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# Poly(Benzodithieno-imidazole-*alt*-carbazole) based $\pi$ -conjugated copolymers: Highly selective and sensitive *turn-off* fluorescent probes for Hg<sup>2+</sup>

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## **Graphical abstract**



Poly(benzodithieno-imidazole-*alt*-carbazole) based  $\pi$ -conjugated copolymer probes with nitrogen and sulphur binding sites exhibit remarkable selectivity and sensitivity towards Hg<sup>2+</sup> as *turn off* fluorescent chemosensor.

# Poly(benzodithieno-imidazole-*alt*-carbazole) based $\pi$ -conjugated copolymers: Highly selective and sensitive *turn-off* fluorescent probes for Hg<sup>2+</sup>

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#### Abstract

In this work, highly emissive and soluble  $\pi$ -conjugated poly(benzodithieno-imidazole-*alt*carbazole)  $\pi$ -conjugated copolymers (P1 and P2) have been synthesized through Pd(0)-catalyzed Suzuki coupling polymerization protocol from the corresponding monomers. For solubilizing in common organic solvents, heptyl (in P1) or 2-(2-(2-methoxyethoxy)ethoxy)ethyl (in P2) substituents have been introduced at benzodithieno-imidazole and 9-position of carbazole unit. The well-defined and soluble  $\pi$ -conjugated polymers have been characterized by multinuclear NMR spectra as well as by tetradetector GPC studies showing molecular weight ( $M_n$ ) of 16.5 and 14.3 kDa with the polydispersity indices of 1.36 and 1.31 respectively. The emissive  $\pi$ conjugated polymers show remarkable selectivity and sensitivity towards Hg<sup>2+</sup> ion as *turn-off* fluorescent probes as a result of *molecular wire* effect, without interference by other competing metal ions. The detailed photophysical and sensing studies have been demonstrated to understand the insight of polymer-metal ion interaction which is responsible for selective fluorescence quenching of the  $\pi$ -conjugated polymers. DFT studies have been performed to gain the insight of the electronic properties of the sensor by determining the frontier molecular orbitals and the HOMO-LUMO energy levels for a model probe (M1). The polymeric probes (P1 and P2) are reversible in nature, and can also act as secondary sensors for  $S^{2-}$ . The limit of detection of the polymer probes towards  $Hg^{2+}$  is found to be in the range of 40-50 ppb with high association constant in the order of  $10^5 \text{ M}^{-1}$  suggesting its high applicability as chemosensor for  $Hg^{2+}$ . The polymers have also been explored as thin film polymeric sensor towards  $Hg^{2+}$  to demonstrate its practical utility.

#### Introduction

In the recent years, the development of chemosensors for the recognition of biologically and environmentally concerned toxic metal ions, especially  $Hg^{2+}$ , has attracted considerable research interest, due to its detrimental effects on the human health and natural ecosystem [1]. Mercury contaminations are originated from both natural and anthropogenic activities such as volcanic eructation, mining waste, leather tanning and from several industrial products such as battery, painting, electrical equipments [2]. Marine aquatic organisms convert inorganic mercury into neurotoxin methyl-mercury, that bioaccumulates through the food chain in the tissues of fish and marine mammals. The results lead to a severe human health problems such as brain damage, kidney failure, Minamata disease, Hunter-Russell syndrome, damaging to the central nervous system, various cognitive and motion disorders [3]. United States Environmental Protection Agency (EPA) fixes the upper limit of  $Hg^{2+}$  in drinking water as 10 nM (2 ppb) [4]. In this context, the environmental contamination resulting from mercury ion is alarming attention throughout the world. Therefore, it is necessary to build up convenient and straightforward sensors for rapid, sensitive, and versatile detection of mercury ion with no interference.

Various research groups have developed different analytical methods for the detection of toxic analytes, such as atomic absorption spectroscopy [5], cold vapour atomic fluorescence spectroscopy [6], gas chromatography [7], inductively coupled plasma mass spectroscopy [8], neutron activation analysis [9], and electrochemical [10] with good sensitivities and selectivities. However, each approach has some drawbacks due to bulky instrumentation, operational inconvenience, analysis cost and test speed of detection limiting their applications. In the recent years, design and construction of novel and simple fluorescent and colorimetric chemosensors for selective detection of environmentally toxic heavy metal ions including Hg<sup>2+</sup> have paid much more attention due to their quick response to the analyte, operational simplicity, high sensitivity and selectivity, cost-effectiveness and synthetic ease [11]. Therefore, the interest in developing simple and highly sensitive optical fluorescent chemosensors with *turn-off* or *turn-on* fluorescent strategy for specific recognition of a heavy toxic analyte has grown steadily for chemical, biological, and medical applications.

For the detection of toxic  $Hg^{2+}$  a number of chemosensors have been developed by various groups. Most of the fluorescent chemosensors for  $Hg^{2+}$  are based on small molecules,

such as cationic porphyrin core [12], BODIPY based [13], Rhodamine B [14], coumarin [15], pyrene core [16], cyclodextrin based probes [17], DNA-functionalized probes [18], functionalized calixarene [19], fluorescein [20], aza-oxacrown and cryptand derivatives [21]. However, compared to the small molecular organic chemosensor,  $\pi$ -conjugated polymers based optical chemosensors possesses several important advantages. The high sensitivity of the  $\pi$ conjugated polymers originates from the sensory signal amplification which attributed to energy migration along the  $\pi$ -conjugated polymer backbone upon light excitations as a result of *molecular wire* effect as demonstrated by the pioneering work by Swagar [22]. In the recent years, a number of polymer based probes for the recognition of metal ions have been developed by various research groups [23]. In the recent past, significant efforts have been focused on the design and construction of conjugated polymer based sensory materials with appropriate receptors unit to detect the toxic mercury metal ions [24]. However, there are few reports for sensing toxic Hg<sup>2+</sup> by  $\pi$ -conjugated polymer based sensor as efficient "*turn-off*" fluorescence strategy with high selectivity and sensitivity [25].

Herein, we report design and synthetic protocol of highly soluble and emissive poly(benzodithieno-imidazole-*alt*-carbazole)  $\pi$ -conjugated copolymers through Pd(0)-catalyzed Suzuki coupling polymerization. The copolymer probes having nitrogen and sulphur donor atoms act as appropriate chelating sites for selective sensing of Hg<sup>2+</sup> ions. For solubilizing in common organic solvents and in semi-aqueous media, heptyl 2-(2-(2or methoxyethoxy)ethoxy)ethyl side groups have been introduced respectively to benzodithienoimidazole and carbazole skeleton. The corresponding polymers have been investigated for sensory applications towards  $Hg^{2+}$  as a thin-film polymeric sensor.

#### **Results and discussion**

#### Synthesis and characterization

A good and appropriate chelating or a binding site attached to  $\pi$ -conjugated polymer backbone is essential to be a selective and efficient fluorescent chemosensor for toxic metal ions. The favorable binding-site improves the binding constant and as well as enhancing the fluorescence response towards the targeted toxic metal ions. For this reason, the benzodithienoimidazole based ligand containing nitrogen and sulphur donors are unique choice in designing probe for Hg<sup>2+</sup> [23 k,l]. Alkylation to rigid-rod  $\pi$ -conjugated polymer is essential to improve the solubility and solution processability of the synthesized polymer. Accordingly, in this work we have designed the monomers in such a way that one building block (known as binding domain) bears a suitable chelating-site for  $Hg^{2+}$  binding. It is well known that soft  $Hg^{2+}$  ions (soft acid) can preferentially interact with sulphur or nitrogen (of N-heterocyclic aromatic ring) donor atoms. The other block (signaling domain) of 9-Heptyl-9H-carbazole having  $\pi$ -conjugated delocalized backbone with alkyl substituent enhance the emission and sensing signal through *molecular wire* effect [22] and as well as solubility.

The diboronic ester functionalized carbazole monomers (4 and 5) with heptyl and TEGME groups, for Suzuki polymerization were obtained by borylation of 3,6-dibromo-9- alkyl-9H-carbazole on treatment with n-BuLi followed by addition of 2-isopropoxy-4,4,5,5tetramethyl-1,3,2- dioxaborolane (iPrO-Bpin) in dry THF at -78 °C as depicted in scheme 1 [26]. The characterization and purity of the monomers (2, 3, 4 and 5) were determined by multinuclear NMR and mass spectrometry analysis (ESI). Analytically pure 8 and 9 substituted with heptyl (8) and 2-(2-(2- methoxy)ethoxy)ethoxy)ethyl (TEGME) (9) were synthesized (scheme 1) with 50-60% yield following our previously reported work [27]. In <sup>1</sup>H NMR, the four thienyl protons in 8 and 9 resonate as multiplets in the range of 8.03-7.78 and 7.86-7.77 ppm respectively. The four benzene protons resonate as doublet at 7.65 and 7.57 ppm. The triplet signal centered at 4.60 ppm is attributed to the  $-CH_2$ - protons, attached to nitrogen of the imidazole moiety. For the compound 9, the TEGME protons resonate in the range of 4.73 to 3.31 ppm. The characteristic signal at 113.3 ppm in <sup>13</sup>C{<sup>1</sup>H} NMR, and the band centred at 2221 cm<sup>-1</sup> in FTIR spectrum confirm the presence of -CN group. Formation of compounds 8 and 9 was further confirmed by HRMS study showing the molecular ion peak at 430.1414 and 478.1232 respectively. The bromination of 8 and 9 using N-bromosuccinamide yielded the dibromo derivative, 10 and 11 as depicted in scheme 1. Analytically pure 10 and 11 were obtained through chromatographic purification (silica 60-120) using ethylaceate:hexane (20-30%) as an eluent with 85-90 % yield. The thienyl protons resonate as singlet at 7.74 and 7.67 ppm for **10** and 7.73 and 7.68 ppm for **11** respectively in <sup>1</sup>H NMR. The  $-CH_2$ - group of the heptyl attached to nitrogen resonates as triplet centered at 4.41 ppm, whereas the  $-CH_2$ - group of TEGME group attached to nitrogen of 11 appears as triplet at 4.62 ppm. MALDI-TOF study shows the molecular ion peaks at 588.581 and 635.785 for 10 and 11 respectively.



Scheme 1. Synthetic route for the monomers 4-5 and 10-11.



Scheme 2. Synthesis of polymers (P1 and P2), and the model compound (M1).

To access the corresponding polymer, poly(benzodithienoimidazole-*alt*-carbazole) (**P1**) bearing heptyl groups, polycondensation of analytically pure monomers **4** and **10** was carried out in degassed THF using aqueous potassium carbonate as a base and  $Pd(PPh_3)_4$  as a catalyst following Suzuki coupling polymerization protocol as demonstrated in scheme 2. The

polymerization reaction was furnished under refluxing condition with vigorous stirring for 48 h under inert atmosphere. The polymer **P2**, substituted with TEGME unit to the 9-position of carbazole was also synthesized by following the similar strategy from the corresponding monomer **5** and **11**. Quenching of polymerization by adding few drops of methanol followed by precipitation from its concentrated THF solution in ice-cold methanol yielded both the crude polymers (**P1** and **P2**). The polymers **P1** and **P2** were further purified through Soxhlet extractor by using hexanes, followed by MeOH to remove the oligomers and catalyst residue and finally with distilled CHCl<sub>3</sub>. The CHCl<sub>3</sub> part was collected and evaporated to get the dark-brown powder of polymer **P1** and **P2**. The synthesized polymers bearing long heptyl or TEGME groups as side chain are readily soluble in common organic solvents (such as toluene, THF, and chlorinated solvents) and exhibit strong greenish blue to cyan fluorescence emission in solution. Interestingly, both the synthesized poly(benzodithieno-imidazole-*alt*-carbazole copolymers exhibit appreciable amount of fluorescence even in solid state (as thin film).



**Fig. 1.** Tetradetector GPC trace (refractive index response) of the synthesized polymers (**P1** and **P2**) using THF as eluent.

The synthesized luminescent  $\pi$ -conjugated polymers were characterized by multinuclear NMR, FTIR and tetradetector Gel Permeation Chromatography (GPC). <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of polymer **P1** exhibits two multiplets in the region of 7.84-7.77 and 7.73-7.60 ppm, attributed the six aromatic protons of the carbazole unit. The signal at 7.58-7.45 and 7.41- 7.29 ppm as multiplet are assigned to the aromatic protons of thienyl and phenyl group respectively. The *-CH*<sub>2</sub> protons of the heptyl groups attached to 9-position of carbazole and benzodithieno-imidazole groups resonate at 4.44-4.15 ppm as multiplet. The remaining alkyl protons resonate in

the region of 1.89 to 0.87 ppm. In  ${}^{13}C{}^{1}H$  NMR spectrum, the aromatic carbon of **P1** resonates in the region of 134.7 to 118.2 ppm, whereas the -CN carbons resonate at 113.2 ppm. The heptyl carbons appear in the region of 46.5 to 13.9 ppm. Similarly, polymer P2 shows multiplets at the region of 8.14-8.08 and 7.84-7.81 ppm ascribing to the carbazole protons, whereas the aromatic protons of thienyl and benzyl unit resonates as multiplets in the region of 7.80-7.745 and 7.69-7.45 ppm. The TEGME protons resonate in the region of 4.61 to 3.30 ppm. In  ${}^{13}C{}^{1}H$ NMR spectrum, the signal in the range of 151.3 to 118.7 ppm attribute the aromatic carbons of the polymer P2, whereas the carbons of the TEGME unit resonates in the region of 71.8 to 46.3 ppm. In FTIR spectra, the signal at 2228  $\text{cm}^{-1}$  attributes the presence of -CN group in the polymer (P1 and P2). The formation of the polymers was further confirmed by tetradetector Gel Permeation Chromatography (in THF with polystyrene standards) as shown in Fig. 1. The number-average molecular weights  $(M_n)$  of the well-defined  $\pi$ -conjugated polymers (P1 and P2) are 16.5 and 14.3 kDa with the very good polydispersity indices of 1.36 and 1.31 respectively (Table 1) [28]. The lower M<sub>n</sub> can be attributed to the introduction of bulky monomers with long chain alkyl groups during polymerization. The molecular weight of the synthesized  $\pi$ -conjugated copolymers (P1 and P2) is high enough to demonstrate efficient sensing properties. The thermal property of the polymer was also investigated by thermogravimetric analysis (TGA) in a nitrogen atmosphere at heating rate of 10 °C/min to 700 °C, revealing only 5% weight loss at relatively higher temperature of 356 and 305 °C, for P1 and P2 respectively (Fig. S51). A model monomeric probe (M1) has also been synthesized and characterized to establish the coordination and mechanistic studies of  $Hg^{2+}$  sensing (*vide infra*).

Table 1 Characterization data for P1 and P2							
	M <sub>n</sub> (kDa)	$M_w(kDa)^a$	PDI <sup>a</sup>	$T_d^{c} (^{o}C)^{b}$			
P1	16.5	22.4	1.36	356 °C			
P2	14.3	18.7	1.31	305 °C			

<sup>a</sup> obtained from GPC, <sup>b</sup>from TGA studies.

#### **Photophysical study**

Excellent solubility of the synthesized polymers allowed us to evaluate the photophysical properties with UV-vis and fluorescence spectra. The photophysical properties of the synthesized  $\pi$ -conjugated copolymers **P1** and **P2** were conducted in THF in 2 × 10<sup>-5</sup> M concentration as

depicted in Fig. 2. In solution (THF), polymer P1 exhibited absorption maxima at 305 and 361 nm while the polymer **P2** showed similar absorption at  $\lambda_{max}$  of 297 and 356 nm with  $\varepsilon$  values in the range of 2.02  $\times$  10<sup>4</sup> -2.12  $\times$  10<sup>4</sup> M<sup>-1</sup>cm<sup>-1</sup>, which were attributed to the  $\pi$ - $\pi$ \* electronic transition of the  $\pi$ -conjugated polymer backbone. The relatively high energy absorption at  $\lambda_{max}$  of 241 and 237 nm was assigned as  $\pi$ - $\pi$ \* transition for the appended benzonitrile substituent. The  $\pi$ conjugated polymers (P1 and P2) exhibited strong cyan to blue emission centered at 499 nm ( $\lambda_{ex}$ = 361 nm) and 494 nm ( $\lambda_{ex}$ = 356 nm) for **P1** and **P2** respectively. The photoluminiscent quantum yields ( $\Phi$ ) of the polymers are in the range of 22 - 21% in THF as measured by relative method with quinine sulphate (in 0.1 M sulphuric acid) as reference [29]. The absorption and emission properties of the model compound (M1) are very much similar to those of P1 suggesting that the lowest singlet excited state and the  $\pi$ -electron delocalization are almost confined to a single repeating unit in the polymer backbone. The small bathochromic shift in  $\lambda_{em}$  by varying the solvent polarity suggests that the ICT fluorescence is not dominant in these systems (Table S1 and Fig. S62. In thin film (made by spin coating on quartz substrate), the absorption maxima of the polymer P1 and P2 were observed at 365 nm and 361 nm. More interestingly, both the polymers are highly emissive in green to blue spectral region even as thin film showing  $\lambda_{em}$  at 527 nm and 535 nm respectively with a Stoke's shift of 7660 and 7846 cm<sup>-1</sup> respectively. In the solid state (as film) photophysical studies, a red shift by ca. 5 nm (in absorption spectra) and 30-40 nm (in PL spectra), relative to that in solution state, was observed presumably due to the enlarged  $\pi$ -conjugation of the polymer backbone in solid state. The relevant photophysical data of the polymers are tabulated in Table 2.



Fig. 2. (a) Solution state UV-vis and PL spectra for the polymers P1 and P2 in THF with a concentration of  $\sim 10^{-5}$  M (b) Solid state UV-vis and PL spectra for the films (spin coated on quartz plate from CHCl<sub>3</sub> solution of polymers) of the polymers P1 and P2 at 28 °C.

	Absorbance (nm)	Emission (nm)		S	Stoke's shift (cm <sup>-1</sup> )		
Polymer	Solution	Solid	Solution	l	Solid	Solution	Solid
	$\lambda_{max}$ ( $\epsilon x 10^4$ in	$\lambda_{max}$	$\lambda_{em}$	$\Phi$ (%) <sup>a</sup>	$\lambda_{em}$	6	
	$M^{-1}cm^{-1}$ )						
P1	361 (2.09), 305	365,	499	22	527	7660	8272
	(2.12), 241 (3.15)	309, 247					
					()		
P2	356 (2.02), 297	361,	494	21	535	7846	9009
	(2.09), 237 (3.13)	306, 257			$\mathbf{Q}$		
			/	$\sim$			
M1	356 (2.01), 303 (2.10),	363, 303, 256	494	18	-	7660	-
	236 (2.95)						

Table 2 Photophysical data of the polymers (P1, P2) and the model compound (M1).

<sup>a</sup>Measured by relative method with quinine sulphate (in 0.1 M sulphuric acid) as the reference ( $\Phi = 0.54$ ).

To estimate the HOMO and LUMO of the polymers, the cyclic voltammetric experiments of the synthesized  $\pi$ - conjugated polymers were conducted (Fig. S72). For this purpose, films of the polymers were prepared by drop casting the corresponding DCM solution on GC-disc electrode. The measurement was carried out in CH<sub>3</sub>CN solution using n-Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) as supporting electrolytes, Pt wire counter electrode and Ag/AgCl reference electrode. The electrochemical data are summarized in Table 3. HOMO energy levels of **P1** and **P2** are calculated as -4.92 and -5.02 eV respectively from the onset oxidation potentials considering the known reference level for ferrocene (4.80 eV below the vacuum level) according to the equation;  $E_{HOMO}$  (eV) = [ $E_{onset} - E_{ox(ferrocene)}$ ] - 4.80 [30]. We have calculated the  $E_{LUMO}$  levels from the E<sub>HOMO</sub> levels and its optical band gaps ( $E_g^{opt}$ ) using the relation,  $E_{LUMO} = E_{HOMO} + E_g^{opt}$  [31]. The optical energy band gap ( $E_g^{opt}$ ) of the polymer probes was calculated by examining the edge of the solid state absorption spectra by using the equation  $E_g^{opt}(eV) = 1240/\lambda_{cutoff}$ . The optical energy bandgap was found to be 2.54 and 2.55 eV for **P1** and **P2** respectively.

Polymer	E <sub>ox</sub> , V	E <sub>HOMO</sub> ,(eV) <sup>a</sup>	$E_{LUMO}, (eV)^{b}$	$E_g^{opt}(eV)^c$
P1	0.63	-4.92	-2.38	2.54
P2	0.73	-5.02	-2.47	2.55
M1	0.67	-4.96	-2.38	2.58

**Table 3** Electrochemical data and HOMO and LUMO energy levels of**P1** and **P2.** 

<sup>a</sup>From the onset of the oxidation potential, and using the equation,  $E_{HOMO}$  (eV) = [ $E_{onset} - E_{ox(ferrocene)}$ ] - 4.80. <sup>b</sup>( $E_{LUMO} = E_{HOMO} + E_{g}^{opt}$ ). <sup>c</sup> $E_{g}^{opt}$  from solid state absorption spectra.

### Selective recognition to Hg<sup>2+</sup>

The excellent emissive nature of the polymer **P1** and **P2** having dithieno-imidazole binding sites encouraged us to explore their potential application as a fluorescence chemosensor for the selective detection of toxic metal ions. To explore the potential application, the absorbance and fluorescence responses of the highly emissive probes **P1** and **P2** were investigated in 1:1 and 2:3 THF-H<sub>2</sub>O respectively in  $5 \times 10^{-5}$  M concentrations. The photophysical responses of **P1** and **P2** are similar to that in  $5 \times 10^{-5}$  M THF solution.



**Fig. 3** (a) Change in PL response of **P1** towards various metal ions (1 eqv.). (b) Selectivity profile; Blue solid bars: Free sensor or treated with metal ions; Red solid patterned bars: Treated with competing metal ions followed by 1 eqv. of  $Hg^{2+}$ ; 1–15 represent 1) **P1** 2) Na<sup>+</sup> 3) K<sup>+</sup> 4) Mg<sup>2+</sup> 5) Ca<sup>2+</sup> 6) Cd<sup>2+</sup> 7) Co<sup>2+</sup> 8) Cr<sup>3+</sup> 9) Ni<sup>2+</sup> 10) Pb<sup>2+</sup> 11) Cu<sup>2+</sup> 12) Hg<sup>2+</sup> 13) Zn<sup>2+</sup> 14) Fe<sup>3+</sup> 15) Ag<sup>+</sup> 16) Ba<sup>2+</sup> 17) Sr<sup>2+</sup> 18) Al<sup>3+</sup> 19) all. For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

The high stability and the electron rich  $\pi$ -conjugated network of the synthesized polymers make a supreme candidate for sensing of toxic metal ion through the fluorescence quenching

taking advantage of *molecular wire* effect of the  $\pi$ -conjugated polymers. To determine the optimum concentration in which self-aggregation of both the  $\pi$ -conjugated polymeric probes through  $\pi$ - $\pi$  stacking is minimal, we have recorded concentration dependent emission spectra as well as dynamic light scattering (DLS) studies. With increasing concentration from  $10^{-5}$  to  $10^{-3}$ M in THF the emission intensity of P1 and P2 decreased significantly (Fig. S52). The emission intensity of the probes also decreased when the solution was diluted to 10<sup>-6</sup> M. DLS studies of the probes were carried out by varying the concentration, ranging from  $10^{-3}$  to  $10^{-5}$  M (Fig. S53). The average aggregate size  $(D_H)$  of 30-50 nm for both the probes confirmed the negligible selfaggregation and the presence of mainly unimers of the polymeric probes in relatively dilute solution of ca.  $10^{-5}$  M in THF. Henceforth, the sensing application was explored in  $10^{-5}$  M concentration to avoid the self-association behavior of the probes. The metal ion recognition study through the absorbance and fluorescence response was investigated qualitatively by treating the polymer probes in THF:H<sub>2</sub>O with various biologically and environmentally relevant metal ions including alkali metal ions (K<sup>+</sup>, Na<sup>+</sup>), alkaline-earth metal ions (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>), and heavy/transition metal ions (such as Cu<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Ag<sup>+</sup>, Co<sup>2+</sup>, Fe<sup>3+</sup>, and  $Cr^{3+}$ ). Upon addition of these metal ions to the polymer probe P1, absorption band remain unperturbed or no significant change in the absorption intensity was noticed. Similar result was obtained for TEGME functionalized probe P2. However, upon treatment with one equivalent of Hg<sup>2+</sup> per benzodithienoimidazole unit, a remarkable *turn-off* fluorescence response for both the polymer probes was observed. The investigation clearly shows that the polymers P1 and P2 exhibit excellent fluorescent probes for detection of  $Hg^{2+}$ . By contrast, other metal ions only caused marginally fluorescence discrepancies in contrast to  $Hg^{2+}$ , establishing an efficient sensor for  $Hg^{2+}$  ion as illustrated in Fig. 3a. Both the polymers **P1** and **P2** exhibited partial quenching (ca. 10%) upon addition of  $Cu^{2+}$ , however change in fluorescence intensity was indistinguishable by naked eye (ESI). The essential criterion for a selective sensing probe is the ability to sense the particular metal ion in the vicinity of other competing metal ions. The synthesized  $\pi$ -conjugated polymers (P1 and P2) exhibited fluorescence quenching by  $Hg^{2+}$ , which was remained intact in the presence of other competing metal ions and even in more complex mixtures. This observation accomplishes the criterion for an efficient selective probe towards  $Hg^{2+}$  as portrayed in Fig. 3b. Moreover, the fluorescence responses to different mercury (II) salts with various counter anions (such as NO<sub>3</sub>, OAc<sup>-</sup>, S<sup>2</sup>, ClO<sub>4</sub>, SCN<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Br<sup>-</sup>, I<sup>-</sup> and Cl<sup>-</sup>) were also

investigated to ensure the anion-independent '*turn-off*' response (Fig. S59). Thus, it can be established that both the polymer sensors unveiled excellent selectivity towards different  $Hg^{2+}$  salts irrespective of counter ions and in the vicinity of the other competing metal ions.



**Fig. 4.** (a) Fluorescence titration of **P1** upon incremental addition of  $Hg^{2+}$  metal ion with visual change in fluorescence (b) Job's plot of **M1**: $Hg^{2+}$  complexes in 1:1 THF: $H_2O$  medium.

To obtain an insight into the sensing mechanism in depth and to find the binding stoichiometry of the probe with  $Hg^{2+}$ , spectroscopic titration was accompanied with a continuous variation of concentrations of metal ion  $(Hg^{2+})$ . Upon addition of increasing equivalents of  $Hg^{2+}$ , the corresponding emission spectrum showed a gradual decrease in intensity as illustrated in Fig. 4a, and at a higher concentration (2 x  $10^4$  M) of Hg<sup>2+</sup> the fluorescence was completely quenched, which could be presumed to the complete formation of benzodithieno-imidazolebounded  $Hg^{2+}$ -metallopolymer. The selective quenching of the probe (**P1** and **P2**) towards  $Hg^{2+}$ is easily visualized by naked eyes. Interestingly, after addition of one equivalent of  $Hg^{2+}$  per benzodithieno-imidazole unit to the polymer solution leads to almost complete quenching (98.6% for P1 and 98.1% for P2) of fluorescence and the emission intensity almost retained intact after addition of excess equivalent of Hg<sup>2+</sup> presumably due to the unavailability of the vacant coordination sites in the polymer backbone. The fluorescence intensity at 527 and 535  $nm(\lambda_{em})$  of the probe towards Hg<sup>2+</sup> remained unperturbed in the pH range of 5.4–8.5 and 5.6–8.7 for P1 and P2 respectively, establishing the sensing capability in the physiological condition (Fig. S60-S61). The stoichiometric ratio of benzodithieno-imidazole:Hg (II) in P1-Hg<sup>2+</sup>metallopolymer formed through coordination of Hg<sup>2+</sup> to the benzodithieno-imidazole units was estimated to be 0.88 from the saturation behavior of emission spectra, suggesting a 1:1 benzodithieno-imidazole:Hg<sup>2+</sup>-coordination behavior. To further prove the 1:1 coordination, the model monomeric probe (M1) has been treated with  $Hg^{2+}$  in a similar set of condition as performed sensory studies for the polymers. Job's plot indicated the 1:1 M1:Hg<sup>2+</sup> stoichiometry as depicted in Fig. 4b.

The coordination of Hg<sup>2+</sup> to the chelating sites of the probe was investigated by IR spectra and <sup>1</sup>H NMR titration for the model compound (M1). Probably the soft and borderline binding sites having sulphur and nitrogen donor atoms can interact preferentially to the soft Hg<sup>2+</sup>. In the probe, three recognition sites are available for Hg<sup>2+</sup> binding, *i.e.* "S,N-R", "-C $\equiv$ N" and "N,S". The probability of the binding in the "S, N-R" site was ruled out by considering the steric hindrance of the heptyl substituent. In the IR spectral titration, the stretching frequency of "-C=N" group at 2221 cm<sup>-1</sup> remains intact even after the addition of 1.5 equivalent of Hg<sup>2+</sup> metal ion. Hence, the  $Hg^{2+}$  recognition towards the -C=N site was further excluded the possibility of coordination. Therefore, the  $Hg^{2+}$  ion presumably coordinate with the "N,S" coordinating site. The stretching vibration band for C=N (imidazole ring) appeared at 1605 and 1468 cm<sup>-1</sup>, which were gradually shifted to lower energy region upon addition of Hg<sup>2+</sup> ion. The C-N stretching vibration band along with the C-S bond (of dithieno unit) also shifted to lower energy region from 1235 cm<sup>-1</sup> and 800 cm<sup>-1</sup> respectively with incremental addition of Hg<sup>2+</sup> (Fig. S70) [32]. <sup>1</sup>H NMR titration also supports this presumption. As illustrated in Fig. S71, after incremental addition of  $Hg^{2+}$ , the signal for thienyl (H<sub>b</sub>) and carbazole protons (H<sub>c</sub> and H<sub>d</sub>) experienced slight downfield shift by 0.03 ppm. Thus, the results of FTIR spectral and <sup>1</sup>H NMR titration also suggest coordination of Hg<sup>2+</sup> to "N,S" chelating site of dithieno-imidazole unit with 1:1 binding stoichiometry.

To further confirm the coordination mode between the "N,S"-chelating site of **M1** and  $Hg^{2+}$ , the density function distribution analysis was carried out. The geometry of **M1** and  $[M1 \cdot Hg(NO_3)_2]$  were fully optimized by Becke's three parameter hybrid functional using the LYP correlation functional (B3LYP). The LanL2DZ basis set was employed for Hg element while the 6-31G(d,p) basis set was assigned to nonmetal elements (C, H, O, N and S) [33]. To reduce the computational time, the long alkyl groups are replaced by -CH<sub>3</sub> group. The DFT geometry optimization studies also support 1:1 coordination as presumed from fluorescence titration studies (Fig. 5a). Furthermore, the formation of 1:1 **M1**:Hg<sup>2+</sup> complex was unambiguously confirmed by MALDI-TOF analysis showing molecular ion peak, [**M1**·Hg(II)-NO<sub>3</sub>]<sup>+</sup> at 1219.847. The experimental isotopic distribution pattern for the molecular ion peak is in well agreement with the simulated one as presented in Fig. 5b.



**Fig. 5.** (a) Proposed  $\text{Hg}^{2+}$ -coordination with model sensing probe **M1** (obtained from DFT computed optimized structure). (b) Simulated and experimental isotopic distribution pattern for the molecular ion peak,  $[M1 \cdot \text{Hg}(\text{II})\text{NO}_3]^+$  obtained from MALDI-TOF mass spectrometric analysis.



**Fig. 6.** (a) Stern-Volmer plot for the quenching of **P1** by incremental amount of  $Hg^{2+}$ ; (b) The linear dynamic fluorescence response of **P1** against  $Hg^{2+}$  to determine the limit of detection (LOD).

The emission quenching process was also analyzed by the Stern-Volmer (SV) equation  $I_0/I = 1+K_{SV}[Q]$  [34], where  $I_0$  and I are the fluorescence intensities in the absence and presence of the quencher [Q] and  $K_{SV}$  is the Stern-Volmer fluorescence quenching constant. In the analysis, the relative fluorescence intensities ( $I_0/I$ ) were plotted versus the concentration of the quencher ions ( $Hg^{2+}$ ) and the rate of quenching was determined. The decrease in the fluorescence intensity with the linear SV-plot suggests for static fluorescence quenching of the probes in the presence of  $Hg^{2+}$  metal ion with  $K_{SV}$  value of  $4.75 \times 10^5$  and  $4.28 \times 10^5$  M<sup>-1</sup> for the polymers **P1** and **P2** respectively, indicating thermodynamically stable binding between  $Hg^{2+}$  and the chelating site attached to  $\pi$ -conjugated polymer. The fluorescence life time studies of both the

polymer probes also supports the static quenching phenomenon as the life time is invariant with different concentration of the metal ions (Fig. S56). It is noteworthy to mention that the limit of detection (LOD) [35] of **P1** and **P2** for  $Hg^{2+}$  (1.35 × 10<sup>-7</sup> M<sup>-1</sup> and 2.17 × 10<sup>-7</sup> M<sup>-1</sup> respectively) is sufficiently low for practical utility as fluorescent probe, as calculated from the concentration dependent fluorescence titration study shown in Fig. 6.

The plausible sensing mechanisms could be due to the chelating quenched fluorescence (CHQF) by  $Hg^{2+}$  as demonstrated elegantly by Schreckenbach's and Huang's groups [36]. The HOMO orbital is delocalized over the carbazole and benzodithieno-imidazole moiety while the LUMO is mainly distributed over the benzonitrile group. The important frontier orbitals of the free **M1** and  $Hg^{2+}$ -coordinated complexes are presented in Fig. 7 (and Fig. S76). In the coordination process, the **M1** acts as an electron pair donor, while the  $Hg^{2+}$  ion serve as a an electron pair acceptor and coordinates through the available vacant s-orbital. The vacant s-orbital of the  $Hg^{2+}$  (-3.34 eV) metal ion is in between the HOMO (-4.92 eV) and LUMO (-1.72 eV) of **M1** as evidenced from DFT studies. The data in Table 3 indicate similar situation for the polymeric probes **P1** and **P2**. Hence, the chelating quenched fluorescence (CHQF) is induced resulting radiationless decay of the excited state and thus the polymers act as efficient *turn off* probe for toxic  $Hg^{2+}$  (Fig 8 and Fig. S77) [36].



**Fig. 7.** Selected frontier molecular orbitals for **M1** and  $[M1 \cdot Hg(NO_3)_2]$ . Estimated HOMO-LUMO energy levels (eV) from DFT calculations, HOMO: -4.92, -5.66; LUMO: -1.72 and -3.34 respectively. To reduce the computational time, the heptyl group has been replaced by -CH<sub>3</sub>.



Fig. 8. Proposed sensing mechanism for the polymer probe, P1.



**Fig. 9.** (a) Change in PL intensity after incremental addition of  $S^{2-}$  to  $Hg^{2+}$ -metallopolymer in THF-H<sub>2</sub>O medium (reversibility study) (b) Cycles of emission quenching and recovery by exposing the polymer probe (as film on quartz substrate) towards  $S^{2-}$  solution demonstrating reusability.

The reversibility of a sensing probe is another important aspect in view of the reusability and cost-effectiveness of the sensing probes. Reversibility of the chemosensors was demonstrated by the addition of S<sup>2-</sup> to the Hg<sup>2+</sup>-metallopolymer complex ( $\lambda_{ex} = 361$  nm,  $\lambda_{em} =$ 499 nm). The S<sup>2-</sup> ion is well known to bind strongly with Hg<sup>2+</sup>. Incremental addition of S<sup>2-</sup> to a solution of Hg<sup>2+</sup>-metallopolymer showed the opposite trend in the fluorescence intensity due to the formation of stable HgS complex, and subsequently regain of free probe demonstrating reversible nature of the **P1** and **P2** probes. (Fig. 9a). Furthermore, the Hg<sup>2+</sup>-metallopolymers of **P1** and **P2** can act as a secondary sensor to detect the S<sup>2-</sup>.

After the successful sensing studies in solution phase, the recognition of  $Hg^{2+}$  was also investigated for both the polymers **P1** and **P2** as thin film probe. Thin films of the probes for the solid state measurements were casted from THF solution onto quartz plates. Solid state PL studies of the polymeric films were conducted. Cycles of emission quenching and recovery by exposing the probe towards successive treatment of  $Hg^{2+}$  and  $S^{2-}$  demonstrated reusability. Most importantly, the reversible process could be repeated by several times (more than 10 times) with little loss of fluorescent efficiency (Fig. 9b).

Solid state PL studies of the  $Hg^{2+}$ -coordinated polymeric films were also conducted by immersing the polymer film into the various concentrations of  $Hg^{2+}$  aqueous solution (100µM–1µM). Fig. 10a demonstrates a significant amount of quenching of the emission centered at 527 and 535 nm for the polymer probes with a gradually decrease of emission intensity as a function of increasing concentration of  $Hg^{2+}$ . To investigate the practical and real time application of chemosensor, the excellent *turn-off* sensing behaviour of the polymer sensing probes to  $Hg^{2+}$  was

employed. In order to demonstrate the potential utility of the sensing probes towards  $Hg^{2+}$ , testpaper experiment was conducted. The test strips were prepared by immersing filter papers into a THF solution of polymer (0.1 M) and then drying in air. The test strips containing polymer probe was immersed into the aqueous solution of  $Hg^{2+}$  by varying different concentration ( $10^{-4} - 10^{-7}$ M) and the obvious change from green emission to dark green could be detected by naked eye (under 365 nm UV lamp) as shown in Fig. 10b. Similar response was observed for polymer **P2** in the similar set of experimental conditions (Fig. S69). This result demonstrates that **P1** and **P2** are excellent chemosensors for the immediate visual detection of  $Hg^{2+}$  in solution and as test paper strip.



**Fig. 10.** (a) Emission quenching of polymer **P1** by micromolar aqueous solution of  $Hg^{2+}$  metal ion demonstrating trace detection. (b) Change on **P1** test paper strips after treating with different samples of  $Hg^{2+}$  varying concentration ( $10^{-4}-10^{-7}$  M<sup>-1</sup>), under 365 nm light.



**Fig. 11.** FESEM images and EDX line trace analysis of **P1** (left) and after treatment with  $Hg^{2+}$  (right) revealing binding of  $Hg^{2+}$  to polymers.



**Fig. 12.** Bright-field TEM micrographs of (a) monodisperse spherical self-assembled structures of **P1** formed in 45% (v/v) MeOH/THF (b) ribbon like self-assembly after addition of 150  $\mu$ L of Hg<sup>2+</sup> metal ion solution (as 5 x 10<sup>-5</sup> M in water). (c) STEM mapping showing the presence of Hg<sup>2+</sup> in the vicinity of S and N, further proving Hg(II) binding to N,S sites. (d) Comparison of overlaying integrated EDX point spectra. Carbon coated copper grid (300 mesh) was used for the TEM.

The scanning electron microscope image analysis of the polymer probe films (prepared by drop casting of 5 x  $10^{-4}$  M chloroform solution on aluminium substrate) were performed to observe the change in surface morphology of the polymers before and after coordination of Hg<sup>2+</sup>. Typical FESEM images of the morphology are shown in Fig. 11. Line EDX analysis of the film was also carried out before and after Hg<sup>2+</sup> ion coordination, which shows the presence of elemental Hg, confirming the formation of the Hg<sup>2+</sup>-coordinated metallopolymer. The TEM analysis (Fig. 12a,b) was also carried out to understand the self-assembly of the Hg<sup>2+</sup> metallopolymer complex. In order to study solution self-assembly, the polymer **P1** (1.5 mg/ml) was dissolved in dry THF, (a good solvent for the polymer) to give clear greenish-yellow solutions at room temperature (28 °C). After 2 hours, dry and filtered MeOH (passing through a syringe filter, PTFE 0.45 µm) was then added dropwise until the solution consisted of ~45% (v/v) MeOH in THF. This process was accompanied by a colour change from clear greenish-

yellow to turbid yellow coloration. Transmission electron microscopy (TEM) analysis showed the formation of sphere-like self-assembled structure with diameter in the range of 800-950 nm. Interestingly, after  $Hg^{2+}$  coordination, the sphere self-assembled structure transferred to ribbon like aggregates as monitored by TEM analysis. The STEM element mapping of an area of 284 by 284 µm with a pixel resolution of 256×256 (Fig. 12c,d) also clearly revealed the formation of  $Hg^{2+}$ -metallopolymer by showing the signal of N, S and Hg [37].

#### Conclusion

In conclusion, we have designed and synthesized well-defined soluble  $\pi$ -conjugated copolymer (P1 and P2) consisting of carbazole and bezodithieno-imidazole in alternating fashion, through Suzuki coupling polymerization. The synthesized polymers exhibit a simple, facile, low-cost and efficient chemosensor towards  $Hg^{2+}$  through fluorescence quenching responses via CHQF mechanism. Furthermore, no obvious interference was observed upon addition of various metal ions, indicating excellent selective recognition of  $Hg^{2+}$  by the polymeric probe in semi-aqueous environment. The limit of detection of the polymer probes towards  $Hg^{2+}$  was found to be in ppb level with high association constant in the order of  $10^5 \text{ M}^{-1}$ . Naked eyes can detect the distinct and rapid change in fluorescence under 365 nm light. The coordination of the Hg<sup>2+</sup> to the "N,S"-chelating site of the dithieno-imidazole unit was investigated though IR spectra and <sup>1</sup>H NMR spectroscopic titration. To gain an insight into coordination mode of Hg<sup>2+</sup> to "N,S"-chelating site, DFT geometry optimization studies was also performed. The favorable energy of LUMO of  $Hg^{2+}$ , which is in between the HOMO and LUMO of sensors, induces chelating quenched fluorescence (CHQF). Moreover, the polymers serve as a reusable and recyclable probe on successive addition of  $Hg^{2+}$  and  $S^{2-}$ . The paper strip test study was also inspected, to demonstrate its practical utility as convenient and efficient  $Hg^{2+}$  test kit. This work clearly reveals a novel platform to further develop easily processable  $\pi$ -conjugated fluorescent polymer based simple, selective, highly sensitive, low cost and reversible probes by judicious design of coordination site for sensing not only metal ions but also different environmental and biological relevant analytes.

#### **Materials and Instrumentation**

All the air and moisture sensitive reactions and manipulations were carried out under an atmosphere of pre-purified N2 or Ar by using standard Schlenk techniques. The glassware were

oven-dried (at 180 °C) and cooled under vacuum. Tetrahydrofuran and diethyl ether were dried over Na/benzophenone. All chemicals were purchased from Sigma Aldrich unless otherwise noted. Silica gel (60–120 and 100–200 mesh) used for column chromatography, was purchased from Merck. Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and Pd(PPh<sub>3</sub>)<sub>4</sub> were synthesized following the literature method [38].

1H (600 MHz and 400 MHz), 13C{1H} (150 MHz and 100 MHz) NMR spectra were obtained from Bruker Lambda spectrometer using CDCl3 unless otherwise mentioned. Spectra were internally referenced to residual solvent peaks ( $\delta = 7.26$  ppm for proton and  $\delta = 77.23$  for carbon (middle peak) in CDCl3). All coupling constants (J) are given in Hz. The HRMS was recorded in ESI+ mode (70 eV) in Waters mass spectrometer (Model: Xevo-G2QTOF). The absorption and fluorescence spectra were collected using a Shimadzu (Model UV-2450) spectrophotometer and a Hitachi (Model F-7000) spectrofluorimeter, respectively. FTIR spectroscopy was recorded in Spectrum-BX (Perkin Elmer). Solid state PL spectra were recorded in Flurolog Horiba (Model FL-1016, Spectracq). MALDI-TOF study was performed by using Bruker MALDI- TOFUltrafleXtreme instrument. TEM and EDX-STEM analysis of polymer were carried out by JEOL JEM2100F (Japan) Transmittance Electron Microscope with JEOL EDS detector. Scanning Electron Microscope (SEM) analysis was carried out with ZEISS MERLIN (GEMINI2) FESEM with Oxford EDS detector. Thermogravimetric analysis (TGA) was carried out using Perkin Elmer Pyris Diamond TG/DTA instrument. The thermal stabilities of the samples under nitrogen were determined by measuring their weight losses while heating at a rate of 5 °C/min. Molecular weights and polydispersity indices (PDI =  $M_w/M_n$ ) of polymers were obtained by Gel Permeation Chromatography (GPC) using a Viscotek VE 2001 Triple-Detector Gel Permeation Chromatograph equipped with automatic sampler, pump, injector, inline degasser, column oven (30 °C), styrene/divinylbenzene columns with pore sizes of 500 Å and 100,000 Å, VE 3580 refractometer, four-capillary differential viscometer and 90° angle laser and low angle laser (7°) light scattering detector (VE 3210 & VE270). HPLC grade THF was used as the chromatography eluent, at a flow rate of 1.0 mL/min. Samples were dissolved in the eluent (1 mg/ mL) and filtered with a Ministart SRP 15 filter (polytetrafluoroethylenemembrane of 0.2µm pore size) before analysis. Calibration of all three detectors (refractive index, laser light scattering and viscometry) was performed using polystyrene standards (Viscotek). This equipment allows the absolute measurement of homopolymer molecular weights and PDIs. Cyclic voltammetric studies were performed on a BASi Epsilon electrochemical workstation in acetonitrile with 0.1 M tetra-*n*-butylammonium-hexafluorophosphate (TBAPF6) as the supporting electrolyte at room temperature. The working electrode was a BASi Pt disc electrode, the reference electrode was Ag/AgCl and the auxiliary electrode was a Pt wire. The ferrocene/ferrocenium couple occurs at E1/2 = +0.51(70) V versus Ag/AgCl under the same experimental conditions. The dynamic light scattering (DLS) was carried out using Malvern Zeta sizer Nano series equipped with a laser with wavelength of 633 nm and a detector oriented at 173° to the incident radiation.

#### **Experimental**

3,6-Dibromo-9-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-9H-carbazole (3): To a solution of di-bromo-9H-carbazole (1) (1 g, 3.07 mmol), in anhydrous DMF (15 ml), NaH (160 mg, 4 mmol) and 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane (840 mg, 3.7 mmol) were added. The reaction mixture was stirred at 90 °C for 24 h. After consumption of carbazole substrate (the reaction was monitored by TLC, n-hexane: ethyl acetate was used as the eluent) the reaction mixture was poured into water (200 ml), extracted with ethyl acetate (3  $\times$  50 ml) and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed under diminished pressure and the residue was purified by column chromatography eluting with *n*-hexane: ethyl acetate (1:4) to afford colourless liquid with 70% yield (1.01 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.12 (s, 2H, carbazolyl), 7.54 (d, 2H, J = 8 Hz, carbazolyl), 7.34 (d, 2H, J = 8 Hz, carbazolyl), 4.43 (t, 2H, J = 2 Hz, -NCH<sub>2</sub>-), 3.83 (t, J = 2 Hz, -NCH<sub>2</sub>CH<sub>2</sub>-O-), 3.50-3.40 (m, 8H), 3.34 (s, 3H, -OCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 139.4, 128.9, 123.3, 122.3, 112.0 (carbazolyl carbon attached to bromine), 110.7 (carbazolyl carbon attached to bromine), 71.8 (alkyl carbon attached to N), 70.9, 70.5, 70.1, 69.3, 58.9, 43.4 (-OCH<sub>3</sub>). MALDI-TOF (m/z):  $C_{19}H_{21}Br_2NO_3$ , calculated value 471.986 (M)<sup>+</sup>, found 471.521 (M)<sup>+</sup>.

**9-heptyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole(4)**: A solution of *n*-BuLi (1.6 M in hexanes, 9.3 mL, 14.8 mmol) was added dropwise to a solution of **2** (2.03 g, 4.8 mmol) in THF (50 mL) kept at -78 °C. The obtained mixture was vigorously stirred for 1 h at -78 °C before the addition of 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (2.85 g, 15.2 mmol) in one portion. The resulting solution was then allowed to reach room temperature and to react overnight. After removing the solvent under vacuum,  $CH_2Cl_2$  (50 mL) was added and the obtained

solution was washed with water (3 × 50 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum and the obtained crude product was purified by flash column chromatography (silica gel, petroleumether 40-60 °C /CH<sub>2</sub>Cl<sub>2</sub> ¼ 1/1 v/v) to give **3** (1.7 g, 68 %) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.67 (s, 2H, carbazolyl), 7.90 (d, 2H, *J* = 8 Hz, carbazolyl), 7.39 (d, 2H, *J* = 8 Hz, carbazolyl), 4.30 (t, 2H, *J* = 2 Hz, -NC<u>H</u><sub>2</sub>-), 1.88-1.83 (m, 2H, -NCH<sub>2</sub>C<u>H</u><sub>2</sub>-), 1.41-1.37 (m, 32H), 0.89-0.85 (m, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  142.7, 132.1, 128.0, 122.8, 108.1, 83.5, 43.0, 31.7, 29.1, 28.9, 27.2, 26.3, 25.4, 24.9, 22.6, 21.0, 14.2.

### 9-(2-(2-(2-methoxy)ethoxy)ethyl)-3,6-bis(4,4,5,5-tetramethyl-1,3,2-

dioxaborolan-2-yl)-9H-carbazole (5): A solution of n-BuLi (1.6 M in hexanes, 2.5 mL, 4.04 mmol) was added dropwise to a solution of 4 (615 mg, 1.3mmol) in THF(10 mL) kept at -78 °C. The obtained reaction mixture was vigorously stirred for 1 h at -78 °C before the addition of 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (787 mg, 4.17 mmol) in one portion. The resulting solution was then allowed to reach room temperature and to react 24 h. After removing the solvent under vacuum, CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added and the obtained solution was washed with water ( $3 \times 50$  mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum and the obtained crude product was purified by flash column chromatography (silica gel 60-120 mesh, petroleum ether 40 -60 °C /CH<sub>2</sub>Cl<sub>2</sub>1/1 v/v) to give 5 (442 mg, 60%) as a white semisolid.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.64 (s, 2H, carbazolyl), 7.89 (d, 2H, J = 8 Hz, carbazolyl), 7.45 (d, 2H, J = 8Hz, carbazolyl), 4.51 (t, 2H, J = 2 Hz, -NCH<sub>2</sub>-), 3.87 (t, 2H, J = 2 Hz, -NCH<sub>2</sub>CH<sub>2</sub>O-), 3.50-3.33 (m, 8H), 3.33 (s, 3H, -OCH<sub>3</sub>), 1.39 (s, 24H, tetra-methyldioxaboralane proton). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 142.8, 140.6, 132.2, 127.8, 125.7, 122.8, 120.3, 119.5, 108.7, 83.5, 71.8, 70.9, 70.5, 70.1, 69.2, 58.8, 43.6 (-OCH<sub>3</sub>), 24.9 (tetramethyldioxaboralane carbon).

**Synthesis of 7:** A mixture of 4-cyano-benzaldehyde (315 mg, 2.4 mmol), benzo[1,2b:4,3-b']dithiophene-4,5-quinone (484 mg, 2.2 mmol), ammonium acetate (5.5 g, 72.6 mmol) and acetic acid (20 mL) was heated to 100 °C for overnight. The green solution was cooled to room temperature, and 15 mL water was added to stir for 15 min at room temperature. The solution was filtered in a Buchner funnel. The product was washed thoroughly in water and hexane, dried and taken to the next step. General synthesis of 8 and 9: To an oven dried Schlenk, previously prepared compounds (7) (265 mg, 0.8 mmol) in DMF (30 ml) was taken,  $K_2CO_3$  (300 mg, 2.1 mmol) was added and heated to 95 °C for 3 h and then cooled to room temperature. To it 1-iodoheptane (203 mg, 0.9 mmol) or 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane (204 mg, 0.9 mmol) were added slowly. Reaction mixture was heated to 95 °C for overnight. After cooling to room temperature the reaction mixture was poured in 20 mL water. Organic phase was extracted by ethyl acetate via repeated washing in water and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed under rotary evaporation. Crude product was purified by silica gel column chromatography (Ethyl acetate:Hexane = 10:90) to give solid product (8/9) (50-60% yield).

**Compound 8**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.03-7.87 (m, 2H, thienyl), 7.86-7.77 (m, 2H, thienyl), 7.65 (d, 2H, J = 4 Hz, benzyl), 7.57 (d, 2H, J = 4 Hz, benzyl ), 4.60 (t, 2H, J = 2 Hz, -NC<u>H</u><sub>2</sub>-), 1.94-1.93 (m, 2H), 1.28-1.21 (m, 8H), 0.86-0.83 (m, 3H, -CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  149.4, 133.1, 132.5, 132.1, 130.1, 127.9, 124.6, 123.9, 122.5, 120.8, 118.3, 113.3 (-CN), 46.7 (alkyl carbon attached to N), 31.6, 31.4, 28.6, 26.4, 22.5, 14.0 (-<u>C</u>H<sub>3</sub>). HRMS-ESI<sup>+</sup> (m/z): C<sub>25</sub>H<sub>23</sub>N<sub>3</sub>S<sub>2</sub> calculated value 430.1367 (M+H)<sup>+</sup>, found 430.1414 (M+H)<sup>+</sup>. FTIR (KBr, cm<sup>-1</sup>): 2958, 2855 ( $\bar{\nu}_{C-H}$  stretching), 2226 (( $\bar{\nu}_{C=N}$  stretching), 1609, 1451 ( $\bar{\nu}_{C=N}$  imidazole stretching), 1262 ( $\bar{\nu}_{C-N}$  stretching).

**Compound 9**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.16 (m, 2H, thienyl), 7.84 (m, 4H, -Ph), 7.55 (m, 2H, thienyl), 4.73 (t, 2H, J = 2 Hz, -NCH<sub>2</sub>-), 4.05 (t, 2H, J = 2 Hz, -NCH<sub>2</sub>CH<sub>2</sub>O-), 3.51-3.38 (m, 8H), 3.31 (s, 3H, -OCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  150.9, 136.0, 135.1, 132.5, 131.1, 129.6, 127.8, 124.8, 123.7,122.7, 118.7, 113.2 (-CN), 72.0, 71.0, 70.7, 70.6, 70.1, 59.1, 46.6 (-OCH<sub>3</sub>). HRMS-ESI<sup>+</sup> (m/z): C<sub>25</sub>H<sub>23</sub>N<sub>3</sub>O<sub>3</sub>S<sub>2</sub> 478.1241 (M+H)<sup>+</sup>, found 478.1232 (M+H)<sup>+</sup>. FTIR (KBr, cm<sup>-1</sup>): 2910, 2811 ( $\bar{\nu}$ <sub>C-H</sub> stretching), 2221 (( $\bar{\nu}$ <sub>C=N</sub> stretching), 1609, 1421 ( $\bar{\nu}$ <sub>C=N</sub> imidazole stretching), 1248 ( $\bar{\nu}$ <sub>C-N</sub> stretching).

**General synthesis of 10 and 11:** Solution of **8** (812 mg, 1.7 mmol)/**9** (730 mg, 1.7 mmol) in THF (10 mL) was taken in 100 mL oven dried Schlenk RB flask. N-bromosuccinamide (676 mg, 3.8 mmol) was added portion wise in 10 min intervals with continuous stirring at room temperature. Completion of the reaction was monitored by TLC. After completion of the reaction the solvent was then removed by evaporation under reduced

pressure and the crude product was purified by silica gel column chromatography (hexane as eluent) to give a brown solid of **10/11** (85-90% yield).

**Compound 10**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.90 (d, 2H, *J* = 8 Hz, -Ph), 7.85 (d, 2H, *J* = 8 Hz, -Ph), 7.74 (s, 1H, thienyl), 7.67 (s, 1H, thienyl), 4.41 (t, 2H, *J* = 2 Hz, -NC<u>H</u><sub>2</sub>-), 1.92-1.84 (m, 2H), 1.26-1.22 (m, 8H), 0.87-0.84 (m, 3H, -CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-d<sub>6</sub>):  $\delta$  151.0, 134.5, 133.2, 131.6, 130.7, 129.6, 124.4, 127.1, 127.0, 118.8 (-CN), 112.8 (carbazolyl carbon attached to bromine), 112.2 (carbazolyl carbon attached to bromine), 31.8 (alkyl carbon attached to N), 30.7, 28.1, 25.9, 24.2, 22.3, 14.2 (-<u>C</u>H<sub>3</sub>). MALDI-TOF (m/z): C<sub>25</sub>H<sub>21</sub>Br<sub>2</sub>N<sub>3</sub>S<sub>2</sub>, calculated value 588.392 (M)<sup>+</sup>, found 588.581 (M)<sup>+</sup>. FTIR (KBr, cm<sup>-1</sup>): 2961,2851 ( $\bar{\nu}_{C-H}$  stretching), 2223 (( $\bar{\nu}_{C=N}$  stretching), 1605, 1465 ( $\bar{\nu}_{C=N}$  imidazole stretching).

**Compound 11**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.12 (d, 2H, J = 8 Hz, -Ph), 7.84 (d, 2H, J = 8 Hz, -Ph), 7.74 (s, 1H, thienyl), 7.67 (s, 1H, thienyl), 4.62 (t, 2H, J = 2 Hz, -NCH<sub>2</sub>c-), 4.01 (t, J = 2 Hz, -NCH<sub>2</sub>CH<sub>2</sub>O-), 3.51-3.40 (m, 8H), 3.32 (s, 3H, -OCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-d<sub>6</sub>):  $\delta$  151.7, 148.6, 134.3, 133.8, 132.9, 131.5, 130.7, 127.2, 127.0, 126.8, 122.2 (-CN), 112.6 (carbazolyl carbon attached to bromine), 112.2 (carbazolyl carbon attached to bromine), 71.8 (alkyl carbon attached to N), 70.4, 70.0, 69.9, 69.3, 58.3, 43.4 (-OCH<sub>3</sub>). MALDI-TOF (m/z): C<sub>25</sub>H<sub>21</sub>Br<sub>2</sub>N<sub>3</sub>O<sub>3</sub>S<sub>2</sub>, calculated value 635.390 (M)<sup>+</sup>, found 635.785 (M)<sup>+</sup>. FTIR (KBr, cm<sup>-1</sup>): 2925, 2871 ( $\bar{\nu}_{C-H}$  stretching), 2229 (( $\bar{\nu}_{C=N}$  stretching), 1608, 1474 ( $\bar{\nu}_{C=N}$  imidazole stretching), 1094, 1058, 1011 ( $\bar{\nu}_{C-O}$  stretching), 800 ( $\bar{\nu}_{C-S}$  stretching).

Synthesis of M1: Compound 14 (200 mg, 0.52 mmol) and 9 (152 mg, 0.26 mmol) were dissolved in 7 mL of distilled THF in a 100 mL Schlenk flask under argon atmosphere. The reaction flask was degassed three times by *freeze-pump-thaw* technique. In an another 100 mL Schlenk flask,  $K_2CO_3$  (0.74 g, 5.35 mmol) was dissolved in 4 mL of mili-Q water and degassed by purging Ar through a niddle for about 45 min. After that, the  $K_2CO_3$  solution was transferred to the reaction mixture through a cannula. Next,  $Pd(PPh_3)_4$  (18 mg, 0.015 mmol, 3 mol %) was added to it and the reaction mixture was heated to 65 °C for 36 h. The colour of the reaction turned to dark green during the course of the reaction. After cooling to room temperature, the solvent was concentrated to minimum volume and extracted with ethyl acetate (3 × 50 ml) and dried over anhydrous

MgSO<sub>4</sub>. The solvent was removed under diminished pressure and the residue was purified by column chromatography eluting with hexane:ethylacetater to afford brown solid with 58 % yield (280 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.48-8.40 (m, 2H, carbazolyl), 8.20-8.16 (m, 2H, carbazolyl), 7.90-7.86 (m, 10H, carbazolyl), 7.51-7.47 (m, 4H, -Ph), 7.44-7.41 (m, 2H, thienyl), 4.37-4.28 (m, 6H, -NC<u>H</u><sub>2</sub>-), 1.94-1.83 (m, 6H, -NCH<sub>2</sub>C<u>H</u><sub>2</sub>-), 1.30-1.26 (m, 24H, alkyl proton), 0.88-0.85 (m, 9H, -C<u>H</u><sub>3</sub>).<sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>): δ 150.0, 149.5, 149.1, 140.9, 139.5, 133.3, 132.5, 132.3, 130.0, 125.6, 125.123.4, 120.4, 118.9, 112.5, 109.1, 109.0, 108.8, 46.5, 43.2, 31.7, 31.5, 29.1, 29.0, 27.3, 22.6, 22.5, 22.4, 14.1, 14.0 (-CH<sub>3</sub>). MALDI-TOF (m/z): C<sub>63</sub>H<sub>65</sub>N<sub>5</sub>S<sub>2</sub>, calculated value 956.471 (M)<sup>+</sup>, found 956.481 (M)<sup>+</sup>.UV-Vis (THF):  $\lambda_{max}$  (ε, M<sup>-1</sup>cm<sup>-1</sup>): 357 nm (2.03 × 10<sup>4</sup>).

Synthesis of model complex M1·Hg<sup>2+</sup>: A clear solution of M1 (100 mg, 0.10 mmol) in 5 mL THF was taken into a 50 ml RB flask. 2 mL solution of Hg(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O in MeOH was added. The resulting mixture was stirred for 8 h. The brown coloured product was precipitated, filtered off and washed with diethyl ether three times. The brownish coloured [M1.Hg<sup>2+</sup>(NO<sub>3</sub>)<sub>2</sub>] was dried in vacuum (yield: 70%). MALDI-TOF (m/z): C<sub>63</sub>H<sub>65</sub>HgN<sub>6</sub>O<sub>3</sub>S<sub>2</sub>, calculated value 1219.426 for [M1·Hg(NO<sub>3</sub>)] <sup>+</sup>, found 1219.847. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  8.65-8.51 (m, 2H, carbazolyl), 8.30-8.22 (m, 2H, carbazolyl), 8.06-7.98 (m, 10H, carbazolyl), 7.70-7.58 (m, 4H, - Ph), 7.50-7.43 (m, 2H, thienyl), 4.52-4.40 (m, 6H, -NCH<sub>2</sub>-), 1.79-1.70 (m, 6H, -NCH<sub>2</sub>CH<sub>2</sub>-), 1.20-1.07 (m, 24H, alkyl proton), 0.80-0.75 (m, 9H, -CH<sub>3</sub>). FTIR (KBr, cm<sup>-1</sup>): 2956, 2832 ( $\bar{\nu}_{C-H}$  stretching), 2229 ( $\bar{\nu}_{C=N}$  stretching), 1608, 1470 ( $\bar{\nu}_{C=N}$  imidazole stretching), 1219 ( $\bar{\nu}_{C-N}$  stretching).

**Synthesis of P1**: Compound **3** (178 mg, 0.33 mmol) and **9** (195 mg, 0.33 mmol) were dissolved in 7 mL of distilled THF in a 100 mL Schlenk flask under argon atmosphere. The reaction flask was degassed three times by *freeze-pump-thaw* technique. In an another100 mL Schlenk flask,  $K_2CO_3$  (0.74 g, 5.35 mmol) was dissolved in 4 mL of mili-Q water and degassed by purging Ar through a niddle for about 30 min. After that, the  $K_2CO_3$  solution was transferred to the reaction mixture through a cannula. Next,  $Pd(PPh_3)_4$  (7 mg, 0.006 mmol, 2 mol%) was added to it and the reaction mixture was heated to 65 °C for 72 h. The colour of the reaction turned to dark green during the course of the reaction. After cooling to room temperature, the solvent was concentrated to minimum volume and polymer was precipitated to a stirring methanol solution. After the

complete precipitation, the methanol was removed and the brown colour polymer was washed another two times with methanol. After drying under vacuum, the polymer was purified through Soxhlet extraction using distilled hexanes, methanol and at last collected in dry and distilled chloroform. The chloroform part was evaporated to get the brown coloured polymer. The polymer was finally purified by fractional precipitation in cold distilled hexanes from a concentrated dichloromethane solution to achieve well-defined **P1**. Yield: 260 mg (71%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.84-7.77 (m, 2H, carbazolyl), 7.73-7.60 (m, 4H, carbazolyl), 7.58-7.45 (m, 2H, thienyl), 7.41-7.29 (m, 4H, -Ph), 4.44-4.15 (m, 4H, -NCH<sub>2</sub>-), 1.89-1.73 (m, 4H, -NCH<sub>2</sub>CH<sub>2</sub>-), 1.30-1.26 (m, 16H, alkyl proton), 0.91-0.87 (m, 6H, -CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 134.7, 134.3, 132.4, 131.3, 130.5, 129.9, 127.1, 125.6, 125.1, 124.1, 123.3, 121.7, 120.5, 119.2, 118., 118.0, 113.3,112.4, 109.0 46.5 (-NCH<sub>2</sub>-), 43.2 (-NCH<sub>2</sub>-), 31.7, 31.5, 1.3, 29.0, 28.5, 27.2, 26., 22.6, 22.5, 22.4, 14.0, 13.9 (-CH<sub>3</sub>). FTIR (KBr, cm<sup>-1</sup>): 2950, 2854 ( $\bar{\nu}_{C-H}$  stretching), 2228 (( $\bar{\nu}_{C=N}$  stretching), 1605, 1468 ( $\bar{\nu}_{C=N}$  imidazole stretching), 1235 ( $\bar{\nu}_{C-N}$  stretching), 800  $(\bar{\nu}_{C-S} \text{ stretching})$ . UV-Vis (THF):  $\lambda_{max}$  ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>): 361 nm (2.09 × 10<sup>4</sup>). GPC: M<sub>w</sub> = 22.4 kDa,  $M_n = 16.5$  kDa, PDI = 1.36,  $T_d = 356$  °C.

Synthesis of P2: Compound 5 (160 mg, 0.28 mmol) and 11 (179 gm, 0.28 mmol) were dissolved in 7 mL of distilled THF in a 100 mL Schlenk flask under argon atmosphere. The reaction flask was degassed three times by *freeze-pump-thaw* technique. In an another 100 mL Schlenk flask,  $K_2CO_3$  (0.74 g, 5.35 mmol) was dissolved in 4 mL of mili-Q water and degassed by purging Ar through a niddle for about 30 min. After that, the  $K_2CO_3$  solution was transferred to the reaction mixture through a cannula. Next, Pd(PPh\_3)\_4 (8 mg, 0.005 mmol, 2 mol %) was added to it and the reaction mixture was heated to 65 °C for 72 h. The colour of the reaction turned to dark green during the course of the reaction. After cooling to room temperature, the solvent was concentrated to minimum volume and polymer was precipitated to a stirring methanol solution. The polymer P2 was further purified following the procedure described for P1. Yield: 280 mg (65%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.14-8.08 (m, 2H, carbazolyl), 7.84-7.81 (m, 4H, carbazolyl), 7.80-7.745 (m, 2H, thienyl), 7.69-7.45 (m, 4H, -Ph), 4.61-4.56 (m, 4H, -NCH<sub>2</sub>-), 3.98-3.96 (m, 4H, -CH<sub>2</sub>O-), 3.56-3.40 (m, 16H,), 3.33-3.30 (m, 6H, -OCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  151.3, 151.0, 141.0, 134.9, 134.6, 132.3, 130.8,

126.9, 125.6, 125.0, 123.9, 122.9, 121.8, 118.7, 113.4, 112.3, 109.0, 108.6, 71.8(-NCH<sub>2</sub>-), 70.5, 70.4, 69.8, 69.3, 58.9, 46.3 (-CH<sub>3</sub>). FTIR (KBr, cm<sup>-1</sup>): 2960, 2842 ( $\bar{\nu}_{C-H}$  stretching), 2229 ( $\bar{\nu}_{C=N}$  stretching), 1608, 1475 ( $\bar{\nu}_{C=N}$  imidazole stretching), 1260 ( $\bar{\nu}_{C-N}$  stretching). UV-Vis (THF):  $\lambda_{max}$  ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>): 356 nm (2.02 × 10<sup>4</sup>). GPC: M<sub>w</sub> = 18.7 kDa, M<sub>n</sub> = 14.3 kDa, PDI = 1.31, T<sub>d</sub> = 305 °C.

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#### **Conflicts of interest**

There are no conflicts to declare.

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# Poly(Benzodithieno-imidazole-*alt*-carbazole) based $\pi$ -conjugated copolymers: Highly selective and sensitive *turn-off* fluorescent probes for Hg<sup>2+</sup>

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### Highlights

- Synthesis and characterization of well-defined highly soluble  $\pi$ -conjugated poly(benzodithieno-imidazole-*alt*-carbazole)  $\pi$ -conjugated fluorescent polymers.
- Highly selective and sensitive *turn-off* fluorescent probe for selective detection of heavy toxic Hg<sup>2+</sup> in ppb level as a result of *molecular wire* effect.
- Reversible and reusable on-site detection kit for  $Hg^{2+}$ .

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