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Synthesis of novel coumarin containing conjugated fluorescent polymers by Suzuki cross-coupling reactions and their chemosensing studies for iron and mercury ions

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ABSTRACT

Conjugated fluorescent polymers are very useful materials for chemical and biochemical sensors. Herein we report the synthesis of four novel conjugated coumarin-containing fluorescent co-polymers (**P1–P4**) by palladium catalyzed Suzuki-Miyaura cross-coupling reaction. 4-Methyl/phenyl coumarin ditriflates and diboronic acids such as benzene-1,4-diboronic acid and 9,9-dioctylfluorene-2,7-diboronic acid were used as coupling partners. All the polymers were well-characterized using NMR and gel permeation chromatography. TGA studies revealed that these polymers are stable over 300 °C. The photophysical properties of these novel polymers were studied by UV–Vis and fluorescence spectroscopy. Among these four polymers, polymer **P3** having 4-methylcoumarin and dioctylfluorene as alternating monomers showed intense fluorescence with 0.73 quantum yield in the DMF medium. Polymer **P3** was also found as selective fluorescence "turned-off" chemosensor for the detection of Hg (II) and Fe(II)/Fe(III) ions over the other metal ions dissolved in water.

1. Introduction

Conjugated polymers are important synthetic materials with wide applications in solar cells [1], organic light-emitting diodes [2], thin-film transistors [3], fluorescence imaging [4], electro chromic materials [5], photocatalyst [6], as well as in chemosensors [7]. Specially, fluorescent conjugated polymers are very useful materials for chemosensing studies. Considering the easy preparation, rigid structure, and high sensitivity due to the molecular wire effect of conjugated polymers, the design and development of novel fluorescent conjugated polymers has remained a popular and very useful research topic [8]. In addition to these, polymer-based chemosensors often show better selectivity and binding efficiency due to the presence of multiple recognition sites for analytes in the polymer backbones [9]. Metal catalyzed coupling reaction is one of the most widely used strategies for the synthesis of conjugated polymers [10]. Recently, Zhao and Tang et al. reported synthesis of through-space conjugated polymers by Suzuki and Stille coupling reactions, and studied their optical and explosive detection properties [11]. Foster and Turner et al. reported synthesis of spherical and rod-like conjugated nanoparticles in emulsions from the palladium catalyzed Suzuki-Miyaura cross-coupling reactions of different dibromoarenes and 9,9-dioctylfluorene-2,

7-diboronic acid bis(1,3-propanediol) ester monomers [12]. Using similar polycoupling, synthesis of copolymer poly(9,9-dihexadecyl fluorene-2,7-diyl-alt-2,2'-bithiophene-5,5'-diyl)s was reported by Cimrová et al. under microwave conditions and studied their electroluminescent properties [13]. Likewise, Wang et al. reported a novel conjugated polymer having coumarin, carbazole, fluorene and phenylene moieties for the naked-eye detection of DNA [14]. From this literature survey, we realized the potential and scope of conjugated polymers and its usefulness as chemosensors.

Rapid detection of environmentally harmful and biologically important metal ions dissolved in water has remained an ever-enduring topic in the field of chemosensing [15]. Considering the advantage of polymers over the small molecule-based chemosensors, recently attention has been shifted towards developing novel polymers for the selective detection of transition and heavy metals [16]. Water pollution due to the presence of excess amounts of dissolved metal ions is a major concern for the health of humans and other living organisms [17]. Although metals are very important in various biochemical reactions, however, excess intake of metal ions such as iron and mercury are very harmful, toxic and can cause severe health issues [18]. In view of these, an effective method for the detection of these ions in very low concentration in the aqueous medium has lots of scopes. Fluorescence

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spectroscopy is a relatively simple and highly sensitive tool for chemosensing studies [19]. Recently, many methods have been developed for the detection of iron [20] and mercury [21] ions using either small molecule or polymers as fluorescent chemosensors. However, to the best of our knowledge, there is no report of a single fluorescent polymer-based chemosensor for the simultaneous detection of iron and mercury ions dissolved in water. Thus, in continuation of our work on synthesis and studies of fluorescent molecules and chemosensors [22], we were motivated to develop a novel fluorescent conjugated polymer to use as fluoroprobe for the detection of important metal ions such as iron and mercury dissolved in water.

Although polymers with coumarin as pendant are known in the literature with diverse applications [23] however, to the best of our knowledge, conjugated polymers having only coumarin-fluorene or coumarin-arene in alternating copolymers are not yet explored. In this paper, we are reporting the synthesis of four novel coumarin containing conjugated fluorescent copolymers by palladium-catalyzed Suzu-ki–Miyaura cross-coupling reaction of coumarin ditriflate and diboronic acids and studied their photophysical properties and thermal stabilities. We have also studied the chemosensing properties of one of the polymers.

2. Results and discussion

Initially, pre-monomers (dihydroxy coumarin derivatives) **PM-1** (where R = Me) and **PM-2** (R = Ph) were prepared using iodine mediated reaction of phloroglucinol dihydrate (1) and β -keto esters **2a** and **2b** (ethyl acetoacetate or ethyl benzoyl acetate) under neat conditions following literature reported procedure [24]. Then these two pre-monomers were converted to the corresponding ditriflates **M-1** and **M-2** by reacting with trifluoromethanesulfonic anhydride in the presence of pyridine as a base in dichloromethane medium at room temperature (Scheme 1). Next, all these synthesized pre-monomers and monomers were fully characterized by recording melting point, IR spectroscopy, ¹H and ¹³C NMR as well as by HRMS.

Before trying the Suzuki poly coupling reaction, a model reaction was tried by reacting monomer **M-1** with 2.0 equivalents of phenylboronic acid in the presence of palladium acetate as catalyst. Interestingly, this model reaction provided our desired biscoupling product **MD-1** with 58% yield within 24.0 h (Scheme 2). This compound was then characterized by recording IR, ¹H & ¹³C NMR as well as by recording HRMS. Langer et al. also prepared this biscoupling product **MD-1** using Pd(PPh₃)₄ as catalyst, and K₃PO₄ as base in toluene–1,4-dioxane (1:1) solvent system [25].

With the success of this biscoupling reaction with monomer M-1, next, we tried polymerization reaction of M-1 with benzene-1,4diboronic acid for the preparation of coumarin containing conjugated polymer P1 having alternate coumarin-arene monomers. The optimization table for the preparation of polymer P1 under various reaction conditions is shown in Table 1. Among all the screened reactions, entry 8, Table 1 using 10-mol% Pd catalyst in dioxane-water medium (20:1 v/ v) at 120 °C for 72 h provided the best result in terms of yield obtained and molecular weight of the polymer. The average molecular weights (Mw and Mn) of this polymer were determined by GPC in DMF medium. It is noteworthy to mention that GPC technique has some limitations for determining molecular weights of rigid-rod polymers, which often shows higher molecular weights [26].

Next, polymer P1 was characterized by ¹H NMR in DMSO- d_6 and solid-state ¹³C NMR. For the characterization of the polymer P1, we first compared the ¹H NMR peak positions of various protons of the polymer with ¹H NMR of the model compound **MD-1**. In the model compound, CH₃ attached with the coumarin ring at 4-position appears at 1.79 ppm, and in the polymer P1 corresponding peak appears at 1.77 ppm. Similarly, the = CH proton of the coumarin ring appears at 6.19 ppm, and in polymer P1 corresponding peak appears at 6.32 ppm. In the solid-state 13 C NMR, the presence of one peak at 24.4 ppm is due to the –CH₃ group attached with coumarin ring and carbonyl carbon appears at 159.78 ppm. These informations confirmed the presence of the coumarin moiety in the polymer backbone. In the ¹H NMR of polymer **P1**, the presence of another three peaks in the aromatic region implies the presence of an aryl linker connected with the coumarin moiety. In the FTIR spectra of the model compound C=O stretching appears at 1733, and in the polymer **P1** corresponding C=O appears at 1701 cm⁻¹.

After having this successful result for the polymer P1, next this Suzuki polycoupling strategy was applied for the preparation of another polymer P2, using M-2 and benzene 1,4-diboronic acid as monomers. In this case also a similar result was observed. Similarly, another two conjugated polymers P3 and P4 were prepared by replacing benzene-1,4-diboronic acid with 9,9-dioctylfluorene-2,7-diboronic acid and taking monomers M-1 and M-2 respectively under the standard reaction conditions (Scheme 3). After preparing these conjugated polymers, we characterized all of them by recording ¹H NMR in DMSO-d₆ or CDCl₃ and solid-state ¹³C NMR. The detailed reaction procedure and characterization data are given in the experimental section and the NMR spectra of all these polymers are shown in the supporting information.

Thermal stability is one of the very important parameters for assessing the usefulness of a polymer and deciding its applications in harsh conditions. To check the thermal stability of our newly synthesized polymers, thermogravimetric analysis (TGA) was performed using an SDTQ600 (TA Instruments) at a scan rate of 10 °C/min under nitrogen flow (100 mL/min). The initial decomposition temperature at which 5% weight loss of the initial weight of **P1** was found at 450 °C while **P2**, **P3** and **P4** are stable in the range between 300 and 320 °C (Fig. 1).

2.1. Optical properties

The absorption and emission properties of these newly synthesized coumarin based polymers were studied in DMF solution. The absorption peaks of **P1**, **P2**, **P3**, and **P4** appear between 335 and 350 nm as shown in Fig. 2a, which may be due to the π - π * transition of the conjugated backbone. All the polymers (**P1** to **P4**) exhibit emission peaks in the range of 407–425 nm in fluorescence spectroscopy (Fig. 2b).

Next, the fluorescence quantum yields (Φ_f) of these four polymers (**P1** to **P4**) were measured in DMF medium, and observed quantum yields were found in the range of 16–73% (Table 2).

Next, considering the high fluorescence quantum yield of **P3** polymer, we wanted to explore this polymer as a fluorescent probe for selective metal ion detection from drinking water. Before, screening the chemosensing properties of **P3**, we have recorded UV–Vis and fluorescence spectra of this polymer in different concentrations. The absorbance and the fluorescence intensity were found gradually increasing



Scheme 1. Preparation of pre-monomer and monomers.



Scheme 2. Pd catalyzed Suzuki biscoupling of M-1 with two equivalents of phenylboronic acid.

Table 1

Optimization of reaction conditions for the preparation of polymer P1.^a



Entry	Pd(OAc) ₂ (mol%)	Solvent	Temp./ºC	Reaction time/h	M _n	Mw	PDI	% Yield
1	1	1,4-Dioxane	70	24	400	559	1.39	25
2	2	1,4-Dioxane	70	24	521	768	1.47	30
3	10	1,4-Dioxane	80	48	3778	4495	1.18	46
4	10	1,4-Dioxane-water(20:1)	80	48	4171	5019	1.2	56
5	10	1,4-Dioxane-water (20:1)	90	48	4384	5043	1.15	58
6	10	1,4-Dioxane-water(20:1)	100	48	4370	5054	1.16	57
7	10	1,4-Dioxane-water(20:1)	120	48	5319	6857	1.29	68
8	10	1,4-Dioxane-water (20:1)	120	72	5934	12231	2.06	85
9	10	THF	120	72	3820	4423	1.15	54
10	10	DMF	120	72	3950	4018	1.01	59

^a Reaction conditions: M-1 (0.5 mmol), benzene 1,4-diboronic acid (0.5 mmol), Pd(OAC)₂, PPh₃ heating under sealed conditions.



Scheme 3. Synthetic routes to coumarin containing fluorescent polymers P1 to P4.

with the increase in the concentration of P3 from 1 to 15 $\mu g/mL$ (Fig. 3a and b).

Next, to check whether **P3** will show any solvatochromic effect, we recorded the UV–Vis and fluorescence spectra of polymer **P3** in four different solvents THF, chloroform, DMSO, and DMF. In all the four solvents, a very similar kind of absorption pattern having absorption maxima at 345 nm was observed (Fig. 4a). The fluorescence spectra of **P3**, in DMSO, DMF, and CHCl₃ showed emission maxima at 425 nm whereas THF showed at 442 nm (Fig. 4b). On the other hand, the fluorescence intensity of **P3** was found similar in DMF and THF. Interestingly, fluorescence intensity slightly decreased in DMSO, and increased in CHCl₃ medium. We also calculated the quantum yields of **P3** in these four different solvents and the results are summarized in Table 3.



Fig. 1. Thermograms of polymers P1, P2, P3 and P4.

After having these results in hand, the recognition ability of **P3** toward different metal-cations such as Zn^{2+} , Mg^{2+} , Cu^{2+} , Fe^{3+} , Cd^{2+} , Ni^{2+} , Mn^{2+} , Na^+ , K^+ , Al^{3+} , Co^{2+} , Hg^{2+} as well as anions like SO₄²⁻, Br⁻, NO₂⁻, Cl⁻, N₃, I⁻, SO₃²⁻, CO₃²⁻, NO₃⁻ and F⁻ which are generally found in the water were studied by the naked eyes, UV–Vis and fluorescence spectroscopic methods. In the naked eye, the solution of **P3** in DMF is



Fig. 2. (a) UV-vis spectra and (b) Fluorescence spectra of polymers P1, P2, P3 and P4 in DMF with a concentration of 2.5 µg/mL.

Table 2							
Molecular	weight and	fluorescence	quantum	vields of	polymers	in DMF	medium.

Sr. No.	Polymer	M _w (g/mol)	DP	PDI	Yield (%)	Excitation $\lambda^{ex}(nm)$	A _s	Emission λ^{em}_{max} (nm)	Stokes' shift (nm)	$\Phi_{\rm f}$
1.	P1	12231	52	2.06	85	339	0.48	416	77	0.16
2.	P2	5778	19	1.19	78	360	0.32	423	63	0.18
3.	P3	6963	12	1.48	80	345	0.25	425	63	0.73
4.	P4	6337	10	1.22	82	340	0.21	407	67	0.49



Fig. 3. (a) UV–Vis spectra of polymer P3 in DMF medium at different concentrations, (b) The fluorescence spectra of polymer P3 in DMF at different concentrations.

colourless, however, on the addition of Fe²⁺ solution a faint pink colour and on the addition of Fe³⁺ solution, the colour of the polymer solution changed to light brown colour. On the other hand, a sharp colour change from colourless to yellow for Hg²⁺ was observed, whereas other metal ions did not show any colour change under visible light. Interestingly, under the UV light fluorescence quenching because of these three ions were clearly visible (Fig. 5, second row).

Next, we have studied the fluorescence property of **P3** in DMF solution using a spectro -fluorimeter. The fluorescence properties of polymer **P3** in DMF medium in absence of any metal ions as well as in the presence of various cations with 10 μ g/mL concentration are shown

in Fig. 6.

Similarly, fluorescence spectra of polymer **P3** in the DMF medium in the absence of any quencher, and in the presence of salts having different anions as well as in the presence of Fe(III) is shown in Fig. 7.

From these studies, it was evident that **P3** is a selective "turn-off" fluorescent sensor for $\text{Fe}^{3+/2+}$ and Hg^{2+} ions. Next, to understand the counter ion effects, we recorded the fluorescence spectra of **P3** solution in the presence of metal ion solutions of the same concentrations having different counterions. Fe(III) salts having chloride, nitrate and sulphate as counterions showed very similar type of quenching with **P3** solution in DMF as shown in Fig. 8.



Fig. 4. (a) UV–Vis spectra of polymer P3 (1 µg/mL) in different solvents, (b) Fluorescence spectra of polymer P3 (1 µg/mL) in different solvents.

Table 3Quantum yields of P3 in different solvents.

Solvent	λ^{abs}_{max} (nm)	Excitation $\lambda^{ex}(nm)$	A _s	Emission $\lambda^{em}_{max}(nm)$	$\Phi_{\rm f}$
DMF	345	345	0.145	425	73
DMSO	345	345	0.151	425	69
THF	345	345	0.166	442	66
CHCl ₃	345	345	0.164	425	78

Similarly, for the Fe(II), effects of counter ions were checked, by taking iron (II) salts having chloride, sulphate and bromide as counter ions. In this case, also, we did not find any significant change in fluorescence quenching due to the different counterions as shown in Fig. 9.

Interestingly, in the case of mercury sensing, we found that quenching of fluorescence in the presence of $Hg(OAc)_2$ is more as compared to $Hg(NO_3)_3$ (Fig. 10). This difference in quenching properties may be due to the reactive nature of $Hg(NO_3)_3$ which undergo fast hydrolysis in water to give a turbid solution.

2.2. Limit of detection (LOD) calculation

To calculate the limit of detection for these three cations, solutions of P3 (concentration 1 µg/mL in DMF) with a varying concentration of Fe³⁺ (1–100 µg/mL), Fe²⁺ (1–188 µg/mL) and Hg²⁺ (1–200 µg/mL)

were prepared and the fluorescence measurements were performed at room temperature (Figs. 11a, 12a and 13a). LOD was calculated by using the linear regression method, and the fluorescence recovery graph was obtained by plotting $(F_0-F)/F_0$ against metal-ion concentration. The linear range was obtained within 3–13 μ g/mL of Fe³⁺ concentration (Fig. 11b). The linear equation was fitted as Y = 0.0257X - 0.0316 with a linear correlation coefficient of $R^2 = 0.9967$. For Fe²⁺, the linear range was found within 1–11 µg/mL concentration (Fig. 12b). The linear equation was fitted as Y = 0.024X - 0.0031 with a correlation coefficient of $R^2 = 0.9946$. Similarly, the linear range was obtained within 1–19 µg/ mL of Hg^{2+} concentration (Fig. 13b). For Hg^{2+} , the linear equation was fitted as Y = 0.011X+0.0073 with a correlation coefficient of R^2 = 0.9978. The limit of detection was obtained by the following equation $3\sigma/m$ (Where σ is the standard error of the blank for 11 replicate measurements and m is the slope of calibration curve). The LOD for $Fe^{3+} =$ 1.25 μ M, Fe²⁺ = 2.9 μ M and for Hg²⁺ = 2.98 μ M were obtained.

Next, to understand the quenching process, the Stern-Volmer constants were calculated using the equation $F_0/F = 1 + K_{SV}$ [Q] [27]. Here F_0 and F are the fluorescence intensities in the absence and presence of metal-ion respectively. [Q] is the metal-ion concentration and K_{SV} is the Stern-Volmer constant. The linear fitting of the plot F_0/F vs [Q] gives the slope K_{SV} . The K_{SV} for Fe (III) was found to be $7.65 \times 10^3 \, L \, mol^{-1}$, for Fe (II) $4.13 \times 10^3 \, L \, mol^{-1}$ and for Hg(II) $3.54 \times 10^3 \, L \, mol^{-1}$ (obtained from Fig. 14a, b and c). This indicates that these three metal ions have binding affinity towards the polymer. In addition to these, from the life time



Fig. 5. The change of colour of P3 solution in DMF (10 μ g/mL) on addition of 50 μ L different metal-ion solutions (4.0 mM) (above) and the quenching of fluorescence intensity under the uv light (bellow). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 6. Fluorescence spectra of P3 in DMF (1 μ g/mL) in the absence and presence of various metal ions dissolved in water (10 μ g/mL).



Fig. 7. Fluorescence spectra of P3 in the DMF medium(1.0 $\mu g/mL$), measured in the absence and presence of aqueous solutions of different salts with different anions and Fe $^{3+}$ containing solution having 10 $\mu g/mL$ concentration.

measurement we found that the average fluorescence lifetime of polymer **P3** is 0.86 ns in the absence of any quencher. We did not observe any significant change in the fluorescence lifetime of **P3** in the presence of Hg^{2+} and Fe^{3+} solutions (Fig. 15a and b). This clearly indicates that the quenching of fluorescence of **P3** by Hg^{2+} and by Fe^{3+} is static in nature (see Table 4).

To further investigate the quencing mechanism we considered fluorescence quencing of model substrate **MD1** in the presence of Hg(II) and Fe(III) solutions. Interestingly, our model compound **MD1** also showed a similar type of quenching pattern of polymer **P3** in the presence of Hg(II) and Fe(III) solutions. The fluorescence intensity of **MD1** was found decreasing with the increase of concentration of both Hg(II) and Fe(III) solutions as shown in Fig. 16a and b. The decrease in fluorescence intensity of **MD1** with an increase in the concentration of quenchers (Hg²⁺ or Fe³⁺) may be due to the selective ion induced aggregation caused quenching(ACQ). We believe that these cations help to form aggregates



Fig. 8. Fluorescence spectra of P3 in DMF (2.5 μ g/mL) in the presence of different Fe(III) salts having 0.1 mM concentration.



Fig. 9. Fluorescence spectra of P3 in DMF (2.5 $\mu g/mL)$ in the presence of different 0.1 mM Fe(II) solutions.

by weakly interacting with the ester moieties of the coumarin ring. Next, to further prove that quenching of fluorescence of polymer P3 is due to aggregation caused quenching (ACQ), we have recorded both absorption and emission spectra of P3 in the highly soluble DMF medium as well as in mixtures of DMF-water mixtures. Interestingly, we found that initially, absorption increases with an increase in water content, and after that further increase do not give any significant change in absorption (Supporting information Fig. S2). On the other hand fluorescence emission drastically reduces in the presence of higher amount of water, a poor solvent which forces polymers to have aggregation and precipitation by hydrophobic interaction (Supporting information, Fig. S3). Finally, we recorded the UV-visible spectrum of P3 solution in DMF in the presence of Hg^{2+} and Fe^{3+} solutions with different concentrations (see supporting information, Fig S4, and S5). Interestingly, we found that in both cases absorptions gradually increase with increasing the quencher concentrations. Based on the literature reports [28,29] and our present studies by using UV-vis and fluorescence spectroscopy we proposed that quenching of fluorescence of polymer P3



Fig. 10. Fluorescence spectra of P3 (2.5 μ g/mL) in the presence of different 0.1 mM Hg (II) salt solutions.

in the presence of quenchers Hg and Fe ions is due to the ion induced aggregation caused quenching.

Solubility of polymers at room temperature: The solubility of our synthesized coumarin containing polymers were checked in various solvents and their results are summarized below: Copolymers **P1** and **P2**, where coumarin is connected with phenyl linker are not soluble in most of the organic solvents except polar aprotic solvents such as DMF, DMSO and THF. Both **P1** and **P2** were found sparingly soluble in acetonitrile and 1,4-dioxane. However, other two polymers **P3** and **P4** having dioctyl fluorene (having hydrophobic chain) as one of the monomer showed better solubility and was found soluble in most of the organic solvents as shown in Table 5.

3. Experimental section

3.1. Materials and methods

All starting materials, solvents, and the catalyst were purchased from commercial suppliers and were used as such without further purifications. Benzene-1,4-diboronic acid, 9,9-Dioctylfluorene-2,7diboronic acid, phloroglucinol, ethyl acetoacetate and palladium acetate were purchased from Sigma-Aldrich. Ethylbenzoyl acetate, trifluoromethane sulfonic anhydride and potassium tert-butoxide were purchased from TCI chemicals. Chloroform-*d* and DMSO- d_6 were purchased from Sigma-Aldrich. The monomers were prepared using reported methods. The progress of the reactions was monitored by TLC. The purification of premonomers and monomers as well as the products of the model reactions were done by silica gel column chromatography using ethyl acetate/hexane (in different ratios) solvent system as mobile phase.

3.2. Instrumentation

FTIR spectra were recorded by ATR mode with the absorption in cm^{-1} . NMR spectra of all compounds were recorded in a Bruker 400 MHz instrument. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded in either in DMSO- d_6 or CDCl₃ as solvent. To define the multiplicities: s = singlet; d = doublet; t = triplet; m = multiplet; dd (doublet of doublets); td (triplet of doublets); bs (broad singlet), coupling constants (J, in Hz) has been used as abbreviations. Solid-state ¹³C cross-polarization magic angle spinning (CP-MAS) NMR spectra were recorded at a spinning rate of 8 kHz and CP contact time of 2 ms with a delay time of 2s. BRUKER Impact HD mass spectrometer (Impact HD UHR-TOF, ESI with positive mode) was used for the HRMS data. Melting points were recorded using an SRS EZ-Melt automated melting point apparatus by capillary methods without correction. The average molecular weights and polydispersity of polymers (sample concentration:1 mg/mL in DMF) were determined using Agilent PL-GPC 50 integrated GPC instrument using DMF as eluent and the molecular weight of polymer sample were calculated using standard calibration curve based on polystyrene standards at a flow rate of 1.0 mL/min. Thermal stability (TGA) analysis was performed using SDTQ600 (TA Instruments) at a scan rate 10 °C/min under nitrogen flow (100 mL/min). Absorption measurements were done by using Shimadzu-UV2550 spectrophotometer using 1 cm path-length quartz cuvettes. Fluorescence emission spectra were measured using Fluoromax-4P spectrofluorometer (Horiba Jobin Yvon). The fluorescence lifetime was measured using picosecond time-correlated single photon counting (TCSPC) technique by a time-resolved fluorescence spectrophotometer (LifeSpec-II, Edinburgh Instruments, UK).



Fig. 11. (a). Fluorescence spectra of P3 (1.0 μ g/mL) in DMF measured with increasing concentration of Fe³⁺ ion, (b). The plot of (F₀–F)/F₀ vs Fe³⁺concentration. Inset: The linear range of the plot with Fe³⁺ concentration over the range of 3–13 μ g/mL.



Fig. 12. (a). Fluorescence spectra of P3 (1 μ g/mL) in DMF measured with increasing concentration of Fe²⁺ ion. (b) The plot of (F₀–F)/F₀ vs Fe²⁺ concentration. Inset: The linear range of the plot with Fe²⁺ concentration over the range of 1–11 μ g/mL.



Fig. 13. (a). Fluorescence spectra of **P3** (1 μ g/mL) in DMF medium measured with increasing concentration of Hg²⁺ ion. (b) The plot of (F₀–F)/F₀ vs Hg²⁺ concentration. Inset: The linear range of the plot with Hg²⁺ concentration over the range of 1–19 μ g/mL.

4. Synthesis of premonomers (PM-1,PM-2)

5,7-dihydroxy-4-methyl-2H-chromen-2-one (PM-1). In a 50 mL round bottom flask 10.0 mmol of phloroglucinol, 10.0 mmol of ethyl acetoacetate and 100 mg of iodine were stirred at 80 °C. The reaction was monitored by TLC, after the completion of the reaction, the reaction mixture was cooled and poured into ice and iodine was neutralised by using 20.0 mL 10% sodium thiosulphate solution. The light yellow precipitate was filtered and washed with water for several times and allowed to dry. The air dried product was further dried under vacuum and purified by recrystallization in hot ethanol.

Yield 92%; white solid; mp 260–264 °C. IR (ATR) 3421, 3112, 1662, 1616, 1547, 1509, 1376, 1359, 1298, 1234, 1156, 1075, 823, 754, 638 cm⁻¹. ¹H NMR (400 MHz, **DMSO-d**₆) δ 10.52 (s, 1H, OH), 10.29 (s, 1H, OH), 6.25 (d, *J* = 4.0 Hz, 1H, Ar), 6.16 (d, *J* = 4.0 Hz, 1H, Ar), 5.84 (d, *J* = 2.0 Hz, 1H, Ar), 2.48 (s, 3H, CH₃) ppm.¹³C NMR (100 MHz, **DMSO-d**₆) δ 161.1, 160.1, 158.0, 156.5, 155.0, 108.9, 102.1, 99.1, 94.5, 23.5 ppm. HRMS (ESI-TOF): *m*/*z* [M + H]⁺ calcd for C₁₀H₉O₄ 193.0495; found 193.0504.

5,7-dihydroxy-4-phenyl-2H-chromen-2-one (PM-2). Same procedure of PM-1was followed for the synthesis of PM-2 and the product was purified by column chromatography. Yield 75%; brick red solid; mp 242–245 °C. IR (ATR) 3305, 3184, 1665, 1610, 1587, 1550, 1367, 1234, 1139, 1059, 945, 823, 696, 560 cm^{-1. 1}H NMR (400 MHz, **DMSO-d**₆) δ 10.44 (bs, 1H, OH), 10.17 (bs, 1H, OH), 7.37–7.32 (m, 5H, Ar), 6.27 (d, J = 2.0 Hz, 1H, Ar), 6.16 (d, J = 2.0 Hz, 1H, Ar), 5.74 (s, 1H, Ar) ppm.¹³C NMR (100 MHz, **DMSO-d**₆) δ 161.8, 160.0, 157.2, 156.8, 156.1, 139.6, 127.9, 127.5, 127.4, 110.2, 100.7, 99.2, 94.7 ppm. HRMS (ESI-TOF): m/z [M + H]⁺ calcd for C₁₅H₁₁O₄ 255.0652; found 255.0663.

5. Synthesis of monomers (M-1 and M-2)

Trifluoro-methanesulfonic acid 4-methyl-2-oxo-6-trifluoromethanesulfonyloxy-2H-chromen-8-yl ester (M-1). 5.0 mmol of PM-1 was taken in a 50.0 mL two necked round bottom flask equipped with a magnetic stir bar and flashed with nitrogen gas three times then 20.0 mL dichloromethane and 20.0 mmol of pyridine were injected and the reaction mixture was placed on an ice bath with the constant stirring for



Fig. 14a. Linear fitting of the plot F_0/F vs Fe^{3+} concentration for calculating Stern-Volmer constant K_{SV}.



Fig. 14b. Linear fitting of the plot F_0/F vs Fe^{2+} concentration for calculating Stern-Volmer constant K_{SV}.



Fig. 14c. Linear fitting of the plot F_0/F vs Hg^{2+} concentration for calculating Stern-Volmer constant K_{SV}.



Fig. 15a. The time-resolved fluorescence emission spectra of polymer P3 (1 μ g/mL) in the absence and in presence of Hg²⁺ (150 μ M) in DMF. The red line plot (IRF) shows the instrument response function. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 15b. The time-resolved fluorescence emission spectra of polymer P3(1 $\mu\text{g}/$ mL) in the absence and in presence of Fe^{3+} (150 $\mu M)$ in DMF. The red line plot (IRF) shows the instrument response function. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Га	ble	4	

Fluorescence life time data.									
Sample Name	τ_1 (ns)	τ_2 (ns)	a ₁	a ₂	(τ) _{average} (ns)	χ^2			
P3	0.45	1.24	0.48	0.52	0.86	0.99			
P3+Hg ²⁺	0.46	1.20	0.48	0.52	0.84	1.04			
P3+Fe ³⁺	0.47	1.22	0.52	0.48	0.83	1.03			

15 min to keep the temperature bellow 5 °C. Next, trifluoromethanesulfonic anhydride (15.0 mmol) was added drop wise by syringe. After the addition, the reaction was kept stirring at room temperature for 2 h. After the completion of the reaction, the reaction mixture was poured into 20.0 mL water and extracted by adding 2x 20 mL dichloromethane. The organic layer was collected using a separating funnel and washed three times with water and 10% HCl solution. The



Fig. 16. (a) Fluorescence spectra of model compound MD1 (2.5 µg/mL) in DMF in the presence of Hg(II) solutions at different concentrations (left). (b) Fluorescence spectra of model compound MD1(2.5 µg/mL) in DMF in the presence of Fe(III) solutions at different concentrations (right).

able 5	
olubility of the polymers P1-P4 (mg/mL) in different solvents.	

Polymer	CHCl ₃	DCM	DMF	THF	DMSO	WATER	Methanol	ACN	1,4-Dioxane
P1	Х	Х	430	160	200	Х	Х	12	35
P2	Х	Х	400	161	190	Х	Х	10	30
P3	170	190	840	460	50	Х	Х	45	480
P4	165	180	770	410	43	Х	Х	41	360

X = insoluble.

combined organic extracts were dried over anhydrous Na_2SO_4 . The solvent was removed by rotavapor and the crude product was finally purified by column chromatography. After purification, a white crystalline compound was obtained.

Yield 75%; white solid; mp 126–130 °C. IR (ATR) 1726, 1613, 1431, 1200, 1127, 1055, 991, 835, 795, 757, 728, 705, 659, cm^{-1.} ¹H NMR (400 MHz, **DMSO-d**₆) 8.01 (d, J = 2.0 Hz, 1H, Ar), 7.70 (d, J = 4.0 Hz, 1H, Ar), 6.66 (s, 1H, Ar), 2.56 (s, 3H, CH₃) ppm.¹³C NMR (100 MHz, **DMSO-d**₆) δ 157.6, 154.9, 149.0, 148.9, 145.2, 126.6, 119.0, 114.6, 112.1, 111.9, 21.9 ppm. ¹⁹F NMR (376 MHz, **DMSO-d**₆) δ –72.28, –72.50 ppm. HRMS (ESI-TOF): m/z [M + H]⁺ calcd for C₁₂H₇F₆O₈S₂ 456.9481; found 456.9507.

Trifluoro-methanesulfonic acid 2-oxo-4-phenyl-8-trifluoromethanesulfonyloxy-2H-chromen-6-yl ester(M-2). Same procedure as mentioned for M-1 was followed for M-2. Yield 70%; white solid; mp 92–96 °C. IR (ATR) 1741, 1610, 1428, 1353, 1208, 1130, 1110, 1041, 997, 887, 818, 705, 586 cm^{-1. 1}H NMR (400 MHz, **DMSO-d**₆) δ 8.13 (d, J = 2.0 Hz, 1H, Ar), 7.84 (d, J = 2.0 Hz, 1H, Ar), 7.51–7.48 (m, 5H, Ar), 6.61 (s, 1H, Ar) ppm.¹³C NMR (100 MHz, **DMSO-d**₆) δ 157.5, 155.2, 150.6, 149.3, 144.8, 135.3, 129.9, 128.3, 120.2, 119.8, 119.3, 113.8, 113.3, 112.2 ppm.¹⁹F NMR (376 MHz, **DMSO-d**₆) δ –72.09, –72.32 ppm. HRMS (ESI-TOF): m/z [M + H]+ calcd for C₁₇H₉F₆O₈S₂ 518.9638; found 518.9666.

6. Procedure for the synthesis of model compound (MD-1)

Monomer M-1 (0.5 mmol) was transferred to a 10.0 mL sealed tube equipped with a magnetic stirrer and 2.0 mL of 1,4-dioxane. To this solution palladium acetate (10 mol%) and triphenylphosphine (20 mol%) were added. The reaction mixture was kept at 65 °C under stirring conditions. After 10 min, 1.0 mmol of phenylboronic acid and 1.5 mmol of K₂CO₃ was added to the reaction mixture followed by four drops of

water. The tube was sealed properly and the reaction was continued for 24 h at 120 $^{\circ}$ C. After completion of the reaction, 30.0 mL water was added to the reaction mixture and extracted with ethylacetate 3 x 20.0 mL. The combined organic layer was collected and dried over sodium sulphate and filtered. Finally, the solvent was removed using rotavapour and the crude product was purified by column chromatography using a mixture of ethyl acetate and hexane.

4-methyl-5,7-diphenyl-2H-chromen-2-one (MD-1). Yield 58%; white solid; mp 126–128 °C. IR (ATR) 3060, 2928, 2852, 1733, 1208, 1601, 1503, 1427, 1355, 1222, 1140, 1001, 964, 856, 825, 699 cm⁻¹. ¹H NMR (400 MHz, **CDCl**₃) δ 7.66–7.61 (m, 3H, Ar), 7.48–7.41 (m, 6H, Ar), 7.39–7.36 (m, 3H, Ar), 6.19 (s, 1H, Ar), 1.79 (s, 3H, CH₃) ppm.¹³C NMR (100 MHz, **CDCl**₃) δ 155.3, 154.2, 143.4, 142.4, 142.3, 138.9, 129.6, 129.4, 129.0, 128.44, 128.37, 127.5, 126.8, 120.8, 117.7, 115.1, 24.4 ppm. HRMS (ESI-TOF): *m/z* [M + H]⁺ calcd for C₂₂H₁₆O₂ 313.1223; found 313.1229.

7. Procedure for the synthesis of polymers (P1, P2, P3 and P4)

Monomer **M-1/M-2** (0.5 mmol) was taken in a 10.0 mL sealed tube equipped with a magnetic stirrer and 3.0 mL of 1,4-dioxane. The solution was then heated to 65 °C and palladium acetate (10 mol%) and triphenylphosphine (20 mol%) were added. After 10 min, 0.5 mmol of benzene-1,4-diboronic/9,9-dioctylfluorene-2,7-diboronic acid and 1.5 mmol of K₂CO₃ was added to the reaction mixture followed by four drops of water. The tube was sealed properly and the reaction was kept at 120 °C under constant stirring for 72 h. After 72 h, methanol was used for the precipitation of the polymer. All the polymers were characterized by recording ¹H and ¹³C NMR as well as GPC (¹H and ¹³C NMR of all these polymers as well as GPC data are given in supporting information.).

P1: IR (ATR) 3417, 3033, 2981, 2932, 2342, 2097, 1701, 1600,

1438, 1389, 1352, 1297, 1236, 1190, 1138, 1083, 1029, 965, 936, 829 cm^{-1.} ¹H NMR (400 MHz, DMSO- d_6) δ 7.93 (bs), 7.83 (bs), 7.51(bs), 6.32 (bs), 1.77 (bs) ppm.¹³C NMR (solid state) δ 159.8, 154.6, 140.9, 127.2, 116.4, 23.7 ppm.

P2: IR (ATR) 3059, 3027, 2926, 2325, 1716, 1603, 1444, 1389, 1352, 1257, 1190, 1121, 1078, 1034, 976, 869, 829, 757, 696, 642 cm^{-1.1} H NMR (400 MHz, DMSO-*d*₆) δ 8.04–7.83 (m), 7.68–7.55 (m), 7.47–7.41 (m), 7.28 (bs), 7.08(bs), 7.04(bs), 6.99 (bs) ppm.¹³C NMR (solid state) δ 156.3, 140.3, 127.7, 114.9 ppm.

P3: IR (ATR) 2923, 2851, 1701, 1603, 1459, 1404, 1375, 1352, 1260, 1179, 1121, 1078, 1003, 818, 737, 722, 693 cm^{-1.1} H NMR (400 MHz, CDCl₃) δ 7.81 (bs), 7.65 (bs), 7.55–7.48 (m), 7.34 (bs), 2.05, 1.09, 0.80 ppm.¹³C NMR (solid state) δ 151.6, 140.8, 127.1, 120.0, 55.5, 40.7, 29.9, 23.0, 14.2 ppm.

P4: IR (ATR) 3515, 3062, 3012, 2926, 2854, 1701, 1609, 1493, 1462, 1438, 1409, 1306, 1213, 1167, 1118, 1046, 999, 910, 817, 751, 722, 693, 667, 549 cm^{-1. 1}H NMR (400 MHz, CDCl₃) δ 7.78 (bs), 7.68–7.60 (m), 7.50–7.43(m), 2.08, 1.10, 0.80 ppm.¹³C NMR (100 MHz, CDCl₃) δ 155.8, 145.7, 132.4, 132.3, 132.1, 130.0, 129.4, 128.9, 128.7, 128.2, 127.6, 127.3, 126.3, 121.6, 55.6, 40.5, 31.9, 30.1, 29.3, 24.0, 22.7, 14.2 ppm.

8. Conclusion

In summary, we have reported synthesis of four novel coumarin containing conjugated polymers by using palladium catalyzed poly coupling reaction of coumarin ditriflate and diboronic acids. These novel polymers showed good thermal stability. The photophysical properties of these conjugated polymers were studied by UV–Vis and fluorescence spectroscopy. Polymer **P-3** was found selective chemosensor for the detection of iron (II and III) and mercury (II) ions dissolved in water medium both by colorimetric and fluorometric analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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