

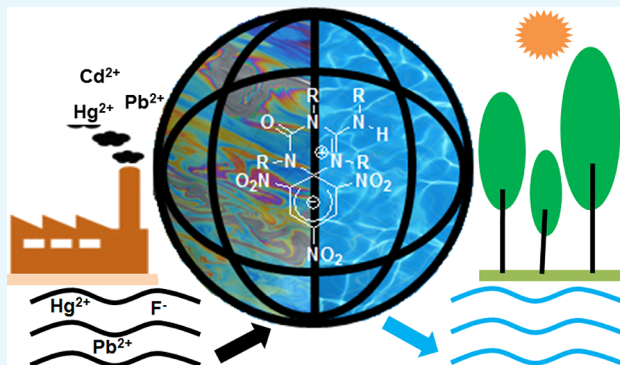
Mopping up the Oil, Metal, and Fluoride Ions from Water

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Supporting Information

ABSTRACT: The recycle, cleaning, and reuse of water are highly important for environmental remediation. This issue is addressed by creating a fluorescent zwitterionic spirocyclic Meisenheimer complex with high chelating propensity for toxic metals using low-cost starting materials and a one-pot synthesis technique. The resulting material is able to detect fluoride up to 12.8 ppb level and remove 82% aqueous fluoride from 1000 mL of 100 ppm fluoride solution in a single contact. The material demonstrates rapid kinetics and is capable of dropping the toxic metal ion (Pb/Hg/Cd) concentration below 0.2 ppb within 10 min. A resin-free, precipitation-free, and reusable technique has been developed for the removal of toxic metal ions and fluoride from extremely polluted water. Moreover, utilizing its extreme hydrophobicity, polystyrene sponges have been coated with the Meisenheimer complex to mop up oil spill and organic solvents from a biphasic mixture.



INTRODUCTION

With rapidly increasing world population, it has become extremely challenging to provide clean water to each and every citizen.^{1,2} In the agricultural sector, increasing demand for food production is forcing us to use underground water for farming. This has increased the fluoride and arsenic level in groundwater in some parts of the world. Industrial waste as well as pesticides and synthetic dyes is critically polluting the surface water. Therefore, there is a growing interest in recognition, sensing, and removal of hazardous chemicals which are responsible for water pollution. Among different anionic species, sensing of fluoride ion is very interesting as it plays malevolent as well as benevolent role in human beings.³ At a low concentration (around 1 ppm) in drinking water, fluoride is beneficial for our dental health. It strengthens our tooth enamel by converting hydroxyapatite present on the teeth surface to fluoroapatite which is much harder and prevents tooth decay.⁴ Fluoride is also potentially useful for osteoporosis treatment. The human body absorbs fluoride very easily, but the excretion process is rather slow.⁵ Therefore, at a high concentration, fluoride accumulation in the body can lead to osteoporosis, neurological and metabolic dysfunctions, and cancer.⁶ Fluoride is extremely useful in industrial processes such as steelmaking, aluminum refining, organic compound synthesis,⁷ military purposes such as uranium refinement, and so forth.⁸ Therefore, these industries are highly prone to affect the local water resources. Fluoride is also released from the hydrolysis of nerve gases such as sarin, cyclosarin, soman, and so forth. Therefore, for a nerve gas attack, detecting fluoride in the victim's body as well as in the surrounding environment is very important.^{9,10} In the last

decade, various strategies have been applied to sense fluoride anions.^{11–22}

With enhancement in living standards and to fulfill basic human needs, a rapid growth in industrial activity has been observed in the last couple of centuries.²³ Water is the main component for daily works in almost every industry. In most of the cases, wastewater discharged from industries contains toxic metals such as Cu, Ni, Cd, Hg, Cr, and Pb. As a result, the surface water or groundwater gets contaminated by them.²⁴ By virtue of biomagnification, the concentrations of these metals start to increase in the food chain pyramid, and human beings are the worst affected. Therefore, detection and removal of these toxic metals are very much crucial.²⁵ Various methods have been developed for metal ion removal from drinking water and industrial wastewater. Coagulation–flocculation and chemical precipitation are often applied for the removal of metal ions.²⁶ Ion exchange,²⁷ electrolytic reduction,²⁸ and membrane technologies are also very common methods.^{29,30} Adsorption has also been proven to be a very effective removal process.^{31,32} Agricultural waste materials³³ and zeolites³⁴ are being used as adsorbing materials. Recently, carbon nanotubes,³⁵ ionic liquids,³⁶ metal–organic frameworks,^{37–39} covalent organic frameworks,⁴⁰ porous organic polymers,^{41,42} nanoparticles, fullerenes, biosorbents, and ion-imprinted polymers have been explored as solid-phase sorbents.⁴³ However, the selective removal of different toxic metal ions has been reported in the literature, but the universal removal is

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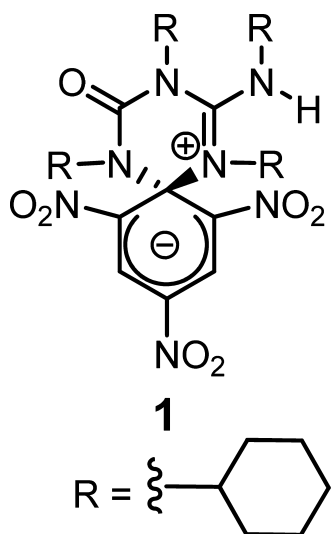
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very less.^{44–48} In general, an ideal material for metal removal application must be cheap, water-insoluble, easy to synthesize, of high removal capacity, reusable, and with an affinity for a wide variety of metal ions.

Another important aspect in water processing is the oil spill removal. Over the years, oil spill accidents had taken place around the world during oil transportation by ships or from natural calamities in oil fields.^{49–53} These accidents pose serious threats to the marine ecosystem and species (such as birds) relying on the marine ecosystem.⁵⁴ Therefore, it is very crucial and challenging to remove spread oils.^{55–59} There are different methods for oil spill recovery. For example, absorption of the oil phase using some hydrophobic porous materials,^{60–62} use of dispersing agents followed by burning or left for natural degradation,^{63,64} application of solidifiers,^{65,66} and bioremediation⁶⁷ can be mentioned. Among them, the first method being quick, with no environmental pollution and reusable, is the most effective one. For this, different oleophilic and hydrophobic porous materials were utilized throughout the last decade.^{68–72} In this report, a single Meisenheimer complex (Scheme 1) has been applied to overcome all these issues.

Scheme 1. Chemical Structures of Meisenheimer Complex 1



RESULTS AND DISCUSSION

Zwitterionic spirocyclic Meisenheimer complex **1** was synthesized from picric acid and *N,N'*-dicyclohexylcarbodiimide.⁷³ The crystal structure of **1** reveals the distribution of a negative charge over five carbons in the 2,4,6-trinitrocyclohexadienyl anion system.⁷³ This is reminiscent of the cyclopentadienyl anion system which is known to form different sandwich complexes with transition metals, such as ferrocene. We have studied the effect of various metal ions on compound **1** using absorption and emission spectroscopy. Compound **1** has two absorption maxima at 405 and 527 nm which are the characteristic bands of a trisubstituted Meisenheimer complex (Figure 1a).⁷⁴ Addition of a divalent or trivalent metal ion to the methanolic solution of **1** causes the suppression of these bands (Figure 1a). This is the direct proof of interaction of metal ions with the π -cloud of **1**. Meisenheimer complexes are known to be fluorescent.⁷⁵ This fluorescence arises from the electron-rich cyclohexadienyl anion system. Therefore, if the electron cloud of **1** interacts with a metal ion, the electron density of the π -

cloud diminishes and so does the fluorescent intensity. Compound **1** is highly fluorescent ($\phi = 0.67$), and its fluorescent intensity decreases with increasing concentration of metal ions (Figure 1b). This also confirms the metal– π -cloud interaction. Both divalent and trivalent metal ions interact with **1** in the same manner as revealed by absorption spectroscopy (Figure S1). The stoichiometry of binding was determined by Job's method. **1** binds with Fe^{3+} ion ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in 2:1 fashion (Figure S2).

Compound **1** is a zwitterionic species, and it is only the negative charge which participates in the metal binding process. Therefore, to know the fate of the positive charge within the molecule and to further investigate every detail of the binding event, we performed the NMR titration experiment (Figure 1c). The NMR spectrum of compound **1** (in CDCl_3) was studied with an increasing concentration of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (in CD_3OD). The NMR titration experiment reveals the loss of a proton from the guanidinium group of **1** as soon as **1** starts to bind with the Fe^{3+} ion. The intensity of the signal at 4.53 ppm due to the guanidinium N–H starts to diminish with an increasing concentration of the Fe^{3+} ion. On the basis of the demand of the electron, the metal ion can bind with **1** in two possible modes to produce either **2** or **3** (Figure 2a). As the fluorescence intensity of **1** is quenched by aqueous bivalent or trivalent metal ions, the methanolic solution of **1** can be utilized as a preliminary detection kit for these metal ions. The kit can detect wide varieties of transition metal ions such as Cr^{3+} , Fe^{3+} , Fe^{2+} , Co^{3+} , Co^{2+} , Ni^{2+} , and Cu^{2+} along with other toxic metal ions such as Hg^{2+} , Cd^{2+} , and Pb^{2+} . Compound **1** also interacts with the main group metal ions such as Mg^{2+} , Ca^{2+} , and so forth. A solution of compound **1** is orange colored. This color arises due to charge transfer from ring π -electrons to the nitro groups.⁷⁶ Upon interacting with a metal ion, this intramolecular charge transfer stops. As a result, the typical orange color and fluorescence of **1** vanish (Figure 2b,c).

Compound **1** is extremely hydrophobic because of the presence of four bulky cyclohexyl groups. This makes compound **1** water-insoluble. It has just been discussed that compound **1** interacts with a wide variety of metal ions. On the basis of these two important observations, compound **1** was used as a metal-ion-removing agent from industrial wastewater. Two different strategies were successfully applied to remove metal ions from water. The first method deals with the addition of compound **1** to the aqueous solution of the metal ion and then sonication of the solution for a certain time. Pure water is obtained by filtering the sonicated mixture (Figure 3 and Video S1). The second method is based on immobilization of compound **1** on the silica surface and then running the polluted water through a column packed with the immobilized compound (Figure 4). Fresh water is eluted from the outlet. This method is more effective than the previous one. Different metal salts mostly of perchlorate or nitrate were dissolved in deionized water. Different aqueous metal solutions (1000 mL) of concentration 1 mM were passed through a column freshly filled with 2 g of compound **1** immobilized over 60 g of 60–120 silica gel. The absorption spectra were measured, and inductively coupled plasma-mass spectrometry (ICP-MS) was performed for each solution before and after the treatment. From the absorption spectroscopy as well as ICP-MS, we can conclude that in each case there is more than 99.99% removal of metal ions. After several cycles, whenever the adsorption capacity of the metal ion significantly decreases, the column has to be regenerated. The regeneration process is very simple and

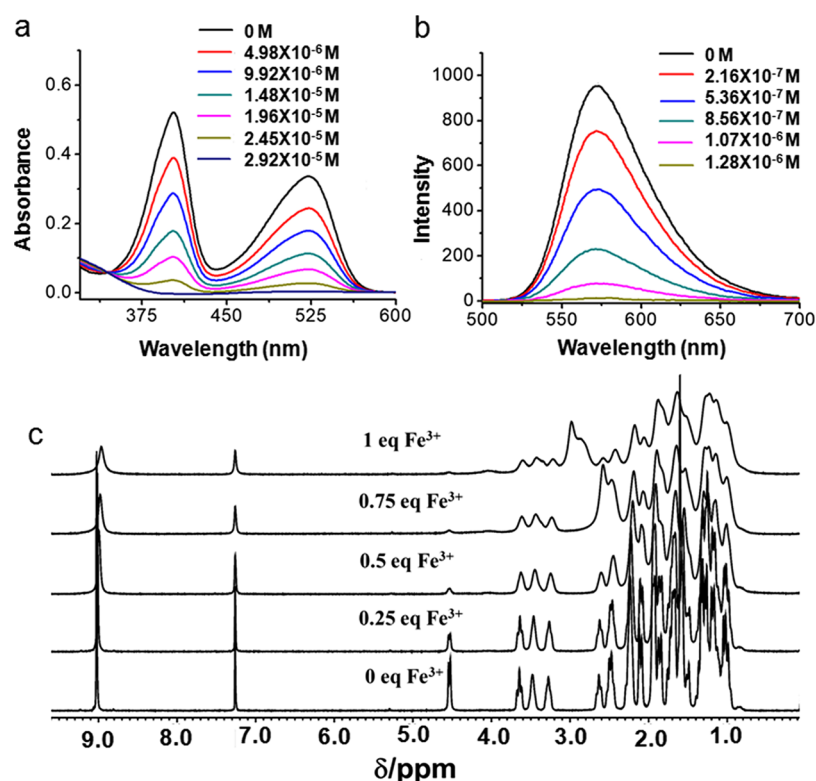


Figure 1. (a) Change of absorption spectra of **1** with gradual addition of the Fe^{3+} ion (aqueous FeCl_3 solution). (b) Fluorescence quenching of **1** with gradual addition of the Fe^{3+} ion (aqueous FeCl_3 solution). (c) ^1H NMR titration of **1** with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (dissolved in CD_3OD) in CDCl_3 .

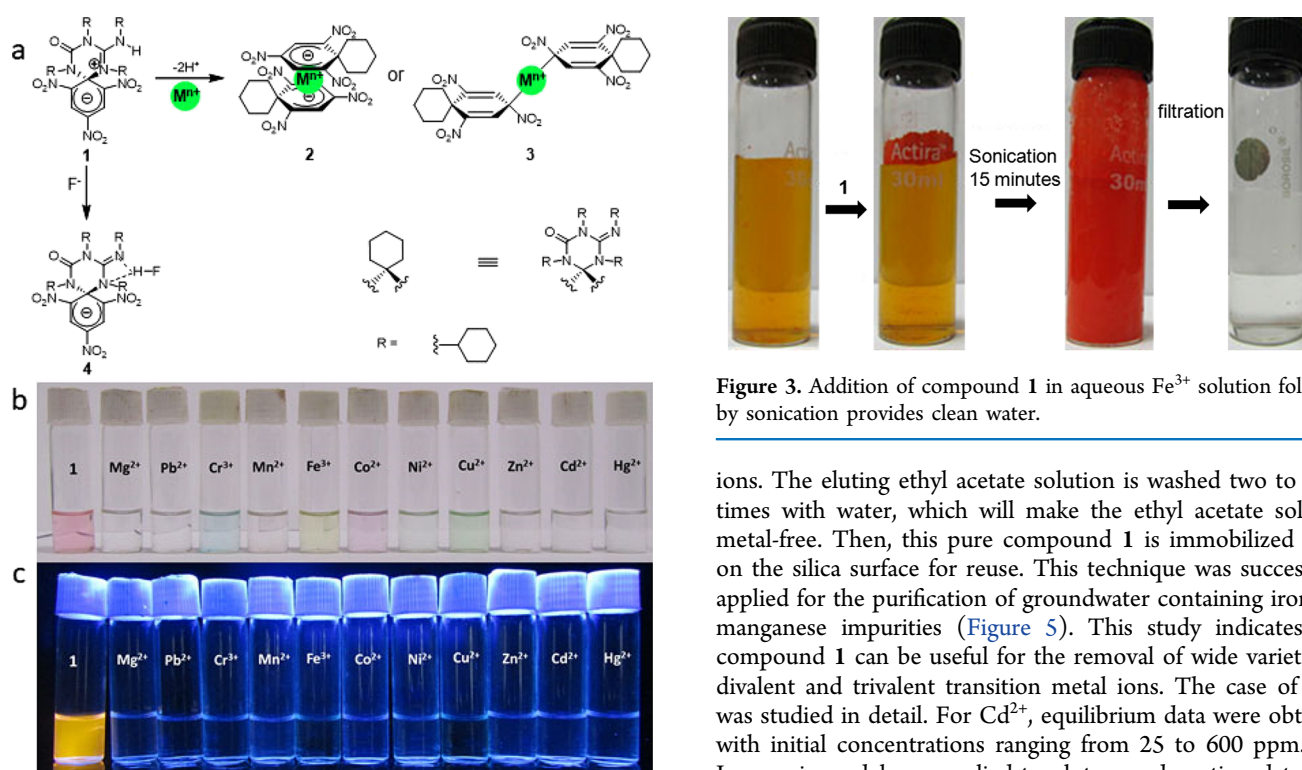


Figure 2. (a) Possible mode of binding of **1** with different metal ions and the fluoride anion. Methanolic solution of **1** in the presence of different metal ions (10 equiv) under (b) natural light and (c) 366 nm irradiation.

quantitative. For that, ethyl acetate is run through the column, which dissolves compound **1** along with the adsorbed metal

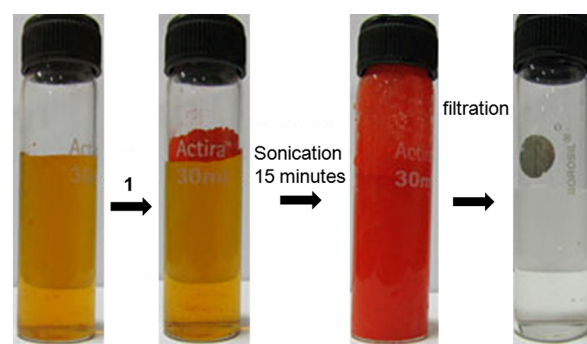


Figure 3. Addition of compound **1** in aqueous Fe^{3+} solution followed by sonication provides clean water.

ions. The eluting ethyl acetate solution is washed two to three times with water, which will make the ethyl acetate solution metal-free. Then, this pure compound **1** is immobilized again on the silica surface for reuse. This technique was successfully applied for the purification of groundwater containing iron and manganese impurities (Figure 5). This study indicates that compound **1** can be useful for the removal of wide varieties of divalent and trivalent transition metal ions. The case of Cd^{2+} was studied in detail. For Cd^{2+} , equilibrium data were obtained with initial concentrations ranging from 25 to 600 ppm. The Langmuir model was applied to plot our adsorption data. The data fitted nicely with a correlation coefficient of 0.995 (Figure 6). The uptake capacity was calculated in each step, and the maximum uptake capacity was found to be 712 mg/g with an equilibrium concentration of 180 ppm. The recyclability of compound **1** was also investigated for three consecutive cycles (Figure 7a). The compound also showed similar uptake capacities for Cd^{2+} in second and third cycles. The effect of



Figure 4. (a) Column packed with **1** coated on 60–120 mesh silica particles, (b) 2000 ppm aqueous Cu^{2+} solution, (c) after purification of 2000 ppm aqueous Cu^{2+} solution, (d) 300 ppm aqueous Fe^{3+} solution, and (e) after purification of 300 ppm aqueous Fe^{3+} solution.

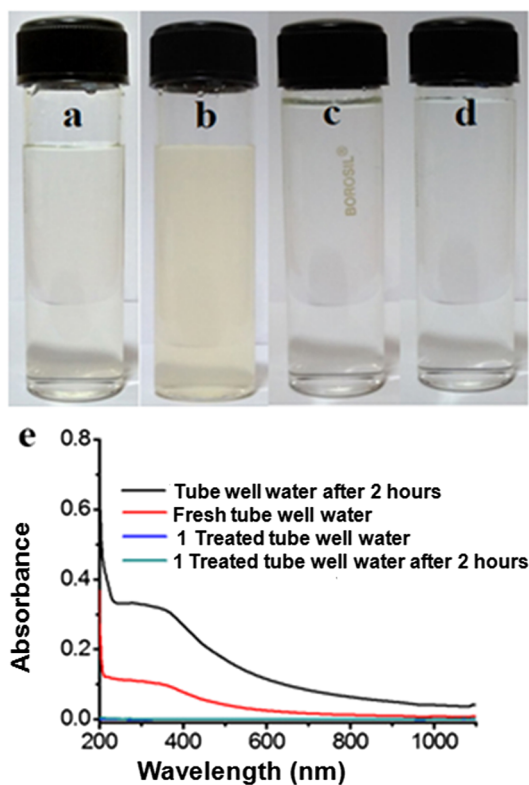


Figure 5. (a) Fresh tube well water, (b) tube well water after 2 h, (c) treated tube well water, (d) treated tube well water after 2 h, and (e) absorption spectra of all these four water samples.

pH on the uptake capacity of Cd^{2+} for compound **1** was also investigated (Figure 7b). The uptake capacity was measured at different pH values ranging from 3 to 9. The results indicated

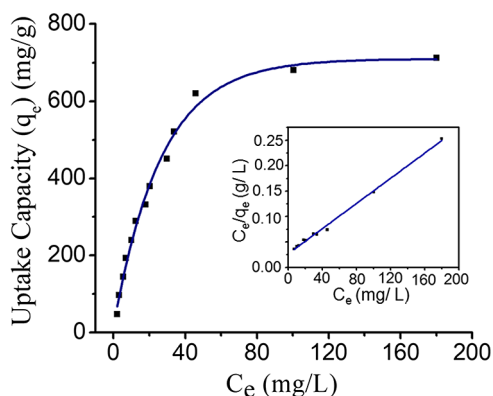


Figure 6. Cd^{2+} adsorption isotherm for compound **1**. The inset shows the linear regression by fitting the equilibrium adsorption data with the Langmuir adsorption model.

that pH 7 is the ideal one for the maximum removal of Cd^{2+} from water. At pH 2, the para carbon of 2,4,6-trinitrocyclohexadienylate system becomes protonated, and the complex remains no longer a Meisenheimer complex.⁷³ Therefore, in the absence of a negatively charged π -cloud, the protonated compound is unable to bind with the metal ions. While at pH 10, the guanidium proton is abstracted, and its zwitterionic state is lost.⁷³ Moreover, a decrease in the uptake capacity is observed. Time-dependent removal of metal ions was also studied. The cases of Fe^{3+} and Cd^{2+} were also studied. Highly concentrated aqueous solutions of Fe^{3+} (100 ppm) and Cd^{2+} (48.7 ppm) were treated with compound **1**, and concentrations of the metal ions were calculated with the progress of time. More than 99.99% removal was achieved within 30 and 40 min for Fe and Cd, respectively (Figures S3 and 7c). To evaluate the affinity of adsorbent **1** for metal ions, distribution coefficient values (K_d) were calculated. For Cd^{2+} and Fe^{3+} , the K_d values are, respectively, 9.74×10^7 and 1.66×10^8 mL g^{-1} . These K_d values are very good, which indicate that compound **1** has higher binding affinity for a trivalent metal ion than for a divalent metal ion. Now according to the World Health Organization (WHO), the permissible limits of Cu^{2+} , Pb^{2+} , Hg^{2+} , Cd^{2+} , and Fe^{3+} in drinking water are 1 ppm, 50, 1, 5, and 100 ppb, respectively. To check whether these metal concentrations can be dropped below the safe limit by our material, ICP-MS was performed. For concentration such as 5 ppm, the concentration level dropped below 0.2 ppb for Cu^{2+} , Pb^{2+} , Hg^{2+} , Cd^{2+} , and Fe^{3+} within 10 min after treating with compound **1**. A breakthrough experiment was performed by passing a solution containing Cu^{2+} , Hg^{2+} , Cd^{2+} , Pb^{2+} , Fe^{3+} , K^+ , and Na^+ each having a concentration of around 5 ppm through a column packed with compound **1**. Cd^{2+} , Hg^{2+} , Fe^{3+} , Pb^{2+} , and Cu^{2+} concentrations dropped much below the WHO permissible limits for these metal ions (Figure 7d). This study indicates the effectiveness of **1** as a highly promising adsorbent for the removal of toxic metals from water.

The uptake capacity of **1** for other metal ions was also checked. For Pb^{2+} , Hg^{2+} , Cu^{2+} , and Fe^{3+} , the uptake capacity values are 817, 830, 451, and 511 mg/g, respectively.

Being a zwitterionic species, compound **1** possesses a positive charge. Therefore, some anionic species were applied such that the positive charge of that zwitterion interacts with the anion. Different anions were added to the THF solution of **1**, but only in the presence of a fluoride anion, significant changes in the absorption and emission spectra were observed. The

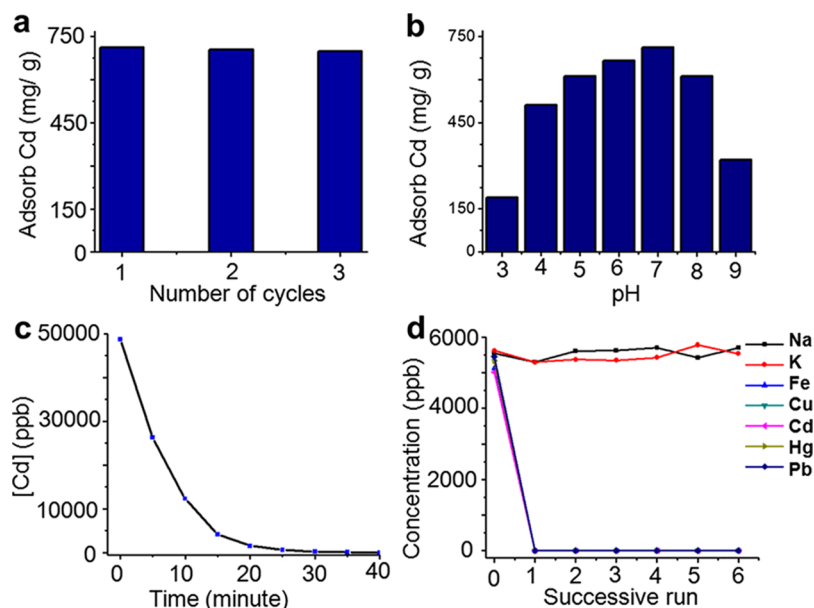


Figure 7. (a) Cadmium uptake capacity in consecutive cycles after the regeneration of compound **1**. (b) Effect of pH on the fluoride uptake capacity of **1** at different pH values. (c) Cd^{2+} sorption kinetics of **1** with an initial Cd^{2+} concentration of 48.7 ppm at a V/m ratio of 2000 mL g^{-1} . (d) Concentrations of metal ions after the breakthrough experiment of **1** collected at 4 mL intervals. The initial concentration of various ions is approximately 5 ppm.

fluorescent orange-colored THF solution of **1** becomes nonfluorescent, and the color of the solution becomes deep red (Figure 8a,b). The binding interaction was studied using

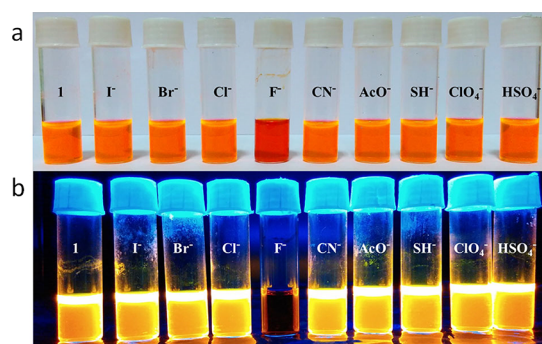


Figure 8. (a) Possible mode of binding of **1** with different metal ions and fluoride anion. (b) THF solution of **1** in the presence of different tetra-*n*-butylammonium anions (1 equiv) under (a) natural light and (b) 366 nm irradiation.

absorption (Figure 9a) and fluorescence spectroscopy (Figure 9b). Out of the two bands, the one at 527 nm starts to diminish slowly with increasing concentration of tetra-*n*-butylammonium fluoride (TBAF). The band at 405 nm starts to diminish rapidly, and a new maximum arises at 437 nm. In the case of the emission spectroscopy, the fluorescence intensity of compound **1** starts to decrease with increasing concentration of TBAF. The presence of two absorption maxima in between 400 and 600 nm confirms that after interacting with the F^- ion, the 2,4,6-trinitrocyclohexadienate system in **1** remains intact. It proves that the F^- ion interacts only with the positive charge of the guanidium moiety of **1**. A binding stoichiometry of 1:1 was obtained from Job's plot (Figure S4). To know the details of the binding interaction, we performed NMR titration with TBAF (Figure 9c). Upon addition of 1 equiv TBAF, the signal at 4.53 ppm for the N–H proton vanishes. Therefore, the F^-

ion takes the proton from a zwitterionic Meisenheimer complex **1**, resulting into a negatively charged Meisenheimer complex (Figure 2a). In this new species **4**, photoinduced electron transfer (PET) occurs from the triazene moiety to the 2,4,6-trinitrocyclohexadienate system.⁷⁷ This is the reason for the fluorescence quenching in **4**. Addition of 1 equiv strong acid such as trifluoroacetic acid (TFA) to a solution of **4** causes the regeneration of compound **1** (Figure S5). Therefore, compound **1** can show a fluoride and proton-mediated fluorescence switching phenomenon. As compound **1** responds to only F^- ion, it can be used as a fluoride sensor. The binding constant calculated from the Benesi–Hildebrand plot is $2.55 \times 10^5 \text{ M}^{-1}$ (Figure S6). The detection limit is $6.76 \times 10^{-7} \text{ M}$ or 12.8 ppb (Figure S6).

This fluoride sensor is equally effective in detecting the fluoride present both in organic medium and in water. Figure S7 shows the detection of aqueous fluoride. After successfully sensing the F^- anion, we thought whether we could apply compound **1** for fluoride removal from drinking water. In general, there are different methods such as (i) coagulation and precipitation, (ii) membrane-based methods, (iii) ion-exchange process, (iv) electro-coagulation process, (v) adsorption, and so forth.⁷⁸ Among them, adsorption is the mostly used method because it is of low cost, easier to apply, and very effective. We were also successful in applying compound **1** for fluoride removal using the same setup used for metal ion removal. We passed 1000 mL 100 ppm aqueous F^- solution through that column. Removal of the F^- ion (82%) was achieved after the first elution. Just like the case of metal ion removal, whenever the fluoride removal efficiency decreases, the column should be regenerated though the regeneration process is different. In this case, the eluting solvent is 1:99 TFA/ethyl acetate. After eluting the solvent, the solution was made neutral using triethylamine and by washing two to three times with water. Then the ethyl acetate solution was evaporated to get back compound **1** for further use.

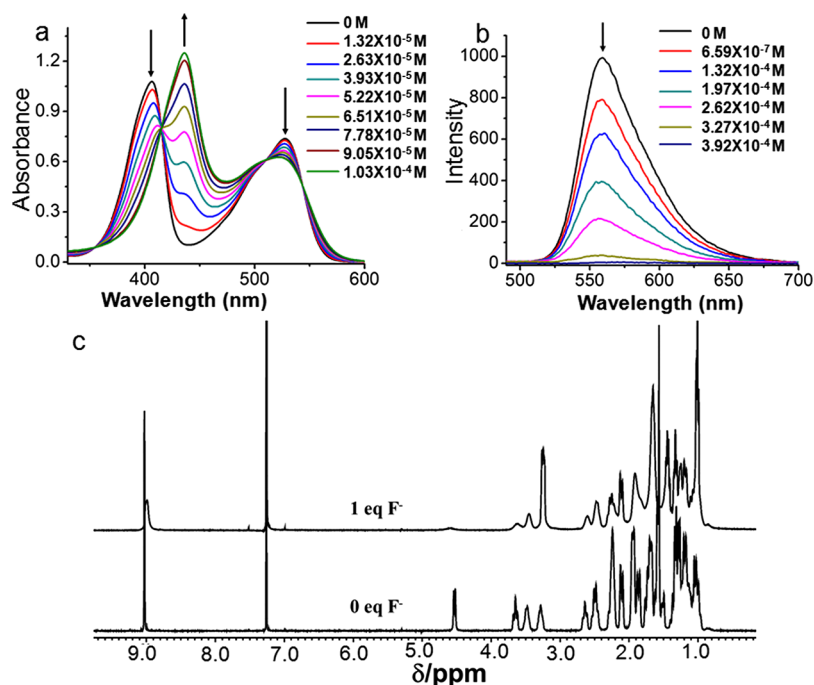


Figure 9. (a) Change of absorption spectra of **1** with gradual addition of F^- ion (TBAF). (b) Fluorescence quenching of **1** with gradual addition of the F^- ion (TBAF). (c) 1H NMR titration of **1** with TBAF in $CDCl_3$.

Adsorption studies for F^- removal were also performed. In this case, equilibrium data were obtained with initial concentrations ranging from 5 to 40 ppm. Also for fluoride removal, the equilibrium adsorption isotherm data fitted nicely with the Langmuir model having a correlation coefficient of 0.995 (Figure 10). The uptake capacity in each step was measured, and the maximum uptake capacity was found to be 60 mg/g with an equilibrium concentration of 8 ppm.

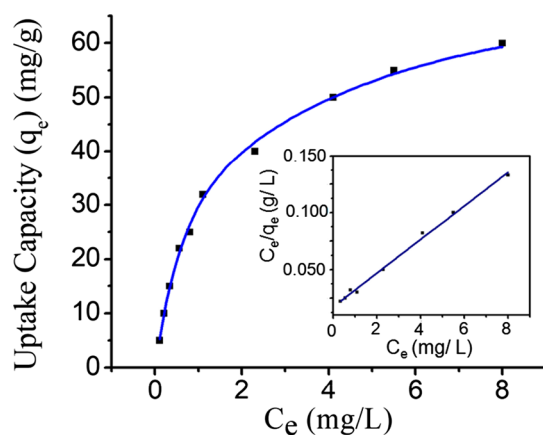


Figure 10. F^- adsorption isotherm for compound **1**. The inset shows the linear regression by fitting the equilibrium adsorption data with the Langmuir adsorption model.

The uptake capacity of compound **1** for three consecutive cycles was observed (Figure S8). No significant drop in the uptake capacity was observed even after the third cycle. This quality makes this compound a very promising material for a large-scale fluoride removal process. A pH-dependent adsorption study was further performed (Figure 11a). Also, in this case, it was found that pH 7 is the best condition for maximum fluoride removal. Moving from pH 7 toward both higher and

lower pH values causes a decrease in the uptake capacity. At pH 10, the guanidium proton can be easily abstracted and then the fluoride anion is not any longer able to bind with that guanidine unit.⁷³ That is why adsorption at higher pH is not favorable. For lower pH such as 2, the structure of the guanidine unit also changes significantly and the complex is no longer a Meisenheimer complex.⁷³ Therefore, at a lower pH, the uptake capacity value decreases sharply. The removal of fluoride with time was also studied (Figure 11b). The time-dependent adsorption study also indicated that the removal process is kinetically favorable. To evaluate the affinity of adsorbent **1** for the fluoride ion, the distribution coefficient value (K_d) was calculated which is 2.99×10^6 mL g^{-1} . According to WHO, the maximum permissible limit of fluoride in drinking water is 1.5 ppm. To check whether the fluoride concentration can be dropped below the safe limit by our material, fluorescence spectroscopy was performed with the treated water. However, in this case, a final concentration below 10 ppb was achieved from a heavily polluted water having 10 ppm fluoride concentration within 10 min.

We have already mentioned that compound **1** is extremely hydrophobic and we have utilized this concept for oil spill removal from water. Normal polystyrene sponge absorbs both water and oil at the same rate. However, after soaking a concentrated dichloromethane solution of **1**, the sponge becomes extremely hydrophobic. The modified sponge does not absorb water (Figure 12a,b). The water contact angle was measured to check the surface wettability (Figure 12c,d). The contact angle of normal sponge was 58° (Figure 12d). After coating the sponge with compound **1**, the contact angle value increased to 131° (Figure 12c). Oil droplets were immediately absorbed by the coated sponge. These facts suggest that there is an increment in the hydrophobicity after coating the sponge with compound **1**. FE-SEM images of the normal sponge as well as the coated sponge were recorded (Figure S9). The modified sponge exhibits significant changes in morphology,

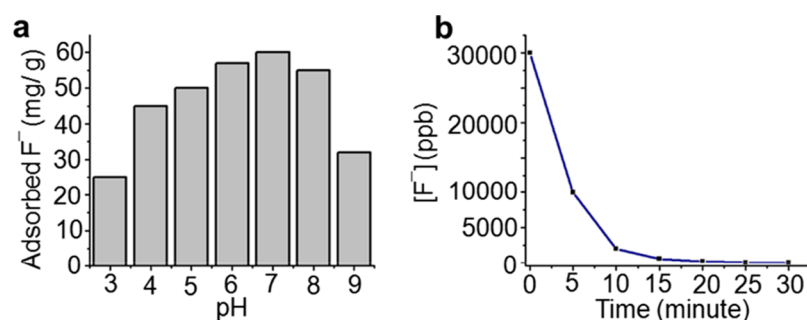


Figure 11. (a) Effect of pH on the fluoride uptake capacity of **1** at different pH values. (b) F⁻ sorption kinetics of **1** with F⁻ initial concentration of 30 ppm at a V/m ratio of 1000 mL g⁻¹.

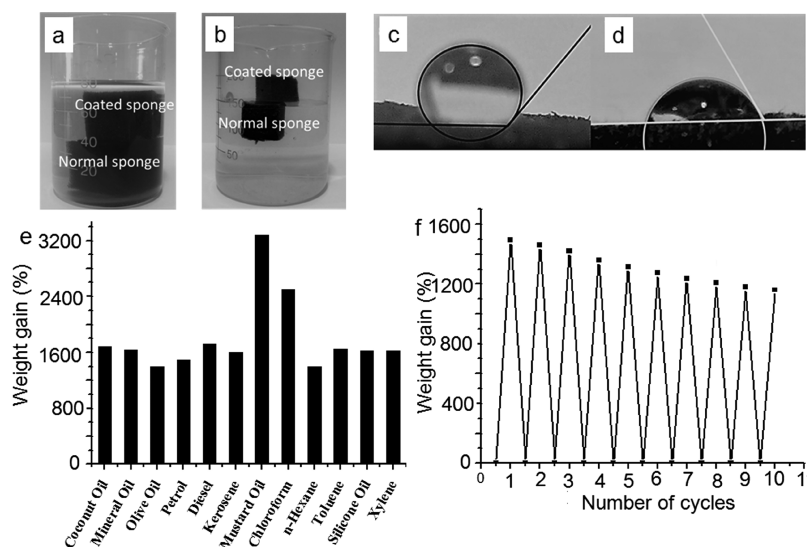


Figure 12. (a) Coated sponge and normal sponge in ethyl acetate. (b) Coated sponge and normal sponge in water. (c) Water contact angle of coated sponge (131°). (d) Water contact angle of normal sponge (58°). (e) Weight gain (%) of the modified sponge for different oils. (f) Weight gain (%) of the modified sponge (in the case of petrol) for 10 consecutive cycles.

suggesting that the sponge surface has been coated with compound **1** (Figure S9). This modified sponge can absorb a wide variety of oils and organic solvents. It has been utilized to remove oil spill and organic solvents from the water surface (Figure S10 and Video S2).

The sponge can remove heavier organic solvents such as chloroform from the bottom of the water layer (Figure S11 and Video S3). With the help of a suction pump, oils and lighter organic solvents were removed using this modified hydrophobic sponge (Video S4). The oils separated by this method can also be used after a normal distillation process. The weight gain (%) of the sponge was calculated in the presence of different oils and organic solvents (Figure 12e). Being a charged species, compound **1** is well-adsorbed on the surface of the sponge. As a result, compared to other neutral hydrophobic compounds, leaching of **1** from the sponge surface occurs slowly. The consecutive weight gain (%) of the sponge was also determined for 10 cycles for the recovery of petrol from water (Figure 8f).

CONCLUSIONS

This study explored the use of a zwitterionic spirocyclic Meisenheimer complex for its ability to remove 99.99% toxic metal ions from water for environmental remediation purposes. A zwitterionic spirocyclic Meisenheimer complex was successfully utilized as a highly efficient fluoride sensor which can

detect fluoride present both in organic and in aqueous media. An eco-friendly and cheap sorbent was developed for the removal of oil spills from water by coating the zwitterionic spirocyclic Meisenheimer complex on a porous matrix. Normal polystyrene sponge was chosen as the matrix, and the Meisenheimer complex was chosen as the surface modifier to convert the sorbent hydrophobic. Because of the hydrophobic nature and high porosity of the modified sponge, it absorbs the oil into the voids instantaneously. The modified sponge does not absorb water. Moreover, the sponge can remove heavier organic solvents such as chloroform from the bottom of the water. Using pressure or a suction pump, the oil can be easily collected from the modified sponge. The modified sponge shows very high oil soaking capacity with different kinds of crude oils. The modified sponge is also superior to all the known sorbents as it overcomes all the usual limitations such as secondary spill containment and uptake of water, thus making this system attractive toward the implementation in the industrial scale. This strategy of mopping up the oil, metals, and fluoride ions through hierarchical encapsulation by a zwitterionic spirocyclic Meisenheimer complex not only provides pure water but also cleans the environment and recovers the valuable resources.

EXPERIMENTAL SECTION

General. All chemicals were purchased from Sigma chemicals.

Synthesis. Compound **1** was synthesized following our previous report.⁶⁸

NMR Experiments. All NMR studies were carried out on a JEOL 400 MHz spectrometer at 278 K. Compound concentrations were in the range of 1–10 mM.

Absorption Spectroscopy. All the absorption spectra were recorded on a PerkinElmer UV/vis spectrophotometer (LAMBDA 35). During the measurement of absorption spectra, a 1 cm path length quartz cell was used.

Fluorescence Spectroscopy. All the fluorescence spectra were recorded on a PerkinElmer fluorescent spectrometer (LS 55). A 1 cm path length quartz cell was used during the measurement.

Field Emission Scanning Electron Microscopy. The morphologies of the sponge surfaces were investigated using field emission scanning electron microscopy (FE-SEM). The images were taken using an FE-SEM apparatus (ZEISS scanning microscope-ZSM-S 55 VP).

ICP-MS. The initial as well as residual metal ion concentrations were measured using ICP-MS (model-XSeries2) (Thermo Scientific).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01379.

Detection limit and binding constant determination, breakthrough experiment, and sorption isotherm and sorption kinetics (PDF)

Purification, sonication, and filtration of pure water (AVI)

Removal of mustard oil from the water surface (AVI)

Removal of dichloromethane from the bottom of the water layer (AVI)

Removal of ethyl acetate above the water surface (AVI)

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Author Contributions

T.D. has synthesized the compound and done the experiments. D.H. has done the analysis and wrote the manuscript.

Notes

The authors declare no competing financial interest.

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