PPT−I^- solution in a 4:1 THF/water solution upon the addition of metal salts under UV light. The concentration of each metal salt is 5 × 10^{-5} M.

environment, as well as a mixture of aqueous and organic-based environments by I^- remains unreported.

We further noticed that the quenched fluorescence of PPT−I^- complex was restored in the presence of an aqueous solution of Hg^{2+} salts (see Figure 6). Significant color changes that could be both visualized with the naked eye, as well as fluorescent enhancement, occurred at a very low concentration of Hg^{2+} in the presence of other metals salts of cadmium, zinc, iron, etc. The quenched fluorescence intensity of PPT−I^- was ~60% recovered upon the addition of Hg^{2+} in concentrations as low as 8.3 × 10^{-6} M (Figure 7). Titration performed with various other metal ions (Figure 8) that are known to compete with Hg^{2+} showed no significant effect on the enhancement of the fluorescence intensity of PPT−I^-. The detection limit is calculated using the equation

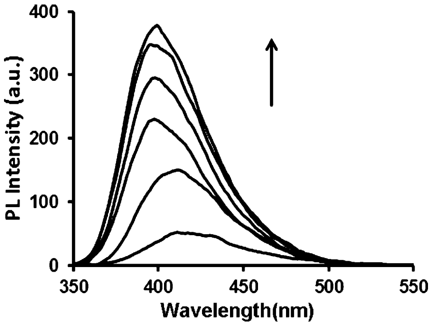

Figure 7. PL spectra of PPT−I^- in a 4:1 THF/water solution with increasing concentration of Hg^{2+}. Dequenching was ~60% at a concentration of 8.3 × 10^{-6} M.

$$\text{detection limit} = \frac{3\sigma}{K}$$

where σ is the standard deviation and K is the slope of the plot of Hg^{2+}; the detection limit was found to be 2.1 nM (see Figure S3 in the Supporting Information).

Analysis of Real Water Samples. The real tap water samples were collected and filtered through a 0.2-μm membrane. The water samples were spiked with standard iodide and mercury solutions separately at certain concentrations and then used for sensing purposes. The amounts of iodide and mercury in tap water were estimated after preparing a standard calibration curve and comparing it with the changes caused in the fluorescence spectra of the polymer PPT upon the addition of these tap water samples. (See Figures S4 and S5, and Tables S1 and S2 in the Supporting Information.)

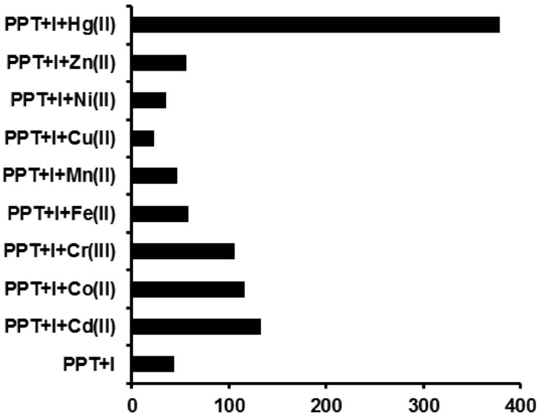

Figure 8. Bar diagram depicting the effects of various metals on the fluorescence intensity of PPT−I^-. PL titration of different metal ions (5 × 10^{-5} M) was performed with PPT−I^- in a 4:1 THF/water solution at room temperature.

Interaction between the PPT-I^- and Hg^{2+} was also monitored via UV-Vis spectroscopy (see Figure 9). Significant changes in peaks were observed after adding 2 equiv of mercury. Upon the addition of Hg^{2+} salts to PPT−I^-, the 365-nm absorption peak of PPT−I^- disappeared completely and a new peak was obtained at 260 nm with the clear formation of an isosbestic point at 276 nm. The formation of this new peak may be due to the formation of a new complex between a thiazole moiety of PPT−I^- and Hg^{2+}. The absorption peak at 295 nm showed a remarkable red shift of 15 nm, which indicates interaction of the PPT−I^- complex with mercury. Since the initial absorption peak of PPT does not

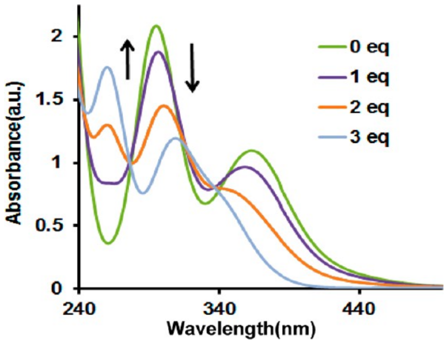

Figure 9. UV-Vis titration spectra of PPT−I^- in a 4:1 THF/water solution with increasing concentration of Hg^{2+} in water.

recover after the addition of mercury salts to PPT−I^-, we can say that a new complex of PPT−I^- with mercury has formed. This was further confirmed by treating different metal salts including Hg^{2+} with PPT, but no significant changes were observed in the UV-Vis and fluorescence spectra. This shows that the Hg^{2+} cation has an affinity to bind with the PPT−I^- complex, rather than the PPT, in the absence of I^-.

Evaluating the Sensing Properties of PPT in the Membrane Form. Most of the I^- and Hg^{2+} detection systems are generally solution-based, which is difficult and sometimes not practical for carrying out analyses in distant places. Hence, to realize practical applications, the fluorescence response of the PPT had to be utilized on a solid-support-based platform for better mobility. Since CPs can form films on desired substrates or membranes with any other polymer, we utilized these properties to make a handy membrane of PPT with commercial polystyrene and performed membrane-based I^- and Hg^{2+} detection in an aqueous medium. This technique is an energy- and cost-effective method if the concentration levels of the pollutants are very low (ca. ppm or sub-ppm). A membrane film was prepared by doping 1% PPT in a polystyrene (PS) solution dissolved in THF (w/w) and cast gently over a glass slide (see Figure 10) and peeled off upon drying and cut into desired shapes and sizes. The bright fluorescence of the PPT film being completely quenched is clearly visualized in the presence of a 3.3 × 10^{-5} M I^- solution. This film was dipped in a fresh 5 × 10^{-5} M solution of Hg^{2+} to visualize fluorescence recovery that could also be easily distinguished. The PPT-based polymeric sensory system shows outstanding optical selectivity and sensitivity for I^-, as well as Hg^{2+} anions in water, and in the presence of competing anions and cations. The lowest Hg^{2+} detection limit visible by the naked eye, using the membrane method, was determined to be 1.6 μM.

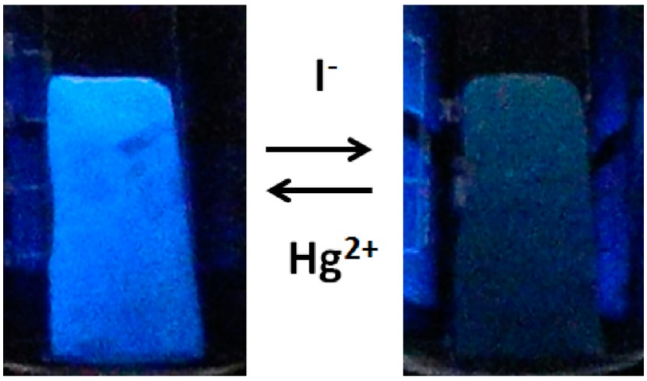

Figure 10. A bright blue PS + PPT membrane (left image) under UV light in water loses its fluorescence (right image) upon being dipped in a 3.3 × 10^{-5} M I^- solution in water. This film regains its fluorescence upon being dipped in a fresh 5 × 10^{-5} M solution of Hg^{2+}.

CONCLUSIONS

A neutral conjugated polymer (CP), poly(1,4-bis-(8-(4-phenylthiazole-2-thiol)-octyloxy)-benzene) (PPT), was synthesized using an oxidative polymerization reaction. The polymer PPT showed high optical activity in the presence of I^- and Hg^{2+}, which could be detected by fluorescence spectroscopy as well by colorimetric responses in very low quantities by the naked eye. The colorless PPT solution changed to a deep yellow color upon the addition of iodide salts. The yellow color disappeared in the presence of very dilute Hg^{2+} salts, which could also be visualized by the naked eye. The PPT-based detection platform was further extended to the solid state by preparing a membrane using 1% PPT in polystyrene, and this free-standing membrane also showed the capability to detect and respond to both iodide and mercury salts. The PPT-based detection system is very simple and economical to prepare, highly sensitive, and can rapidly detect iodide and mercury in competitive environments.

ASSOCIATED CONTENT

Supporting Information

Details of polymer interactions with various iodide salts studied by UV-visible spectroscopy, fluorescence spectroscopy, figure of the detection limit studies for mercury salts, quantum yield calculations, details of estimation studies of iodide and mercury in real sample water are mentioned in the electronic supporting information file. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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