

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

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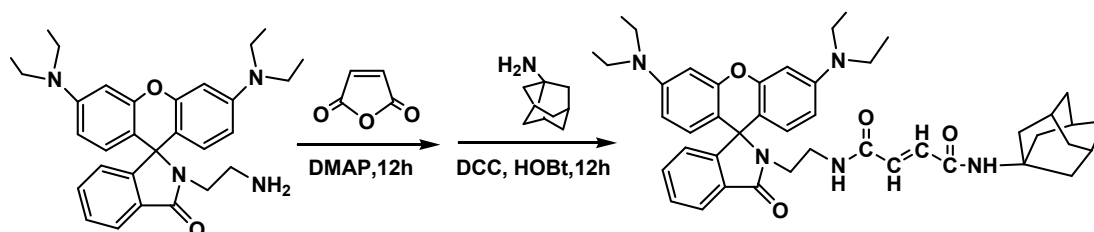
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1. Synthesis of AD-MAH-RhB.

The chemsensor was synthesized as following (Scheme 1). Maleic anhydride (1 mmol), RhB (1 mmol) and 4-dimethylamiopyridine (DMAP, 0.15 mmol) were dissolved in DMSO. Then, 1-ethyl-3-(3-Dimethylaminopropyl) carbodiimide (EDC, 1 mmol), hydroxybenzotriazole (HOBT, 1 mmol) and 1-aminoadamantane (AD-NH₂, 1 mmol) were added into the above solution. After predetermined time, solvent was removed under reduced pressure to give an red powder and purified by silica gel column chromatography in CH₂Cl₂ to give purified AD-MAH-RhB probe. Figure S1 shows ¹H NMR spectrum in CDCl₃. Peaks at 7.87, 7.45-7.423, 7.8, and 6.3 ppm assigned to the protons in benzene and double carbon groups. Peaks at 3.31, 2.11, 1.8 ppm assigned to methylene and adamantyl groups, and peak at 1.18 belonged to methyl groups. From the results, AD-MAH-RhB was successfully synthesized.



Scheme S1. Synthesis of AD-MAH-RhB.

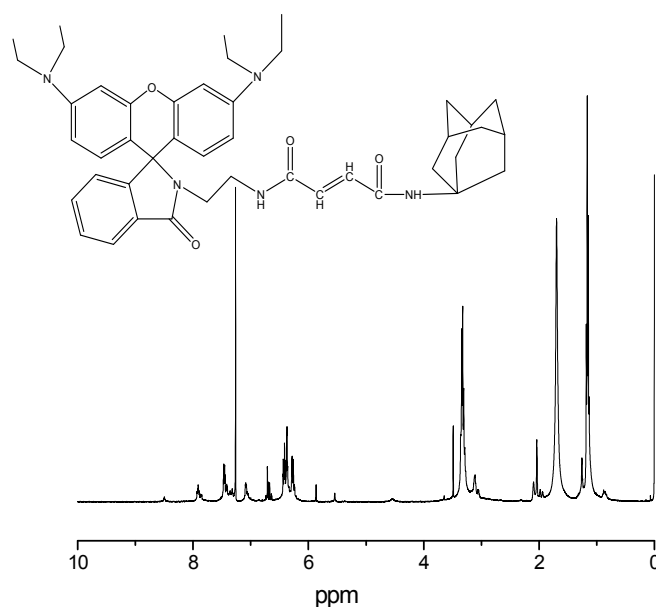


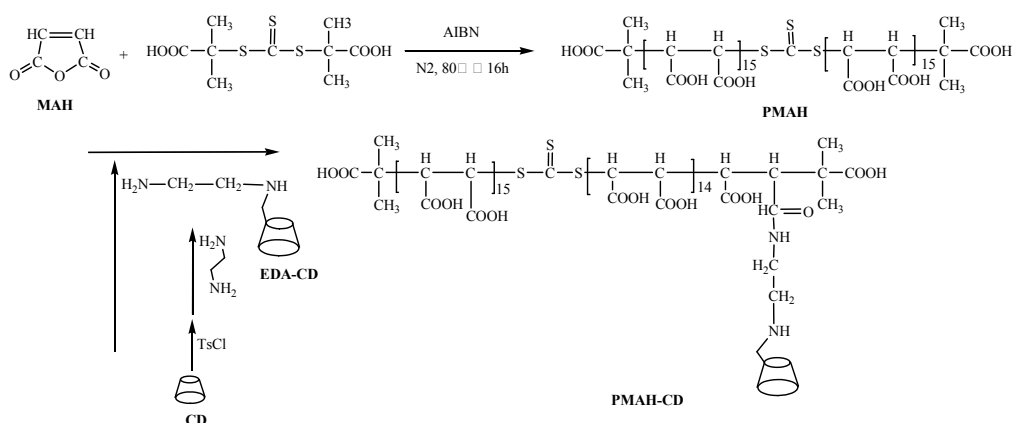
Figure S1. ¹H NMR spectrum of AD-MAH-RhB in CD₃Cl.

2. Synthesis of CD-functionalized magnetic nanoparticles (CD-MNP)

Polymaleicanhydride (PMAH) can be synthesized by Reversible Addition-Fragmentation Chain Transfer Polymerization (RAFT) using a chain transfer agent which prepared in a reported method^[27]. 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 °C under N₂ atmosphere. PMHA was obtained by dialyzed and dried after reacted at 80 °C for 8 h. The molecular weight of PMAH is 3714.

EDA- β -CD was synthesized according to the reported methods^[28]. Then PMAH (0.0376 g), 4-dimethylaminopyridine (DMAP, 20 mg), hydroxybenzotriazole (HOBT, 137 mg), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (191 mg) and EDA- β -CD (12 mg) were dissolved in 10 ml of DMF. After reacted for 12 h, the product PMAH-CD was dialyzed and dried.

Figure S2 shows ¹H NMR spectrum of PMAH-CD in D₂O. Peak at 5.1 ppm assigned to C1 in CD. Peaks at around 3.26-3.91 belonged to the proton in methine methyl groups.



Scheme S2. Synthesis of PMAH-CD.

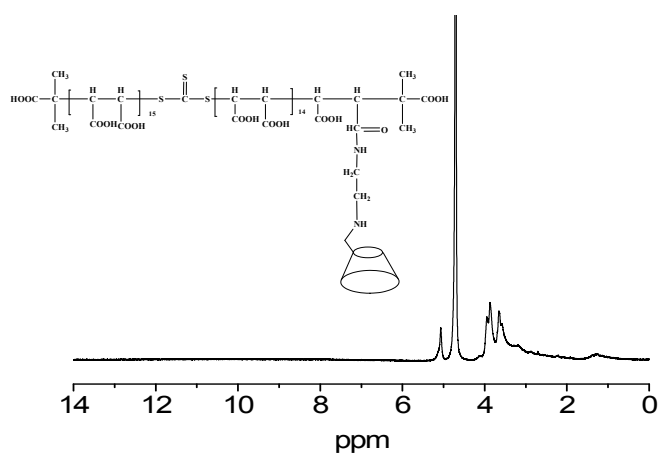


Figure S2. ¹H NMR spectrum of PMAH-CD in D₂O.

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

5.5×10^{-6} mol of PMAH-CD 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].

Figure S3 shows ^1H NMR spectrum of PMAH-CD/AD-MAH-RhB complex in D_2O . Peaks at around 7.2~7.8 and 6.2~6.7 ppm assigned to benzene and double carbon groups in AD-MAH-RhB, respectively. Peaks at 2.2~4 ppm assigned to methine, ethylene groups C1 in AD and CD. Peak at 1.1 ppm belonged to methyl groups. These results confirmed the supramolecular complex formation.

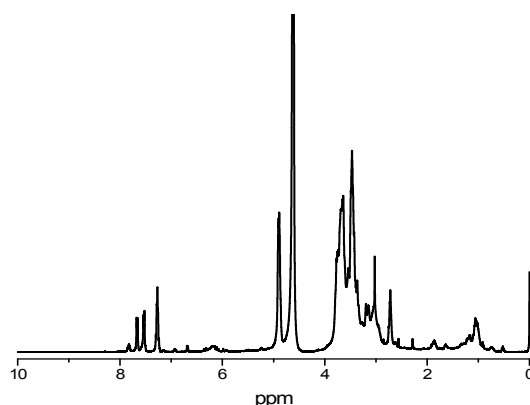


Figure S3. ^1H NMR spectrum of PMAH-CD/AD-MAH-RhB complex.

4. Calibration curve of standard Fe^{3+} solutions

A calibration curve was obtained using a certain range of the Fe^{3+} concentrations from 3 to 30 ppm by UV-vis spectra, as shown in Figure S4. Then, two standard Fe^{3+} solutions, 10.6 and 23 ppm, were selected to measure UV-vis adsorption again. After calculated based on the calibration curve, the actual concentrations of these two standard solutions were 12.5 and 24.0 ppm, respectively, and the deviations were ± 1.9 and ± 1.0 . These results were added into the supporting information.

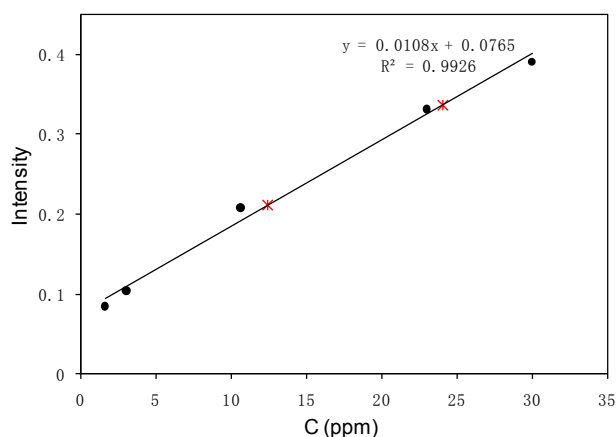


Figure S4. Calibration curve of standard Fe^{3+} solutions.

5. Mechanism studies by $^1\text{H-NMR}$ spectra

The binding position of the complexes were also determined by $^1\text{H-NMR}$ spectra (Figure S5). It could be seen that the chemical shift of the double carbon group on AD-MAH-RhB@ Hg^{2+} (Figure S5a) had an obviously changed from 6.3 ppm to 6.7 ppm, compared with AD-MAH-RhB (Figure S5b). This indicated the unsaturated olefin was changed by addition of Hg^{2+} . For AD-MAH-RhB@ Fe^{3+} complex (Figure S5c), an obviously shift at 2.5 ppm that belongs to the methylene adjacent to nitrogen atoms was observed, suggesting formation the AD-MAH-RhB@ Fe^{3+} complex between nitrogen atoms and Fe^{3+} .

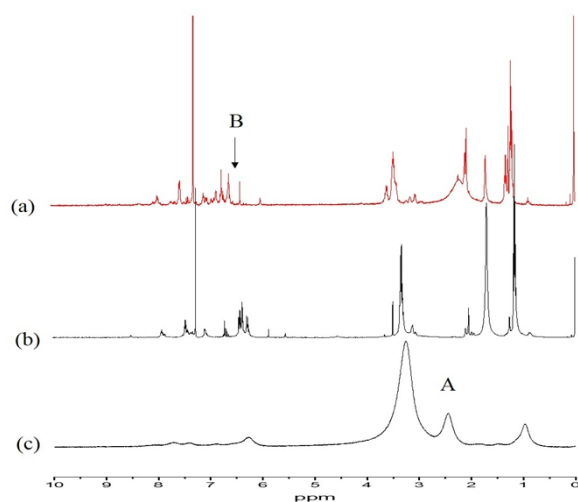


Figure S5. ^1H NMR spectra of AD-MAH-RhB@ Hg^{2+} (a), AD-MAH-RhB (b) and AD-MAH-RhB@ Fe^{3+} (c)