

Highly sensitive and selective fluorescence turn-on detection of lead ion in water using fluorene-based compound and polymer†

Cite this: *J. Mater. Chem. A*, 2014, 2, 5024

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A fluorene-based sensory compound and polymers were designed and synthesized for the fluorescence turn-on detection of lead ions in aqueous media. The fluorene unit is used as a fluorophore and also as the building block for making a conjugated fluorene-based polymer. A dicarboxylate pseudo crown was selected as a receptor, which is highly selective towards the lead ion and imparts a good water-solubility to sensory compounds and polymers. The water-soluble sensory compound and fluorene-based polymer show high sensitivity and selectivity towards lead ions in aqueous media. Sensory compound **7a** and polymer **P2** are highly selective and sensitive for the fluorescence turn-on detection of lead ions in water with a concentration of 4 μM . Fibre-optic sensing for lead ions in water using sensory compound **7a** has also been demonstrated.

Received 18th October 2013
Accepted 20th January 2014

DOI: 10.1039/c3ta14209d

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Introduction

Besides the contamination of heavy metal ions to the environment by volcanic activity and erosion in nature, more and more heavy metal ions are entering the soil and water *via* industrial, municipal and agricultural waste water.¹ Among all the heavy metals, arsenic, mercury, lead and cadmium are highly toxic and can be absorbed by plants and animals and then enter the human body. Lead, cadmium, and mercury ions are banned in electrical and electronic equipment by the European Union's Restriction on Hazardous Substances (RoHS).² The World Health Organization (WHO) and Environmental Protection Agency (EPA) have strictly defined the concentration limits of these heavy metal ions that are allowed in drinking water.³ Low-level lead exposure is known to cause a number of adverse health effects, for example delayed physical or mental development in infants and children and damage to the kidney, nervous system, liver, brain, reproductive system and high blood pressure in adults.^{4,5} Severe exposure to lead has been associated with sterility, abortion, stillbirth and neonatal deaths.⁶

Flame atomic absorption spectrometry,⁷ atomic absorption spectrometry,⁸ inductively coupled plasma emission spectrometry,⁹

inductively coupled plasma–mass spectrometry,¹⁰ and voltammetry¹¹ have been widely applied to the determination of heavy metals at low levels. All these methods require expensive instrumentation and a well-equipped lab set up, and are also time consuming.^{12–15} Fluorescence spectroscopy is widely used because of its high sensitivity, selectivity, simple application, and low cost. Much research on molecular probes for fluorescence detection has been done in the past few decades.^{16,17} A variety of fluorescent probes based on nucleic acids,¹⁸ peptides,¹⁹ proteins,²⁰ nanoparticles²¹ and quantum dots²² have been designed, successfully synthesized and applied for the selective detection of lead ions. Some small molecules have been demonstrated to be useful for the fluorescence turn-on detection of lead ions (*i.e.*, Pb^{2+}) in mixtures of water and organic solvents or in a buffer solution.²³ In particular, Chang *et al.* reported a water-soluble fluorescent probe (leadfluor-1) with a detection limit of 23 μM for lead ions.²⁴

Conjugated polymers have been explored particularly for amplified fluorescence detection of aromatic nitro-containing compounds and other hazardous chemicals.²⁵ However, there have been relatively few reports on fluorescent turn-on polymer sensors for the selective detection of Pb^{2+} .²⁶ In addition, conjugated polymers have received increasing interest in fibre-optic sensing (FOS) applications because of their film-forming ability, structural flexibility, fast response time, and ease of processing. FOS can offer several advantages, such as flexibility, cost effectiveness, being hand-held, longevity in various harsh environment and corrosion resistant. It has been used for the detection of explosive TNT vapour.^{27,28} However, it has not been extensively explored for the detection of heavy metals, except for a recent report on the fluorescence turn-on detection of Cu^{2+} in water.²⁹

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† Electronic supplementary information (ESI) available: ¹H NMR, ¹³C NMR, IR and MS spectra for compounds **1–8**; IR, TGA and DSC for polymers **P1–P2**; Absorption and emission spectra of compound **7a** and polymers **P1–P3**; Photographs of the precipitate formation of compound **7a** and polymer **P2** with Pb^{2+} . See DOI: 10.1039/c3ta14209d

In this work, we designed and synthesized a fluorescence turn-on sensory compound and the related conjugated polymers with high selectivity and sensitivity for the detection of Pb^{2+} in water. In addition, a coaxial optic-fibre setup has been demonstrated for the first time to detect the fluorescence turn-on signal from the aqueous solution of the sensory compound in the presence of Pb^{2+} .

Experimental section

Materials

2-Anilinoethanol, 2-(2-chloroethoxy)ethanol, fluorene, 2-bromoacetic acid, phosphorus oxychloride, thionyl chloride, pyridine, acetic anhydride, 1,5-cyclooctadiene, 2,2'-bipyridine, lead(II) acetate trihydrate, copper(II) chloride, nickel bromide, cobalt chloride hexahydrate, calcium chloride, cadmium chloride, potassium bromide, ferric chloride, zinc sulfate, manganese chloride, magnesium chloride, and mercury chloride were purchased from Aldrich Chemicals Canada. Lithium hydroxide was purchased from Matheson Coleman and Bell. $\text{Ni}(\text{COD})_2$ was purchased from Strem Chemicals and used as received. *N,N*-Dimethylformamide (DMF) and toluene were dried and distilled over CaH_2 under an atmosphere of dry argon. *tert*-Butyl alcohol was refluxed over CaH_2 for one day and then distilled under an atmosphere of dry argon. Tetrahydrofuran (THF) was distilled over benzophenone and sodium under an atmosphere of dry argon. The water used in this work was purified using a Millipore™ Milli-Q™ Advantage A10 water purification system from Fisher Scientific. Column chromatography was done using silica gel (Silicycle Chemical Division, 70–230 mesh) as the stationary phase.

Measurements

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance Digital 300 MHz. Resonances are quoted on the δ scale relative to tetramethylsilane (TMS, $\delta = 0$) as an internal standard. For ^1H NMR spectra, the following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The UV-vis spectra were recorded on a Perkin-Elmer Lambda 900 UV-vis-NIR spectrometer at room temperature. Infrared measurements were performed on a Varian 1000 FT-IR Scirinitar spectrophotometer. The bands are expressed in cm^{-1} . Mass spectra were measured with a Micromass Quattro LC ESI (EI). Fisher-John's melting point apparatus was used for recording the melting points of all the synthesized compounds. Thermogravimetric analysis was carried out in nitrogen on a Hi-Res TGA 2950 thermo gravimetric analyzer with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. Differential scanning calorimetric analysis was carried out in nitrogen on a TA DSC Q100 with a heating rate $10\text{ }^\circ\text{C min}^{-1}$.

2-[[2-(2-Hydroxyethoxy)ethyl]phenylamino]ethanol (1)

A suspension of 2-anilinoethanol (27.60 g, 200.0 mmol), 2-(2-chloroethoxy)ethanol (40.80 g, 328.0 mmol) and CaCO_3 (14.00 g, 140.0 mmol) in 600 mL of water was refluxed with vigorous stirring under argon for 24 h. The progress of the reaction was monitored by thin-layer chromatography (TLC) (hexane–acetone,

5 : 1 v/v). After cooling to room temperature, the reaction mixture was filtered and the filtrate was extracted with dichloromethane. The organic extract was dried over MgSO_4 and the solvent was removed using a rotary evaporator. After purification by column chromatography (hexane–acetone, 5 : 1), compound 1 was obtained as a colourless oil (40.00 g, 75.0% yield). ^1H NMR (300 MHz, CDCl_3): δ 7.26 (2H, m), 6.74 (3H, m), 4.03 (1H, OH, br), 3.83 (2H, m), 3.74 (4H, m), 3.66 (2H, m), 3.58 (4H, m), 3.01 (1H, OH, br). ^{13}C NMR (75 MHz, CDCl_3): 147.87, 129.33, 117.11, 112.61, 72.87, 69.24, 61.64, 61.06, 56.06, 52.57. IR (NaCl plate, cm^{-1}): 3369, 2925, 2876, 1598, 1506, 1056.

2-[[2-(2-Acetoxyethoxy)ethyl](phenylamino)ethyl acetate (2)

Under an argon atmosphere in a two-neck flask, a mixture of compound 1 (34.00 g, 151.1 mmol), acetic anhydride (46.24 g, 649.0 mmol), and pyridine (35.80 g, 453.2 mmol) was added and refluxed for 20 h. The reaction was monitored by TLC (hexane–acetone, 5 : 1). The mixture was then cooled to room temperature and poured into ice water. The resulting mixture was extracted with dichloromethane and the extracts were dried over MgSO_4 . The solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography using hexane and acetone (5 : 1) as the eluting solvent. Compound 2 was obtained as a viscous oil (31.00 g, 66.0% yield) after removing the solvent. ^1H NMR (300 MHz, CDCl_3): δ 7.24 (2H, m), 6.73 (3H, m), 4.26 (4H, m), 3.65 (8H, m), 2.06 (6H). ^{13}C NMR (75 MHz, CDCl_3): 170.96 ($\text{CH}_3\text{-C=O}$), 147.55, 129.40, 116.58, 111.85, 69.15, 68.70, 63.52, 61.46, 50.90, 49.84, 20.88, 14.18. EI-MS calculated for $[\text{M}^+]$: 309.16, found 309.16. IR (NaCl plate, cm^{-1}): 2955, 2890, 1739, 1599, 1506, 1235.

2-[[2-(2-Acetoxyethoxy)ethyl](4-formylphenyl)amino]ethyl acetate (3)

In a flame dried two-neck round bottom flask, under an argon atmosphere 55 mL of dry DMF was added. Then the flask was cooled in an ice bath. Phosphorous oxychloride (11.2 mL, 120.6 mmol) was added dropwise with stirring. After 1 h, a solution of compound 2 (31.00 g, 100.2 mmol) in 20 mL of dry DMF was added to the flask. The mixture was heated at $95\text{ }^\circ\text{C}$ for 3 h and then poured onto crushed ice in a beaker. A saturated solution of sodium acetate was added dropwise to adjust the pH to 7. The mixture was then extracted three times with dichloromethane and dried over MgSO_4 . The solvent was removed under reduced pressure. The crude product was purified by column chromatography using hexane–acetone (3 : 1) as the eluting solvent. Compound 3 was obtained as a viscous oil (30.0 g, 88.7% yield) after removing the solvent. ^1H NMR (300 MHz, CDCl_3): δ 9.75 (1H, CHO, s), 7.75 (2H, d), 6.80 (2H, d), 4.29 (2H, t), 4.21 (2H, t), 3.74 (2H, t), 3.68 (6H, m), 2.05 (6H). ^{13}C NMR (75 MHz, CDCl_3): 190.04 (Ar, CHO), 170.84 ($\text{CH}_3\text{-C=O}$), 152.33, 132.15, 125.88, 111.15, 69.25, 68.44, 63.30, 60.96, 50.93, 49.80, 20.82. EI-MS calculated for $[\text{M}^+]$: 337.15, found 337.15. IR (NaCl plate, cm^{-1}): 2958, 2900, 2816, 2738, 1739, 1668, 1597, 1525, 1235.

4-[[2-(2-Hydroxyethoxy)ethyl](2-hydroxyethyl)amino]-benzaldehyde (4)

Compound 3 (30.00 g, 88.92 mmol) was dissolved in methanol (7.0 mL) and an aqueous sodium hydroxide solution (25%, 8.43 g, 210.9 mmol). The reaction mixture was heated to reflux for 3 h, while being monitored by TLC (hexane–acetone, 1 : 1). The mixture was cooled and neutralized with concentrated hydrochloric acid and extracted with dichloromethane. The mixture was washed with distilled water two times and dried with MgSO_4 . The solvent was evaporated under reduced pressure and purified by column chromatography where hexane and acetone (1 : 1) were used as the eluting solvent. Compound 4 was obtained as a viscous oil (20.00 g, 88.8% yield). ^1H NMR (300 MHz, CDCl_3): δ 9.75 (1H, CHO, s), 7.75 (2H, d), 6.74 (2H, d), 3.89 (2H, t), 3.78 (6H, m), 3.68 (2H, t), 3.60 (2H, m). ^{13}C NMR (75 MHz, CDCl_3): 190.28 (Ar, CHO), 152.58, 132.05, 125.90, 111.75, 72.84, 68.62, 61.60, 60.69, 55.65, 52.19. EI-MS calculated for $[\text{M}^+]$: 253.13, found 253.13. IR (NaCl plate, cm^{-1}): 3393, 2925, 2875, 2750, 1655, 1596, 1526, 1057.

2-[[4-(((9H-Fluoren-9-ylidene)methyl)phenyl)(2-(2-hydroxyethoxy)ethyl)amino]ethanol (5a)

In a flame dried two-neck round bottom flask, potassium *tert*-butoxide (0.70 g, 6.25 mmol) was added to a solution of fluorene (0.455 g, 2.74 mmol) in 14 mL of dry *tert*-butanol and THF (1 : 1). The reaction mixture was heated up for half an hour at 60 °C and then cooled down to room temperature. A green solution formed. Then a solution of compound 4 (0.70 g, 2.77 mmol) in 7 mL of dry THF was added and the mixture was refluxed for 1 h. The reaction was monitored by TLC (hexane–acetone, 1 : 1). The reaction mixture was neutralized by concentrated hydrochloric acid and evaporated to dryness under reduced pressure. The residue was extracted three times with dichloromethane and the extracts were dried over MgSO_4 . The crude product was purified by column chromatography using hexane as the eluting solvent first, then with a mixture of hexane and acetone (3 : 1). A yellow solid (5a) was obtained after evaporating all the solvents and was further purified by recrystallization in methanol (0.80 g, 72.1% yield). M.p. 107–109 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.97 (1H, d), 7.78 (3H, m), 7.65 (1H, s), 7.59 (2H, d), 7.35 (3H, m), 7.16 (1H, m), 6.79 (2H, d), 3.92 (2H, m), 3.85 (2H, t), 3.78 (4H, m), 3.68 (4H, m). ^{13}C NMR (75 MHz, CDCl_3): 147.82, 140.90, 140.06, 138.61, 136.75, 133.81, 131.22, 128.06, 127.93, 127.45, 126.76, 126.47, 125.00, 123.97, 72.97, 69.21, 61.72, 61.13, 56.08, 52.56. EI-MS calculated for $[\text{M}^+]$: 401.20, found 401.20. IR (KBr, cm^{-1}): 3313, 3100, 2931, 2888, 1610, 1596, 1518, 1042.

2,7-Dibromofluorene³⁰

In a solution of fluorene (18.00 g, 108.4 mmol) in 60 mL of chloroform, bromine (16.2 mL, 314.2 mmol) in 10 mL of chloroform was added dropwise through a dropping funnel under an argon atmosphere. A rubber tube with a funnel in one end was connected between the flask and a solution of sodium hydroxide (1 M). Using this setup, the resulting HBr can go out

of the reaction system and be trapped and neutralized. After vigorous stirring for 1 h, TLC in hexane showed that the reaction was complete. A part of the product precipitated as a white solid. The reaction mixture was filtered and washed with hexane. The liquid part was neutralized by 15% Na_2CO_3 solution and then extracted with chloroform and dried over MgSO_4 . The solvent was evaporated under reduced pressure and a white solid were obtained. The two white solids were combined and recrystallized from hexane and ethyl acetate to afford the pure product as a white crystal (30.00 g, 85.0% yield). M.p. 166 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.69 (2H, s), 7.62 (2H, d), 7.53 (2H, m), 3.89 (2H, s). ^{13}C NMR (75 MHz, CDCl_3): 144.80, 139.70, 130.15, 128.31, 121.19, 120.94, 36.42.

2-[[4-(((2,7-Dibromo-9H-fluoren-9-ylidene)methyl)phenyl)(2-(2-hydroxyethoxy)ethyl)amino]ethanol (5b)

In a flame dried two-neck flask under an argon atmosphere, potassium *tert*-butoxide (4.427 g, 39.53 mmol) in 35 mL of *tert*-butanol was added to a solution of 2,7-dibromofluorene (6.403 g, 19.76 mmol) in 50 mL of dry THF. The reaction mixture was heated up for half an hour at 60 °C and then cooled to room temperature. A green solution formed. Then a solution of compound 4 (5.0 g, 19.76 mmol) in dry THF (50 mL) was added and the mixture was refluxed for 1 h. The reaction mixture was neutralized by concentrated hydrochloric acid and all the solvents were evaporated under reduced pressure. The residue was extracted three times with dichloromethane and the extracts were dried over MgSO_4 . The crude product was purified by column chromatography using hexane as the eluting solvent first, then with a mixture of hexane and acetone (3 : 1). A reddish oily compound (5b, 9.0 g) was obtained after evaporating all the solvents. The compound 5b was further purified by recrystallization in methanol. The final product was obtained as a yellow crystal (8.00 g, 72.4% yield). M.p. 109–110 °C; ^1H NMR (300 MHz, CDCl_3): δ 8.15 (1H, d), 7.90 (1H, d), 7.64 (1H, s), 7.57 (4H, m), 7.47 (2H, m), 6.81 (2H, d), 3.92 (2H, m), 3.85 (2H, m), 3.79 (4H, m), 3.72 (2H, m), 3.65 (2H, m). ^{13}C NMR (75 MHz, CDCl_3): 148.52, 141.79, 138.63, 138.31, 136.28, 131.48, 131.26, 130.98, 130.73, 130.23, 126.76, 123.69, 123.19, 120.99, 120.94, 120.80, 120.55, 112.06, 72.98, 68.98, 61.72, 61.05, 55.98, 52.43. EI-MS calculated for $[\text{M}^+]$: 559.02, found 559.02; IR (KBr, cm^{-1}): 3402, 2919, 2874, 1600, 1590, 1519, 1062, 1015.

Diethyl 6-[4-((9H-fluoren-9-ylidene)methyl)phenyl]-3,9,12-trioxa-6-azatetradecane-1,14-dioate (6a)

Potassium *tert*-butoxide (0.44 g, 3.89 mmol) was added to a solution of compound 5a (0.13 g, 0.32 mmol) in *tert*-butanol (8 mL) and THF (4 mL) under an argon atmosphere and the mixture was refluxed for 2 h. Then a solution of bromoacetic acid (0.090 g, 0.65 mmol) in 3 mL of *tert*-butanol was added dropwise into the reaction under vigorous stirring. The reaction mixture was then refluxed overnight and monitored by TLC (hexane–acetone, 1 : 1). It was cooled to room temperature and quenched with 1 M HCl. All the solvents were evaporated and anhydrous ethanol was added to the residue. The mixture was stirred and the white solid part was filtered. The filtrate was

collected and 1.50 g of SOCl_2 was added to the solution under argon. The mixture was stirred overnight and monitored by TLC (hexane–acetone, 3 : 1). The mixture was neutralized by 10% NaHCO_3 and extracted three times with dichloromethane. The solvent was evaporated under reduced pressure and purified by silica gel column chromatography using hexane and acetone (3 : 1) as the eluting solvent. Compound **6a** was obtained as a yellow viscous oil (0.11 g, 60.0% yield) after removing the solvent. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.01 (1H, d), 7.78 (3H, m), 7.64 (1H, s), 7.58 (2H, d), 7.33 (3H, m), 7.15 (1H, m), 6.86 (2H, d), 4.24 (4H, m), 4.17 (2H, s), 4.13 (2H, s), 3.76 (12H, m), 1.29 (6H, m). EI-MS calculated for $[\text{M}^+]$: 573.27, found 573.28. IR (NaCl plate, cm^{-1}): 3100, 2950, 2870, 1751, 1600, 1596, 1519, 1219.

Diethyl 6-[4-(2,7-dibromo-9H-fluoren-9-ylidene)methyl]phenyl]-3,9,12-trioxa-6-azatetra decane-1,14-dioate (**6b**)

Potassium *tert*-butoxide (11.22 g, 100.1 mmol) was added to a solution of compound **5b** (5.00 g, 8.35 mmol) in 70 mL *tert*-butanol under an argon atmosphere and the mixture was refluxed for 2 h. Then a solution of bromoacetic acid (8.57 g, 61.68 mmol) in *tert*-butanol was added dropwise into the reaction under vigorous stirring. The reaction mixture was then refluxed overnight and monitored by TLC (hexane–acetone, 1 : 1). It was cooled to room temperature and quenched with 1 M HCl. All the solvents were evaporated and 200 mL of anhydrous ethanol was added to the residue. The mixture was stirred and the white solid part was filtered. The filtrate was collected and 18.0 g of SOCl_2 was added to the solution under argon. The mixture was stirred overnight, then neutralized by 10% NaHCO_3 and extracted three times with dichloromethane. The solvent was evaporated under reduced pressure and purified by silica gel column chromatography using hexane and acetone (3 : 1) as the eluting solvent. Compound **6b** was obtained as a yellow viscous oil (5.50 g, 84.1% yield) after removing the solvent. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.17 (1H, d), 7.90 (1H, d), 7.63 (1H, s), 7.58 (3H, m), 7.52 (1H, s), 7.46 (2H, m), 6.83 (2H, d), 4.24 (4H, m), 4.16 (2H, s), 4.14 (2H, s), 3.76 (12H, m), 1.29 (6H, m). EI-MS calculated for $[\text{M}^+]$: 731.1, found 731.0. IR (NaCl plate, cm^{-1}): 2979, 2904, 1752, 1600, 1591, 1519, 1196.

Compound 7a

A solution of compound **6a** (0.060 g, 0.11 mmol) in a mixture of methanol and toluene (1 : 1 v/v, 10 mL) was cooled at 0 °C and then LiOH (0.080 g, 16 mol equiv.) was added to the solution. The solution was stirred for two days at room temperature under an argon atmosphere. The reaction was monitored by TLC for complete hydrolysis of the ester. The reaction mixture was evaporated to dryness and the residue was dissolved in a minimum amount of methanol. The methanol solution was passed through a short column of silica gel eluting with acetone and methanol (1 : 1 v/v). Compound **7a** was obtained as a yellow solid (0.047 g, 85.5% yield); m.p. 170 °C; $^1\text{H NMR}$ (300 MHz, D_2O): δ 7.75 (1H, d), 7.57 (3H), 7.38 (1H), 7.20 (5H), 6.95 (1H), 6.45 (2H), 3.76 (4H), 3.35 (12H). ESI-MS calculated for $[\text{M}^+]$: 517.21, found 517.40. IR (KBr, cm^{-1}): 3429, 2923, 1607, 1518, 1430.

Polymer P1

Under an argon atmosphere, a solution of $\text{Ni}(\text{COD})_2$ (0.28 g, 1.03 mmol), COD (0.48 mL, 3.92 mmol) and bipyridine (0.16 g, 1.03 mmol) in toluene (4 mL) was heated to 80 °C. Then, a solution of compound **6b** (0.30 g, 0.41 mmol) in 4 mL of toluene was added to the reaction and the mixture was heated at 90 °C in dark. After 20 h, a mixture of methanol–acetone–1 M hydrochloric acid (1 : 1 : 1 v/v, 30 mL) was added and the solution was left to stir for 2 h. The yellow polymer **P1** was precipitated into methanol and then collected by filtration (0.20 g, 85.0% yield). The polymer was not fully soluble in common organic solvents. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 6.85–8.5 (aromatic CH), 4.11 (m), 3.67 (m), 1.27 (m). IR (NaCl plate, cm^{-1}): 2960, 2908, 1750, 1594, 1601, 1518, 1204. **P1** has a maximal emission at 534 nm in DMF (excitation wavelength = 400 nm).

Polymer P2

LiOH (0.20 g, 8.33 mmol) in methanol (15 mL) was added to a solution of polymer **P1** (0.16 g) in DMF (10 mL). After refluxing overnight, the resulting reddish precipitate was collected by filtration (0.120 g, 81% yield). IR (KBr, cm^{-1}): 3429, 2923, 1607, 1518, 1430.

Polymer P3

Polymer **P2** was washed twice with 2 mL of water to get rid of LiOH and then with 20% HCl and dried in a vacuum oven at 70 °C for 12 h. IR (KBr, cm^{-1}): 3442, 2950, 2871, 1724, 1591, 1517.

Preparation of fluorometric titration solutions

Stock solutions (0.01 M) of different salts, including Pb^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , Ca^{2+} , Mg^{2+} , Hg^{2+} , Mn^{2+} , Zn^{2+} , Fe^{3+} , Cu^{2+} and K^+ , and compound **7a** (2.8×10^{-4} M) were prepared in pure water. The fluorescence spectroscopic titration for the sensitivity of **7a** was carried out by sequentially adding 2, 6, 10, 14, 16, 22, 30, 34, 38, 50, 60, 70, 80 and 100 μL aliquots of Pb^{2+} solution to 5 mL of the solution of **7a**. The fluorescence turn-on titration for FOS was carried out by sequentially adding 5, 10, 15, 20, 25, 35, 45, 55, 65, 75 and 95 μL aliquots of Pb^{2+} solution to 3 mL of the solution of **7a**. A solution of polymer **P2** (2.8×10^{-4} M) in THF–water (1 : 1 v/v) was prepared and used for the experiments. The titration for sensitivity of **P2** was carried out by sequentially adding 2, 12, 22, 32, 42, 52, 62, 72, 82, 102, 112, 122, 142, 202 and 232 μL aliquots of Pb^{2+} solution to 5 mL of the polymer solution. The solutions of compound **7a** and polymer **P2** with Pb^{2+} were stirred for 1 minute and placed in a quartz cuvette, respectively. The fluorescence spectra were recorded at room temperature each time at the excitation wavelength of 400 nm.

Results and discussion

Design, synthesis and characterization

To have a fluorescence turn-on sensory compound with high sensitivity and selectivity towards Pb^{2+} in aqueous media, a receptor and a fluorophore with the desired properties are required. The lead ion has a multivalent binding site and binds

easily with a carboxylate unit.³¹ Chang's probe consists of a dicarboxylate pseudo crown as a receptor, which is highly selective towards Pb^{2+} and is able to impart water-solubility to the probe (Fig. 1). For this probe to work properly, the pH of the medium needs to be maintained in a given range. Upon binding with the lead ion, the fluorescence intensity of Chang's probe increases 18-fold. The fluorophore is a fluorescein with a quantum yield of 0.013. Thus, to design a new sensory probe, the dicarboxylate pseudo crown from Chang's probe is an ideal receptor and should be kept. However, the fluorescein fluorophore could be replaced preferably with one with a high fluorescence quantum yield. The fluorene derivatives and polyfluorene are known to be highly fluorescent with a high quantum yield. Accordingly, fluorene was chosen as a fluorophore in design, owing to its high fluorescence quantum yield (e.g., $\Phi_F = 0.87$ in chloroform for a fluorene-containing polymer³²) and its feasibility for functionalization for further polymerization.³³ Since it is known that conjugated polymers can amplify the signals, a conjugated fluorene-polymer was also designed as a target polymer probe for lead detection. Fig. 1 shows the designed fluorene-based sensory probe and polymer, in comparison with Chang's probe, for the fluorescence turn-on detection of Pb^{2+} in water.

The synthesis of a small molecular probe and monomer for a polymer probe is depicted in Scheme 1. As shown in Scheme 1, diol **1** with a 75% yield was synthesized by the reaction of 2-aminoethanol with 2-(2-chloroethoxy) ethanol.²⁴ The protection of the hydroxyl groups in **1** was carried out in pyridine using acetic anhydride.^{34,35} The Vilsmeier reaction with electron-rich compound **2** and POCl_3 -DMF afforded aldehyde **3** in an 89% yield.³⁴ After deprotection with 25% NaOH,³⁵ aldehyde **4** was reacted with fluorene or 2,7-dibromofluorene in the presence of potassium *tert*-butoxide in *tert*-butanol-THF to give the expected fluorene derivatives **5a** and **5b** with yields of 72% and 85%, respectively.^{36,37} Subsequent etherification with bromoacetic acid followed by esterification produced diesters **6a** and **6b** in 72% and 60% yields, respectively.^{24,38} **6b** is considered to be the potential monomer for making conjugated polymer

probes. The basic hydrolysis of the diester in methanol with LiOH yielded the target molecular probes **7a** and **7b** in 85% and 90% yields, respectively.^{24,39}

The structures of monomer **6b** and sensory compound **7a** were confirmed by IR, NMR and MS spectroscopy. Compounds **6b** and **6a** are structurally similar and the former contains two bromines at the 2 and 7 positions in fluorene. The peaks at 8.17 and 7.90 ppm in the ^1H NMR spectrum of **6b** indicate the protons at positions 1 and 8. The singlet peak at 7.63 ppm indicates the alkene proton, which is almost the same for compounds **6a** and **6b**. All other aromatic peaks for the fluorene part (at positions 3, 4, 5 and 6) are in the region of 7.52 to 7.58 ppm. Peaks at 7.46 and 6.83 ppm indicate the *meta* and *ortho* aromatic protons with respect to the nitrogen atom. The peak at 1.29 ppm represents the methyl proton of the ester. Two singlet peaks at 4.14 and 4.16 ppm are assigned to the $\text{O}=\text{C}-\text{CH}_2-\text{O}$ moiety. Peaks at 4.24 and 3.76 are from the NCH_2 and OCH_2 moieties. The IR spectrum of compound **6b** shows the sharp and intense band at 1752 cm^{-1} for $\text{C}=\text{O}$ of the ester group. The mass spectrum of **6b** shows a molecular ion peak at m/z 731.0, which is consistent with its structure.

The IR spectrum of **7a** displays the asymmetric $\text{O}=\text{C}-\text{O}^-$ band at 1607 cm^{-1} and symmetric $\text{O}=\text{C}-\text{O}^-$ at 1430 cm^{-1} , which are the characteristic peaks for the acid salt form. There is no peak around 1750 cm^{-1} , indicating that all the ester groups were hydrolyzed and converted to the carboxylic acid salt (Fig. S34†). The ^1H NMR spectrum of **7a** shows that all the aromatic protons are in the region of 6.45–7.75 ppm. There are no peaks at 1.30 ppm for the methyl protons, thus indicating that the ester groups are completely hydrolyzed (Fig. S33†). The mass spectrum of **7a** shows a molecular ion peak at m/z 517.40, which is consistent with its structure. To further confirm the structure of compound **7a**, a methyl-ester compound **8** was synthesized by treatment of **7a** with methanol and thionyl chloride (Scheme S1†). The ^1H NMR spectrum of compound **8** displays two singlets at 4.19 and 4.16 ppm, assigned to the moiety of $\text{O}-\text{CH}_2-\text{C}=\text{O}$. The total 18 protons in the region of 3.7 to 4.0 ppm indicate the presence of the $\text{O}-\text{CH}_2$, $\text{O}-\text{CH}_3$, and NH_2

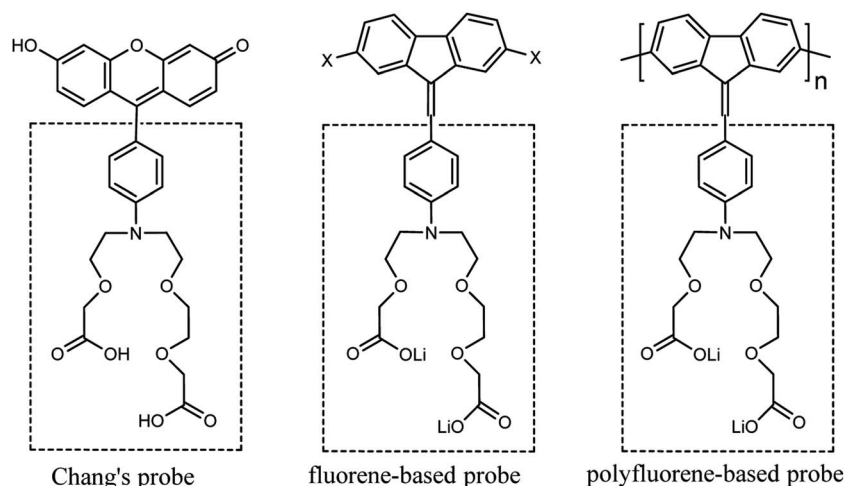
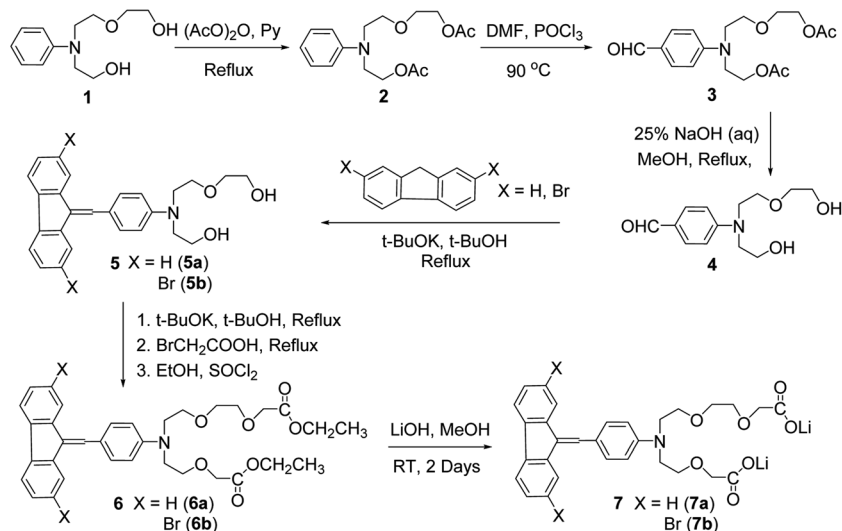


Fig. 1 Molecular and polymer probes for the fluorescence turn-on detection of Pb^{2+} in water.



Scheme 1 Synthetic route to monomer **6b** and sensory compound **7a**.

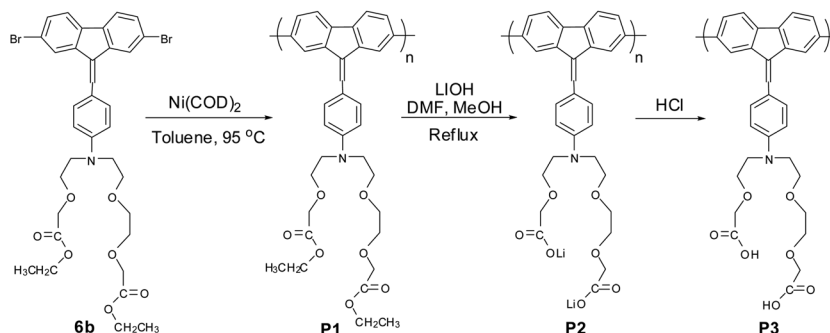
moieties (Fig. S37[†]). Its IR spectrum has a sharp peak at 1754 cm^{-1} characteristic of the C=O band of the ester (Fig. S34[†]). The mass spectrum of compound **8** shows a molecular ion peak at $m/z\ 546.22\ [M + H^+]$, which is consistent with its structure.

All the spectroscopic measurements for compound **7a** were performed in pure water at room temperature. Compound **7a** displays a maximal absorption peak at 402 nm. A very weak emission centered at 489 nm indicates the presence of π -conjugation between the fluorene and the lead receptor, the electron transfer from the amino group to the fluorene moiety in **7a** effectively causes fluorescence quenching of the fluorene fluorophore.

Polymers **P2** and **P3** are derived from polymer **P1**, which was synthesized by the polymerization of the dibromo-substituted monomer **6b** (Scheme 2). **P1** was obtained by the polymerization of **6b** in an 85% yield using the Yamamoto coupling reaction in the presence of $\text{Ni}(\text{COD})_2$ in toluene.^{40,41} In the ^1H NMR spectrum of **P1**, the peaks from 6.5 to 8.5 ppm are assigned to the aromatic protons and those at 4.11 and 3.67 ppm come from the NCH_2 and OCH_2 moieties, resembling the same protons in monomer **6a**. The peak at 1.27 ppm represents the methyl proton of the ester (Fig. S39[†]). The IR

spectrum of polymer **P1** shows the sharp and intense band at 1750 cm^{-1} for C=O of the ester group. The onset temperature for thermal decomposition was found to be quite high ($232\text{ }^\circ\text{C}$). The DSC trace showed multiple melting transitions at about $176\text{ }^\circ\text{C}$. Polymer **P1** is fully soluble in a polar solvent like DMF and partially soluble in chloroform. In comparison with the maximal absorption of **6a** (400 nm), polymer **P1** absorbs at a longer wavelength (426 nm), due to the extended conjugation of the fluorene backbone.

Polymer **P2** was obtained by hydrolysis of polymer **P1** using LiOH in a mixture of DMF and methanol in an 81% yield.⁴² Its IR spectrum displays the asymmetric stretching $\text{O}=\text{C}-\text{O}^-$ at 1607 cm^{-1} and symmetric stretching $\text{O}=\text{C}-\text{O}^-$ at 1430 cm^{-1} , which is characteristic of the acid salt form. There is no peak at 1750 cm^{-1} , confirming complete ester hydrolysis. Polymer **P2** is more soluble in a mixture of water-THF. By washing **P2** with 20% HCl in water, polymer **P3** was formed and its carboxylic acid groups were confirmed by IR (1724 cm^{-1}). The resulting polymer **P3** became less soluble in water than **P2** and soluble only in DMF. Polymer **P3** was not soluble in a water-THF mixture due to the low polarity and only became soluble in water-THF upon addition of LiOH.



Scheme 2 Synthesis of polymers **P1**–**P3** for detection of Pb^{2+} .

The absorption spectra of polymers **P2** (in water-THF, 1 : 1) and **P3** (in DMF) have the same maximal absorption at 372 nm and a shoulder at 420 nm. When the polymer is in the salt form (**P2**), it has a weak emission centered at 509 nm; whereas its acidic form (**P3**) has a longer emission centred at 529 nm (Fig. S44[†]). The hydrophilic nature of the polymer in its salt form may decrease the aggregation of the polymer in the solution, and as a result the emission maximum is at a shorter wavelength. The emission peak is still at a longer wavelength than that of **7a**, which is due to the extended conjugation of the fluorene backbone.

Detection of Pb²⁺ in water using compound **7a**

The high sensitivity of compound **7a** towards Pb²⁺ was revealed by a fluorescence spectroscopic titration experiment. Fig. 2 displays the changes in fluorescence of **7a** with different concentrations of Pb²⁺.

Compound **7a** is virtually not fluorescent. Upon addition of the Pb²⁺ solution in a concentration as low as 4 μM, its fluorescence turns on noticeably. The emission intensity at 489 nm increased sharply, nearly 152-fold after an increase in the Pb²⁺ concentration up to 200 μM. For Chang's probe, after addition of 75 μM of Pb²⁺ solution to Leadfluor-1, its fluorescence intensity increased 18-fold;²⁴ whereas the same fold of intensity was achieved by **7a** with the addition of only 24 μM of Pb²⁺ solution. The addition of 15 ppb of Pb²⁺, which is the maximum EPA limit for allowable level of lead in drinking water, to a solution of **7a** (1.4×10^{-4} M) triggers a 23% increase in fluorescence intensity, which is stronger than the reported probe (15% increase).²⁴ Upon addition of Pb²⁺ the absorption wavelength (402 nm) of compound **7a** in solution (5×10^{-5} M) does not change but the absorption intensity gradually decreases (Fig. S49[†]). These results indicate that the fluorene is a suitable fluorophore, which makes compound **7a** a highly sensitive molecular probe for Pb²⁺ detection in aqueous media.

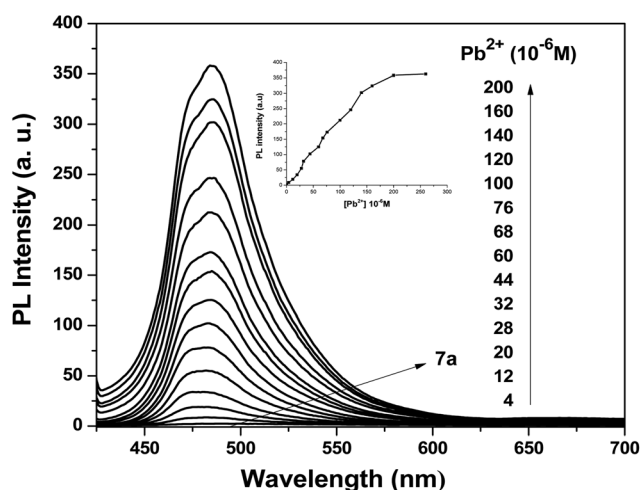


Fig. 2 Changes of fluorescence spectra of **7a** in water (2.8×10^{-4} M) upon addition of Pb²⁺ (0 to 200×10^{-6} M) (excitation at 400 nm).

The stoichiometry for Pb²⁺-**7a** binding was determined using the Job's plot method.^{43,44} For the measurement of the Job's plot, aqueous solutions of Pb²⁺ and **7a** in various molar ratios (2 : 8, 3 : 7, 4 : 6, 5 : 5, 6 : 4, 7 : 3, 8 : 2, 9 : 1, 10 : 0) were prepared. The relationship between relative emission intensity *versus* various mole fraction shows that compound **7a** exhibits a mole fraction close to 50%. Therefore, the **7a**-Pb²⁺ complex is formed in a 1 : 1 molar ratio (Fig. S50[†]).

The fluorescence turn-on mechanism can be explained as follows: the Pb²⁺-pseudo-macrocyclic complex facilitates electron transfer from the nitrogen to the lead ion. Thus, the redox potential of the electron donor in the **7a**-Pb²⁺ complex is raised so that the relevant HOMO level becomes lower than that of the free fluorophore. As a result, photoinduced electron transfer (PET) is no longer possible in the system and the fluorescence of the fluorophore turns on.

The selectivity of compound **7a** in the presence of different alkali, alkaline earth, transition and heavy metal ions (K⁺, Ca²⁺, Mg²⁺, Mn²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Hg²⁺) was investigated using a spectroscopic method. After addition of 200 μM of individual metal ions to a solution of **7a** (2.8×10^{-4} M in water), the emission intensity at 489 nm from each spectrum was taken and compared against each metal ion (Fig. 3). A relatively strong emission of compound **7a** towards Pb²⁺ over these 11 metal ions clearly indicates its high selectivity for the detection of Pb²⁺ in an aqueous medium. Some metal ions such as Ca²⁺, Cd²⁺, Hg²⁺ and Mn²⁺ are known to interfere with the detection of Pb²⁺.²³ In our case, Cd²⁺, Co²⁺ and Cu²⁺ show little interference. The selectivity of compound **7a** towards Pb²⁺ over these 11 metals demonstrates that the dicarboxylate pseudo crown receptor can selectively bind with Pb²⁺ (Fig. 3).

Detection of Pb²⁺ in an aqueous medium using a polymer

Electrons in conjugated polymers are highly mobile and can migrate throughout the polymer chain. This migration increases the frequency of interaction with the bound quencher, and as a result the sensitivity becomes higher.^{45,46} The sensitivity of polymer **P2** (2.8×10^{-4} M) towards Pb²⁺ was

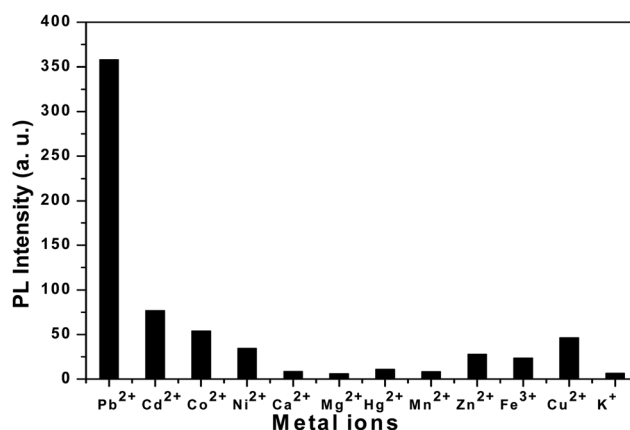


Fig. 3 Relative fluorescence intensity of **7a** solution (2.8×10^{-4} M in water) towards different metal ions.

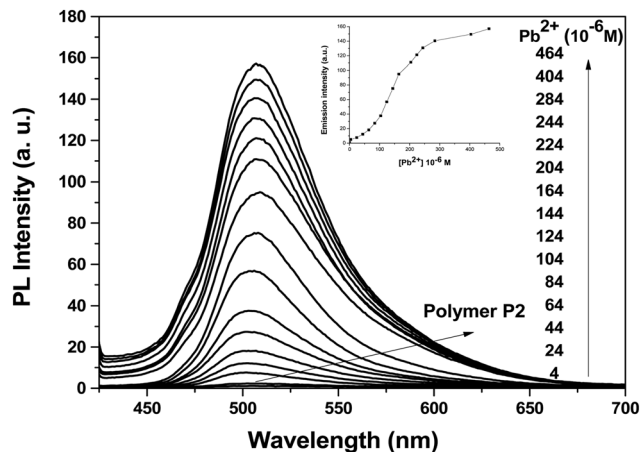


Fig. 4 Changes of fluorescence spectra of polymer P2 (2.8×10^{-4} M) in pure water–THF (1 : 1) upon addition of Pb^{2+} (0 to 464×10^{-6} M) (excitation at 400 nm).

determined by a fluorescence spectroscopic titration experiment (Fig. 4). Upon addition of $4 \mu\text{M}$ of Pb^{2+} , the fluorescence of P2 turned on noticeably. The emission intensity of polymer P2 at 509 nm increased sharply in a water–THF (1 : 1 v/v) solution by nearly 134 fold with an increase of the concentration of Pb^{2+} from 0 to 464×10^{-6} M. Polymer P2 shows the same sensitivity towards Pb^{2+} as compound 7a. The addition of 15 ppb of Pb^{2+} (the maximum EPA limit) to a solution of polymer P2 (2.8×10^{-4} M) triggered an increase in fluorescence intensity of 26%.

As an analog to P2, polymer P3 is in the acidic form, and a 20 nm bathochromic shift in the maximum emission wavelength from 509 nm to 529 nm was observed. Upon addition of Pb^{2+} up to 584×10^{-6} M, the fluorescence intensity of P3 (2.8×10^{-4} M in DMF) at 529 nm increased only 26 fold (Fig. S51†). Inefficient binding to Pb^{2+} by P3 is mainly due to the nature of the carboxylic acid and by converting the acid to the salt, the sensitivity of P3 towards the lead ion should increase. Thus, after addition of LiOH to the solution of P3, the fluorescence intensity at 509 nm increased 164 fold in the presence of Pb^{2+} (Fig. S52†). Accordingly, sensory compound 7a and polymers P2 or P3 in the salt state are active to detect Pb^{2+} in water. Both compound 7a and polymer P2 give the same level of fluorescent signals towards 15 ppb of Pb^{2+} .

Optic-fibre detection of Pb^{2+} in an aqueous medium with compound 7a

The fibre-optic sensing of the lead ion in water offers some advantages, such as on-site detection, being a small hand-held device, and quick detection with less sample preparation. As shown in Fig. 5, a coaxial fibre-optic probe with optimized performance demonstrated before²⁷ was used for the titration measurement. The FOS setup consists of seven identical fibres with core/cladding diameters of $400 \mu\text{m}/430 \mu\text{m}$ and a numerical aperture (NA) of 0.22, where the e-lead contains six fibres and delivers the 400 nm excitation light to the sample solution. At the same time, the center fibre (r-lead) receives the fluorescent signal light and sends it to the spectrometer or detector.

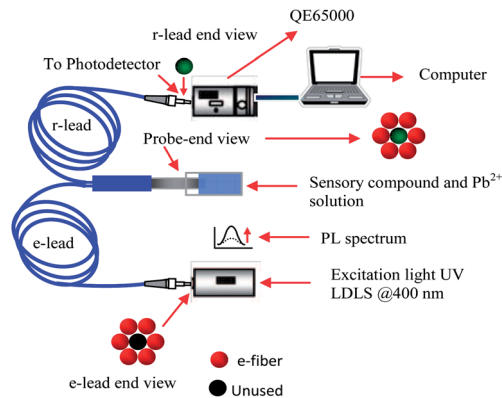


Fig. 5 A schematic drawing of an experimental set up for fibre-optic sensing of Pb^{2+} in water.

The Ocean Optics Spectra Suite software package is used to record all spectra for titration measurements. A standard 15×45 mm quartz cuvette (3.7 mL capacity) is used to contain the 7a solution. In the experiment, the probing end of the fibre-optic probe is immersed into the solution when observing and recording the fluorescent spectrum upon addition of Pb^{2+} .

Fig. 6 shows the fluorescence spectra obtained from the FOS experiments using compound 7a as a probe (2.8×10^{-4} M in water). Initially, there is a very weak signal from the solution of compound 7a. The fluorescence of 7a increased noticeably and gradually with gradual addition of Pb^{2+} . When $33 \mu\text{M}$ of Pb^{2+} was added to 7a, a noticeable fluorescence turn-on signal was observed. The fluorescent intensity increased rapidly with further increases of Pb^{2+} . With $316 \mu\text{M}$ of Pb^{2+} , the emission intensity increased nearly 50 fold. This indicates compound 7a has a very close detection limit in both the fluorometer and fibre-optic set up. The fluorescence detection of Pb^{2+} in water has been demonstrated using the fibre-optic sensing setup with the sensory compound 7a. P2 is the best candidate among the synthesized polymers for further lead sensing application in fibre-optic sensors.

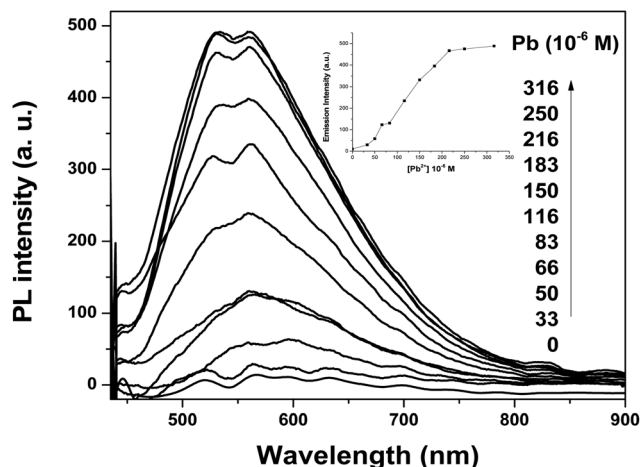


Fig. 6 Changes of fluorescence spectra of compound 7a (2.8×10^{-4} M) in pure water by FOS (excitation at 400 nm) upon addition of Pb^{2+} (0 to 316×10^{-6} M).

Conclusions

The sensory compound **7a** and polymer **P2** are suitable for the fluorescence turn-on detection of Pb^{2+} in water with a concentration of $4 \mu\text{M}$. Upon addition of $200 \mu\text{M}$ of Pb^{2+} , the fluorescence intensity increased 152 fold for **7a** and 134 fold for **P2**. Both probes show a high selectivity towards the lead ion amongst 11 other metal ions. The fluorescence detection of Pb^{2+} in water has also been demonstrated using a fibre-optic sensing setup.

Acknowledgements

We thank the support for research from the Natural Sciences and Engineering Research Council of Canada and the Canada Research Chairs program.

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