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Fabrication of Novel Chemosensors Composed of Rhodamine Derivative for Detection of Ferric Ion and Mechanism Studies on the Interaction between Sensor and Ferric Ion

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Abstract

Although many rhodamine based fluorescence sensors were reported to detect metal ions with high sensitivity and selectivity, there are very few reports to study the mechanisms of detection and the interaction between probe and metal ions. This paper presents to detect ferric ions by novel fluorescence chemosensors and study the mechanism in detail. A novel probe AD-MAH-RhB was designed and synthesized from rhodamine B (RhB), adamantyl (AD), ethylene diamine and maleic anhydride (MAH). AD-MAH-RhB could detect Fe^{3+} in aqueous solution. The mechanism was explored by HSAB principle and FTIR and mass spectra. The results suggested that Fe^{3+} bound with amine and oxygen atoms in AD-MAH-RhB to form a complex composed of 2:1 stoichiometry of Fe^{3+} and the probe. Moreover, computational simulations were employed to further investigate the detection mechanism. The calculated results showed that Fe^{3+} could conjugate with AD-MAH-RhB probe to form stable complex, which induced by synergetic effects of the suitable space and distance of Van der Waals. However, Hg^{2+} was found to disturb this detection and formed a complex with 1:2 stoichiometry of Hg^{2+} and AD-MAH-RhB. Then, another probe, β-cyclodextrin modified polymaleicanhydride (PMAH-CD) inclusive AD-MAH-RhB (PMAH-CD/AD-MAH-RhB) was fabricated by inclusion interaction between CD and AD. PMAH-CD@AD-MAH-RhB showed high selectivity and sensitivity to Fe^{3+} in aqueous solution by eliminating the interruption of Hg^{2+}, possibly due to the high hydrogen interaction among the probes to inhibit the form stable complex with Hg^{2+}.

Keywords: fluorescence sensor, Rhodamine derivative, detection, mechanism study

1. Introduction

Metal ions such as Fe^{3+}, Hg^{2+}, Cr^{3+}, from industrial effluents become significant pollution for the environment. Since these pollutants can be easily absorbed by aquatic organisms, bioaccumulated and spread along the food chain, the analysis and detection of the metal ions in water are important subjects for biology and environmental chemistry[1]. Consequently, over the last few decades, considerable efforts have been devoted to developing fluorescent chemosensors for metal ions with high selectivity, sensitivity and reliability[2-9]. Some fluorescent chemosensors that composed of chromophores such as fluorescein[10-11], rhodamine[12], coumarin[13] and recognition groups such as crown ether[14], calixarene[15], polyamine[16], have been prepared for detection of metal ions.

Rhodamine scaffold is an ideal template chromophore for the construction of chemosensors because they have large molar extinction coefficient, long excitation and emission wavelengths and high fluorescence quantum yields [17-18]. Moreover, rhodamine derivatives with a spirolactam structure are colorless and nonfluorescent, whereas a ring-opened amide form of rhodamine derivative gives rise to both chromogenic and fluorogenic response to facilitate an OFF/ON-type fluorescent detection. Therefore, a number of fluorescence sensors have been developed based on rhodamine derivatives with different recognition groups for detection of metal ions. Li group[19] reported a fluorophore dye containing rhodamine and a naphthalimide moiety to be as a Cr^{3+}-selective fluorescent probe. Hu et al. [20] reported a colorimetric and fluorescent chemosensor based on a rhodamine 6G phenylurea conjugate could

recognize Fe(III) ions. Yook and Tae groups[21-22] prepared a series of rhodamine-based fluorescent and colorimetric sensors for the detection of Hg and Pt ions. These reported probes showed highly selective and sensitive to special metal ions. However, the recognition mechanism was seldom studied in these examples. Thus, some existing problems should be explained and solved, such as why the recognition groups showed the selectivity towards different metal ions although they containing similar cooperative atoms or groups, what is the interaction between sensors and metal ions, how to construct a fluorescence sensor to detect a designated metal ion, and which principle should be followed during the structure design of the sensor.

Since the structure of a probe-metal ion complex is complicated and the binding interaction between probe and metal is concerned several aspects such as metal size, outer shell electrons of metal, Van der Waals force, and so on, it is difficult to explain the recognition mechanism very well by experiment method. Compared with experimental methods, computational simulations are time-saving and eco-friendly[23]. They have been employed to design a desired structure with excellent performance in quantum-chemical (QC) area. However, there are few researches to calculate the structure of rhodamine based fluorescent chemosensor and investigate the relationship between probe and metal ion by computational simulations.

Ferric ions are very important to our body, and will cause anemia and breathing problems if deficient, while will be toxic to body when they are at levels exceeding the capacity of safe consumption[24]. Thus, our aim is to detect ferric ions in aqueous

solution by a designed rhodamine derivative with high sensitivity and selectivity. In order to design a probe for recognition of ferric ions, we should firstly know the chemical properties of the recognition groups and metal ions. Metal ions can be divided into two parts: hard acid and soft acid, and the recognition groups were also divided into hard base and soft base. According to HSAB principle that "hard likes hard and soft likes soft", which was reported by Pearson[25], Fe(III) ion is a hard acid and can form a stable complex with the hard bases such as carbonyl and amide groups. Thus, in this work, ethylene diamine and maleic anhydride (MAH) were selected as receptors to recognize Fe(III) ion, and rhodamine B (RhB) was as a fluorophore. Adamantyl (AD) was also introduced into the probe for further modification of the probe structure with cyclodextrin via host-guest interaction. Then, the novel fluorescent probe (AD-MAH-RhB) was developed based on RhB, ethylene diamine, MAH and AD, as Scheme 1a. The sensitivity and selectivity of the probes to Fe ions were detected. The relatively recognition mechanisms were investigated in detail by HSAB Principle, FTIR and mass spectra. Moreover, computational simulation was employed to investigate the relationship between the structure and the selectivity of the probe, and to determine what the key factors are that will improve the selectivity of the probe. Furthermore, for improvement of the selectivity to Fe^{3+}, another probe with complicated structure (Scheme 1b) was designed and prepared by AD-MAH-RhB and cyclodextrin funtionalized polymaleicanhydride (PMAH-CD) via host-guest interaction. The high selectivity of the probe to Fe ion was detected. These probes could be used as sensor to the great potential application for detection. The

mechanism study might help to design a fluorescence sensor effectively for detection of a desired metal ion.

2. Experimental Section

2.1 Materials and instruments

Tosyl chloride (TsCl), 1-aminoadamantane (AD-NH_2), ethylene diamine (EDA), and maleic anhydride (MAH) were bought from Sigma-Aldrich Chem. Co., and used without further purification. β-Cyclodexrin (CD) was perchased from Sigma-Aldrich Chem. Co., and purified by recrystallization. All metallic salts, such as $Ba(NO_3)_2$, $CdCl_2{\cdot}2.5H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $FeCl_3{\cdot}6H_2O$, $MgCl_2$, KCl, $Ni(NO_3)_2{\cdot}6H_2O$, $AgNO_3$, $CuCl_2$, and $Hg(NO_3)_2$, were purchased from Sinopharm Chemical Reagent Co. Ltd, and theirs aqueous solutions were prepared with ultrapure water from a Millipore autopure WR600A system (Millipore, Ltd. USA).

UV-vis spectrum was recorded on a TU-1901 spectrophotometer (Beijing Purkinje General Instrument Co. Ltd). Fourier transform infrared spectroscopy (FTIR) spectrum (Nicolet iN10) was recorded on an attenuated total reflection (ATR) method with a FT-IR spectrometer. Fluorescence emission spectrum was recorded with a varianinc Cary Esclipse spectrophotometer at an excitation wavelength of 541nm. All the spectroscopic measurements were performed at least in triplicate and averaged. All the computational simulations were performed with GAUSSIAN03[26].

2.2 Synthesis of AD-MAH-RhB probe

Rhodamine B was synthesized in a similar manner to reported methods[25]. Then, MAH (1 mmol)，RhB (1 mmol) and 4-dimethylamiopyridine (DMAP, 0.15 mmol)

were dissolved in DMSO. 1-Ethyl-3-(3-Dimethylaminopropyl) carbodiimide (EDC, 1 mmol) and hydroxybenzotriazole (HOBt, 1 mmol) were added into the above solution. By activated for 1 h, 1-aminoadamantane (AD-NH_2, 1 mmol) was added and started reaction at room temperature (Scheme S1). After predetermined time, red powder was obtained by removing solvent under reduced pressure and purified by slilica gel column chromatography in CH_2Cl_2 to give purified AD-MAH-RhB (367 mg, 53 %). ^{1}H NMR (400MHz, $CDCl_3$, ppm, Figure S1): 7.88-7.85 (1H), 7.45-7.42 (2H), 7.09-7.07 (1H), 6.44-6.26 (8H), 3.37-3.26 (12H), 1.90-1.70 (15H, adamantyl imine), 1.18-1.14 (12H). ESI m/z[M+Na^+] : 738.5.

2.3 Synthesis of cyclodextrin functionalized polymaleicanhydride (PMAH-CD)

Polymaleicanhydride (PMAH) was synthesized by Reversible Addition Fragmentation Chain Transfer Polymerization (RAFT) using a chain transfer agent which prepared in a reported method[27]. As shown in Scheme S2, MAH (5 g), S,S'-bis(α,α'-dimethyl-α'-acetic acid)-trithiocarbonate (143 mg) and AIBN (84 mg) were dissolved in toluene at 0 ^{o}C under N_2 atmosphere. PMHA was obtained by dialyzed and dried after reacted at 80 ^{o}C for 8 h, and the yield was about 30 % (1.5 g). The molecular weight of PMAH was 3710, which was measured by GPC.

Ethylene diamine mono-substituted β-cyclodextrin (EDA-β-CD) was synthesized according to the reported methods[28]. Then, PMAH (0.0376 g), DMAP (20 mg), HOBt (137 mg), EDC (191 mg) and EDA-β-CD (12 mg) were dissolved in 10 ml of DMF (Scheme S2). After reacted for 12 h, 40 mg of product PMAH-CD was dialyzed and dried. The yield was 80 %. ^{1}H NMR (400MHz, D_2O, ppm, Figure S2): 5.0-5.19

(7H), 3.26-3.91 (42H), 1.13-1.15 (12H).

2.3 Preparation of the supramolecular complex PMAH-CD/AD-MAH-RhB

PMAH-CD (5.5×10^{-6} mol) was dissolved in 40 mL of deionized water. Then, the same concentration of AD-MAH-RhB in 10 mL of ethanol was added slowly into the PMAH-CD aqueous solution. The mixed solution was stirred for 2 d at room temperature. The inclusion complex was obtained by dialysis and drying under reduced pressure [29].

2.4 Detection procedure

Standard solution of Fe^{3+} (7×10^{-3} mol L^{-1}) was obtained by dissolving 189.2 mg $FeCl_3\cdot6H_2O$ solid in ultrapure water. The binding complex solutions of AD-MAH-RhB and Fe^{3+} were obtained by mixing 5 mL of the stocked AD-MAH-RhB solution and 0.2，0.5，0.7，1.0，1.5，2.0，2.5 mL of Fe^{3+} standard solution in a 25 mL volumetric flask, respectively. The PMAH-CD/AD-SRhB@Fe complex solutions were the same process as mentioned above. The concentrations of Fe^{3+} in the resultant solutions were 0, 1, 9, 10, 15, 23, 30 and 38 mg L^{-1}. The fluorescences of all the samples before and after formed complexes were measured by excitation at 514 nm. FTIR spectra of the AD-MAH-RhB solution and the complexes with Hg^{2+} and Fe^{3+} were carried out by ATR method. The complex for mass spectrum measurement was prepared by mixing AD-MAH-RhB and metal ions in methanol.

3. Results and Discussion

3.1 Sensitivity and selectivity of AD-MAH-RhB

Depending on HSAB principle, Fe^{3+} is a hard acid and likes hard base ligand. The

prepared AD-MAH-RhB contains the carbonyl and amine groups. Thus, AD-MAH-RhB could detect Fe^{3+}. The solution of AD-MAH-RhB was colorless and did not exhibit any absorption, which was coincident with the property of the spirocycle RhB derivatives by UV/vis spectrum. By adding Fe^{3+} ions to the AD-MAH-RhB solution, the color of the mixture changed to rose red immediately. UV-vis spectra confirmed that Fe^{3+} induced an increment in the absorption of AD-MAH-RhB at 564 nm, as shown in Figure 1a, indicating addition of Fe^{3+} can promote the formation of the open-ring sate of the RhB moieties. The absorption intensity increased with increasing the Fe^{3+} concentration. Figure 1b shows the fluorescence changes in the probe-metal complex upon addition of Fe^{3+}. By excitation at 541 nm, there was almost no emission profile of RhB in the absence of Fe^{3+}. Upon addition of Fe^{3+}, a strong emission peak at around 587 nm appeared and increased gradually with increasing the concentration of Fe^{3+}. The detection limit was calculated to reach 8.3 mg L^{-1}. These results confirmed that the probe could detect Fe^{3+} in aqueous solution with low detection limit.

High selectivity is an important index to know whether the rhodamine probe is an excellent probe. Thus, fluorescent and absorption spectra of AD-MAH-RhB to other traditional metal ions were examined, such as Hg^{2+}, Cd^{2+}, Cu^{2+}, Ba^{2+}, Ag^{+}, Zn^{2+}, Co^{2+}, K^{+}, Mg^{2+}, Ni^{2+} and Pb^{2+}. Figure 2 shows the fluorescence intensity of the AD-MAH-RhB aqueous solution (1.4×10^{-4} M) upon addition of different metal ions with the concentration of 1×10^{-2} M in pH 7.0. From Figure 2, it clearly showed that Fe^{3+} and Hg^{2+} induced a prominent fluorescence increment, whereas other metal ions

did not show any obvious fluorescence enhancement at 587 nm of emission peak as well as no color change. Depending on the HSAB principle, Fe^{3+}, Ba^{2+} and K^{+} are hard acid, whereas Hg^{2+}, Cd^{2+} and Ag^{+} are soft acid, and Cu^{2+}, Zn^{2+}, Co^{2+}, Mg^{2+}, Ni^{2+} and Pb^{2+} are borderline acid. Accordingly, Cd^{2+}, Cu^{2+}, Ag^{+}, Zn^{2+}, Co^{2+}, Mg^{2+}, Ni^{2+} and Pb^{2+} could not conjugate with AD-MAH-RhB to form stable complexes, which were the same as the experimental results. However, AD-MAH-RhB exhibited a specific selectivity to Hg^{2+} as well as Fe^{3+}, although Hg^{2+} is just a soft acid.

3.2 Mechanism studies on the interaction between AD-MAH-RhB and metal ions

In order to know the reason why AD-MAH-RhB could detect Fe^{3+} and Hg^{2+}, the interactions between AD-MAH-RhB and metal ions were investigated. In RhB-metal ion complexes, vibrational spectroscopy can provide information on coordination bond of metal ions and probes[30]. Thus, FTIR spectra of solid AD-MAH-RhB, AD-MAH-RhB@Zn^{2+}, AD-MAH-RhB@Fe^{3+} and AD-MAH-RhB@Hg^{2+} were recorded, and the resultant spectra are shown in Figure 3. Peaks at 3076 and 1676 cm^{-1} assigned to the cis-acylamino and amide groups (Figure 3a), respectively. After adding Fe^{3+}, the peak at 3076 cm^{-1} disappeared and the peak at 1676 cm^{-1} shifted to 1670 cm^{-1} ((Figure 3c), indicating that Fe^{3+} influenced the acylamino and amide groups. After AD-MAH-RhB conjugated with Hg^{2+}, peaks at 3076 and 1676 cm^{-1} chemical shifted to 3056 and 1674 cm^{-1}, and the peaks decreased slightly (Figure 3d). However, there was almost no change when adding Zn^{2+} and other metal ions (Figure 3b, AD-MAH-RhB@Zn^{2+} as an example). These results suggested that Fe^{3+} and Hg^{2+} (especially Fe^{3+}) bound with acylamino and amide groups in AD-MAH-RhB, whereas

other metal ions have no reaction with AD-MAH-RhB. Moreover, peak at 1632 cm^{-1} assigned to double carbon groups. After adding Hg^{2+} (Figure 3d), the absorbance at 1632 cm^{-1} decreased, and a new peak at 1530 cm^{-1} appeared, which belonged to cyclic olefin, suggesting that Hg acted as a bridge to cooperate with the two double bonds to form the cyclic olefin. These results indicated that Fe^{3+} mainly bound to amide and carbonyl groups to form AD-MAH-RhB@Fe^{3+} complex, while Hg^{2+} conjugated with amide, carbonyl and double carbon groups to from the AD-MAH-RhB@Hg^{2+} complex.

Since mass of probe changed after conjugated with metal ions[31], mass spectroscopy was carried out to investigate the selectivity of AD-MAH-RhB to Fe^{3+} and Hg^{2+}. The theoretical mass of AD-MAH-RhB@Hg^{2+} is about 916. However, the related peak was not captured. On the contrary, peak at m/z ~815 assigned to [AD-MAH-RhB@Hg^{2+}@AD-MAH-RhB]/2 (Figure 4a) was clearly observed in the mass spectrum of the AD-MAH-RhB@Hg^{2+} complex, indicating formation of 1:2 stoichiometry complex of Hg^{2+} and AD-MAH-RhB, as shown in Scheme 2a. In the case of AD-MAH-RhB@Fe^{3+}, a peak at m/z 851.4 emerged in the MS spectrum for the AD-MAH-RhB@Fe^{3+} complex (Figure 4b). This result suggested the formation of [Fe^{3+}@AD-MAH-RhB@Fe^{3+}] complex, i.e. formation of a 2:1 stoichiometry complex of Fe^{3+} and AD-MAH-RhB. Based on the results of FTIR spectra and mass analysis, the possible sensing mechanisms of AD-MAH-RhB complex with Hg^{2+} and Fe^{3+} are proposed in Scheme 2.

For further understand the selectivity of AD-MAH-RhB to Fe^{3+}, but not to Ba^{2+} and

K^+, computational simulations were performed with GAUSSIAN03[26]. Ab initio DFT using the well-established Becke three-parameter hybrid functional[32] with the correlation functional of Lee, Yang and Parr[33] (B3LYP) was used, combined with 6-31G* basis set, of which the abilities to calculate the structure and energy of the probe have been widely demonstrated. The optimized structure was checked to be a true minimum and not a saddle point by calculation, as shown in Figure 5a. From the result of the ab initio calculation, the bond lengths of C-N, N-N and O-N are 2.34, 3.0 and 2.86 Å, respectively. Then, the spaces of the probe constituted by amine and oxygen atom could be calculated to 3.28 Å. Therefore, Fe ion (d_{Fe}=2.52 Å, d means diameter) was perfectly suitable for the spaces, whereas the same hard acid such as Ba^{2+} (d_{Ba}=4.3 Å) and K^+ (d_K=4.4 Å) were too big to suit the spaces.

On the other hand, when a probe and metal ion forms a stable complex, the bond distance of Van der Waals between recognition groups and metal ion should be less than the sum of Van der Waals radius of elements[34]. Otherwise, it is considered that there is no interaction between the probe and metal ion. In the optimized structure of AD-MAH-RhB@Fe^{3+} complex by computational simulations (Figure 5b), the distances of Fe-O and Fe-N are 1.9 and 1.95 Å, which are less than the sum of Van der Waals radius of N (1.5 Å), O (1.5 Å) and Fe (2.23 Å) [35,36]. Therefore, Fe^{3+} could conjugate with AD-MAH-RhB probe to form stable complex, which induced by synergetic effects of the suitable space and distance of Van der Waals.

3.3 Improving sensitivity and selectivity of PMAH-CD/AD-MAH-RhB

In order to improve the selectivity of the AD-MAH-RhB probe towards Fe ions, the

interaction between Hg^{2+} and AD-MAH-RhB should be prevented. Increasing inter- and intra- molecular interactions of AD-MAH-RhB might be a good way to reduce the reaction chance between AD-MAH-RhB and Hg^{2+}. Therefore, PMAH-CD was employed to prepare a supermolecular complex with AD-MAH-RhB by host-guest interaction. The inclusive complex formation was confirmed by ^{1}HNMR spectrum, as shown in Figure S3. Fluorescence and UV-vis spectra confirmed that the colorless PMAH-CD/AD-MAH-RhB solution did not exhibit any absorption, which was coincident with the property of the spirocycle RhB derivatives. Addition of Fe^{3+} into the PMAH-CD/AD-MAH-RhB solution induced a significant color change to rose pink (inset photo in Figure 6a). Meanwhile, obvious changes in the absorption spectra at 564 nm appeared with addition of Fe^{3+}, which was similar to Figure 1a, due to the formation of the open-ring sate of the RhB moieties. While, there was negligible absorbance of PMAH-CD/AD-MAH-RhB in the present of Hg^{2+} and other metal ions such as Cd^{2+}, Cu^{2+}, Ba^{2+}, Ag^{+}, Zn^{2+}, Co^{2+}, K^{+}, Mg^{2+}, Ni^{2+} (Figure 6a). Moreover, a dramatic change at 587 nm in the fluorescence spectrum was also observed upon addition of Fe^{3+}, while no obvious fluorescence appeared with addition of other metal ions, even Hg^{2+}, as shown in Figure 6b. These results confirmed that PMAH-CD/AD-MAH-RhB could detect Fe^{3+} to form binding complex, whereas not conjugate with Hg^{2+}.

The selectivity of PMAH-CD/AD-MAH-RhB towards Fe^{3+} over other metal ions was also investigated by the competitive experiments. Figure 7 shows the fluorescence intensity of PMAH-CD@AD-MAH-RhB in the present of Fe^{3+} only and

Fe^{3+} mixed with 100 equiv of various metal ions at 587 nm of emission peak. The results showed that the Fe^{3+} induced fluorescence enhancement was not obviously affected in the presence of other ions. The selectivity and comptetition experiments revealed that PMAH-CD@AD-MAH-RhB has a remarkable selectivity towards Fe^{3+}.

3.4 Mechanism studies on the interaction between PMAH-CD/AD-MAH-RhB and metal ions

When AD-MAH-RhB is as a guest to form the complex with PMAH-CD, PMAH-CD/AD-MAH-RhB can dissolve in ultrapure water and from lots of interactions of intramolecular and intermolecular hydrogen bonds, inducing the chains entangled and network formation. Since one Hg^{2+} needed two AD-MAH-RhB molecules to form a complex, as mentioned above, the high hydrogen interactions of among PMAH-CD/AD-MAH-RhB probes might prevent AD-MAH-RhB from closing each other and also prevent Hg^{2+} from conjugating with two PMAH-CD/AD-MAH-RhB. However, Fe^{3+} ions just need one molecule AD-MAH-RhB, and these hydrogen bonds had no effect on the reactive space and distance of Van der Waals. This is why PMAH-CD@AD-MAH-RhB has a good selectivity for Fe^{3+} in the presence of Hg^{2+}. Unfortunately, the interactions between PMAH-CD/AD-MAH-RhB probes and between PMAH-CD/AD-MAH-RhB and metal ions are difficult to calculate by computational simulations, because of complicated structure of the supermolecular structure. Anyway, the modified probe showed the high selectivity towards Fe^{3+}.

4 Conclusion

A novel probe composed of rhodamine derivative AD-MAH-RhB was synthesized, and it showed sensitivity to Fe^{3+}. However, Hg^{2+} was found to disturb the detection. The mechanism and interaction between the probe and metal ions were studied based on computational simulations, HSAB principle, and FTIR and mass spectra. The results suggested that Fe^{3+} was suitable to the probe structure and the bond distance of Van der Waals was less than the sum of Van der Waals radius of elements. Moreover, Fe^{3+} bound with amine and oxygen atoms in AD-MAH-RhB to form a complex composed of 2:1 stoichiometry of Fe^{3+} and AD-MAH-RhB, whereas Hg^{2+} bound with amine, oxygen atoms and double carbon groups in AD-MAH-RhB to form a complex composed of 1:2 stoichiometry of Hg^{2+} and AD-MAH-RhB. For improvement of the selectivity of the probe, PMAH-CD was employed to inclusive AD-MAH-RhB to form another probe. PMAH-CD/AD-MAH-RhB showed excellent selectivity and sensitivity towards the detection of Fe^{3+} in aqueous solution. The high hydrogen interactions existing among the probes might inhibit the form stable complex with Hg^{2+}. The novel probes could be used as the fluorescence sensors to detect metal ions in aqueous solution. The mechanism studies might help to design and construct novel fluorescence sensors effectively and well understand the interaction between the probe and metal ions.

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Figure Captions

Scheme 1. Schematic representative of structures of AD-MAH-RhB (a) and PMAH-CD/AD-MAH-RhB (b).

Figure 1. (a) Absorption spectra and (b) Fluorescence spectra of AD-MAH-RhB aqueous solution at pH 7.0 with increasing concentration of Fe^{3+} from 0 to 38 mg L^{-1}. Inset photo shows the color change of AD-MAH-RhB solution upon the addition of Fe^{3+}.

Figure 2. Fluorescence intensity of the AD-MAH-RhB aqueous solution (1.4×10^{-4} M) at 587 nm upon addition of different metal ions with the concentration of 1×10^{-2} M in pH=7.0 by excitation at 541 nm. Inset photos show the colors of AD-MAH-RhB upon addition of different metal ions with the concentration of 1×10^{-2} M.

Figure 3. FTIR spectra of AD-MAH-RhB (a), AD-MAH-RhB/Zn^{2+} (b), AD-MAH-RhB/Fe^{3+} (c), and AD-MAH-RhB/Hg^{2+} (d).

Figure 4. MS spectra of AD-MAH-RhB/Hg^{2+} (a) and AD-MAH-RhB/ Fe^{3+} (b).

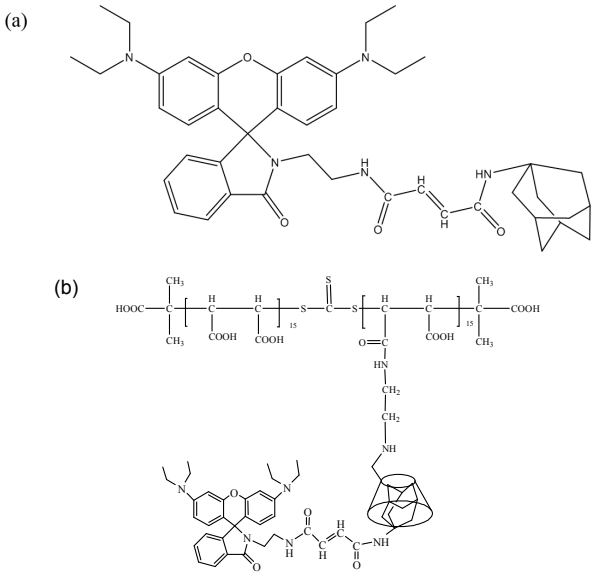
Figure 5. Visualization of the DFT-optimized (calculated at the B3LYP 6-31G* level) structure of AD-MAH-RhB, nitrogen atoms are shown in blue, oxygen atoms in red, carbon atoms in dark gray, hydrogen atoms in white, and Fe ions in red brown.

Scheme 2. Proposed mechanisms for interactions of AD-MAH-RhB with Hg^{2+} (a) and Fe^{3+} (b).

Figure 6. (a) Absorption and (b) Fluorescence intensity of the PMAH-CD/AD-MAH-RhB aqueous solution (1.4×10^{-4} M) at 587 nm upon addition of different metal ions with the concentration of 1×10^{-2} M in pH=7.0 by excitation at 541

nm. Inset photos show the colors of PMAH-CD/AD-MAH-RhB upon addition of different metal ions with the concentration of 1×10^{-2} M.

Figure 7. Fluorescence intensity of the PMAH-CD/AD-MAH-RhB aqueous solution (1×10^{-4} M) upon addition of Fe ion (1×10^{-4} M) in the presence of various metal ions (1×10^{-2} M) in pH=7.0 at 541 nm of excitation wavelength.



Scheme 1. Shi et al.

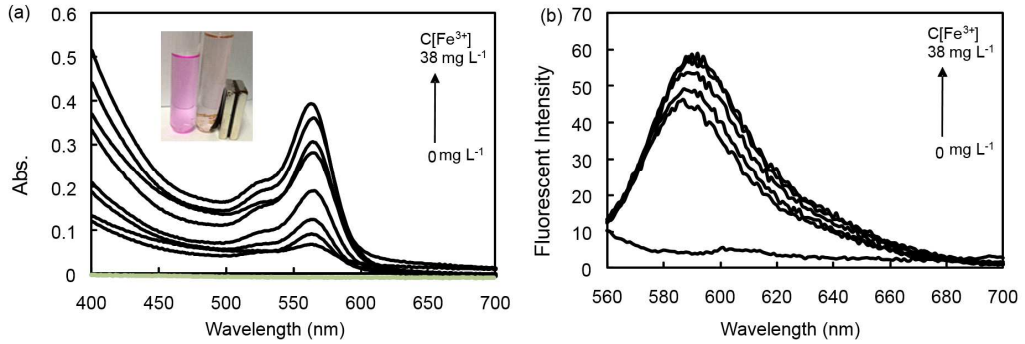


Figure 1. Shi et al.

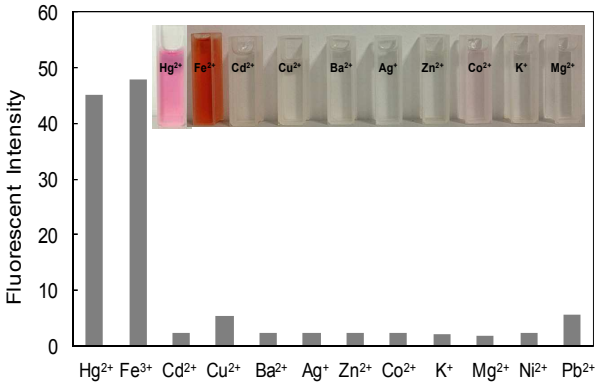


Figure 2. Shi et al.

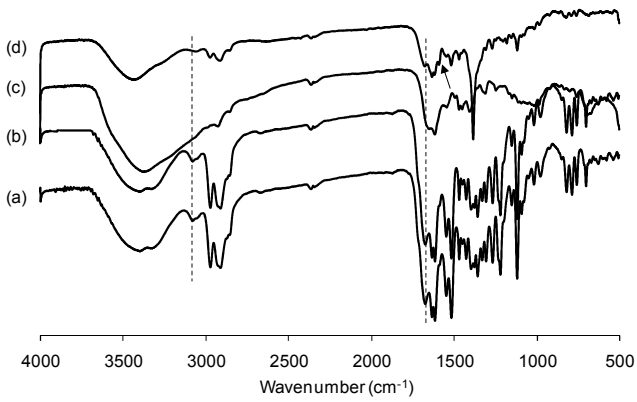


Figure 3. Shi et al.

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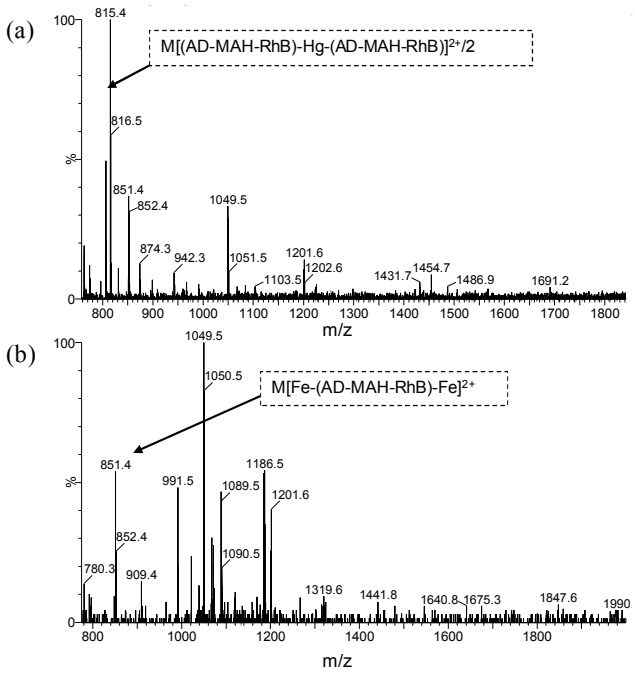

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496 Figure 4. Shi et al.

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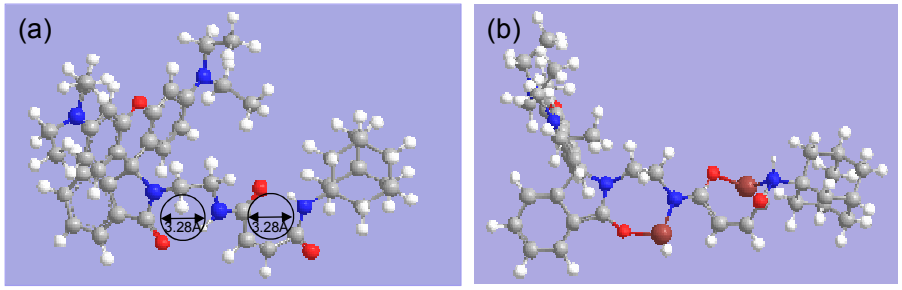
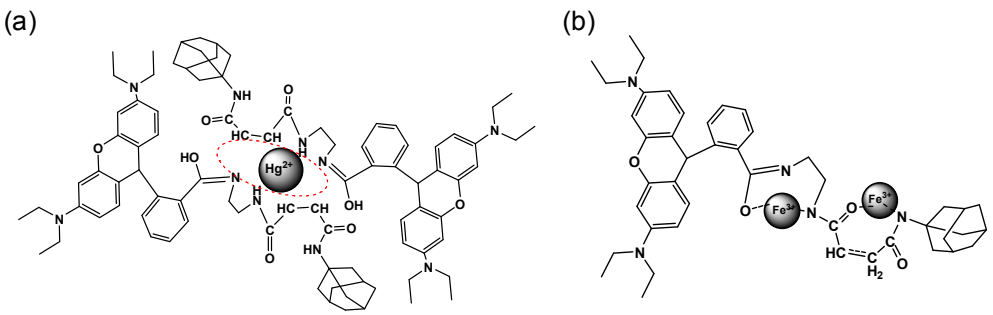


Figure 5. Shi et al.



Scheme 2. Shi et al.

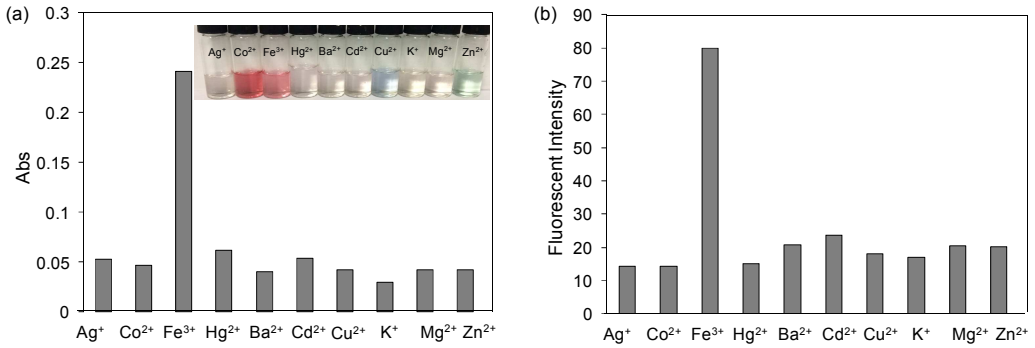


Figure 6. Shi et al.

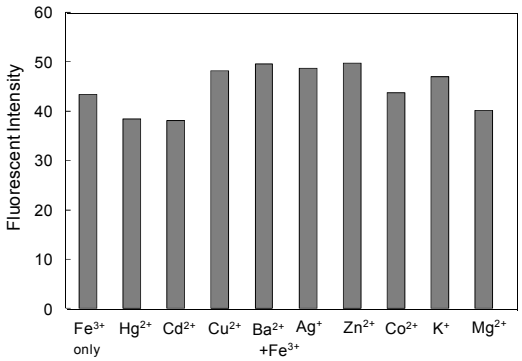


Figure 7. Shi et al.