

<Research Paper>

Anthraquinone-carbamodithiolate Assembly as Selective Chromogenic Chemosensor for Fe³⁺

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Abstract: A new assembly derived from 2,3-dibromo-5,6,7,8-tetrafluoroquinizarin and sodium diethyl-carbamodithiolate, was prepared as an efficient Fe³⁺ colorimetric chemosensor with high selectivity over other cations Fe³⁺, Na⁺, Mg²⁺, Pb²⁺, Cd²⁺, Ni²⁺, Ca²⁺, Cu²⁺, Hg²⁺, Zn²⁺: from the dark blue to brown color change that is visible by eyes. This assembly produced large bathochromic shift of 228 nm in the presence of Fe³⁺ compared with the corresponding absorption maximum of the parent dye.

Keywords: anthraquinone, Fe³⁺ sensing, colorimetric, chemosensor, carbamodithiolate, intramolecular charge-transfer dye

1. Introduction

The sensing of metal cations using dye sensors has attracted much attention owing to its application in both chemical and environmental processes¹⁻⁴. There are already many chromogenic chemosensors developed for selective recognition of different species so far due to their high selectivity, sensitivity and simplicity⁵⁻⁷. Iron is one of the most important elements amongst the transition and heavy metals for metabolic processes, being indispensable for plants and animals and therefore it is extensively distributed in environmental and biological materials⁸. If iron concentration of iron varies from the normal level it may become a potential health hazard e.g. it is well-known that an iron deficiency leads to anemia. Therefore, it is important to explore new chromogenic chemosensors for selective detection of iron. Over the past years, some examples for iron detection, including chromogenic⁹ and fluorescent¹⁰⁻¹⁶ chemical sensors, electrochemical devices¹⁷ have been reported. Currently, colorimetric sensors are popular due to their capability to detect analytes visually without resorting to any expensive

instruments¹⁸. Therefore, to develop a simple-to-use and visual diagnostic tool for the selective detection of iron is an interesting and timely research topic. Anthraquinone dyes are the second most important class after azo dyes. We have reported a number of different types of anthraquinone dyes for optical recording media¹⁹⁻²¹. Herein, we report new colorimetric chemosensor based on a covalent assembly between an anthraquinone derivative and a carbamodithiolate, which have shown specifically specificity towards the Fe³⁺ ion.

2. Experimental

Anthraquinone dye 4 was synthesized according to the literature method^{20,21}. All chemicals, including the perchlorate salts of various cations, namely Fe³⁺, Na⁺, Mg²⁺, Pb²⁺, Cd²⁺, Ni²⁺, Ca²⁺, Cu²⁺, Hg²⁺, Zn²⁺ and solvents were of the highest purity grade available and were used without further purification. UV-Vis spectra were measured using an Agilent 8453 spectrophotometer.

3. Results and Discussion

We designed and synthesized a highly selective chemosensor based on anthraquinone-carbamodithiolate assembly

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(ASSEM) for Fe^{3+} as shown in Scheme 1.

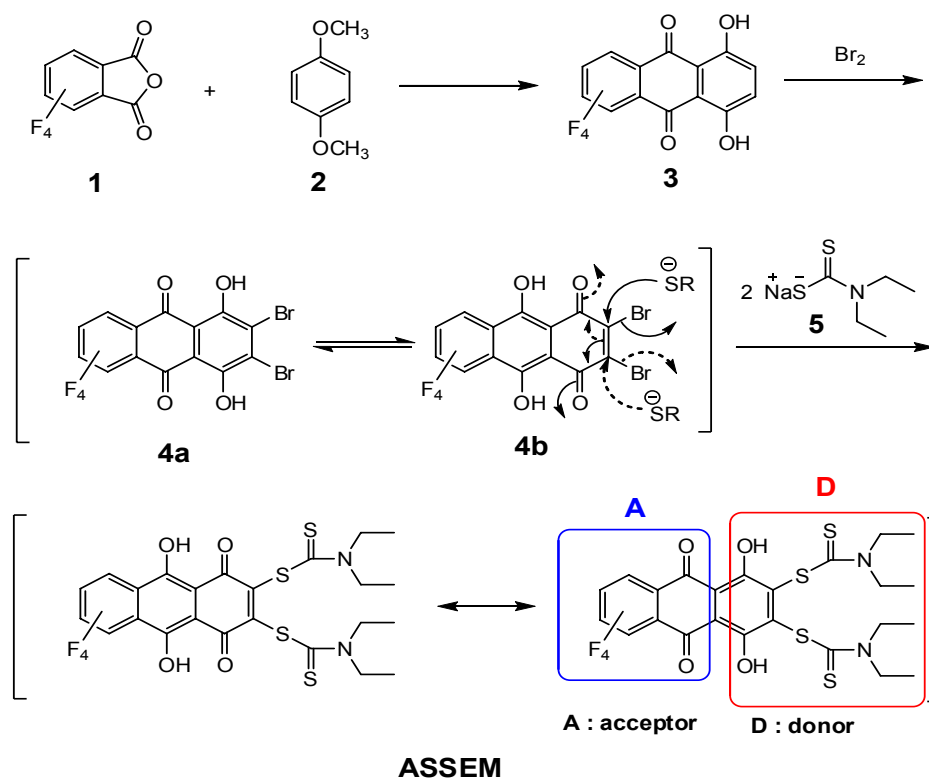
Tetrafluoroquinizarin **3** was synthesized by Friedel-Crafts reaction of tetrafluorophthalic anhydride **1** with 1,4-dimethoxybenzene **2** in a 48% yield. Bromination of compound **3** was carried out in sulfuric acid with excess bromine. The action of compound **4** with sodium diethylcarbamodithiolate **5** gave 4-5 assembly ASSEM. Compound **4a** subsequently tautomerized to tautomer **4b** under the reaction condition. Thus, tautomer **4b** was much more reactive than **4a**. Tautomerism between **4a** and **4b** in solution was not observed. Michael type nucleophilic substitution of the bromine atom by the carbamodithiolate anion gives the 9,10-anthraquinone derivative ASSEM.

We have quantitatively evaluated the color-structure relationship of anthraquinonoid dyes by means of the Pariser-Parr-Pople molecular orbital method (PPP MO)^{22,23}. The first transition of anthraquinone dyes is caused by the intramolecular charge-transfer character²², and the synthetic design of deep colored anthraquinone dyes is shown by Scheme 1, in which introduction of donor groups to 1-4 positions and/or that of acceptor

groups such as fluorine atoms to 5-8 positions of anthraquinone may produce bathochromic shift of the first band. From these results, it was found that introduction of carbamodithiolate donor groups at 2- and 3- position of anthraquinone nucleus may produce a bathochromic shift of the absorption maximum and studied the preparation of ASSEM. Figure 1 show the UV-Vis spectra of dye ASSEM ($5 \times 10^{-5} \text{ molL}^{-1}$) upon addition of 2 equivalents of carbamodithiolate **5** in CH_3CN solution. Upon addition **5**, we found new absorption bands appeared including the absorption at wavelength peak at 652 nm and 709 nm. The color changed from brown to dark blue. ASSEM produces a bathochromic shift of 228 nm in comparison with the parent compound **4**.

Here we report the cation sensing properties of a ASSEM containing dithionate groups. Owing to the well-defined assembly that contains an dithionate groups, it was anticipated that assembly could function as a host molecule for the recognition of cations via coordination.

This was investigated by adding various cations such



Scheme 1. Preparation and synthetic design of ASSEM

as Fe³⁺, Na⁺, Mg²⁺, Pb²⁺, Cd²⁺, Ni²⁺, Ca²⁺, Cu²⁺, Hg²⁺, Zn²⁺, in their perchlorate salt, to a 5 × 10⁻⁵ molL⁻¹ solution of ASSEM in acetonitrile and recording the changes in absorption spectra that occurred during the titration of the solution of ASSEM. Figure 2 shows, upon the addition of Fe³⁺ to the solution of ASSEM, the absorption band at 652 and 709 nm progressively decreased in intensity.

The mechanism for the decrease in absorbance was probably that the coordination to Fe³⁺ inactivated the sulfur atom in the electron transfer to the tetra-fluoroanthraquinone moiety. In ASSEM, the sulfur atom having dithionate groups could be used as an electron donor with strong electron-donating ability.

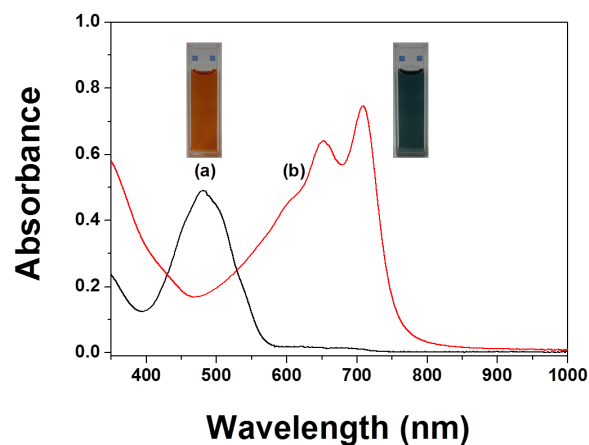


Figure 1. UV-Vis. spectra of CH₃CN solution of (a) compound 4 (5 × 10⁻⁵ molL⁻¹), (b) compound 4 in the presence of 2 equivalents of sodium carbamodithiolate 5 (5 × 10⁻⁵ molL⁻¹).

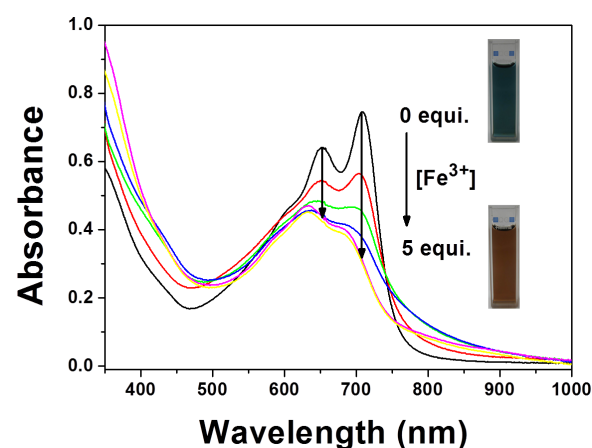


Figure 2. UV-Vis. spectra of ASSEM (5 × 10⁻⁵ molL⁻¹) upon addition of Fe³⁺ in CH₃CN solution.

Herein, the addition of Fe³⁺ might result in the binding of Fe³⁺ with dithionate S, and then the D-π-A structure transformed to A-π-A structure, which decreased the intramolecular charge-transfer from sulfur atom to the electron-accepting tetrafluoroanthraquinone moiety. However, none of the other anions investigated, namely as Fe³⁺, Na⁺, Mg²⁺, Pb²⁺, Cd²⁺, Ni²⁺, Cu²⁺, Hg²⁺, Zn²⁺ had any noticeable effect on absorption, as shown in Figure 3.

Theoretical calculations have been carried out to understand the nature of the binding between ASSEM and Fe³⁺: Fe³⁺ cation is bridged between N atom together with dithiolate S in electron donor unit (Figure 4).

All theoretical calculations were performed by DMol³ program in the Materials Studio 4.2 package^{23,24} which is the quantum mechanical code using density functional theory.

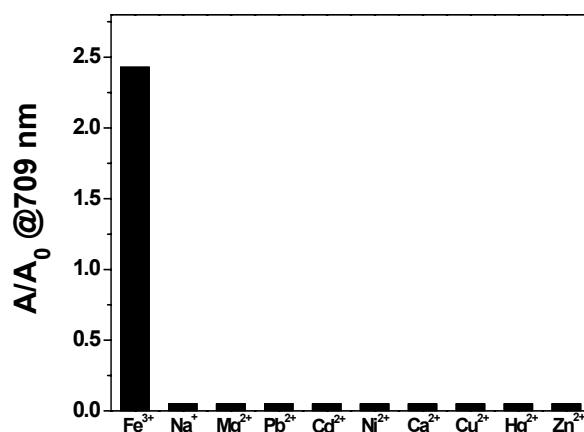


Figure 3. Comparison of absorption ratio for various cations.

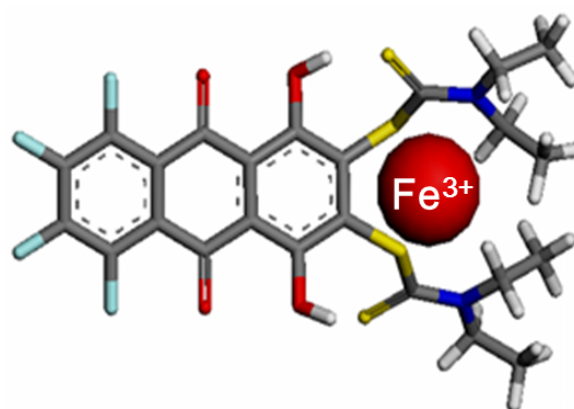


Figure 4. Optimized structure of ASSEM-Fe³⁺ complex.

4. Conclusion

In conclusion, a new chromogenic chemosensor based on anthraquinone-carbamodithiolate assembly, ASSEM, was developed. It shows a good selectivity for Fe³⁺. ASSEM was not observed by absorption changes upon addition of other metal ions. The prepared ASSEM could be utilized as selective good chemosensor for Fe³⁺ in chemical, environmental and biological system.

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