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〈Research Paper〉

Synthesis of Chemosensor Based on Pyrene and Study for Its Sensing Properties Toward Fluoride Ion

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Abstract: In this study, pyrene based chemosensor was synthesized by two step reaction. The chemosensor showed that high selectivity toward fluoride in DMSO. The fluorescence intensity was drastically increased by binding between chemosensor and fluoride ion. Absorption and fluorescence spectra were obtained by UV-Vis spectrometer and fluorescence spectrophotometer. The binding ratio between chemosensor and fluoride ion was also investigated by job's plot method and Benesi-Hildebrand plot. The HOMO/LUMO energy levels and electron distribution were calculated and simulated by *Material studio 6.0 Package*.

Keywords: *pyrene, chemosensor, fluoride, fluorescence, DMSO*

1. Introduction

The chemosesnor for recognizing specific ion such as cation and anion in solution has been taken notice from many researchers[1)]. The effective chemosensor is the system possible to detect specific ion with showing a change of fluorescence properties. The changes of wavelength for emission, appearance of a new fluorescence band can be included for signaling system of chemosensor[1)].

For signaling system, various kinds of fluorophores such as anthraquinone, coumarin, rhodamine, bodipy, fluorescein, quinolone and pyrene have been investigated[2-8)]. Especially, pyrene has been steadily studied because of its efficiency fluorescence properties. The pyrene has a singlet excited state with showing high emission quantum yields, long life time and also interesting diverse photophysical properties[9)]. In addition, the large planar conjugated aromatic characteristic of pyrene also showed strong pi electron delocalization energy. According to this, the pyrene has been also studied for DNA labels and OLED materials[10)].

Various anions have been used for target material in chemosensor field. In particular, fluoride ion has been concentrated for analyte due to relation of environmental and biological processes[11)]. Dental care application and inhibition of certain enzyme functions are associated with fluoride[11)]. In addition, overexposure to fluoride can lead urolithiasis with changing nephrotoxic in humans and animals[11)].

In this study, pyrene based chemosensor was synthesized by two step reaction. The chemosensor showed that high selectivity toward fluoride with showing fluorescence enhancement in DMSO. This phenomenon was induced by binding between chemosensor and fluoride ion. Absorption and fluorescence spectra were obtained by UV-Vis spectrometer and fluorescence spectrophotometer. The binding ratio between chemosensor and fluoride ion was also investigated by Job's plot method and Benesi-Hildebrand plot. The HOMO /LUMO energy levels and electron distribution were calculated and simulated by *Material studio 6.0* package.

2. Experimental

2.1 Chemosensor

1-amino pyrene (1mmol) and triethylamine (5mmol)

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were dissolved in dichloromethane at 0°C. Then 2-bromoacetyl bromide (5mmol) was added. The mixture was warmed to room temperature and allowed to react overnight. The precipitate was filtered and washed with dichloromethane. The white solid was obtained. Without further purification, 2-bromo- n-(pyrene-1-yl) acetamide (1mmol) and triethylamine (5mmol), potassium iodie (10mg), 2-aminothiophenol (5mmol) were dissolved in THF. The reaction mixture was refluxed for 6hrs. After cooling to room temperature, the solvent was removed by evaporation. After dissolving with dichloromethane, impurities were removed by filtration. The white powder was obtained by evaporating dichloromethane. The yield was 57%. ^{1}H-NMR (600MHz, *DMSO-d$_6$*) : 10.41 (1H, s), 8.30-8.26 (3H, q), 8.18-8.07 (6H, m), 7.43-7.42 (1H, d), 7.12-7.10 (1H, t), 6.78-6.71 (1H, d), 6.58-6.56 (1H, t), 5.52 (2H, s), 3.83 (2H, s). ^{13}C-NMR (600MHz, *DMSO-d$_6$*) : 168.90, 150.28, 135.94, 131.96, 131.27, 130.93, 130.31, 128.86, 127.69, 127.53, 127.16, 126.89, 125.73, 124.77, 124.49, 125.44, 125.39, 124.28, 123.86, 122.81, 116.93, 115.65, 115.02, 67.490. ESI-MS : 383.2 $[Chemosensor + H]^+$.

2.2 Measurements

All materials used for the synthesis were purchased from Aldrich and Alfa Aesar and were used without further purification. All inorganic salts used to analyze the sample were purchased from Aldrich and Alfa Aesar in the form of perchlorate salts series.

^{1}H-NMR and ^{13}C-NMR spectra were recorded in BRUKER AVANCE III 600 (Germany) operating at 600 MHz. ESI-Mass (Electrospray Ionization) was employed using a Jeol MStation [JMS-700] Mass Spectrometer. Absorption and fluorescent spectra were measured with an Agilent 8453 and Shimadzu RF-5301PC fluorescent spectrophotometer.

3. Results and Discussion

To investigate the selectivity property for chemosensor, we measured absorption and fluorescence spectra as shown in Figure 1 and Figure 2. The chemosensor (10μM) were dissolved in DMSO. Various kinds of anions such as F^-, Br^-, Cl^-, I^-, CN^-, N_3^-, NO_2^- and HSO_4^- were added for 10 equivalents to the solution. In Figure 1, F^- and chemosensor mixture showed that little different shape compared with other anion mixtures. However specific change was not observed. In fluorescence spectra, significant change was observed as shown in Figure 2. The chemosensor and F^- mixture resulted in an obvious enhancement in fluorescence intensity, while other anion mixtures only showed a minor change in fluorescence intensity. The result indicated that the chemosensor have a high selectivity function toward F^- compared with other anions.

We also calculated quantum yields (Φ_F) in order to further investigate the selectivity chemosensor toward various anions in the Table 1 using reported calculation

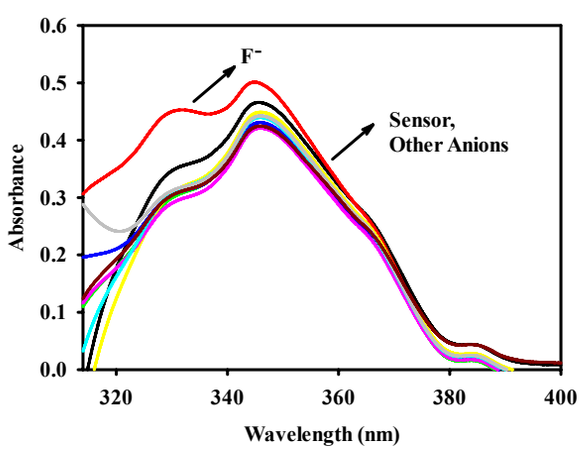
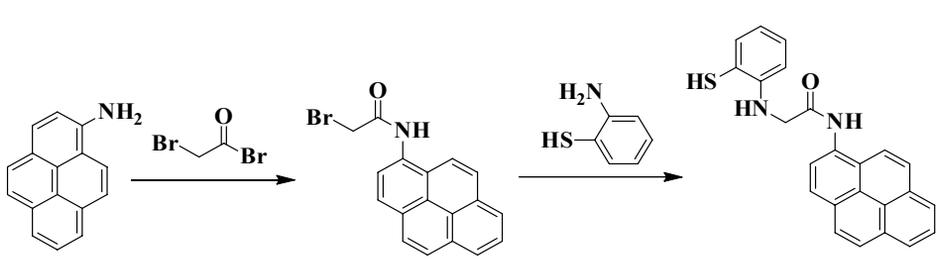


Figure 1. UV-Vis spectra of chemosensor (10μM) with addition of different kinds of anions (10 equivalents) in DMSO.



Scheme 1. The synthetic method for Chemosensor.

method[12]. 9,10-diphenylanthracene was used for the reference. The quantum yield (Φ_F) of F^- and chemosensor mixture was calculated for 3.92. This value was 3 times higher than values for other anions. This result also can be evidence indicating that the chemosensor has the function of high selectivity toward F^-.

Through these results, the chemosensor showed the potential ability to monitor F^- using fluorescence change of the signal system.

The quantitative evaluation is also important factor in chemosensor properties. According to this, fluorescence spectra of chemosensor (10μM) was recorded upon addition of different mole concentrations for F^- ion (0 ~ 12 equivalents) in Figure 3.

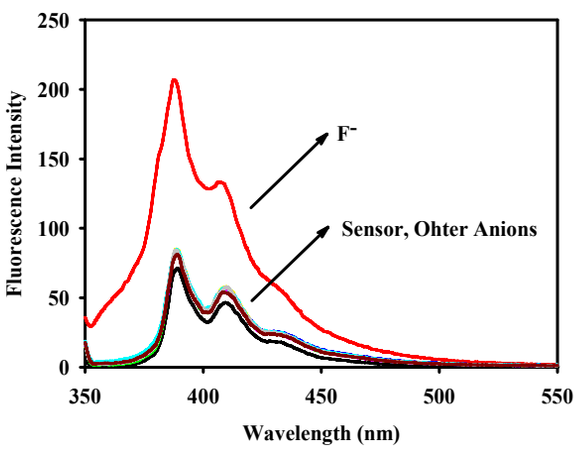


Figure 2. Fluorescence spectra of chemosensor (10μM) with addition of different kinds of anions (10 equivalents) in DMSO (λ_{ex} = 346nm).

Table 1. The quantum yield of chemosensor toward various kinds of anions

Anion	Quantum Yield (ΦF)
Blank	1.17
F^-	3.92
Br^-	1.36
Cl^-	1.31
I^-	1.45
CN^-	1.29
N_3^-	1.40
NO_2^-	1.41
HSO_4^-	1.47

The blank displayed a weak emission band by showing two peaks for 389nm and 409nm. However, the fluorescence intensity was enhanced as much as F^- mole concentration was added. The good linear relationship between chemosensor and F^- was also observed as shown in Figure 3 inset graph. The binding between chemosensor and F^- ion is a reason for this phenomenon.

The binding stoichiometry is important to understand the binding ability between chemosensor and F^-. In this regard, Job's plot methods was studied[13,14].

The Figure 4 showed that the graph of Job's plot method and the highest intensity of fluorescence was recorded when chemosensor and F^- ratio was 5:5.

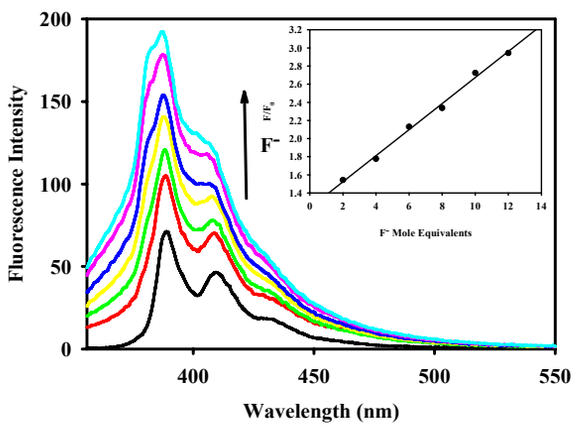


Figure 3. Fluorescence spectra of chemosensor (10μM) upon addition of different mole concentrations for F^- (0~12 equivalent) in DMSO (λ_{ex} = 346nm). Inset: titration profile at 387nm upon addition of various mole concentrations of F^- in DMSO (λ_{ex} = 346nm).

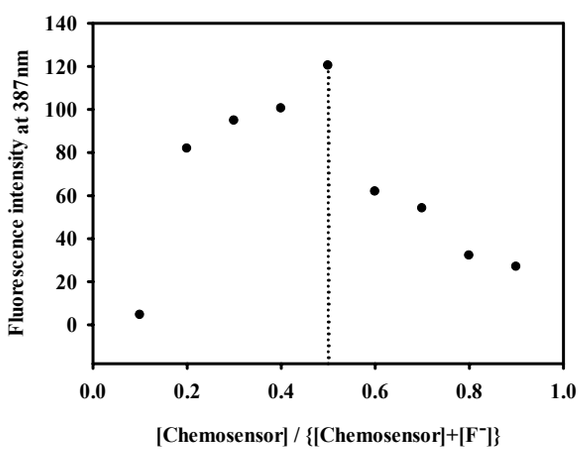


Figure 4. Job's plot method of the chemosensor toward F^- in DMSO.

In addition, Benesi-Hildebrand method[15,16] was also progressing as shown in Figure 5 to investigate K association constant value. This value was evaluated graphically by plotting $1/[F^-]$ against $1/[F\text{-}F_0]$ and calculated by the graph. The result showed the good linear relationship. K association value was obtained from the slope and intercept of the line. 1.62×10^4 was obtained for the K association value. R value was also observed, indicating that 0.98. Through the results, the 1:1 binding ratio between chemosensor and F^- was found.

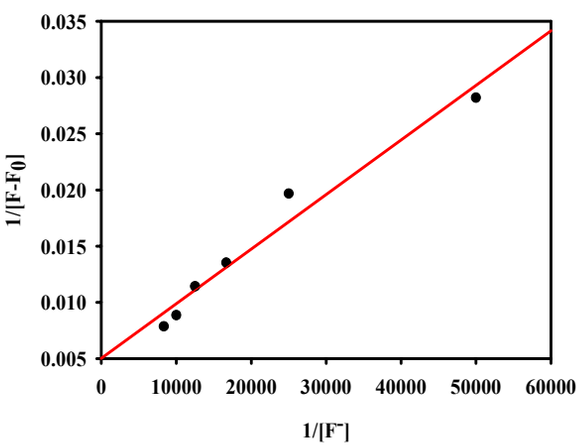
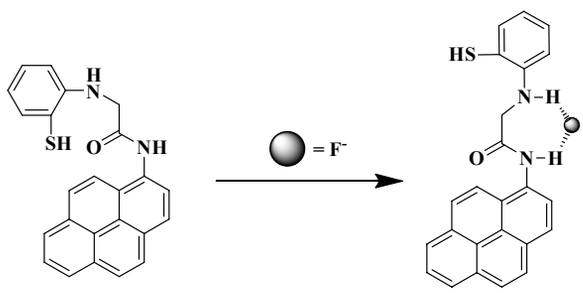


Figure 5. Benesi-Hildebrand plot for binding between the chemosensor and F^- in DMSO.

Depending on the above results, the binding mechanism of chemosensor + F^- structure was proposed in Scheme 2. The structure referred to reported papers[17-21]. In structure of chemosensor, the NH-fragments can be involved to bind the F^- by hydrogen bonding donors.



Scheme 2. The probable binding mechanism of Chemosensor and F^-.

The electron distributions and HOMO/LUMO value-scan be also affected by the complexation between chemosensor and F^-. The Figure 6 showed that the electron distributions and HOMO/LUMO values of respective chemosensor and chemosensor + F^- structures were obtained by computational method using *Material Studio 6.0* package. Most of electrons were delocalized to pyrene fluorophore part.

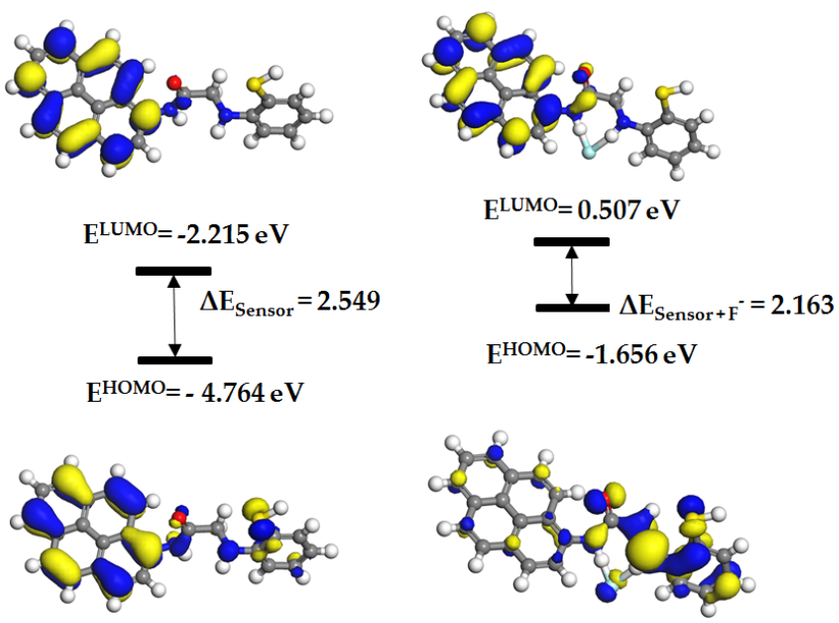


Figure 6. Electron distributions and HOMO/LUMO values for the chemosensor and F^- complexed structures.

In complexed structure between chemosensor and F^-, electrons moved from amine group binding with F^- to pyrene fluorophore when HOMO was changed to LUMO. In addition, HOMO and LUMO values and their bandgap energy were also calculated. The values of chemosensor + F^- structure decreased compared with values of only chemosensor structure. According to the results, binding process can be affected to HOMO /LUMO values and energy electron distributions.

4. Conclusions

In this study, pyrene based chemosensor was designed and synthesized. Toward various kinds of onions, the sensing properties of chemosensor were investigated by UV-Vis and fluorescence spectrometer. The chemosensor showed high selectivity toward F^- with showing fluorescence enhancements. Quantum yield also indicated that chemosensor and F^- mixture showed the highest value compared with other anion mixtures. In addition, 1:1 binding ratio between chemosensor and F^- was found with Job's plot method and Benesi-Hilderbrand plot. With these results, the binding mechanism was also proposed, indicating NH- fragments of chemosensor structure were involved to bind F^-. The electron states were also simulated and calculated by computational methods. HOMO and LUMO values were also obtained. All the investigated results support that the pyrene based chemosensor is useful to monitor F^-.

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