# Optical, Electrochemical, and Sensing Properties of Polyfluorenes Bearing Thiazole or Oxazole and Triphenylamine in the Main Chain

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**ABSTRACT:** Polyfluorenes bearing thiazole (PFTH) or oxazole (PFOX) heterocyclic units as well as triphenylamine (TPA) in the main chain were synthesized. The ratio of thiazole or oxazole/TPA in the polymer chain varies from 100/0 to 25/75. The optical properties of polymers depend on thiazole or oxazole contents. Cyclic voltammetry reveals that thiazole or oxazole hinder the oxidation of polymers and only polymers with TPA show reversible oxidation. The Electron Affinities do not practically depend on composition of the polymer chain. The sensing properties of polymers **PFTH100** and **PFOX100** are investigated toward several cations and anions. Polymers detect two analytes, Fe<sup>2+</sup> and Hg<sup>2+</sup>. PL quenching shows linear

response to Fe<sup>2+</sup> in wide concentration region 1–800  $\mu$ M. I<sup>-</sup> anions quench the emission of polymers. Hg<sup>2+</sup> turns on the emission of the polymer/I<sup>-</sup> complex at concentrations as low as 1  $\mu$ M. Enhancement of polymer/I<sup>-</sup> emission exhibits linear response to Hg<sup>2+</sup> concentration. **PFTH100** is able to detect Fe<sup>2+</sup> and Hg<sup>2+</sup> that coexist in a solution. © 2016 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, *00*, 000–000

**KEYWORDS**: chemosensor; conjugated polymers; fluorescence; iron(II); iodide; mercury(II); oxazole; polyfluorene; sencors; thia-zole; triphenylamine

**INTRODUCTION** Three decades since the discovery of  $\pi$ conjugated semiconducting polymers they still attract scientific interest. A vast number of  $\pi$ -conjugated polymers has been synthesized and used in the fields of light-emitting diodes (LED),<sup>1</sup> field-effect transistors,<sup>2</sup> solar cells,<sup>3-5</sup> and laser devices.<sup>6</sup>  $\pi$ -Conjugated polymers offer a unique combination of superior mechanical properties and the ability to tune their electronic/optical properties by structural modification.

A huge progress has been made in the field of polymeric LED (PLED) and polymeric solar cells (PSC). However, the improvement of the external quantum efficiency of PLED and power conversion efficiency of PSC always remains a challenge. Molecular engineering plays the most important role in this efforts.<sup>7</sup> Most  $\pi$ -conjugated polymers favor the injection and transport of holes (p-type materials) rather than electrons due to high LUMO levels. High efficiency of PLED requires, balanced injection and transport of electrons and holes in polymeric materials. One approach to increase the electron accepting character of  $\pi$ -conjugated polymers is their molecular modification through the insertion of

electron-deficient units in the polymer backbone.<sup>8</sup> Aromatic N-heterocyclic compounds such as oxadiazole,<sup>9</sup> triazole,<sup>10</sup> benzimidazole,<sup>11</sup> quinoxaline,<sup>12,13</sup> quinoline,<sup>14</sup> and 2,1,3benzothiadiazole<sup>12,15</sup> have been used as electron accepting units in  $\pi$ -conjugated polymers. However, it has been reported that the insertion of N-heterocyclic moiety in the main chain of polymer transformed p-type polymers into electron-accepting polymer.<sup>16</sup> Detailed tuning of electrooptical properties of semiconducting polymers is achieved by introducing electron-accepting and electron-reach donor units in the main chain.<sup>17-20</sup> This approach offers the ability to finely tune the frontier orbital levels of polymer, hence their optical properties. The donor-to-acceptor ratio as well as their electron-donating and electron-accepting strengths tune the electronic levels of these bipolar polymers. In bulk heterojunction PSC, the donor-acceptor architecture is used to tune the band gap of the polymer to match the solar spectrum and facilitate the photoinduced electron transfer.<sup>21</sup> Therefore, the synthesis of new  $\pi$ -conjugated polymers with optical and electronic properties tuned to fulfill specific requirements constantly attracts the scientific interest.22-26

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Semiconducting polymers have been proved to be efficient chemosensors. They showed higher sensitivity than low molecular weight sensor due to signal amplification along the polymer backbone because of the transfer of the excitation energy along the polymer backbone (molecular wire effect).<sup>27</sup> Molecular modification of semiconducting polymers allows to tune their structure so as to response to diverse analytes like explosives,<sup>28</sup> biomolecules,<sup>29</sup> nitric oxides,<sup>30</sup> and several metal ions<sup>31,32</sup> as well as anions like cyanide.<sup>33</sup> Among all cations, Hg<sup>2+</sup> is of particular interest because of its high toxicity. Although many low molecular weight sensors for  $Hg^{2+}$  have been developed,<sup>34-38</sup> there are a few polymeric fluorescent probes based on fluorescence quenching<sup>39,40</sup> or fluorescence "turn-on"<sup>41,42</sup> mechanism. Among transition metals iron is the most abundant in cells. Fe<sup>2+</sup> and Fe<sup>3+</sup> ions play an important role in cellular life. Ferrous ions are associated with the generation of high reactive hydroxyl radicals.43 Low molecular fluorescent probes have been developed for ferrous ions detection.<sup>44,45</sup> To the best of our knowledge there are a few publications on Fe<sup>2+</sup> fluorescent probe based on p-conjugated polymer.<sup>46,47</sup>

This article describes the synthesis and characterization of polyfluorenes containing 4,5-diphenylthiazole (PFTH100) or 4,5-diphenyloxazole (PFOX100) in the main chain. In addition, polyfluorenes containing electron-accepting thiazole or oxazole and electron-donating triphenylamine units in the main chain were prepared (PFTH50, PFTH25, and PFOX50, PFOX25). The optical and electrochemical properties of polymers were investigated and correlated to their structure. The chemosensing properties of polymers PFTH100 and PFOX100 were also studied. The polymers were dual fluorescent chemosensors. They detected Fe<sup>2+</sup> through fluoresquenching and Hg<sup>2+</sup> cence through fluorescence enhancement. Polymer response from  $Fe^{2+}$  to  $Hg^{2+}$  was switched by means of iodide.

#### **EXPERIMENTAL**

#### **Characterization Methods**

IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum BX spectrometer with KBr pellets. <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) spectra were obtained using a Brucker spectrometer. The NMR spectra were recorded using CDCl<sub>3</sub> as solvent. Chemical shifts ( $\delta$  values) are given in parts per million with tetramethylsilane as an internal standard. GPC analysis was conducted with a Waters Breeze 1515 apparatus equipped with a 2410 differential refractometer as detector (Waters Associate) and Styragel HR columns using polystyrene as standard and THF as eluant. Differential scanning calorimetry (DSC) was performed on a Netzsch 200F3 DSC thermal analyzer at a scan rate of 10 °C/min in N<sub>2</sub> with a flow rate of 20 cm<sup>3</sup>/min. Elemental analyses were carried out with a Carlo Erba model EA1108 analyzer. UV-vis spectra were recorded on Thermo Evolution 201 UV-visible Spectrophotometer. Fluorescence measurements were carried out on Perkin Elmer LS 55 Fluorescence Spectrometer. Cyclic voltammetry (CV) was performed on a Basi Epsilon potentiostat

equipped with C-3 cell stand. Grassy carbon (GC) disc, Ag/ AgCl, and Pt wire were used as working, reference, and auxiliary electrode, respectively.

## **Reagents and Solvents**

Toluene and tetrahydrofuran (THF) were dried by distillation over  $CaH_2$ . 9,9-Dihexylfluorene-2,7-diboronic acid bis(1,3propanediol)ester was recrystallized from a mixture of ethyl acetate/n-hexane. All other reagents and solvents were commercially purchased and were used as supplied.

## Synthesis of Monomers (Scheme 1) Synthesis of 4,5-Bis(4-Bromophenyl)-2-Methylthiazole (TH)

A flask was charged with 4-bromophenylacetic acid (2.00 g, 9.30 mmol) and SOCl<sub>2</sub> (8 mL). The mixture was heated at 50 °C for 6 h. During this time the solid was dissolved. The excess of SOCl<sub>2</sub> was removed by distillation and bromobenzene (4.38 g, 27.90 mmol), AlCl<sub>3</sub> (1.61 g, 12.11 mmol) were added. The mixture was stirred at 0 °C for 1 h and then at room temperature overnight. Subsequently, the mixture was poured into water (100 mL). The white precipitate was filtered and recrystallized from ethanol to afford 1,2-bis(4-bromophenyl)ethanone (1) as a white solid (2.63 g, 80.0%). FTIR (KBr): v = 3090, 2891, 1689, 1581, 1486, 1336, 1199, 1071, 992. <sup>1</sup>H-NMR (400 MHz,  $CDCl_3$ ,  $\delta$ ): 7.86–7.83 (d, 2H, aromatic), 7.62-7.60 (d, 2H, aromatic), 7.46-7.44 (d, 2H, aromatic), 7.13-7.11 (d, 2H, aromatic), 4.20 (s, 2H, aliphatic).  $^{13}$ C-NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 196.00, 135.05, 133.04, 132.09, 131.86, 131.20, 130.04, 128.65, 121.17, 44.77.

Br<sub>2</sub> (1.86 g, 11.63 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (7 mL) was added dropwise in 3 h to a solution of **1** (3.75 g, 10.71 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The mixture was stirred overnight at room temperature. The solvent was distilled off and the precipitate was recrystallized twice from ethanol to afford *2bromo-1,2-bis*(4-*bromophenyl*)*ethanone* (**2**) as white solid (3.70 g, 79.8%). FTIR (KBr): v = 1681, 1585, 1487, 1485, 1217, 1069, 993. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.85–7.83 (d, 2H, aromatic), 7.62–7.60 (d, 2H, aromatic), 7.52–7.50 (d, 2H, aromatic), 7.40–7.38 (d, 2H, aromatic), 6.22 (s, 1H, aliphatic).



SCHEME 1 Synthesis of monomers TH and OX.



SCHEME 2 Synthesis of polymers PFTH100, PFTH50, and PFTH25.

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, *δ*): 189.76, 134.46, 132.63, 132.27, 132.22, 130.84, 130.59, 129.32, 123.64, 48.97.

A solution of **2** (0.80 g, 1.85 mmol) and thioacetamide (0.17 g, 2.26 mmol) in DMF was heated at 60 °C overnight. The solution poured into water (60 mL) to give a white precipitate. It was filtered off, washed thoroughly with water and recrystallized from acetonitrile to afford compound **TH** as white solid (0.73 g, 96.4%). Anal. Calcd for C<sub>16</sub>H<sub>11</sub>Br<sub>2</sub>NS: C, 46.97; H, 2.71; N, 3.42. Found: C, 46.38; H, 2.68; N, 3.44. FTIR (KBr): v = 1654, 1586, 1489, 1392, 1186, 1070, 1010, 961, 820. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.46–7.41 (m, 4H, aromatic), 7.36–7.34 (d, 2H, aromatic), 7.17–7.15 (d, 2H, aromatic), 2.74 (s, 3H, aliphatic). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 164.51, 148.62, 133.52, 132.08, 131.60, 131.05, 130.86, 130.57, 122.42, 122.08, 19.26.

Synthesis of 4,5-Bis(4-Bromophenyl)-2-Methyloxazole (OX) A mixture of compound 2 (1.00 g, 2.31 mmol), sodium acetate (0.21 g, 2.56 mmol), 18-crown-6 (0.10 g), and acetonitrile (10 mL) was reflux under N<sub>2</sub> overnight. Subsequently, the solvent was evaporated and the residue was triturated with methanol (12 mL). The mixture was filtered to remove the insoluble materials and the filtrate was concentrated under reduced pressure. The resulting solid was purified by flash chromatography (SiO<sub>2</sub>,  $CH_2Cl_2/n$ -hexane 1:1 v/v) to give 1,2-bis(4-bromophenyl)-2-oxoethylacetate (3) as a white solid (0.62 g, 65%). FTIR (KBr): v = 3091, 2939, 1740, 1695, 1586, 1486, 1368, 1373, 1234, 1060, 1011, 977, 925. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.77-7.57 (d, 2H, aromatic), 7.57-7.49 (m, 4H, aromatic), 7.32-7.30 (d, 2H, aromatic), 6.73 (s, 1H, aliphatic), 2.20 (s, 3H, aliphatic). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, δ): 192.55, 170.32, 133.10, 132.46, 132.14, 130.19, 130.17, 129.05, 123.91, 70.29, 20.70.

A mixture of **3** (0.60 g, 1.46 mmol), ammonium acetate (0.56 g, 7.27 mmol) and glacial acetic acid (5 mL) was refluxed. After a short time the solid was dissolved. Heating continued for 24 h. The solution was cooled to room temperature. The white precipitate was filtered, washed with chilled methanol and dried. It was purified by flash chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/n-hexane 1:1 v/v) to afford compound **OX** as

white solid (0.31 g, 54%). Anal. Calcd. for  $C_{16}H_{11}Br_2N0$ : C, 48.89; H, 2.82; N, 3.56. Found: 48.42; H, 2.83; N, 3.53. FTIR (KBr): v = 1580, 1492, 1478, 1396, 1286, 1264, 1072, 1010, 962. <sup>1</sup>H-NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.52–7.41 (m, 8H, aromatic), 2.55 (s, 3H, aliphatic). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 161.28, 145.56, 135.59, 132.96, 132.83, 132,13, 130.13, 128.88, 123.61, 123.24, 14.92.

## Synthesis of Polymers (Schemes 2 and 3)

Polymers were prepared by coupling the synthesized dibromides (TH or OX) and 4,4'-dibromotriphenylamine with 9,9dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol)ester. The compositions of polymers were tuned by adjusting the feed ratio of dibromides TH, OX, and 4,4'dibromotriphenylamine.

## General Procedure of Polymerization

A flask was charged with 1.00 equivalent of dibromide and 1.00 equivalent of 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester. The flask was purged with argon and then 0.02 equivalent of  $Pd(PPh_3)_4$ , 16 equivalent of  $K_2CO_3$  as 2 M solution and toluene were added. The mixture was vigorously stirred at 80 °C, under argon, for 48 h. Then 10 mg of phenylboronic acid and 1 mg of  $Pd(PPh_3)_4$  were added. After 2 h bromobenzene (10 mg) was added and heating continued for two more hours. After cooling to room temperature the organic layer was separated filtered and poured in methanol. The precipitate was filtered, redissolved in  $CH_2CI_2$  and precipitated again in methanol. The resulting yellow solid was filtered and dried in vacuum to afford polymer.

Polymer **PFTH100** prepared as a yellow solid in 62% yield.  $M_{\rm n} = 17,200, PDI = 2.1. T_{\rm g}$  67 °C. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.80–7.75 (m, 4H, aromatic), 7.69–7.65 (m, 4H, aromatic), 7.57–7.55 (m, 2H, aromatic), 7.43–7.25 (m, 4H, aromatic), 2.80 (s, 3H, aliphatic), 1.08–1.01 (m, 20H, aliphatic), 0.75– 0.73 (m, 6H, aliphatic). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 160.52, 152.16, 145.53, 143.55, 140.98, 139.16, 132.55, 131.81, 129.50, 127.93, 127.40, 126.84, 55.15, 40.44, 31.53, 29.77, 22.63, 19.35, 14.02.



SCHEME 3 Synthesis of polymers PFOX100, PFOX50, and PFOX25.



Polymer **PFTH50** prepared as a yellow solid in 76% yield.  $M_{\rm n} = 20,100, PDI = 2.6. T_{\rm g}$  78 °C. <sup>1</sup>H-NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.79–7.66 (m, 12H, aromatic), 7.57–7.43 (m, 12H, aromatic), 7.36–7.22 (m, 6H, aromatic), 7.16–6.92 (m, 3H, aromatic), 2.80 (s, 3H, aliphatic), 1.09–1.02 (m, 40H, aliphatic), 0.75– 0.73 (m, 12H, aliphatic). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$  m): 163.95, 152.64, 147.52, 146.85, 146.56, 141.13, 140.06, 139.36, 135.97, 132.53, 131.86, 130.88, 129.31, 128.80, 127.90, 125.42, 124.62, 123.71, 121.01, 119.17, 55.20, 40.42, 31.52, 29.76, 23.77, 22.61, 19.31, 14.00.

Polymer **PFTH25** prepared as a yellow solid in 59% yield.  $M_{\rm n} = 22,500, PDI = 1.8. T_{\rm g}$  90 °C. <sup>1</sup>H-NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.79–7.60 (m, 12H, aromatic), 7.50–7.26 (m, 12H, aromatic), 7.17–6.96 (m, 9H, aromatic), 2.78 (s, 3H, aliphatic), 1.11–1.01 (m, 40H, aliphatic), 0.76–0.73 (m, 12H, aliphatic). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 163.98, 151.73, 147.58, 146.91, 146.55, 141.21, 139.83, 139.37, 135.95, 132.55, 132.11, 130.02, 129.48, 128.51, 127.89, 125.60, 124.59, 124.30, 123.46, 120.97, 119.96, 55.26, 40.54, 31.50, 29.73, 23.84, 22.60, 19.31, 14.02.

Polymer **PFOX100** prepared as a yellow solid in 79% yield.  $M_{\rm n} = 10,700, PDI = 2.5. T_{\rm g} 55$  °C. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.78–7.70 (m, 4H, aromatic), 7.65–7.52 (m, 4H, aromatic), 7.45–7.25 (m, 6H, aromatic), 2.57 (s, 3H, aliphatic), 1.09–1.00 (m, 20H, aliphatic), 0.75–0.72 (m, 6H, aliphatic). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 160.44, 149.68, 146.35, 143.29, 140.08, 139.65, 132.70, 131.90, 129.42, 127.93, 127.47, 126.46, 55.06, 40.36, 31.53, 29.76, 23.76, 22.65, 15.12, 14.01.

Polymer **PFOX50** prepared as a yellow solid in 56% yield.  $M_n = 13,500$ , PDI = 3.1. Tg 42 °C. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.77–7.65 (m, 12H, aromatic), 7.59–7.43 (m, 12H, aromatic), 7.34–7.25 (m, 6H, aromatic), 7.06–6.92 (m, 3H, aromatic), 2.56 (s, 3H, aliphatic), 1.09–0.99 (m, 40H, aliphatic), 0.75– 0.72 (m, 12H, aliphatic). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 160.42, 150.32, 146.57, 143.54, 140,64, 136.38, 135.91, 134.55, 132.34, 131.91, 129.54, 129.39, 128.62, 127.94, 127.88, 127.45, 125.41, 124.61, 123.75, 121.02, 54.90, 40.38, 31.52, 29.76, 23.77, 22.65, 15.12, 14.01.

Polymer **PFOX25** prepared as a yellow solid in 81% yield.  $M_{\rm n} = 16,700, PDI = 3.7. T_{\rm g} = 61$  °C. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.76–7.74 (m, 8H, aromatic), 7.67–7.54 (m, 8H, aromatic), 7.47–7.22 (m, 8H, aromatic), 7.15–6.92 (m, 9H, aromatic), 2.57 (s, 3H, aliphatic), 1.10–1.05 (m, 40H, aliphatic) 0.76–0.74 (m, 12H, aliphatic). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 160.58, 149.91, 146.9, 144.41, 140,57, 136.36, 135.96, 134.42, 132.35, 132.25, 132.17, 129.60, 129.45, 128.81, 128.49, 127,98, 127.90, 127.22, 125.33, 124.62, 124.38, 121.05, 55.35, 40.52, 31.49, 29.74, 23.83, 22.59, 15.08, 14.01.

## Fluorescence Titration Experiments

Fluorescence experiments were carried out in a 1  $\times$  1 cm quartz cuvette. The emitted light was collected 90° relative to excitation beam. To examine polymers chemosensing properties, an aliquot of a 10<sup>-2</sup> M aqueous stock solution of cation or anion was added to a solution of polymer (20  $\mu$ g/mL) in THF to obtain final concentration 100  $\mu$ M. Emission

of polymer was measured in a minute after mixing. The emission spectra of polymer before and after cation or anion addition were compared.

For fluorescence titration experiments, in case of Fe<sup>2+</sup> and Hg<sup>2+</sup>, three aqueous stock solutions  $10^{-2}$ ,  $10^{-3}$ , and  $10^{-4}$  M were prepared. About 3 mL of polymer's solution (20  $\mu$ g/mL) in THF were added in a cuvette. Aliquot of the appropriate stock solution was added so as the concentration of the cations in polymer solution gradually increased from 1 to 800  $\mu$ M.

## **RESULTS AND DISCUSSION**

### **Monomers Synthesis**

Scheme 1 shows the method for the preparation of monomers **TH** and **OX**. These monomers were derivatives of thiazole and oxazole and they were used as starting materials for the preparation of polymers. They were synthesized via a multistep procedure. The key step for the synthesis of **TH** and **OX** derivatives was the preparation of a-bromo ketone **2**. It was prepared by bromination of ketone **1**. The condensation of **2** with thioacetamide gave **TH**. On the other hand, **2** reacted with sodium acetate to give keto-ester **3**. The later was condensated<sup>48</sup> with CH<sub>3</sub>COONH<sub>4</sub> to give **OX**. The monomers were characterized by FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR as well as elemental analysis.

#### **Polymers Synthesis and Characterization**

The monomers TH and OX were used as starting materials for the preparation of polymers via Suzuki coupling. Two series of polyfluorenes containing thiazole or oxazole as well as triphenylamine (TPA) moieties were prepared. In polymers' names TH or OX stands for thiazole or oxazole, respectively, while numbers 100, 50, and 25 indicate the ratio of thiazole or oxazole in polymer chain, relative to TPA. More particularly, Suzuki coupling of TH and 4,4'-dibromotriphenylamine with 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3propanediol) ester gave polymers PFTH100, PFTH50, and PFTH25 (Scheme 2). These polymers differ in the content of thiazole moieties which was achieved by changing the feed ratio of dibromides TH/4,4'-dibromotriphenylamine. In the same way, polymers PFOX100, PFOX50, and PFOX25 (Scheme 3), containing oxazole moieties, prepared by Suzuki coupling of dibromides OX/4,4'-dibromotriphenylamine with 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester. The polymers' structures were verified by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy. Molecular weights were determined by GPC and the  $M_n$  range from 10,700 to 22,500. All these data are shown in "Experimental" section.

All polymers were readily soluble in organic solvents such as dichloromethane, chloroform, and THF. Polymer solutions with concentration up to 2% were prepared. Transparent and pinhole-free films were formed by casting polymers' solutions. Thermal properties of polymers were investigated by DSC. The  $T_{\rm g}$  of polymers were determined from second heating scan and range from 42 to 90 °C (see "Experimental" section). The rather low  $T_{\rm g}$  should be attributed to the

## **TABLE 1** Optical Properties of Polymers

Polymer	Solution <sup>a</sup>			Film		
	$\lambda_{a,\max}^{b}$	$\lambda_{f,\max}^{c}$	${\varPhi_{f}}^{d}$	$\lambda_{a,\max}^{b}$	$\lambda_{f,max}^{c}$	$E_{g}^{e}$
PFTH100	339	428	0.50	344	445	2.70
PFTH50	344	431	0.64	345	456	2.77
PFTH25	371	438	0.91	383	488	2.56
PFOX100	322, <u>344</u>	418	0.84	319, <u>345</u>	444	2.64
PFOX50	322, 343	426	0.85	319, 341	483	2.60
PFOX25	377	437	0.95	396	493	2.70

<sup>a</sup> In THF.

<sup>b</sup> Absorption maxima in solution or in thin film. Underlined values indicate a shoulder peak.

 $^{\rm c}$  PL maxima (obtained by excitation at the corresponding  $\lambda_{\rm a,max}).$   $^{\rm d}$  PL quantum yield in solution.

<sup>e</sup> Optical band gap calculated from the absorption edge.

kinked 4,5-diphenylthiazole or 4,5-diphenyloxazole and to the propeller-like TPA units that reduced the stiffness of backbone.

## **Optical Properties**

Optical properties of polymers were investigated by means of UV-vis and photoluminescence (PL) spectroscopy. UV-vis and PL spectra were obtained in both solution and thin film. These data are summarized in Table 1. Figures 1 and 2 depict the absorption and emission spectra of polymers in solution. Except PFOX100 and PFOX50, the polymers showed single absorption maxima at 339-377 nm in THF solutions. The former polymers presented a main peak around 322 nm which was attributed to the diphenyloxazole moieties and a shoulder at 344 and 343 nm from  $\pi\text{-}$  $\pi^*$  transition of the main chain. Emission spectra of polymers were recorded in THF solutions with photoexcitation at the corresponding absorption maxima. The emission of PFOX100 and PFOX50 was obtained with excitation at the shoulder absorption peak, 344 and 343 nm, respectively. All polymers displayed the typical pure blue emission of polylfuorene49 with maxima at 418-438 nm. The fluorescence quantum yields ( $\Phi$ ) in solution were measured using quinine sulfate as reference. The polymers exhibited high



The synthesized polymers showed a large hypsochromic shift of absorption maxima relative to PF<sup>49</sup> which showed absorption maximum at about 380 nm. This suggests a reduction in electron delocalization due to the introduction of kinked TH or OX units. The absorption maxima were more than 30 nm red-shifted as the percentage of heterocyclic segments reduced in going from **PFTH100** to **PFTH25** or from **PFOX100** to **PFOX25**. This verifies that the presence of TH or OX moieties disrupted the conjugation length of polymer chain. This behavior has also been observed for PF bearing kinked quinoxaline units.<sup>13</sup>

In contrast to the absorption, the emission maxima were comparable to PF emission maximum. PF showed well



**FIGURE 1** Absorption and emission spectra of PFTH100, PFTH50, and PFTH25 in THF solution.



FIGURE 2 Absorption and emission spectra of PFOX100, PFOX50, and PFOX25 in THF solution.



**FIGURE 3** Absorption and emission spectra of PFTH100, PFTH50, and PFTH25 films.

resolved emission spectra with maxima around 420 and 445 nm.<sup>49</sup> The PL maxima of present polymers were 418–438 nm but there was a loss of vibronic emission bands of PF. This is attributed to kinked TH or OX units that reduced the chain ordering. In a series of polymers with the same heterocyclic unit (**PFTH** or **PFOX**) the PL maxima were redshifted as the content of heterocyclic units TH or OX decreased. The same trend was observed for absorption maximum too, but the emission maxima showed smaller redshift on going from **PFTH100** to **PFTH25** or from **PFOX100** to **PFOX25**. All the polymers showed a large Stokes shift (60–90 nm) which implies a possible conformational change upon photoexcitation.

In order to get insight in polymer optical properties, their absorption and emission spectra were recorded in different solvents like toluene, CH<sub>2</sub>Cl<sub>2</sub>, THF, and DMF (Supporting Information Figs. 1S and 2S). The absorption spectra of all polymers were almost insensitive on solvent polarity, which indicates that there is no strong charge transfer in the ground state. Therefore, the conjunction of donor and acceptor units stemmed from their  $\pi$  orbitals interactions, without evidence of charge transfer. Interestingly, for emission spectra we observed two different trends. The emission maxima of PFTH100 and PFOX100 were practically independent on solvent. The PL maxima of the rest polymers, that contained TPA units, strongly depended on solvent polarity and they were shifted to low-energy region with the increase in solvent polarity. The magnitude of the solvatochromic shift depended on the contents of TPA units in polymer chain. For example, the bathochromic shift for PFTH50 was 13 nm from toluene (422 nm) to DMF (435 nm), while for PFTH25 was 41 nm from toluene (426 nm) to DMF (467 nm). The dependence of emission on solvent polarity indicates that photoinduced charge transfer in the excited state. Obviously, the existence of strong electron donor TPA in polymer chain facilitated this progress. This behavior has been observed for molecules bearing TPA and certain electron-accepting units.<sup>50-52</sup> In contrast, polymers PFTH100 and PFOX100, which lack TPA units, did not display such behavior.

Thin films of polymers were prepared by spin-casting on quartz substrate from THF solutions. The UV-vis and PL spectra of polymers' films are shown in Figures 3 and 4. The absorption spectra of films were slightly broader than the corresponding solution spectra, except PFOX25 which showed a much broader spectrum. The absorption maxima of polymers' films ranged from 319 to 396 nm. They were 0 to 19 nm red-shifted relative to absorption maxima of solutions. These indicate that some polymer form aggregates in solid state. Polymers PFTH100 and PHOX100 exhibited limited tendency to form aggregates, judging from the negligible red-shift of their absorption maxima. The optical band gaps were estimated from absorption edges and they were 2.56-2.77 eV. They were in good agreement with the optical band gap of PF containing quinoxaline<sup>12</sup> or 2,5-diphenyloxazole units.<sup>53</sup> PL spectra of films were recorded by excitation to their absorption maxima. The films showed pure blue emission with maxima 444-493 nm. All polymers displayed bathochromic shifts 17-57 nm relative to emission maxima in solution. This red shift on going from solution to film was more intense for emission spectra than for absorption spectra. In addition polymers presented much larger Stokes shifts in films (97-142 nm) than in solutions (60-89 nm). This behavior indicated that the emission of polymers in solid state stemmed from interchain or intrachain species.

The absorption and emission maxima of polymers were compared with those of polyfluorene **PFTPA** containing TPA moieties (Chart 1) in order to gain further information. **PFTPA** was prepared form equimolar amount of 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester and 4,4'dibromotriphenylamine according to the general procedure for polymerizations (see "Experimental" section). It showed absorption and emission maxima at 380 and 433 nm in solution as well as 379 and 487 nm in film, respectively. These values are in good agreement with bibliography.<sup>54</sup> Within a series of polymers with the same heterocyclic ring (TH or OX), the absorption and emission maxima were reduced with increase of heterocyclic moieties in the polymer chain



**FIGURE 4** Absorption and emission spectra of PFOX100, PFOX50, and PFOX25 films.



CHART 1 Polymer PFTPA.

(Supporting Information Fig. 3S). Eventually, **PFTH100** and **PFOX100** presented the lower absorption and emission maxima. On the other hand polymers **PFTH25** and **PFOX25**, bearing the highest percentage of TPA moieties, had the highest absorption and emission maxima among the polymers. These values were almost equal to absorption and emission maxima in both solution and film was detected as the ratio of TH or OX/TPA in polymer chain increased from 25/75 to 50/50. Interestingly, when equimolar amounts of TH or OX and TPA exist in the polymers chain, the optical properties of polymers were defined by heterocyclic segments. When the molar amount of TPA was higher than that of TH or OX the optical properties of polymers were governed by TPA.

#### **Electrochemical Properties**

Cyclic voltammetry was used to estimate the redox properties of polymers in thin film. Polymers' films were prepared by drop-casting on working electrode and dried in air. Tetrabutylammonium hexafluorophosphate ( $Bu_4NPF_6$ ) 0.1 M in acetonitrile was used as supporting electrolyte. The potential values obtained in reference to Ag/AgCl electrode. Ferrocene was used as internal reference. HOMO and LUMO levels were estimated from the onset ( $E_{ons}$ ) of oxidation or reduction peak, respectively, on the basis of the reference energy level of ferrocene (4.8 eV below the vacuum level) with the equations<sup>45</sup>

$$HOMO/LUMO = -(E_{ons}-E_{fer}) - 4.8 \text{ eV}$$

The Ionization Potential (IP) and Electron Affinity (EA) of polymers were estimated from HOMO and LUMO levels.

Figures 5 and 6 present the CV traces of polymers. The data are summarized in Table 2. The polymers were separated into two groups on the base of oxidation features. Polymers PFTH100 and PFOX100 showed no obvious oxidation process up to 2.0 V. Probably the electron-accepting character of thiazole and oxazole units complicated the oxidation process of polyfluorene. This feature was previously observed for polyfluorene containing 2,5-diphenyloxazole<sup>53</sup> or quinoxaline<sup>12</sup> electron-acceptors. However, the introduction of these acceptors along the polymer chain increased the oxidation potential of PF but they did not prevent the oxidation. Probably, the kinked structure of heterocyclic units TH and OX, which disrupted the backbone conjugation, contributed to oxidation prevention of PFTH100 and PFOX100. PF containing bithiazole units showed irreversible oxidation.55 In contrast, the rest polymers, with both heterocyclic and TPA moieties in the backbone, showed reversible oxidations. Obviously, this feature was assigned to TPA units. During anodic scan these polymers showed oxidation onset  $(E_{ox})$  at 0.93-1.01 V relative to Ag/AgCl. These values were comparable to the oxidation potential (1.04 eV vs. SCE) of triphenylamine.<sup>56</sup> The Ionization Potentials (IP) were determined from the oxidation onset and they were estimated to be 5.28-5.36 eV. These values were higher than IP of 5.25 eV of PFTPA which contains only the triphenylamine in the main chain (Supporting Information Fig. 4S). The higher IP of PFTH and PFOX polymers relative to PFTPA indicate that the insertion of electron-deficient TH or OX units made the oxidation process of polymers more difficult. Generally, these polymers showed more facile p-doping than poly(9.9-di-noctylfluorene) which showed an IP 5.80 eV.<sup>57</sup>

Upon cathodic scan irreversible reduction waves were observed for the polymers. The reduction onsets ( $E_{red}$ ) were comparable and in the range 0.64–0.67 V relative to Ag/ AgCl. Consequently, the estimated Electron Affinities (EA)



**FIGURE 5** CV traces (a) anodic scan and (b) cathodic scan of PFTH100, PFTH50, and PFTH25 films on glassy carbon disc electrode (Bu<sub>4</sub>NPF<sub>6</sub> 0.1 M in acetonitrile, scan rate 100 mV/s).

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solutions of salts at a final concentration 100  $\mu$ M. The

absorption and emission of polymers' solution were recorded within 1 min. Figure 7 presents the effect of certain cations

on PL intensity of polymers PFTH100 in THF solution. Gen-

erally, the addition of cations in polymer solution did not

shift the absorption and emission maxima. This indicates

that cations did not form new species in polymer chain. However, they caused PL quenching which may be attributed

to heavy atom effect.<sup>59</sup> Except Fe<sup>2+</sup>, the other cations did

not quench significant the PL of polymers. Fe<sup>2+</sup> quenched PL

about 50%. Analogous results were obtained for PFOX100

(Supporting Information Fig. 5S). Therefore, we tried to

exploit this quenching behavior for detection and quantifica-

tion of the  $Fe^{2+}$ . When  $Fe^{2+}$  was added to a solution of

PFTH100 or PFOX100 containing other cations like Ba<sup>2+</sup>,

 $Co^{2+}$ ,  $Pd^{2+}$ ,  $Cd^{2+}$ ,  $Cu^+$ , or  $Hg^{2+}$  caused a drastic quenching

of PL of polymers. Therefore, it was possible to detect  $Fe^{2+}$  in the presence of other ions. Fluorescent titration studies

were applied to further evaluate quenching behavior of  $Fe^{2+}$ .

Upon addition of Fe<sup>2+</sup> to PFTH100 solution in THF the

emission intensity at 428 nm was quenched gradually. Figure

8 depicts the fluorescence quenching of PFTH100 in THF

solution upon increase of quencher  $Fe^{2+}$  concentration. The Stern-Volmer plot for **PFTH100** reveals a fine linear rela-

tionship ( $R^2 = 0.9979$ ) between the PL quenching (ratio  $F_0/F$ ) and Fe<sup>2+</sup> concentration over a large region (1–800  $\mu$ M).



**FIGURE 6** CV traces (a) anodic scan and (b) cathodic scan of PFOX100, PFOX50, and PFOX25 films on glassy carbon disc electrode (Bu<sub>4</sub>NPF<sub>6</sub> 0.1 M in acetonitrile, scan rate 100 mV/s).

were comparable (Table 2). This means that the reduction process was not affected by structural variation of the main chain. This suggests that the LUMO levels are localized on the heterocyclic electron-deficient unit (oxazole or thiazole) with limited contributions from adjacent TPA and fluorene moieties. This feature has also been reported for donoracceptor polymers containing isoindigo units.<sup>25,26</sup> In contrast to HOMO levels (see above), the LUMO levels of polymers were independent on structure polymer chain. Calculations of Density Functional Theory on donor-acceptor polymers have shown that the HOMO is delocalized over the conjugated backbone while LUMO is localized on the acceptor monomer.58 No significant dependence of LUMO on the kind of heterocyclic unit was observed. It has been reported that PF bearing quinoxaline or thieno[3,4-b]-pyrazine<sup>12</sup> electronacceptor showed irreversible reduction. In contrast, incorporation of 2,5-diphenyloxazole units<sup>53</sup> in PF chain resulted in polymer with reversible reduction. The band gaps  $(E_{\alpha})$  were estimated electrochemically from the HOMO-LUMO difference and they fairly agreed with optical band gap.

## **Sensing Properties**

The potential use of polymers **PFTH100** and **PFOX100** as fluorescent chemosensors was investigated toward several cations and anions. The sensing properties were studied using polymer solution 20  $\mu$ g/mL in THF by adding aqueous

Polymer	$E_{\rm ox}$ (V) <sup>a</sup>	$E_{\rm red}$ (V) <sup>a</sup>	IP <sup>b</sup> (eV)	EA <sup>c</sup> (eV)	$E_{g elec}^{d}$
PFTH100	ND <sup>e</sup>	-0.67	-	3.68	-
PFTH50	1.01	-0.65	5.36	3.70	1.66
PFTH25	0.97	-0.64	5.32	3.71	1.61
PFOX100	ND	-0.66	-	3.69	-
PFOX50	0.95	-0.66	5.30	3.69	1.61
PFOX25	0.93	-0.65	5.28	3.70	1.58

TABLE	2	Cvclic	Voltammetry	Data
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<sup>a</sup> Onset of oxidation or reduction potential versus Ag<sup>+</sup>/AgCl.

<sup>b</sup> lonization potential.

<sup>c</sup> Electron affinity.

<sup>d</sup> Band gap calculated from  $E_{g elec} = HOMO - LUMO$ .

<sup>e</sup> ND not detected.



FIGURE 7 Change of PFTH100 emission in THF solution (20  $\mu g/$  mL) upon addition of 100  $\mu M$  of metal ions.

The  $K_{\rm sv}$  was  $0.43 \times 10^4 \,{\rm M}^{-1}$ . The results indicate that polymer **PFTH100** quantify Fe<sup>2+</sup> with no interference from other metal ions. For **PFOX100** a fine linearity between the PL quenching and Fe<sup>2+</sup> concentration was detected up to 80  $\mu$ M Fe<sup>2+</sup> (Fig. 9). The corresponding  $K_{\rm sv}$  was  $0.5 \times 10^4 \,{\rm M}^{-1}$ . The shorter linearity of **PFOX100**/Fe<sup>2+</sup> than **PFTH100**/Fe<sup>2+</sup> system could be attributed to the lower molecular weight of **PFOX100**.

The fluorescence response of **PFTH100** and **PFOX100** in presence of certain anions was also investigated. Figure 10 shows the PL quenching of **PFTH100** in the presence of 100  $\mu$ M CO<sub>3</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, AcO<sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>. A selective response to iodide is clearly observed. Iodides quenched PL intensity of polymers in THF solution up to 40%. The other anions had negligible effect on polymer's emission. Analogous behavior has been reported for polyphenyls with laterally attached thiazole rings.<sup>42</sup> In case of **PFOX100**, fluorescence was quenched about 30% by iodide



**FIGURE 8** Change of fluorescence of PFTH100 in THF solution (20  $\mu$ g/mL) with increasing Fe<sup>2+</sup> concentration. Inset shows the Stern–Volmer plot.





**FIGURE 9** Change of fluorescence of PFOX100 in THF solution (20  $\mu$ g/mL) with increasing Fe<sup>2+</sup> concentration. Inset shows the Stern–Volmer plot.

ion (Supporting Information Fig. 6S). This indicates that the heterocyclic segment of polymers influenced the interaction of iodide quencher with polymers. Moreover, after iodide addition the solution adopted a yellow color which indicates the creation of a new species. Therefore there was an interaction of polymers with iodide in ground state. Figure 11 presents the changes of UV-vis spectrum of PFOX100 upon iodide addition. It is seen that a new band at about 296 nm is gradually generated as the concentration of iodides increase. Moreover the absorption maximum of polymer is bathochromically shifted up to 15 nm. The same results were obtained for **PFTH100** (Supporting Information Fig. 7S). The findings verify electronic interaction of polymers PFTH100 and PFOX100 with iodide in ground state. Therefore the quenching by iodide could be attributed to static quenching.<sup>59</sup> In contrast Fe<sup>2+</sup> quencher did not influence the absorption spectra of polymers. The interaction of polymers with iodide could be detected with naked eyes as a yellow



**FIGURE 10** Change of PFTH100 emission in THF solution (20  $\mu$ g/mL) upon addition of 100  $\mu$ M anions.

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FIGURE 11 Change of UV-vis spectrum of PFOX100 in THF solution (20  $\mu$ g/mL) upon addition of 50, 100, and 250  $\mu$ M I<sup>-</sup>.

color developed upon iodide addition. The intensity of yellow color increased with the time. In case of **PFTH100** the was fully developed in 5 min (Supporting Information Fig. 8S) but the interaction **PFOX100**/I<sup>-</sup> was slower taking 10 min to develop the final color. The time dependent on PL quenching by iodide has also been observed.<sup>60</sup>

The ability of **PFTH100** and **PFOX100** to detect selectively iodide ions was investigated. To a **PFTH100**/I<sup>-</sup> solution 100  $\mu$ M of anions (CO<sub>3</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, AcO<sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>) or cations (Ba<sup>2+</sup>, Co<sup>2+</sup>, Pd<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>+</sup>, Hg<sup>2+</sup>) were added. No changed of **PFTH100**/I<sup>-</sup> emission was detected upon addition of anions. Except Hg<sup>2+</sup>, the other cations did not significantly affect the emission of **PFTH100**/I<sup>-</sup>. Hg<sup>2+</sup> ions caused a significant increase in the emission of the complex



**FIGURE 12** Emission "turn-on" of PFTH100/I<sup>-</sup> in THF solution (20  $\mu$ g/mL) upon addition Hg<sup>2+</sup>. Line with open cycles is PFTH100/I<sup>-</sup>emission, line with solid cycles is the emission of pristine PFTH100 in THF solution (20  $\mu$ g/mL), the other lines are PFTH100/I<sup>-</sup>emission upon addition Hg<sup>2+</sup> (1–800  $\mu$ M). Inset: Plot of emission enhancement (*F*/*F*<sub>0</sub>) at 433 nm of PFTH100/I<sup>-</sup> versus Hg<sup>2+</sup> concentration (1–10  $\mu$ M).



**FIGURE 13** Polymer PFTH100 detected and distinguished Fe<sup>2+</sup> and Hg<sup>2+</sup> coexisting in a solution. (i) Emission of pristine PFTH100 (line with squares) in THF solution (20  $\mu$ g/mL), (ii) emission quenching upon addition of 100  $\mu$ M Fe<sup>2+</sup> and 100  $\mu$ M Hg<sup>2+</sup> (line with triangles), (iii) emission "turn-on" upon addition of 100  $\mu$ M I<sup>-</sup> (line with circles).

**PFTH100**/I<sup>-</sup>, restoring the PL intensity of **PFTH100** (see Fig. 12). This feature has been described for polyphenyls containing thiazole rings.<sup>42</sup> Upon addition of  $Hg^{2+}$  the yellow color of **PFTH100**/I<sup>-</sup> solution faded resulting in a transparent colorless solution. Therefore **PFTH100**/I<sup>-</sup> complex could be a chemosensor for naked eyes detection of  $Hg^{2+}$ .

Fluorescent titration experiments were carried out in order to explore if **PFTH100**/I<sup>-</sup> response to Hg<sup>2+</sup> could be used for quantification. About 100  $\mu$ M iodide was added to a solution of PFTH100 or PFOX100 in THF (20 mg/mL) and the mixture was allowed standing 5 or 10 min, respectively. This incubation time was necessary in order to complete the interaction of polymers with I<sup>-</sup> (see above). After that, the titration experiments were carried out. The Hg<sup>2+</sup> concentration ranged from 1 to  $800\mu$ M. As the concentration of Hg<sup>2+</sup> increased the emission intensity of  $\mathbf{PFTH100}/I^-$  solution gradually increased along with a 5-7 nm blue shift of the emission maximum. After addition of 800  $\mu$ M Hg<sup>2+</sup> the 94% of the original emission intensity (before  $I^-$  addition) of PFTH100 and the 90% of PFOX100 were recovered (Fig. 12 and Supporting Information Fig. 9S). Finally, the pure emission of PFTH100 and PFOX100 were almost restored. In case of PFTH100 the PL "turn-on" was detected with the addition 1  $\mu$ M Hg<sup>2+</sup>. Quantification of Hg<sup>2+</sup> was based on the enhancement of PL intensity at 433 nm. Figure 12 shows the plot of PL intensity at 433 nm of PFTH100/iodide versus Hg<sup>2+</sup> concentration. A fine linear response to analyte  $(R^2 = 0.9963)$  was detected in the region 1–10  $\mu$ M. For **PFOX100**/I<sup>-</sup> complex the quantification of Hg<sup>2+</sup> based on PL enhancement at 422 nm. Emission "turn-on" was observed upon addition of 4  $\mu$ M Hg<sup>2+</sup>. A linear response to Hg<sup>2+</sup> ions at concentration 4–100  $\mu$ M was realized (Supporting Information Fig. 9S). Therefore, the polymers could be considered as probes for detection  $Hg^{2+}$  in a wide range of concentrations.

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**FIGURE 14** Detection of  $Hg^{2+}$  with PFTH100 film. (i) Emission of pristine PFTH100 film (line with squares). (ii) Emission quenching after immersion in 0.01M I<sup>-</sup> solution for several seconds (line with open circles). (iii) Emission "turn-on" after immersion in 0.01 M  $Hg^{2+}$  solution for several seconds (line with solid circles).

The ability of the **PFTH100** to detect simultaneously the two analytes (Fe<sup>2+</sup> and Hg<sup>2+</sup>) was also investigated. For this reason 100  $\mu$ M of both Fe<sup>2+</sup> and Hg<sup>2+</sup> were added at a solution of **PFTH100**. A 60% drop of PL intensity was recorded. This was attributed mainly to Fe<sup>2+</sup> since Hg<sup>2+</sup> decreased PL intensity of **PFTH100** no more than 6% (see Fig. 7). Upon addition of 100  $\mu$ M iodide the PL intensity increased due to formation of **PFTH100**/I<sup>-</sup> complex and subsequent dequenching effect of Hg<sup>2+</sup> (Fig. 13). These findings indicate that indeed **PFTH100** can detect analytes Fe<sup>2+</sup> and Hg<sup>2+</sup> that coexist in a solution. This feature was not observed for polymer **PFOX100**.

Finally, the sensing properties of PFTH100 and PFOX100 were investigated in solid state. Films of polymers were prepared by drop-casting on a quartz substrate. To detect Fe<sup>2+</sup> ions the polymer film was immersed in solution of 0.01 M Fe<sup>2+</sup> for several seconds. A 46% quenching of film's emission was detected for PFTH100 (Supporting Information Fig. 10S) and 30% for **PFOX100**. To examine the response to  $Hg^{2+}$  ions fresh polymer film was fist immersed in solution 0.01 M I $^-$  for several minutes, in order to produce the polymer/I<sup>-</sup> complex and then in solution 0.01M  $Hg^{2+}$  for a few seconds. Treatment of polymer film with iodide solution decreased the PL of films about 87% (PFTH100) and 37% (PFOX100). When, subsequently the polymer film was immersed in  $Hg^{2+}$  solution the 70% (PFTH100) and 90% (PFOX100) of the PL intensity of pristine film was restored (Fig. 14). Therefore the polymers' films can be used for detection of analytes  $Fe^{2+}$  and  $Hg^{2+}$ .

## CONCLUSIONS

Two series of polyfluorenes (PF) containing thiazole (**PFTH**) or oxazole (**PFOX**) as well as triphenylamine (TPA) moieties in the main chain were prepared. The molar ratio of thiazole/TPA or oxazole/TPA in polymer backbone was adjusted

at 100/0, 50/50, and 25/75. Polymers showed absorption maxima blue-shifted relative to PF due to the presence of heterocyclic units. However, their emission maxima were comparable to PF emission maxima. The emission of polymers showed a positive solvatochromism which was depended on TPA content. Polymers containing TPA showed photoinduced charge transfer due to strong electron donor triphenylamine and electron acceptor thiazole or oxazole. Cyclic voltammetry of polymers PFTH100 and PFOX100 containing only thiazole and oxazole units, respectively, did not show clear oxidation. The introduction of TPA in polymers PFTH50, PFTH25 and PFOX50, PFOX25 facilitated the oxidation process and polymers showed reversible oxidation. Irreversible reduction was observed for all polymers. The Electron Affinities of polymers were comparable, which suggests that the LUMO levels are localized on the heterocyclic electron-deficient unit (oxazole or thiazole). The sensing properties of PFTH100 and PFOX100 were investigated. Polymers were able to detected two analytes,  $\mbox{Fe}^{2+}$  and  $\mbox{Hg}^{2+}.$  Iodide switched the fluorescence response of polymers to  $Fe^{2+}$  or  $Hg^{2+}$ .  $Fe^{2+}$  directly quenched the emission of polymers. Linearity between the PL quenching and Fe<sup>2+</sup> concentration over a large region (1-800  $\mu$ M) was detected. Iodide interacted with polymers in ground state and quenched their emission. Addition of Hg<sup>2+</sup> in polymer/I<sup>-</sup> solution almost restored the original emission of polymers.  $\mathrm{Hg}^{2+}$  ions were detected and quantified via emission "turn-on" mechanism. **PFTH100**/I<sup>-</sup> showed fine linear response ( $R^2 = 0.9963$ ) to Hg<sup>2+</sup> concentration. It was able to detect as low as 1  $\mu$ M Hg<sup>2+</sup>. In case of **PFOX100**/I<sup>-</sup> linearity was observed in 4–100  $\mu$ M Hg<sup>2+</sup>. **PFTH100** was able to detect the Fe<sup>2+</sup> and Hg<sup>2+</sup> coexisting in a solution. Net films of polymers could detect both analytes.

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