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Pillar[5]arene-based fluorescent polymer for selective detection and removal of mercury ions†

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A novel pillar[5]arene-based thioacetohydrazone functionalized fluorescent polymer was designed and synthesized. This polymer not only contains pillar[5]arene units as the fluorophore (signal transducer) but also embedded the thioacetohydrazone group as the ionophore (cation receptor). Therefore, it displays specificity response for mercury ion over other common cations (Mg^{2+}, Ca^{2+}, Zn^{2+}, Co^{2+}, Fe^{3+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Tb^{3+}, Cu^{2+}, Eu^{3+}, Fe^{2+}, Cr^{3+}, Ag^{+} and La^{3+}) in DMSO/H_2O (1 : 1, v/v). Competitive cations did not show any significant changes in emission intensity and the fluorescence spectra detection limit was 8.12×10^{-7} M, indicating the high selectivity and sensitivity of the polymer towards Hg^{2+}. Meanwhile, this polymer can efficiently remove Hg^{2+} from water.

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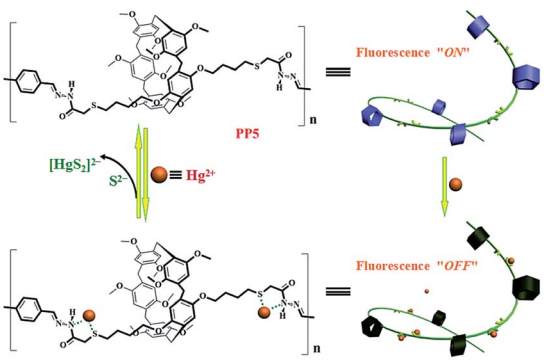
Introduction

Because of their high toxicity and bioaccumulation, heavy metal ions released into the environment can lead to a wide range of severe diseases.[1] Considerable efforts are accordingly being devoted to developing new methodologies for detection and removal of specific toxic metal ions.[2] For example, many types of small molecules have been designed as fluorescent sensors for selective and sensitive detection of metal ions.[3] On the other hand, various absorbents, such as porous silicas,[4] hydrogels,[5] nanoparticles,[6] and metal–organic frameworks (MOFs),[7] are being tested for the possible removal of toxic ions. However, most of the developed methods can only perform either the detection or the removal tasks separately, which limits their practical applications.

Pillararenes, a new kind of macrocyclic compounds, are composed of hydroquinone units linked by methylene bridges at the *para* positions.[8] They have novel host–guest binding properties due to being easier to functionalize by different substituents on the benzene rings,[9] thus functionalized pillararenes attracted a lot of attention of scientists.[10] Since it has multiple benzene ring units, it has a certain luminescent properties.[11] Therefore, pillararenes are used for fluorescence detection of ions,[12] but most of them are used to identify iron ions.[13] In addition, these reports rarely mentioned the corresponding ion can be removed. In order to extend the application of pillararenes, it is quite necessary to design and synthesize novel pillararenes for detection and removal of ions.

Polymers have been widely used as organic light-emitting diodes (OLEDs),[14] thin-film transistors, chemical sensors,[15] and in various photonic and electronic devices.[16] However, the pillar[5]arene-based polymer have rarely been reported.[17] On the other hand, the use of pillar[5]arene-based polymers to detect and remove ions hasn't been reported.

Herein, we designed and synthesized a pillar[5]arene-based fluorescent polymer for detecting and removing the metal ions. As a proof-of-concept, a thioacetohydrazone functionalized fluorescent polymer, **PP5**, was designed and applied for the selective sensing and effective removal of the toxic Hg^{2+} (Scheme 1). Although we have previously studied the selective detection and removal of mercury ions, these sensors are small molecules.[18] However, this report is the use of pillar[5]arene-based polymer for the selective detection and removal of mercury ions. Although it has previously been reported that the



Scheme 1 The pillar[5]arene-based polymer **PP5** was applied for both fluorescent detection and removal of Hg^{2+}.

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use of pillar[5]arene-based pseudorotaxane to detect and remove mercury ions, it is the host–guest complex (no polymer). Importantly, the real-time fluorescence response did show efficient quenching of **PP5** upon the addition of Hg^{2+}. Excellent sensitivity and selectivity toward the Hg^{2+} detection were verified in the presence of other competitive cations. The removal ability of **PP5** was further elucidated by the effective separation of Hg^{2+} from water. Meanwhile, **PP5** can recycle detection and removal of Hg^{2+}.

Experimental

Materials and instruments

1,4-Dimethoxybenzene, boron trifluoride ethyl ether complex, 1,4-dibromobutane and ethyl mercaptoacetate were reagent grade and used as received. Solvents were either employed as purchased or dried by $CaCl_2$. ^{1}H NMR spectra were recorded on a Mercury-600BB spectrometer at 600 MHz and ^{13}C NMR spectra were recorded on a Mercury-600BB spectrometer at 151 MHz. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with solvent resonances as internal standards). Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). Mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker-FranzenAnalytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer. The morphologies and sizes of the polymer were characterized using field emission scanning electron microscopy (FE-SEM, JSM-6701F) at an accelerating voltage of 8 kV. The X-ray diffraction analysis (XRD) was performed in a transmission mode with a Rigaku RINT2000 diffractometer equipped with graphite monochromated CuKα radiation (λ = 1.54073 Å). The infrared spectra were performed on a Digilab FTS-3000 Fourier transform-infrared spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer.

Adsorption experiments

The adsorption experiments were performed at different mercury(II) concentration, corresponding adsorbent and room temperature (Table S1†). The experiments were carried out in 25 mL round-bottom flasks, with continuously stirring (usually for 5 h). The residual concentration of mercury(II) was determined by the inductively coupled plasma (ICP) analysis.

Synthetic procedures

Synthesis of 1,4-bis(4-bromobutoxy)benzene 1. Hydroquinone (2.3 g, 20.0 mmol), K_2CO_3 (16.6 g, 120 mmol), KI (6.6 g, 40 mmol), 1,4-dibromobutane (34.6 g, 160 mmol) and acetone (400.0 mL) were added in a 500 mL round-bottom flask stirred at room temperature. The reaction mixture was stirred at reflux for 1.5 days. After the solid was filtered off, the solvent was evaporated and the residue was dissolved in CH_2Cl_2. Column chromatography (silica gel; petroleum ether : CH_2Cl_2 = 10 : 1) afforded a white solid (6.0 g, 80%). Mp 83–85 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.83 (d, J = 0.8 Hz, 4H), 3.96 (t, J = 6.0 Hz, 4H), 3.52–3.25 (m, 4H), 2.10–1.88 (m, 8H).

Synthesis of a copillar[5]arene 2. To a solution of 1,4-bis(4-bromobutoxy)benzene (1.90 g, 5.0 mmol) and 1,4-dimethoxybenzene (2.76 g, 20.0 mmol) in 1,2-dichloroethane (200 mL), paraformaldehyde (0.75 g, 25.0 mmol) was added under nitrogen atmosphere. Then boron trifluoride diethyl etherate (6.75 mL, 25 mmol) was added to the solution and the mixture was stirred at room temperature for 4 h and concentrated by rotary evaporation. The resultant oil was dissolved in CH_2Cl_2 and washed twice with H_2O. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product, which was isolated by flash column chromatography using petroleum ether/ethyl acetate (20 : 1, v/v) to give **2** (1.69 g, 34%) as a white solid. Mp 187–189 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.84–6.74 (m, 10H), 3.87 (t, J = 5.9 Hz, 4H), 3.83–3.78 (m, 10H), 3.72 (t, J = 19.9 Hz, 24H), 3.33 (s, 4H), 1.94 (s, 4H), 1.84 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.80 (s), 150.75 (s), 150.70 (s), 150.58 (s), 149.84 (s), 128.44 (s), 128.30 (s), 128.08 (s), 114.89 (s), 114.15 (s), 113.92 (s), 113.71 (s), 67.32 (s), 55.95 (d, J = 3.6 Hz), 55.76 (s), 55.70 (s), 33.34 (s), 30.55 (s), 29.75 (s), 29.48 (d, J = 5.2 Hz), 29.19 (s), 28.32 (s). ESI-MS m/z: $(M + NH_4)^+$ calcd for $C_{51}H_{64}O_{10}Br_2N$ 1010.2871; found 1010.2878.

Synthesis of functionalized pillar[5]arene 3. Copillar[5]arene **2** (0.5 g, 0.5 mmol) K_2CO_3 (0.28 g, 2 mmol) and ethyl mercaptoacetate (0.3 mL, 2.75 mmol) were added to acetone (80 mL). The solution was refluxed overnight. After the solid was filtered off, the solvent was evaporated and the residue was dissolved in CH_2Cl_2. Column chromatography (silica gel; petroleum ether : CH_2Cl_2 = 20 : 1) afforded a white solid (6.0 g, 80%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.78 (dd, J = 14.3, 7.1 Hz, 10H), 3.85 (t, J = 5.8 Hz, 4H), 3.79–3.74 (m, 14H), 3.71 (s, 6H), 3.69 (s, 12H), 3.66 (s, 12H), 3.24 (s, 4H), 2.72 (t, J = 7.0 Hz, 4H), 1.87 (ddd, J = 26.5, 14.7, 7.9 Hz, 8H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.88 (s), 151.71–148.89 (m), 129.38–126.85 (m), 116.55–112.46 (m), 67.71 (s), 55.73 (dd, J = 10.4, 5.9 Hz), 52.34 (s), 41.19 (s), 33.42 (s), 32.52 (s), 29.46 (s), 28.86 (s), 25.72 (s).

Synthesis of pillar[5]arene 4. Functionalized pillar[5]arene **3** (0.5 g, 0.5 mmol) and hydrazine hydrate (0.3 mL, 6 mmol) were added to ethanol (20 mL). The solution was refluxed overnight. Then the solvent was removed by evaporation, you can afford a white solid. After white solid was washed by ethanol to obtain **4** as a white solid (0.48 g, 93%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.11 (s, 2H), 6.78 (d, J = 3.4 Hz, 10H), 4.34 (s, 4H), 3.84 (s, 4H), 3.75–3.61 (m, 34H), 3.06 (s, 4H), 2.67 (s, 4H), 1.80 (dd, J = 29.0, 7.3 Hz, 8H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 168.92 (s), 150.32 (s), 127.90 (s), 113.69 (s), 67.84 (s), 55.89 (s), 32.99 (s), 32.09 (s), 29.42 (s), 28.80 (s), 25.96 (s). ESI-MS m/z: $(M + H)^+$ calcd for $C_{55}H_{71}O_{12}N_4S_2$ 1043.44; found 1043.2296.

Synthesis of polymer PP5. To a solution of pillar[5]arene **4** (0.21 g, 0.2 mmol) in ethanol (20 mL), terephthalaldehyde (0.027 g, 0.2 mmol) and acetic acid (0.05 mmol, as a catalyst) was added at room temperature. The mixture was refluxed for 48 h, and yellow solids were precipitated. The solid was isolated by sucking filtration, washed with MeOH, dried at 80 °C under vacuum for 12 h to yield **PP5** as a yellow powder (0.18 g, 75% yield). IR (powder, KBr, cm^{-1}) 3217 (N–H), 1679 (C=O), 1620 (C=N), 834 (Ar–H).

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Synthesis of the model compound M1. To a solution of pillar[5]arene **4** (0.21 g, 0.2 mmol) in ethanol (20 mL), benzaldehyde (45 μL, 0.44 mmol) and acetic acid (0.05 mmol, as a catalyst) was added at room temperature. The mixture was refluxed for 48 h, and white powder were precipitated. The solid was isolated by sucking filtration, washed with MeOH, dried at 80 °C under vacuum for 12 h to yield **M1** as a white powder (0.21 g, 85% yield). ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.47 (s, 1H), 11.37 (s, 1H), 8.18 (s, 1H), 7.97 (s, 1H), 7.65 (dd, J = 17.4, 6.0 Hz, 4H), 7.49–7.26 (m, 6H), 6.75 (s, 10H), 3.81 (s, 4H), 3.63 (s, 34H), 3.29 (s, 4H), 2.71 (d, J = 5.7 Hz, 4H), 1.80 (s, 8H).

Results and discussion

The polymer **PP5** shown in Scheme 1 and the synthesis details are presented in Scheme S1.† The model compound **M1** (as a soluble-molecule counterpart of **PP5**, structure shown in Scheme S2†) also been synthesized. Their intermediate and the model compound **M1** have been characterized by ^{1}H NMR, ^{13}C NMR, and ESI-MS (Fig. S1–S11†). This polymer not only contains pillar[5]arene units as the fluorophore (signal transducer) but also embedded the thioacetohydrazone group as the ionophore (cation receptor). These unique characteristics are expected to be beneficial for the performance in selective detection and facile removal of Hg^{2+}. **PP5** also been characterized by IR (Fig. S10†).

With the robust hydrazone linkage in its structure, **PP5** is insoluble and stable in common organic solvents, such as DMF, THF, DMSO, acetone, acetonitrile, ethanol and $CHCl_3$. Importantly, **PP5** is also insoluble and very stable in water. Thermogravimetric analysis (TGA) indicates that **PP5** is thermally stable up to 285 °C (Fig. S12†). The scanning electron microscopy (SEM) images showed that **PP5** possessed the irregular granular morphology (Fig. S13†). A characteristic vibrational band appeared at 1620 cm^{-1} in the FT-IR spectrum of **PP5** (Fig. S10†), indicating the successful condensation of 1,4-phthalaldehyde and **4** *via* the formation of –C=N– bonds. Meanwhile, we also investigated the crystallinity of this polymer in the solid state using powder XRD measurements (Fig. S14†). However, the peak of the polymer is the bread peak and significantly lower than compound **4**, which indicates that **PP5** is amorphous.

In order to investigate the luminescence properties of **PP5**, the insoluble polymer **PP5** be dispersed in DMSO/H_2O (1 : 1, v/v), and a series of host–guest recognition experiments were carried out. **PP5** toward various cations (including Mg^{2+}, Ca^{2+}, Zn^{2+}, Co^{2+}, Fe^{3+}, Pb^{2+}, Hg^{2+}, Cd^{2+}, Ni^{2+}, Tb^{3+}, Cu^{2+}, Eu^{3+}, Fe^{2+}, Cr^{3+}, Ag^{+} and La^{3+}) were primarily investigated using fluorescence spectroscopy. In the fluorescence spectrum, the maximum emission of **PP5** appeared at 470 nm while excited at λ_{ex} = 340 nm in DMSO/H_2O (1 : 1, v/v). When 10.0 equiv. of Hg^{2+} was added to the dispersed solution of **PP5**, the fluorescence emission band was quenched (Fig. S15†). The same tests were applied using Mg^{2+}, Ca^{2+}, Zn^{2+}, Co^{2+}, Fe^{3+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Tb^{3+}, Cu^{2+}, Eu^{3+}, Fe^{2+}, Cr^{3+}, Ag^{+} and La^{3+} cations, and only Hg^{2+} have significant changes in the fluorescence spectrum, and none of those other cations induced any significant changes in the fluorescent spectrum (Fig. 1).

To further exploit the utility of the polymer **PP5** as cation selective sensor for Hg^{2+}, competitive experiments were carried out in the presence of 10.0 equiv. of Hg^{2+} and 10.0 equiv. of various cations in DMSO/H_2O (1 : 1, v/v). The fluorescence selectivity was examined at an emission wavelength of 470 nm, neither of the competitive metal ions showed an appreciable influence on the Hg^{2+} detection (Fig. 2). These results further identified that **PP5** exhibits a satisfactory selectivity toward Hg^{2+} detection.

The sensitivity of **PP5** toward the Hg^{2+} detection was evaluated *via* the real-time fluorescence response. For this purpose, the stock solution of $Hg(ClO_4)_2$ was gradually added to the suspension of **PP5** in DMSO/H_2O (1 : 1, v/v), and the corresponding fluorescence spectra were measured immediately (Fig. 3). The detection limit of the fluorescent spectrum changes calculated on the basis of 3δ/S is 8.12 × 10^{-7} mol L^{-1} (Fig. S16†), indicating the high sensitivity of the sensor to Hg^{2+}.

To further illustrate the effective removal of Hg^{2+} from water, **PP5** (8 mg) was suspended in a dilute aqueous solution of $Hg(ClO_4)_2$ (100 ppm in 10.0 mL). After the mixture was stirred at room temperature for 5 h. The inductively coupled plasma (ICP) analysis verified that the concentration of the residual Hg^{2+} in

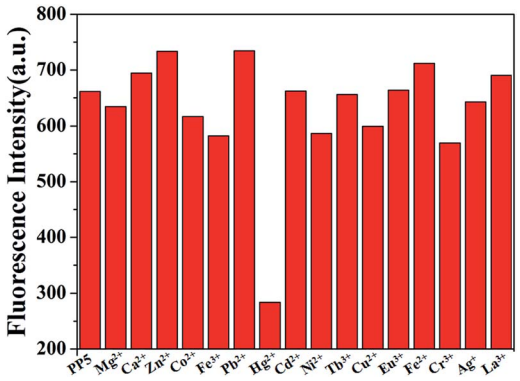

Fig. 1 Fluorescence spectra responses for **PP5** ([RU] = 4 × 10^{-5} M) and each of the various cations (4 × 10^{-4} M) in DMSO/H_2O (1 : 1, v/v).

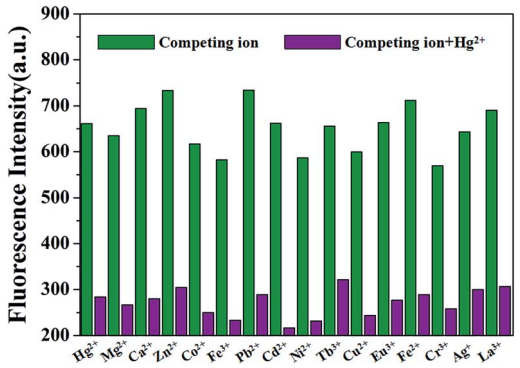

Fig. 2 Fluorescence of **PP5** ([RU] = 4 × 10^{-5} M) at 470 nm with addition of 10.0 equiv. of Hg^{2+} in the presence of 10.0 equiv. of other cations in DMSO/H_2O (1 : 1, v/v).

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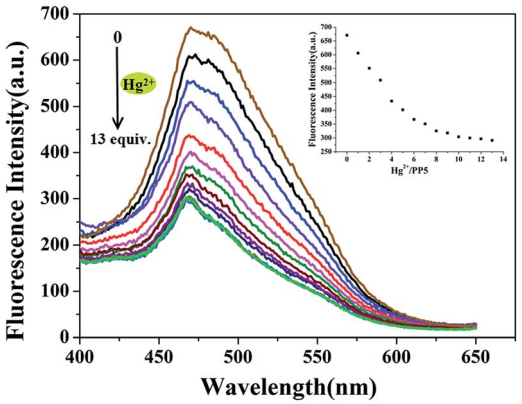

Fig. 3 Fluorescence spectra of **PP5** ([RU] = 4×10^{-5} M) in the presence of different concentration of Hg^{2+} in DMSO/H_2O (1 : 1, v/v). Inset: A plot of emission at 470 nm *versus* number of equivalents of Hg^{2+}.

water was 3.75 ppm, that is, 96.25% of the mercury was removed by polymer **PP5**. Therefore, this polymer could effectively remove Hg^{2+} from water. In addition, the adsorption capacity of adsorbent have been calculated by the adsorption experiment data (Table S1†). The average value of adsorption capacity is 108 mg g^{-1} at room temperature.

On the basis of the excellent Hg^{2+} uptake capacity, we further explored the recycle use of **PP5**. Upon the simple treatment with 5 equiv. of aqueous Na_2S solution to exchange the adsorbed Hg^{2+} out,[19] the fluorescence of **PP5** could be easily recovered. As shown in Fig. 4, this Hg^{2+} adsorption–desorption cycle could be repeated at least four times without significant loss of the sensitivity and responsiveness of **PP5**.

We used model compound **M1** to study the possible mechanism by ^1H NMR titration experiments because **PP5** is difficult to be dissolved. Partial proton NMR spectra of **M1** is shown in Fig. 5(a), and the signal assignments are depicted on the top. Upon the adsorption of Hg^{2+}, H_1 and H_3 signals of **M1** showed a obvious downfield shift (Fig. 5(b)). This result identified Hg^{2+} have the strong interaction with S and N atoms in Hg/**M1**.

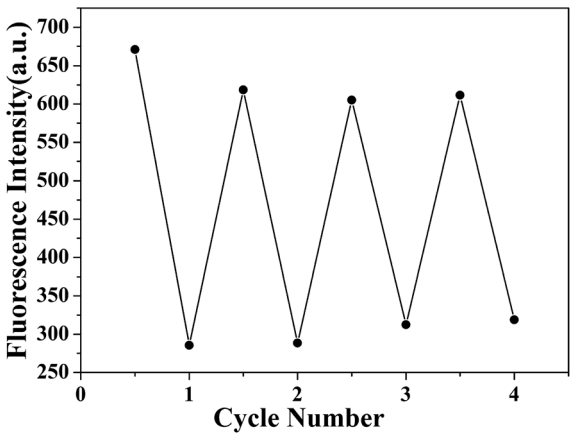

Fig. 4 Recycle use of **PP5** for selective detection and facile removal of the toxic Hg^{2+}. Upon treatment in aqueous Na_2S solution, **PP5** was easily recovered and could be repeatedly used.

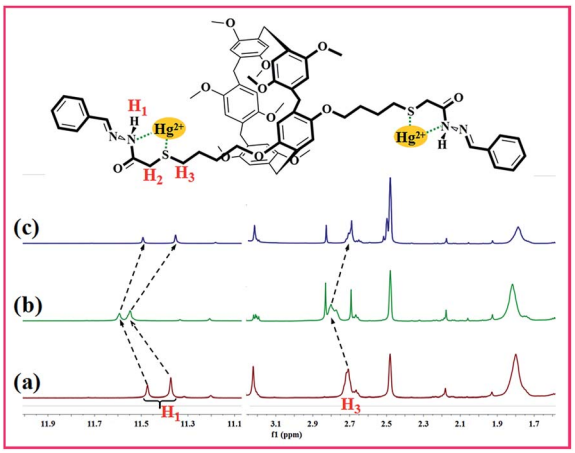

Fig. 5 ^1H NMR spectra of **M1** (a), Hg/**M1** (b), and Hg/**M1** after the treatment with Na_2S (c). H_1 and H_3 signals of **M1** was downfield shifted, which verified that mercury ions have a stronger coordination ability with S and N atoms.

Meanwhile, after the treatment of Hg/**M1** with Na_2S, the ^1H NMR spectrum recorded thereafter (Fig. 5(c)) closely resembles that of fresh **M1**. The results also illustrate the formation of complexes $[HgS_2]^{2-}$. Therefore, the selective detection and effective removal of Hg^{2+} for **PP5** stems indeed from Hg^{2+} have the strong interaction with S and N atoms.

The recognition mechanism of the polymer **PP5** with Hg^{2+} was also investigated by IR spectroscopy. In the IR spectrum of **PP5** (Fig. 6), the N–H bond show the stretching vibrations absorption peak at 3217 cm^{-1}. However, after the addition of Hg^{2+}, this peak shifts to 3448 cm^{-1}. Meanwhile, the ν_{C-S-C} band at 955 cm^{-1} was also changed, which indicates that **PP5** bonds to Hg^{2+} *via* S and N atoms. In addition, the $\nu_{C=O}$ band at 1679 cm^{-1} and the $\nu_{C=N}$ band at 1620 cm^{-1} were almost unchanged, implying that Hg^{2+} does not bind to the –C=O bonds and –C=N bonds (instead, to the S atoms and the N atom of N–H groups) in **PP5**. According to powder XRD measurements (Fig. S14†), no clear new peaks were detected when mercury ions are added to the polymer **PP5**, indicating

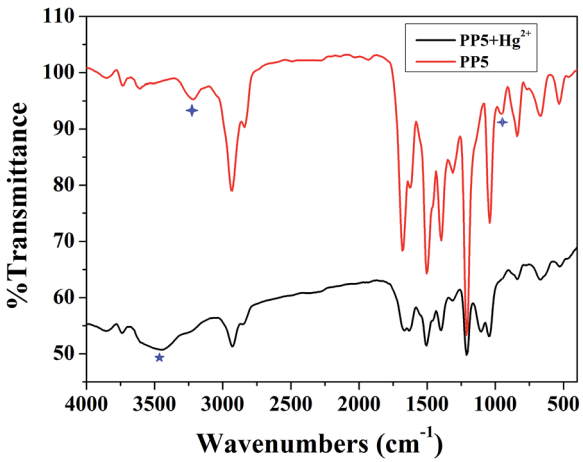

Fig. 6 IR spectra of **PP5** (red) and **PP5**–Hg^{2+} (black) in KBr disks.

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that the amorphous of the polymer is not destroyed. Therefore, the mercury ions should be coordinated with S and N atoms.

Conclusions

In summary, a novel pillar[5]arene-based thioacetohydrazone functionalized fluorescent polymer has been synthesized, and it is used for fluorescence detection and removal of the toxic mercury ions. Meanwhile, this polymer exhibits high selectivity and sensitivity (8.12×10^{-7} M), and it can the efficient removal of Hg^{2+} from water. This research not only explored a new method for the synthesis of pillararene-based polymers but also expanded the pillararene applications about cation sensing/adsorption/removal. Thus, this good example might stimulate wide interest of scientists for further development of new pillararene-based polymers. We also expect that our research will help the environment and industry.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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