

<Research Paper>

Anthraquinone and Indole based Chemosensor for Fluoride Anions Detection

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Abstract: We have designed and synthesized the colorimetric chemosensor through the reactions of 1,2-anthraquinone and indol-3-carboxaldehyde. Due to its well conjugated D- π -A system and the existence of NH- fragment in indole moiety, we expected that the chemosensor can detect target anions with NH- fragment in indole part of the structure. In this regard, UV-Vis absorption spectra were measured to investigate sensing properties of the probe toward different anions in DMSO. This chemosensor shows to detect fluoride anions with absorption change in intensity. These properties are mainly related to the deprotonation effect. ICT system in this molecule was also observed by the computational approach using *Material Studio 4.3* package.

Keywords: chemosensor, absorption, fluoride, deprotonation, anthraquinone, indole

1. Introduction

The development of chemosensor using organic dye molecules has been interested and investigated due to its function to recognize the guest molecules such as cations and anions^{1,2}. The biological and environmental concerns are deeply related to various kinds of anions³. Among well know available anions, fluoride and cyanide ions show considerable interests and concerns as guest analytes in chemosensor fields⁴⁻⁷.

Fluoride ions are biologically important roles in dental care and treatment of osteoporosis. However, an excess of fluoride ion is hazardous^{4,6,7}. Cyanide ions are also vital as raw materials in industrial process and they are also highly toxic to the human body⁵⁻⁷.

In this regard, chemosensor can be an important material to monitor these anions. In addition, chemosensor having dye structure is to be simple and convenient with showing its optical change⁸. In this context, miscellaneous concepts of chemosensor have been studied and introduced^{9,10}.

Herein, to detect fluoride anions, the chemosensor probe was synthesized by the reaction using 1,2-diaminoanthraquinone and indol-3-carboxaldehyde.

UV-Vis absorption spectra were monitored to investigate the detection properties of dye probe toward different anions in solution. With the designed and prepared dye chemosensor, it could detect and recognize fluoride ions with absorption enhancement as expected.

2. Experimental

2.1 Materials and Measurement

All reagents and chemicals were purchased from Aldrich Chemical Co. and TCI. Solvents were purified by normal procedures and used under moisture free atmosphere.

The other materials were commercial products and were used without further purification. Elemental analysis were recorded on a Carlo Erba Model 1106 analyzer.

UV-Vis absorption spectra were measured on an Agilent 8453 spectrophotometer whilst fluorescence spectra were measured on a Shimadzu RF-5301 PC fluorescence spectrophotometer. Mass spectra were recorded on a Shimadzu QP-1000 spectrometer using electron

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energy of 70 eV and the direct probe EI method. $^1\text{H-NMR}$ spectra were recorded using a Varian Inova 400 MHz FT-NMR spectrometer with TMS as internal standard.

2.2 Synthesis

Anthraquinone chemosensor having indole moiety was synthesized according to the established literature procedure^{11,12}. 1,2-Diaminoanthraquinone (0.5g, 2.1 mmol) and indol-3-carboxaldehyde (0.305g, 2.1 mmol) were dissolved in 10 ml of nitrobenzene. The ensuing mixture was refluxed for 20hrs.

After cooling to room temperature, the precipitate was obtained by filtration and washed with hexane. To further purification, the obtained solid was dissolved and boiled in diethyl ether/chloroform and brown solid was obtained using filtration. The product was washed with mixture solvent and dried in vacuum. The purified product was obtained in 65% yield. In Scheme 1, the synthetic procedure of chemosensor was depicted.

$^1\text{H-NMR}$ (400 MHz) DMSO- d_6 : δ (ppm) 7.22 (m, 2H), 7.51 (m, 1H), 7.91 (m, 2H), 8.06 (m, 2H), 8.22 (m, 2H), 8.59 (m, 1H), 8.59 (m, 1H), 11.91 (s, 1H, -NH), 12.93 (s, 1H, -NH). EA: anal. calcd. $\text{C}_{24}\text{H}_{14}\text{N}_2\text{O}_2$: C; 76.02, H; 3.61, N; 11.56. found C; 75.13, H; 3.77, N; 11.61 %. M^+ =363.

3. Results and Discussion

In this work, the chemosensor was designed and synthesized through the reaction between 1,2-diaminoanthraquinone and indol-3-carboxaldehyde. Owing to its well conjugated $D-\pi-A$ system and the existence of NH- fragment in structure, we expected that this chemosensor can detect anion on NH- fragment in

the indole moiety of the structure.

According to the observed results, absorption changes of chemosensor were firstly monitored to determine the selectivity of chemosensor ($2 \times 10^{-5}\text{M}$) toward various kinds of anions (1equiv.) such as F^- , CH_3CO_2^- , Cl^- , HSO_4^- , Br^- , H_2PO_4^- , CN^- , NO_3^- and ClO_4^- in DMSO.

As shown in Figure 1, noticeable absorption changes were observed after addition of F^- to chemosensor solution. However, there were no changes in absorption of other anion mixtures. In naked eye detection, the same results were also obtained as shown in Figure 2. Among various anions, the addition of F^- anions into chemosensor solution only induced the color change from orange yellow to red.

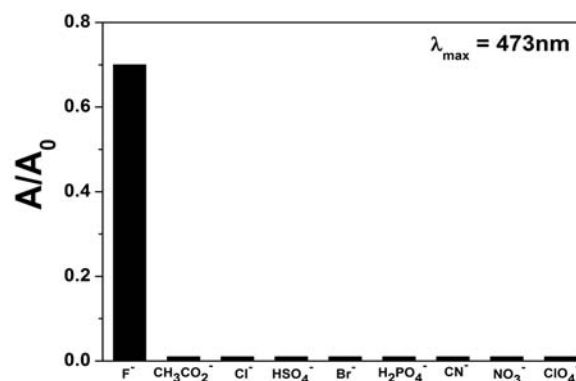
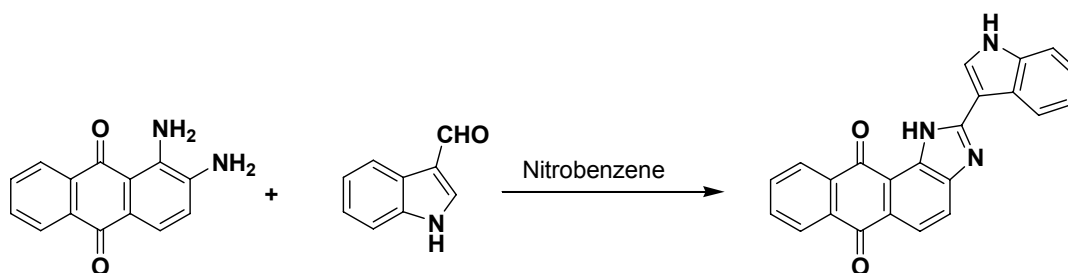


Figure 1. Absorption ratio of chemosensor ($1 \times 10^{-5}\text{M}$) with various guest anions (1equiv.) in DMSO.



Figure 2. Photo images of color changes for chemosensor solutions with various guest anions in DMSO.



Scheme 1. Synthetic procedure of chemosensor

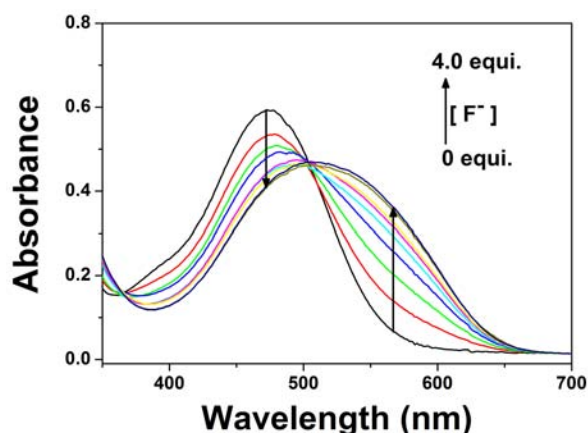


Figure 3. Absorption response of chemosensor ($1 \times 10^{-5} \text{M}$) upon the addition of different mole concentrations for F^- (0–4equiv.) in DMSO.

These findings proposed that the designed chemosensor has been characterized with its sensing potential toward F^- .

The binding efficiency is an important sensing factor toward selected target anion. In this regard, absorption spectra of the chemosensor ($2 \times 10^{-5} \text{M}$) upon the addition of different mole concentrations for F^- (0–4equiv.) anions were investigated as shown in Figure 3. Upon the addition of F^- anion to the chemosensor in DMSO, absorption band at 473nm gradually decreased and a shifted new peak appeared. At the same time, the isosbestic point at 503nm was observed in the spectra. This isosbestic point is good evidence showing that stable complex formations between chemosensor and F^- anion are present in solution¹³.

The binding stoichiometry between chemosensor and F^- was confirmed by Job's plot (Figure 4).

Job's plot was formed by continuous variations with a total concentration of $10 \mu\text{M}$. The maximum absorbance was obtained at 503nm when the molecular fraction of F^- and chemosensor was close to 2:1, suggesting 2:1 stoichiometry for the binding of chemosensor and F^- .

According to the 2:1 stoichiometry supported by the Job's plot, the function can be given as follows. Where A_i and A_0 denote the absorbance of chemosensor in the presence and absence of F^- respectively; A_∞ stands for the absorbance measured when excess

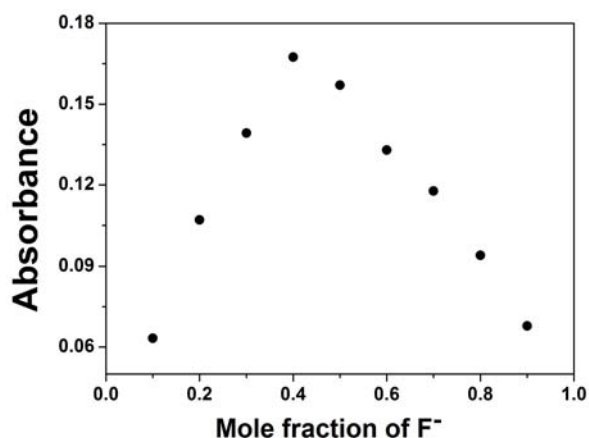
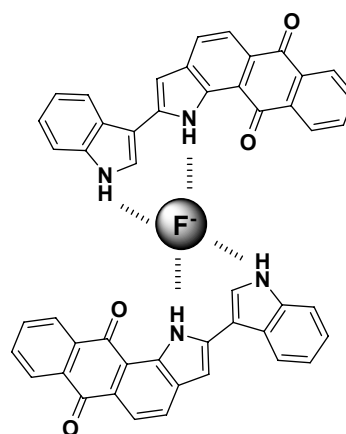


Figure 4. Job's plot of chemosensor and F^- in DMSO solution.



Scheme 2. Proposed 2:1 binding formation

amount of F^- added; K_{ass} is the association constant, and $[\text{F}^-]$ is the concentration of fluoride anions added to the solution. A likely sensing mechanism is proposed in Scheme 2^{14,15-17}.

As shown in Scheme 2, these absorption changes of chemosensor were caused by F^- anions being induced complex formation. Especially, NH- fragment in molecular structure has been studied due to its efficient to detect anions by deprotonation¹⁸. In this connection, $^1\text{H-NMR}$ spectroscopy employed to gain a clear understanding and agreement of the complex structure for chemosensor ($1 \times 10^{-2} \text{M}$) toward F^- (0–2equiv.) in DMSO-d_6 .

Figure 5 showed that $^1\text{H-NMR}$ spectra of chemosensor upon the addition of F^- anion mole concentrations. For the present, proton of NH- fragment in indole and pyrrole moiety for chemosensor was

observed at 10.85ppm and 11.34ppm, respectively and the peaks clearly disappeared as F⁻ anion were added.

This indicated that deprotonation of NH- fragment was induced due to the binding with F⁻ ion. Furthermore, all aromatic and olefinic protons were clearly shifted to the up-field region. These findings indicate that NH + F⁻ increased the electron density of the olefinic and aromatic ring¹¹⁾. The results supported binding process of chemosensor as we expected that NH- fragment was deprotonated by the complex with F⁻ ions.

Modeling calculation of electron density distribution of chemosensor was finally studied using this chemosensor. All theoretical calculations were carried out by DMol³ program of *Material Studio 4.3* package, having the quantum mechanical code using density functional theory¹⁹⁻²¹⁾.

Figure 6 showed electron distributions of chemosensor for HOMO and LUMO states. Electron in HOMO was distributed in indole moiety and was moved to anthraquinone moiety in LUMO.

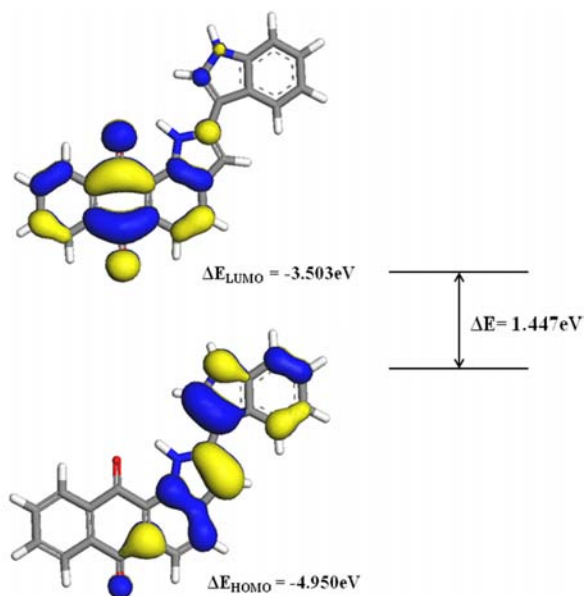


Figure 6. Electron distributions of HOMO and LUMO energy levels for chemosensor.

This finding can suggest the ICT system property: indicating a strong migration characteristic of electrons in chemosensor.

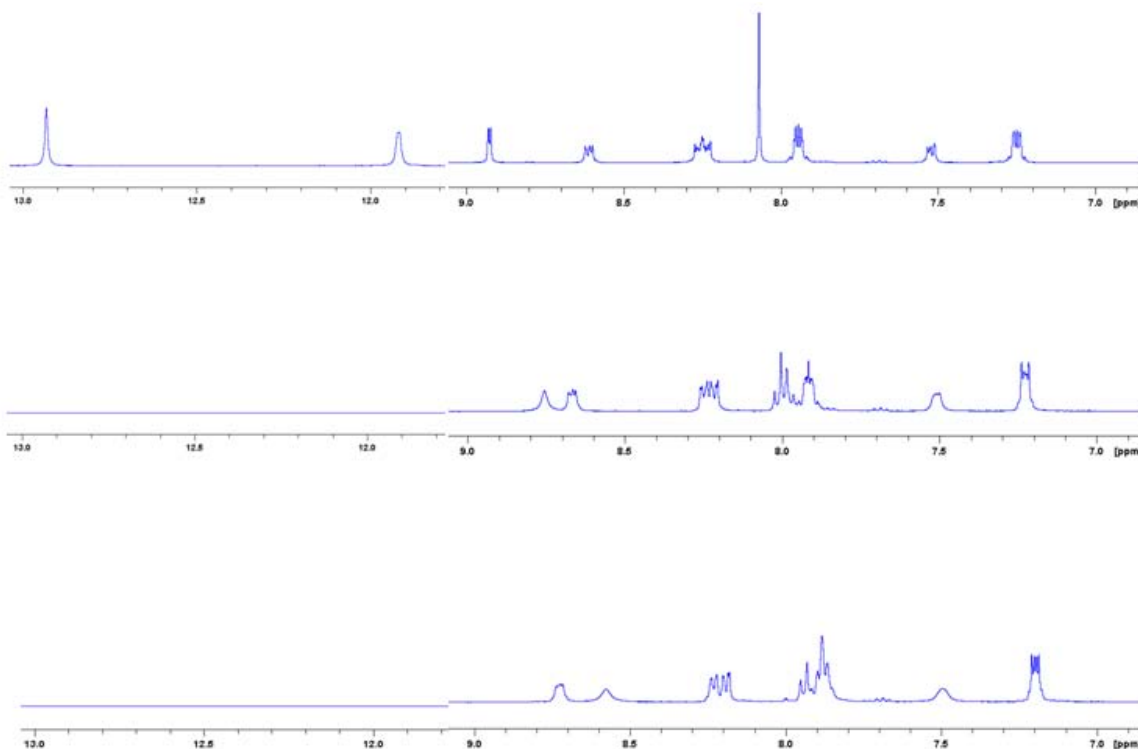


Figure 5. ¹H-NMR spectra of chemosensor (1x10⁻²M) with different mole concentrations of F⁻ (0, 1.0 and 2.0equi.) (400MHz, DMOS-d₆).

In addition, the energy gap between HOMO and LUMO was also calculated in same approaches. The finding of calculated value was $\Delta E=1.447\text{eV}$.

4. Conclusions

In this work, we have synthesized and reported a novel chemosensor through the reaction of 1,2-diaminoanthraquinone and indol-3-carboxaldehyde. This chemosensor displayed that significant changes in absorption intensity upon the addition of F^- anions were induced by the deprotonation of NH - fragment in indole moiety. The molecular fraction of F^- and chemosensor was close to 2:1 stoichiometry for the binding of host and guest molecules. Deprotonation of NH - fragment was induced due to the binding with F^- ions and all aromatic and olefinic protons were clearly shifted to the up-field region.

Acknowledgments

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