CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200700782

# Polymeric Zinc Ferrocenyl Sulfonate as a Molecular Aspirator for the Removal of Toxic Metal Ions

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**Abstract:** A porous bilayered open coordination polymer $[Zn(4,4'\text{-bpy})_2(FcphSO_3)_2]_n$ (**1**; $FcphSO_3Na$ = *m*-ferrocenyl benzenesulfonate), has been assembled from $Zn(NO_3)_2$, *m*-ferrocenyl benzenesulfonate, and the bridging ligand 4,4′-bipyridine (4,4′-bpy). Ion-exchange induced products $[Cd_{0.6}Zn_{0.4}(4,4'\text{-bpy})_2(FcphSO_3)_2]_n$ (**2**), $[Zn_{0.75}Pb_{0.25}(4,4'\text{-bpy})_2(FcphSO_3)_2]_n$ (**3**), and $[Cu_{0.5}Zn_{0.5}(4,4'\text{-bpy})_2(FcphSO_3)_2]_n$ (**4**) could be obtained directly by suspending a big single crystal of **1** into concentrated solutions of $Cd(NO_3)_2$, $Pb(NO_3)_2$, and $Cu(NO_3)_2$, respectively. Most importantly, the big single crystal of **1** could be partly regenerated after immersion into concentrated aqueous solutions of $Zn(NO_3)_2$. On the other hand, powdered **1** could also be used as a metal ion adsorbent because of the well-defined pore size and pore shape. Ion exchange takes place along with the process of ion sorption. The big single crystal of **1** removes harmful metal ions by means of ion exchange, whereas powdered **1** removes toxic metal ions mainly through ion sorption. Also, compound **1** could be employed as a multi-ion analysis fluorescent probe to detect dangerous metal ions, such as $Pb^{2+}$, $Cd^{2+}$, $Ag^{+}$, and $Cu^{2+}$. The compounds described in this study may have potential applications in the design of new molecular devices.

**Keywords:** chemoselectivity · coordination polymers · drug design · ion exchange · single-crystal-to-single-crystal transformations

## Introduction

Nowadays there is a large increase in toxic heavy-metal ion discharge in the waste water effluents from different industries.[1] Heavy-metal poisoning can result in numerous clinical syndromes.[2] For example, exposure to lead may cause diseases of the kidneys, circulatory system, and nervous system;[3] disturbance in the homeostasis of Cu causes Wilson's, Menkes, and Prion diseases.[4] Toxicological data on cadmium indicate that extracellular Cd-containing intracellular metallothionein (MT) might be toxic.[5] To remove toxic heavy metals from the body, multidentate chelators[6] have been used in clinical medicine to form insoluble coordination complexes with the metal ions. However, owing to the strong coordination ability of the chelators, many elements that are vital to health were also removed. To remain healthy, people must continue to ingest the necessary microelements. To some extent, such chelators are not conducive to good health. However, porous coordination polymers (PCPs) may prove to be more suitable than multidentate chelators. They could be used as a metal ion-exchange resin and may not only simultaneously remove large amounts of dangerous metal ions, but also keep the concentration of metal ions that are conducive to health within the body. They are potential candidates for achieving the state-of-the-art in clinical drugs for the removal of harmful metal ions.

Ion sorption could remove dangerous metal ions, whereas ion exchange could supply sanative metal ions. Research on PCPs[7] has shown that they could be used for this purpose by using the mechanism of ion sorption and exchange. A significant feature of these frameworks[8] is their large well-defined pore shape and pore size. These characteristics mean that these frameworks have significant applications in metal ion sorption. Moreover, a regular arrangement of organic sulfonates[9] could also increase the adsorption ability of such materials. Meanwhile, ion exchange in these materials occurs directly by suspending such frameworks in a solution containing metal salts. The search for similar ion-exchange materials with improved properties has continued in recent years.[10] The open framework chalcogenide $(NH_4)_4In_{12}Se_{20}$ has been used for heavy-metal ion capture

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and ion exchange.[11] In addition, various functional groups, including carboxylate, hydroxyl, sulfate, phosphate, amide, and amino groups have been found to be responsible for metal sorption.[12] Among these, the sulfate group is very effective in removing metal ions. PCPs with a regular arrangement of sulfonate groups are believed to have a large adsorption capacity for harmful metal ions. We have gained much experience in designing and synthesizing ferroceyl-substituted carboxylates and phosphonates.[13] Usually these ferrocene-based materials are particularly insoluble and they can be egested easily from the body. Consequently, polymeric metal ferrocenyl sulfonates with sanative elements (e.g., Fe, Zn, Ca) as central metal ions have been successfully applied in drug design. We now present the synthesis and properties of the two-dimensional (2D) ferrocenyl zinc polymeric sulfonate **1** (Scheme 1), a new compound for the effective removal of most of the toxic metal ions. Single-crystal-to-single-crystal (SCTSC) transformations have received considerable interest in crystal engineering.[14] This could also be applied to remove harmful metal ions through ion-exchange induced SCTSC transformation without changing the structure of the solid-state materials. Three ion-exchange induced products **2**, **3**, and **4** were obtained by SCTSC transformation from a big single crystal of **1**. Most importantly, **1** could be partly recovered after it was immersed in a concentrated solution of aqueous $Zn(NO_3)_2$, and this could be beneficial for the repeated application of such materials and for production of analogous metal–organic frameworks with cores that contain different metal ions. Meanwhile, such materials show high selectivity when different metal ions coexist. Powdered **1** only selectively adsorbs $Pb^{2+}$ and small quantities of $Cu^{2+}$, whereas the central metal ions in the big single crystal of **1** could be largely exchanged with $Cd^{2+}$ and partially with $Pb^{2+}$ and $Cu^{2+}$. Also, **1** could be employed as a fluorescent chemosensor and an electrochemical probe for multi-ion analysis.

## Results and Discussion

**X-ray structure of 1**: Compound **1** was prepared by combining $d^{10}$ $Zn^{2+}$ ions with highly conjugated 4,4′-bpy and disodium ferrocene-1,1′-disulfonate. A single-crystal X-ray diffraction study reveals that polymer **1** is a 2D network with the molecular formula $[Zn(4,4'\text{-bpy})_2(FcphSO_3)_2]_n$, which crystallizes in the space group *C*2/*c*. The building unit of **1** is illustrated in Figure 1, in which the central zinc ion adopts a slightly distorted octahedral environment by coordinating to four pyridyl groups of four 4,4′-bpy bridging ligands and two $FcphSO_3^-$ ions.

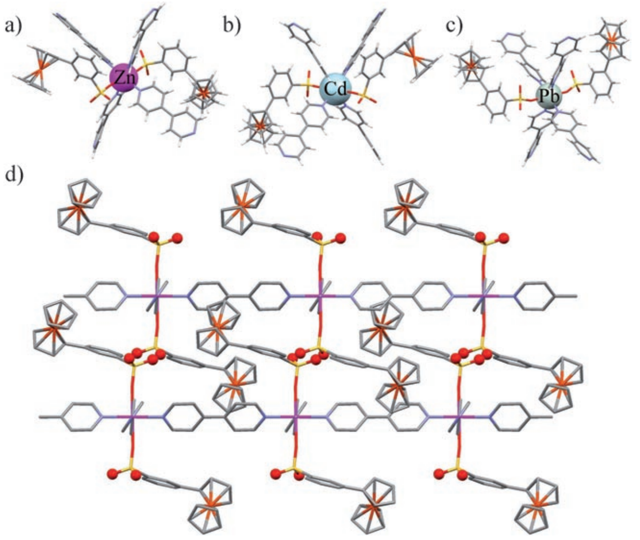
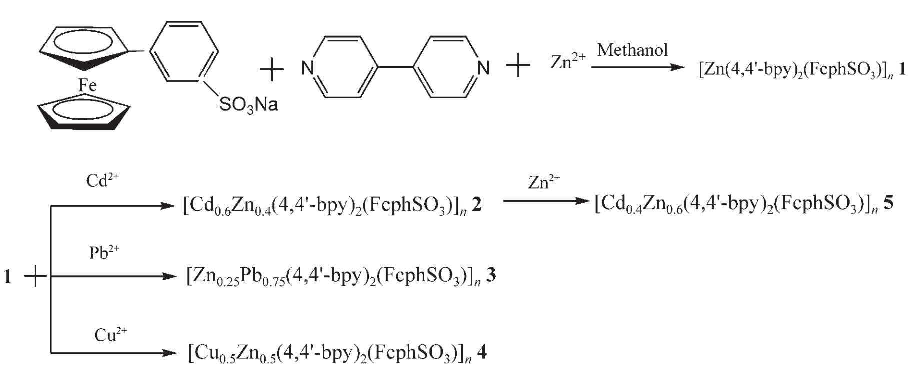


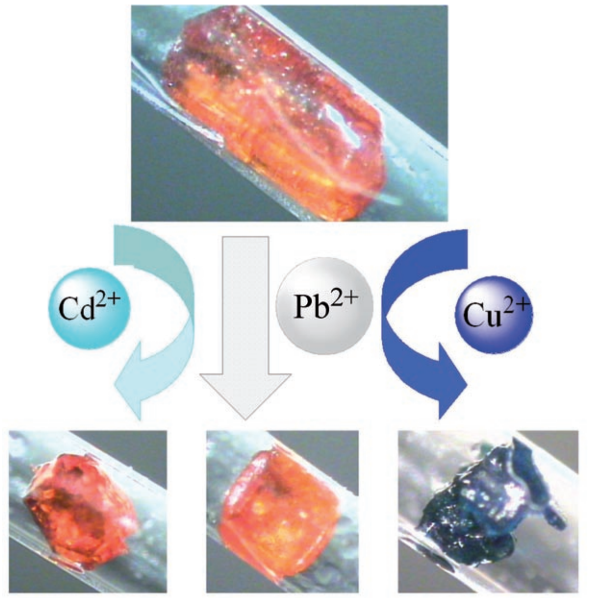
Figure 1. a) The building block of **1**. b) The molecular structure of Cd-exchange-induced product **2**. c) The crystal structure of Pb-exchange-induced product **3**. d) The polymeric structure of **1** viewed along the *b* plane. Cd atom is shown as cyan; Zn purple; O red; N blue; S yellow; C light gray; Fe orange, and hydrogen atoms were omitted for clarity.

In the coordination polymer **1**, there are two types of 4,4′-bipyridine ligands, which are distinguished by the dihedral angles of their two pyridine rings (0 and 29.6°), and these two pyridine linkers join with the Zn atoms to form a 2D (4,4) grid network (Figure 1d). The shortest distances between the two adjacent parallel linkers in this structure are 11.454 and 11.674 Å, respectively. Simultaneously, $FcphSO_3^-$ ions are set in the axis of $Zn^{II}$ nodes. Viewed along the *b* plane, there are numerous face-to-face interlaced unsaturated oxygen atoms of sulfonate groups from the adjacent plane. Overall this gives rise to a 2D bilayered network with the potential for high selectivity for metal ions.



Scheme 1. $FcphSO_3Na$ = *m*-ferrocenyl benzenesulfonate.

**Removal of toxic metal ions upon metal ion-exchange induced SCTSC transformation**: We focused primarily on the ion removal properties of the big single crystal of **1** in 1.0 $mg\,mL^{-1}$ aqueous $Cd(NO_3)_2$. Interestingly, an isomorphous crystal of **1**, namely **2**, was obtained by ion-exchange induced SCTSC transformation. X-ray diffraction analysis of the still intact crystal (Figure 1b) confirmed that an SCTSC phase transformation had occurred, resulting in a Cd–Zn complex. This complex has an analogous crystal structure to **1**. It is notable that in the synthesis of crystalline solid-state materials, an outstanding challenge is to alter the chemical composition without changing the underlying topology.[15] Compound **2** was analyzed carefully by using an atomic sorption spectrophotometer and the content of zinc and cadmium atoms was 37.18 and 62.82 %, respectively (see Figure 2). These results were consistent with the elemental analysis. Nevertheless, transport of cadmium ions through the lattice was not considered to be a homogeneous process, as evidenced by the unambiguous SCTSC transformation that took place over a period of more than a month (Figure 2).



(Cd 62.82%; Zn 37.18%)(Pb 23.57%; Zn 76.43%) (Cu 49.87%; Zn 50.13%)

Figure 2. Photographs of single crystals of **1** in the ion-exchange process.

To gain insight into the mechanism of the phase transition induced by ion-exchange, we conducted a series experiments on the big single crystal of **1** in solutions containing the same concentration of aqueous $Cd(NO_3)_2$ after different time intervals. The plot of the percentage of central metal ions after different periods of time is illustrated in Figure 3. The amount of Cd in the big single crystal of **1** increased rapidly during the first six days, and then more slowly after a week, and then a month later, it stabilized at 62.82 %. In contrast, the percentage of Zn in the big single crystal of **1** decreased rapidly in the first six days, then decreased gradually, and then stabilized at 37.18 % after a month. Such a transformation could be significant in designing new functional materials for eliminating toxic metal ions. The rational mechanism can be postulated on the basis of metal ion exchange. We believe that the relative metal ion exchange properties of this polymer are in good accord with its coordination ability toward transition metal ions. The additional metal ions interact with the unsaturated sulfonate groups, and this interaction closely associates with ion exchange properties and may result in ion exchange.

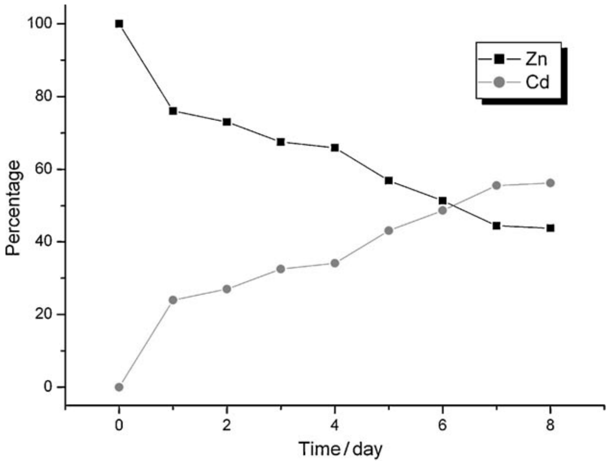


Figure 3. The percentage of central metal of Cd-exchanged product at different times (● and ■ represent the percentage of Cd and Zn ions in ion-exchanged product, respectively).

More significantly, this behavior is observed not only with Cd, but also with Pb and Cu ions. Lead and copper ions can also induce the unambiguous SCTSC transformation of **1**. Reliable evidence for this comes from the central metal ion composition of the Pb-exchange induced product[12] **3** (Figure 1c) and the Cu-exchange induced product **4**, both of which were also measured by atomic absorption spectroscopy (Pb 23.57, Zn 76.43, Cu 49.87, Zn 50.13 %) and confirmed by elemental analysis. The crystal structure of polymer **3** was further determined by single-crystal X-ray diffraction measurements. Although complex **3** was also obtained by metal-ion-exchange induced SCTSC transformation from **1**, the crystal structure of **3** differs from that of **1**. Polymer **1** crystallized in the *C*2/*c* space group, whereas polymer **3** crystallized in the *P*4(3)2(1)2 space group (see Table 1). Unlike the regular reticular polymer **1**, the anionic parts in the building blocks of **3** lie on the same side to form a chiral complex. Thus far, it might be anticipated that the different structures of these products are caused by ion-exchange behavior. Additionally, on the basis of the X-ray diffraction analysis of polymers **2** and **3**, we believe that the removal of toxic metal ions, such as $Cd^{2+}$, $Pb^{2+}$ and $Cu^{2+}$, by the big single crystal of **1** is attributed to the ion-exchange behavior.

**Regeneration of metal-ion-exchanged products**: As we mentioned above, ion-exchange behavior could be used to produce new materials in the big single crystal. Accordingly, we wanted to know whether **1** could be recovered from the Cd-exchanged product **2**. Therefore, we immersed a collection

Table 1. Crystal data and structure refinement for polymers **1**–**3** and **5**.

| Complexes | **1** | **2** | **3** | **5** |
|---|---|---|---|---|
| formula | $C_{104}H_{84}Fe_4N_8O_{12}S_4Zn_2$ | $C_{52}H_{46}Cd_{0.6}Zn_{0.4}Fe_2N_4O_8S_2$ | $C_{52}H_{42}Fe_2N_4O_6S_2Zn_{0.75}Pb_{0.25}$ | $C_{52}H_{46}Zn_{0.6}Cd_{0.4}Fe_2N_4O_8S_2$ |
| $F_w$ | 2120.17 | 1124.06 | 1195.6 | 1114.1 |
| $T$[K] | 291(2) | 291(2) | 293(2) | 293(2) |
| color | red | red | red | red |
| crystal system | monoclinic | monoclinic | tetragonal | monoclinic |
| space group | $C2/c$ | $C2/c$ | $P4(3)2(1)2$ | $C2/c$ |
| $a$[Å] | 17.2333(16) | 17.4198(18) | 11.4381(4) | 17.345(5) |
| $b$[Å] | 11.6743(11) | 11.8550(12) | 11.4381(4) | 11.809(3) |
| $c$[Å] | 22.857(2) | 23.497(2) | 34.847(3) | 23.396(7) |
| $\alpha$[°] | 90 | 90 | 90 | 90 |
| $\beta$[°] | 101.5120(10) | 103.1700(10) | 90 | 103.083(3) |
| $\gamma$[°] | 90 | 90 | 90 | 90 |
| $V$[Å$^3$] | 4506.1(7) | 4724.8(8) | 4559.1(4) | 4668(2) |
| $Z$ | 2 | 4 | 4 | 4 |
| $\rho_{calcd}$[g cm$^{-3}$] | 1.563 | 1.607 | 1.544 | 1.588 |
| $R1$, $wR2$ [$I>2\sigma(I)$] | $R1=0.0335$, $wR2=0.0735$ | $R1=0.0269$, $wR2=0.0717$ | $R1=0.0271$, $wR2=0.0701$ | $R1=0.047$, $wR2=0.1241$ |

of big crystals of **2** in aqueous solutions of $Zn(NO_3)_2$ (2 mL, 10 mg mL$^{-1}$), and after a about 14 days, we obtained the compound **5** (see Scheme 1) in which the Zn content had risen again slightly. As shown in Figure 4, compound **5** has the same space group as **1** and **2**. Compound **5** was also carefully analyzed by using an atomic sorption spectrophotometer and the zinc atom content was found to be 58.8%, whereas that of cadmium was 41.2%. Thus, the swing towards the single crystal **2** could be partly achieved by an ion-exchange induced single-crystal-to-single-crystal transformation. This property is helpful not only for the repeated application of such materials, but also for the synthesis of new solid materials with similar structure and different metal cores.

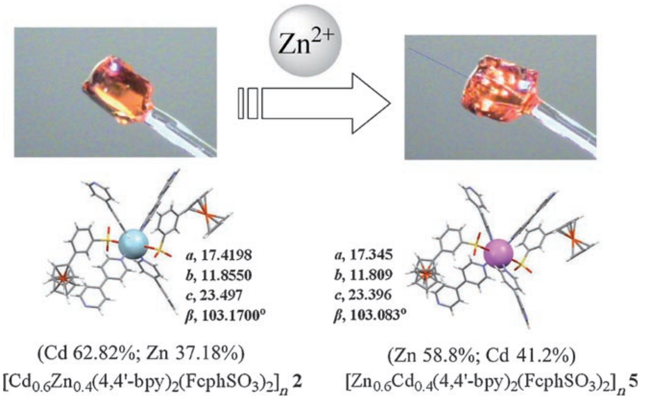


Figure 4. A concentrated aqueous solution of $Zn(NO_3)_2$ was used to regenerate the big single crystal of **2**.

**Removal of harmful metal ions by metal ion sorption and exchange**: Usually, clinical medicines were made into uniform powders to allow the preparation of homogeneous mixtures with starch powder.[16] If our polymers were to be employed as clinical drugs, first of all, they would need to be ground into powders. As we know that there are differences between the ion-removal properties of the big crystal and abrasive powder forms, we decided to test this by using 10.0 mg of powdered **1** to measure its ion-removal properties from solutions of divalent copper, lead, and cadmium salts, (10 mL, 1.0 mg mL$^{-1}$), respectively. Figure 5 displays the different ion-exchange behavior of powdered **1** with these divalent metal salts. In the same solution concentration of these metal ions, besides the exchange of the central zinc ion, powdered **1** could also adsorb a large amount of metal ions from aqueous solutions of such divalent metal ions. This behavior is quite different to that of the big crystal of **1** because the specific surface area of powdered **1** is much larger than that of the big crystal of **1**. Thus, the central zinc ion could be partly replaced by other metal ions, but metal ion sorption also takes place when powdered **1** is used.

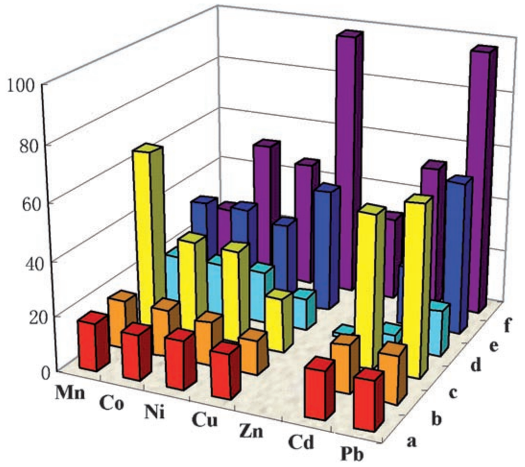


Figure 5. The percentage of adsorbed metal ions and exchanged zinc ions of powdered **1** in different nitrate solution concentrations of $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Pb^{2+}$. The red, orange, and yellow columns represent the percentage of exchanged zinc ions in 10, 100, and 1000 µg mL$^{-1}$, respectively, whereas the brown, blue, and cyan columns represent the percentage of adsorbed metal ions in 10, 100, and 1000 µg mL$^{-1}$, respectively.

As such, we measured the metal ion-removal properties of divalent copper salts, lead salts and cadmium salts, respectively, in solutions (10 mL, 0.01 and 0.10 mg mL$^{-1}$) using employed powdered **1** (10.0 mg). As shown in Figure 5, we find that as the solution concentration of metal salts increases, the percentage of adsorbed metal ions decreases, especially for copper and lead ions. In 0.01 mg mL$^{-1}$ solutions, **1** could adsorb almost all of the metal ions (97.40 and 97.59 %, for copper and lead, respectively), but in 1.0 mg mL$^{-1}$ solutions, although **1** can adsorb a large quantity of lead and copper ions, the percentage of adsorbed metal ions is very low (12.05 and 16.51 %, for copper and lead, respectively). Bearing this in mind, the percentage of exchanged zinc ions and the quantity of adsorbed metal ions increase with the increase of the solution concentration of metal salts. Thus, it might be anticipated that in dilute solution, metal ion sorption is mainly occurring, whereas both ion sorption and exchange are the dominant processes in concentrated solution. From the experimental results, it is clear that **1** could adsorb large amounts of harmful metal ions (especially $Pb^{2+}$ ions) from aqueous metal salts at solution concentrations from 0.01 to 1.0 mg mL$^{-1}$. It is notable that 10 mg of **1** could adsorb more than 1.032 mg $Pb^{2+}$ when exposed to aqueous lead nitrate solutions (10 mL 1.0 mg mL$^{-1}$). It is well known that among the toxic metal ions, $Pb^{2+}$ is one of the important targets because of the adverse health effects of lead exposure, particularly in children.[17] Although considerable efforts have been devoted to removing lead ions over the last few decades,[18] efficient materials are still not readily available. Remarkably, the additional advantage of this kind of material lies in the supplement of nutrient elements with respect to the exchange mechanism. Figure 6a shows the photographs of powdered **1** and activated carbon, which were immersed in aqueous $Cu(NO_3)_2$ solutions (20 mg mL$^{-1}$) for one hour. Although activated carbon is regarded as an excellent adsorbent, the adsorption capacity of powdered **1** in aqueous $Cu(NO_3)_2$ clearly exceeds that of activated carbon. After two days, adsorbed copper ions were released from the activated carbon, whereas the solution in the tube that contained powdered **1** as adsorbent remained the same as it was after immersion for one hour. Thus, it might be anticipated that the adsorption mechanism of **1** is different to other porous activated carbon materials. Clearly, **1** could adsorb a large amount of metal ions because of its porous structure and free functional groups, whereas activated carbons are reliant on their porous structure alone. Additionally, the powder X-ray diffraction (PXRD) pattern (Figure 6b) of **1** resembles that of the product of **1** that has adsorbed $Cu^{2+}$ ions. This means that the crystal structure of **1** could be retained after it has served as a metal ion adsorbent. Furthermore, ion exchange and sorption properties of powdered **1** are also applicable for other harmful metal ions, such as $Mn^{2+}$, $Co^{2+}$, and $Ni^{2+}$.

**Selectivity of 1 for metal ions**: Clearly, powdered **1** could be used to adsorb many metal ions, such as $Pb^{2+}$, $Cu^{2+}$, $Mn^{2+}$, $Co^{2+}$, and $Ni^{2+}$. However, when all these metal ions coexist in solution, powdered **1** selectively adsorbs large amounts of $Pb^{2+}$ ions and very few $Cu^{2+}$ ions. This behavior is different from that of the big cubic single crystal of **1**. When big crystals of **1** were immersed in an aqueous solution containing different metal ions, each at concentration of 1.0 mg mL$^{-1}$, the central zinc ions in single crystal **1** were exchanged primarily with $Cd^{2+}$ ions, and with very few $Pb^{2+}$ and $Cu^{2+}$ ions. Clearly, when different metal ions coexisted in solution, only ion exchange took place in the big cubic single crystal of **1**, whereas in powdered **1**, both ion exchange and ion sorption were dominant processes. This behavior is simi-

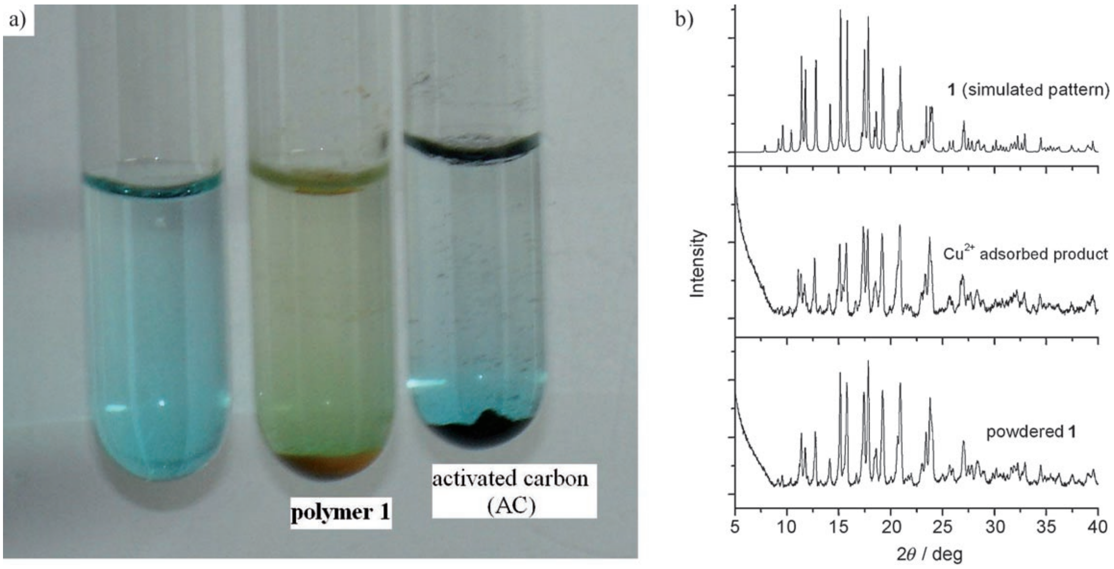


Figure 6. a) Powdered **1** and activated carbon (AC) were respectively immersed in 20 mg mL$^{-1}$ aqueous $Cu(NO_3)_2$ solutions for 1 h. b) PXRD pattern of **1** and the product of **1** that had adsorbed $Cu^{2+}$ ions. The red line represents the XRD pattern of powdered **1**; blue line, the product of **1** that had adsorbed $Cu^{2+}$ ions; black line, simulated pattern from X-ray single-crystal diffraction measurement of **1**.

lar to that for a solution which only contains one type of metal ion. In addition, X-ray diffraction single-crystal analysis reveals that the immersed crystal also has the same space group and analogous cell parameters ($a=17.2765$, $b=11.8306$, $c=23.3679$ Å; $\beta=102.42175°$) as those of **1** ($a=17.2333$, $b=11.6743$, $c=23.857$ Å; $\beta=101.512°$). Thus it is presumed that **1** still retains its solid structure after it had been immersed in solutions containing ions of different metals for a time.

Of course, other reported methods[19] also can effectively remove metal cations such as $Pb^{2+}$ and $Cd^{2+}$. For example, electrodialytic remediation (EDR)[20] was used to remove 79–98 and 91–96 % of Pb and Cd ions, respectively, from contaminated harbor sediment recently. However, rigorous experimental conditions (including pH value) and complicated experimental equipment restrict the scope of these applications. In contrast, polymeric ferrocenyl sulfonate has a very high adsorption capability even under moderate conditions without the necessity of an auxiliary facility, such as acidic conditions, alkaline conditions, surface active agents, dispersing agent, or buffering agents. Most significantly, a small quantity of beneficial zinc metal ions could be exchanged when we employed such polymeric complexes to adsorb toxic metal ions. It is well known that zinc is an element that each of us needs; the daily required dosage is 15 mg per person. However, it should be noted that it is hard to achieve the values below the limits accepted in water through one time simple adsorption of a massive dose of heavy metal ions by the use of complexes such as metal ion adsorbents.

**Multi-ion analysis**: To detect the toxic residue, we must revert to some metal ion probes. Remarkably, compound **1** also could be employed alone as a fluorescent probe to detect dangerous metal ions, such as $Pb^{2+}$, $Cd^{2+}$, $Ag^{+}$, $Cu^{2+}$. The fluorescence responses of **1** in DMF solution in the presence of different concentrations of copper ions are displayed in Figure 7. Analogous to previous observations,[21] fluorescence intensity could be greatly shifted on the addition of the above-mentioned metal ions. Nevertheless, interferences are introduced by the change of the dosages of these metal ions. However, previously reported fluorescent chemosensors are only sensitive to one or two particular metal ions.[22] More importantly, **1** exhibits a highly selective response to most of the heavy-metal ions. Taken together, the sensing properties of **1** might be caused by unoccupied functional groups. To the best of our knowledge, no reports have been published on this type of study to date.

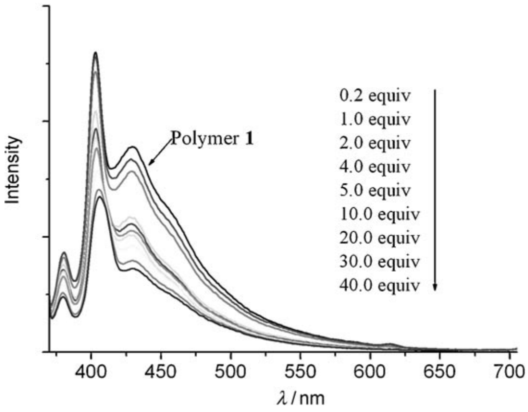


Figure 7. Fluorescence spectra of **1** ($5.0\times10^{-5}$ M) in DMF solution in the presence of different concentrations of $Cu^{2+}$ ions ($\lambda ex=360$ nm).

**Electrochemical cation-recognition investigations**: One of the most interesting attributes of the ferrocenyl sulfonate compound reported here is the presence of metal ion binding sites on the ferrocenyl group, which can be affected by the presence of metal ions and transform chemical information at the molecular level into a macroscopic signal that is easily measurable.[23] Due to this structural feature, the detailed study of its protonation and metal–recognition properties was of interest. An electrochemical study was carried out with the aim of the electrochemical detection of heavy toxic metal ions such as $Pb^{2+}$, $Cd^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Cu^{2+}$, and $Mn^{2+}$.

Reversibility and relative potentials of redox processes of complex **1** were determined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in solutions containing $[(n\mathrm{Bu})_4\mathrm{N}]\mathrm{ClO}_4$ (0.1 M) in DMF ($5\times10^{-4}$ M). CV and DPV were used to evaluate the strength of the interaction between the metal centers and complex **1**. The shift of the oxidation potential of the redox-active groups as a function of the presence and absence of $Pb^{2+}$, $Cd^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Cu^{2+}$, $Zn^{2+}$, and $Mn^{2+}$ ions was monitored in DMF. Electrochemical studies of **1** indicate that this receptor behaves as a selective electrochemical sensor for ions of different metals. Complex **1** shows significant shifts of the oxidation potential of the ferrocenyl groups upon addition of large amounts of metal ions. However, addition of very small amounts of $Cd^{2+}$, $Mn^{2+}$, $Zn^{2+}$, $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$, and $Pb^{2+}$ ions to this complex do not promote any significant change in the corresponding electrochemical responses. For instance, the electrochemical response found for **1** in the presence of different concentrations of copper ions is displayed in Figure 8.

## Conclusion

We have demonstrated a new kind of molecular aspirator for the removal of hazardous metal ions. Most significantly, the big single crystal of **1** could be partly recovered by an ion-exchange-induced single-crystal-to-single-crystal transformation. Furthermore, this kind of compound could also be utilized as a fluorescent chemosensor and electrochemical probe to identify most of the heavy-metal ions. The functional mechanism of such materials might be ascribed to the presence of the free functional groups in this kind of compound. These results provide an entry to a promising new field of metal ion adsorbents, molecular drugs, and chemical probes based on porous coordination polymers with free functional groups.

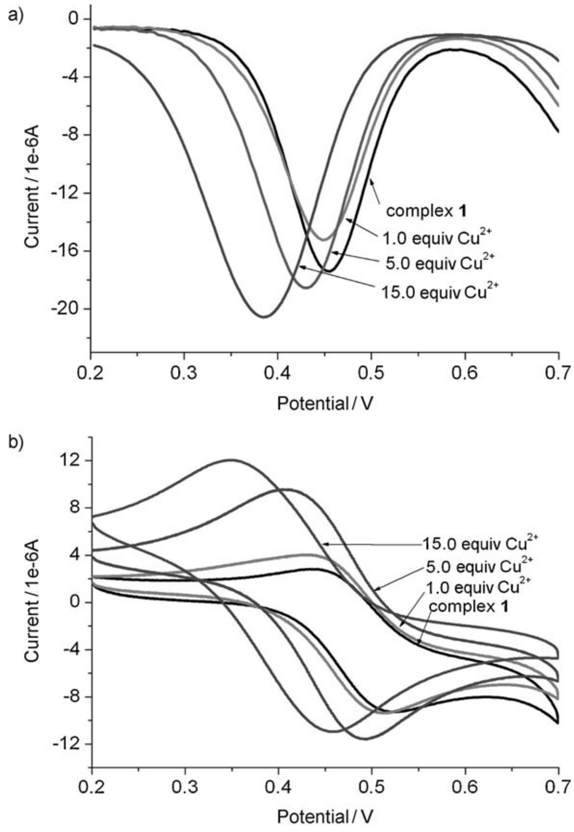


Figure 8. Cyclic voltammograms (a) and DPV (b) of **1**, in DMF solution by using $[(n\mathrm{Bu})_4\mathrm{N}]\mathrm{ClO}_4$ as supporting electrolyte scanned at $100\,\mathrm{mV\,s^{-1}}$ from 0.2 to 0.7 V, after addition of 1.0, 5.0, and 15.0 equivalents of $\mathrm{Cu}^{2+}$ ions.

## Experimental Section

**$[\mathrm{Zn}(4,4'\text{-bpy})_2(\mathrm{FcphSO_3})_2]_n$ (1)**: Two-dimensional polymeric zinc ferrocene-1,1′-disulfonate was prepared by mixing $\mathrm{Zn(NO_3)_2{\cdot}6\,H_2O}$ (0.027 g, 0.1 mmol) with $\mathrm{FcphSO_3Na}$ (2.0 equiv, 0.073 g, 0.2 mmol) and 4,4-bpy (2.0 equiv, 0.033 g, 0.2 mmol) in methanol (4 mL). The desired inclusion complex crystallized by slow evaporation at room temperature as a red crystalline solid (yield 63 %). IR (KBr): $\tilde{\nu}=3445$ (s), 3099 (m), 1609 (s), 1536 (w), 1490 (w), 1416 (s), 1385 (m), 1255 (s), 1219 (m), 1179 (s), 1126 (s), 1067 (s), 1039 (s), 998 (w), 903 (w), 768 (s), 732 (w), 702 (w), 661 (w), 620 (w), 604 (s), 534 (w), 505 $\mathrm{cm^{-1}}$ (m); elemental analysis calcd (%) for $\mathrm{C_{104}H_{84}Fe_4N_8O_{12}S_4Zn_2}$: H 3.99, C 58.91, N 5.28, S 6.05; found: H 4.18, C 59.00, N 5.38, S 6.13.

**$\{[\mathrm{Cd_{0.6}Zn_{0.4}}(4,4'\text{-bpy})_2(\mathrm{FcphSO_3})_2]{\cdot}\mathrm{H_2O}\}_n$ (2)**: A solution of $\mathrm{Cd(NO_3)_2{\cdot}4\,H_2O}$ (0.031 g, 0.1 mmol) in methanol (5 mL) was treated with a collection of big single crystals of **1** (0.024 g). The mixture was left for 30 days and red transparent crystals were obtained at room temperature. The crystals were stable in air. IR (KBr): $\tilde{\nu}=3488$ (m), 3092 (m), 2922 (w), 1604 (s), 1535 (w), 1491 (w), 1416 (s), 1251 (s), 1220 (m), 1178 (s), 1123 (s), 1040 (s), 1001 (w), 826 (s), 801 (s), 767 (w), 702 (w), 660 (w), 621 (s), 536 (w), 501 $\mathrm{cm^{-1}}$ (m); elemental analysis calcd (%) for $\mathrm{C_{52}H_{46}Cd_{0.6}Zn_{0.4}Fe_2N_4O_8S_2}$: H 4.12,C 55.55, N 4.98, S 5.70; found: H 4.17, C 55.27, N 4.95, S 5.59.

**$[\mathrm{Zn_{0.75}Pb_{0.25}}(4,4'\text{-bpy})_2(\mathrm{FcphSO_3})_2]_n$ (3)**: Compound **3** was prepared analogously to compound **2** by using an aqueous $\mathrm{Pb(NO_3)_2}$ solution instead of a solution of $\mathrm{Cd(NO_3)_2}$ in methanol. The mixture was left for 30 days and red transparent crystals were obtained at room temperature. The crystals were stable in air. IR (KBr): $\tilde{\nu}=3426$ (s), 2364 (m), 1605 (s), 1414 (s), 1254 (s), 1177 (s), 1125 (m), 1039 (s), 803 (s), 621 $\mathrm{cm^{-1}}$ (s); elemental analysis calcd (%) for $\mathrm{C_{52}H_{46}Zn_{0.75}Pb_{0.25}Fe_2N_4O_8S_2}$: H 4.10, C 55.19, N 4.95, S 5.67; found: H 4.14, C 54.97, N 4.92, S 5.81.

**$[\mathrm{Cu_{0.5}Zn_{0.5}}(4,4'\text{-bpy})_2(\mathrm{FcphSO_3})_2]_n$ (4)**: Compound **4** was prepared analogously to compound **2** by using a solution of $\mathrm{Cu(NO_3)_2}$ in methanol instead of a solution of $\mathrm{Cd(NO_3)_2}$ in methanol. The mixture was left for 30 days and blue transparent crystals were obtained at room temperature. The crystals were stable in air. Elemental analysis calcd (%) for $\mathrm{C_{52}H_{46}Cu_{0.5}Zn_{0.5}Fe_2N_4O_8S_2}$: H 4.23, C 57.03, N 5.12, S 5.86; found: H 4.34, C 56.89, N 4.99, S 5.91.

**$[\mathrm{Zn_{0.6}Cd_{0.4}}(4,4'\text{-bpy})_2(\mathrm{FcphSO_3})_2]_n$ (5)**: Several big single crystals of **2** (0.011 g) were immersed in an aqueous solution of $\mathrm{Zn(NO_3)_2}$ (2.0 mL, $20\,\mathrm{mg\,mL^{-1}}$). The mixture was left for two weeks and red transparent crystals were obtained at room temperature. The crystals were stable in air. IR (KBr): $\tilde{\nu}=3468$ (m), 3090 (m), 2363 (m), 1603 (s), 1536 (w), 1491 (w), 1416 (s), 1252 (s), 1220 (m), 1178 (s), 1122 (s), 1038 (s), 1002 (w), 827 (s), 802 (s), 766 (w), 701 (w), 660 (w), 621 (s), 536 (w), 500 $\mathrm{cm^{-1}}$ (m); elemental analysis calcd (%) for $\mathrm{C_{52}H_{46}Zn_{0.6}Cd_{0.4}Fe_2N_4O_8S_2}$: H 4.16, C 56.02, N 5.02, S 5.75; found: H 4.17, C 56.17, N 5.05, S 5.59.

**Crystallographic studies**: Diffraction intensity data for a single crystal of **1**–**3** and **5** were collected at room temperature on a Bruker Smart CCD diffractometer equipped with graphite-monochromated $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda=0.71073$ Å) and can be seen in Table 1. Compound **5** was measured at room temperature on a Ragaku Smart CCD diffractometer. The structures were solved by direct methods and refined by using the full-matrix least-squares method on $F^2$ with anisotropic thermal parameters for all non-hydrogen atoms.[24] Hydrogen atoms were located geometrically and refined isotropically. CCDC-630122, CCDC-630123, and CCDC-630124 contain the crystallographic data of **1**–**3** for this paper, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Ion exchange and sorption test**: The sorption behavior of divalent metal salts from aqueous solutions was investigated by using the batchwise method at room temperature. The concentration of the nitrate salts of $\mathrm{Mn^{2+}}$, $\mathrm{Co^{2+}}$, $\mathrm{Ni^{2+}}$, $\mathrm{Cu^{2+}}$, $\mathrm{Zn^{2+}}$, $\mathrm{Cd^{2+}}$, and $\mathrm{Pb^{2+}}$ ions in aqueous solution was determined by atomic absorption spectrometry. The amount of cations adsorbed and cadmium ions exchanged were also determined by using a Z28000 graphite-oven atomic absorption spectrophotometer.

**Fluorescent properties test**: Fluorescence spectra were obtained by using a FluoroMax-P spectrometer with 5 nm excitation and emission slit widths. All solutions of fluorescent chemosensor **1** and metal nitrates were prepared in analytical grade DMF without special effort to exclude water or air. Both the absorption and fluorescence titrations were carried out by the addition of small volumes of metal ion solutions to sensor **1** (2.0 mL, $5.0\times10^{-5}\,\mathrm{M}$) in a quartz cuvette. For all measurements, the excitation wavelength was 360 nm.

**Electrochemistry test**: Electrochemical experiments were performed in a low-volume three-electrode cell in dry, degassed DMF (analyte concentration of $5\times10^{-4}\,\mathrm{M}$). The background electrolyte was $n\mathrm{Bu_4ClO_4}$ (0.1 M). The working electrode was a Pt disk with a diameter of 2 mm, and the auxiliary electrode was a Pt foil. Potentials were reported relative to a commercially available saturated calomel electrolyte. To prevent fouling, the working electrode was polished before each addition of cation. Pure $\mathrm{N_2}$ gas was bubbled through the electrolytic solution to remove oxygen.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (20371042 and 20671082) and NCET.

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Received: May 24, 2007
Revised: August 22, 2007