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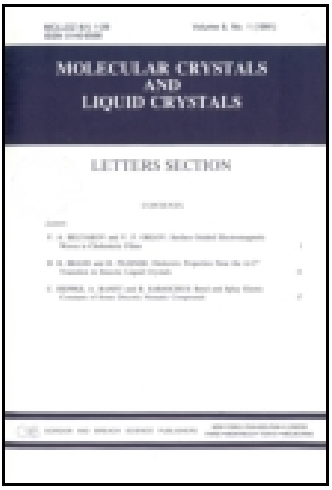

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Chromene and Imidazole Based D-π-A Chemosensor Preparation and Its Anion Responsive Effects

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Chromene and Imidazole Based *D-π-A* Chemosensor Preparation and Its Anion Responsive Effects

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We have designed and synthesized the colorimetric chemosensor through the reactions of 2-(4H-chromen-4-yildene)malonitrile and 4-imidazolecarboxaldehyde. Due to its well conjugated D-π-A system and the existence of NH- fragment in structure, we expected that the chemosensor can detect anion using NH- fragment in the imidazole moiety 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 can detect both fluoride and cyanide ion with absorption change in intensity. In addition, pH sensing property was also investigated upon the addition of hydroxide ion. These properties are related to the deprotonation effect. The ICT system in this molecule was also observed by the computational approach using Material Studio 4.3 *package.*

Keywords Chemosensor; absorption; fluoride; cyanide; hydroxide; deprotonation; ICT

1. Introduction

The development of chemosensor has been noticed and investigated due to its function to recognize the analyte such as cation and anion [1, 2]. The biological and environmental process is deeply related to various kinds of anions [3]. Among these anions, fluoride and cyanide ion show considerable interest in analyte in chemosensor field [4–7]. Fluoride ion is a biologically important role in dental care and treatment of osteoporosis. However, an excess of fluoride ion is hazardous [4, 6, 7]. Cyanide ion is also vital as a raw material in industrial process and it is also highly toxic to the human body [5–7]. 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 change [8]. So far, miscellaneous concepts of chemosensor have been studied and reported [9, 10].

In this work, the chemosensor probe was synthesized by reaction between 2-(4H-chromen-4-yildene)malonitrile and 4-imidazolecarboxaldehyde. UV-Vis absorption spectra were measured to investigate sensing properties of the probe toward different anions in

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solution. This chemosensor can detect both fluoride and cyanide ion with absorption enhancement. In addition, pH sensing potential ability was also investigated upon the addition of OH^-.

2. Experimental

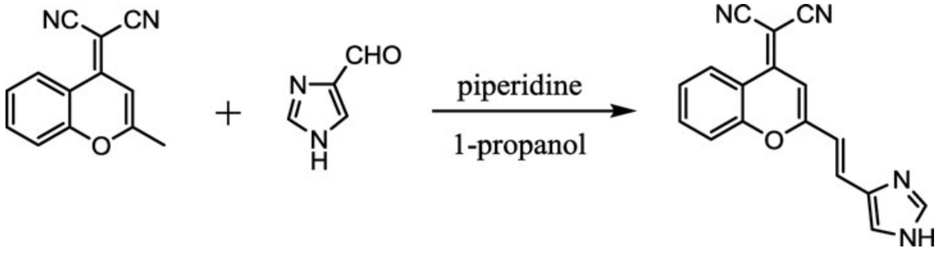
2.1 Measurement

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 analysys were recorded on a Carlo Elba Model 1106 analyzer. UV-visible 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 energy of 70 eV and the direct probe EI method. ^1H NMR spectra were recorded using a Varian Inova 400 MHz FT-NMR spectrometer with TMS as internal standard. Melting point was determined using an Electrothermal IA900.

2.2 Synthesis

The 2-(4H-chromen-4-yildene)malonitrile was synthesized according to the established literature procedure [11, 12]. The 2-(4H-chromen-4-yildene)malonitrile (0.5 g, 2.4 mmol) and 4-imidazolecarboxaldehyde (0.23 g, 2.4 mmol) were dissolved in 30 ml of 1-propanol. Piperidine was added dropwise and the ensuing mixture was refluxed for 12 hrs under N_2 protection. After cooling to room temperature, the precipitate was obtained by filtration and washed with ethanol and hexane. To further purification, the obtained solid was dissolved in $CHCl_3$ and hexane mixture solvent. The solution was stirred for 3 hrs. After filtration, the product was washed with mixture solvent and dried in vaccum. The purified product was obtained in 68% yield. In Scheme 1, the synthetic procedure of chemosensor was depicted.

^1H NMR(400 MHz) DMSO-d_6: δ (ppm) 6.90 (s, 1H), 7.08 (d, $J = 15.6$Hz, 1H), 7.60(t, $J = 7.12$Hz, 1H), 7.64 (s, 1H), 7.68 (t, $J = 15.6$Hz, 1H), 7.76 (d, $J = 8.44$Hz, 1H), 7.86 (s, 1H), 7.90 (t, $J = 7.08$Hz, 1H), 8.71 (d, $J = 8.44$, 1H), 12.54 (s, 1H, -NH). EA: anal. calcd. $C_{17}H_{10}N_4O$: C; 71.32, H; 3.52, N; 19.57. found C; 71.23, H; 3.56, N; 19.81%. $M^+ = 286$. mp: 336-337°C.



Scheme 1. Synthetic procedure of chemosensor.

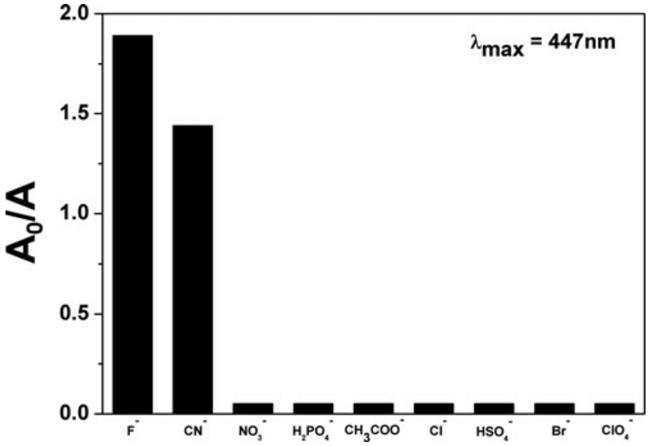


Figure 1. Absorption spectra of chemosensor (2×10^{-5}M) upon the addition of various anions (1equi.) in DMSO. Each absorption intensity at 447 nm was recorded.

3. Results and Discussion

In this work, the chemosensor was designed and synthesized through the reaction between 2-(4H-chromen-4-yildene)malonitrile and 4-imidazolecarboxaldehdyde. Due to its well conjugated *D-π-A* system and the existence of NH- fragment in structure, we expected that the chemosensor can detect anion using NH- fragment in the imidazole moiety of the structure.

According to this finding, absorption changes of chemosensor were firstly investigated to evaluate the selectivity of chemosensor (2×10^{-5} M) toward various kinds of anions (1equi.) such as F^-, CN^-, $NO_3{}^-$, $H_3PO_4{}^-$, CH_3COO^-, Cl^-, $HSO_4{}^-$, Br^- and $ClO_4{}^-$ in DMSO. As shown in Figure 1, noticeable absorption changes were observed after addition of F^- and CN^- to chemosensor solution. However, there are no changes in absorption of other anion mixtures. In naked eye, the same result was also obtained as shown in Figure 2. Among anions, each F^- and CN^- mixed solutions with chemosensor only induced the color change from yellow to red. These result proposed that the chemosensor characterized its sensing ability toward F^- and CN^-.

The binding efficiency is an important sensing ability toward selective ion. In this regard, absorption spectra of the chemosensor (2×10^{-5} M) upon addition of different mole concentrations for respective F^- (0∼6equi.) and CN^- (0∼7equi.) ions were investigated as shown in Figs. 3 and 4. Upon the addition of F^- ion to the chemosensor in DMSO,

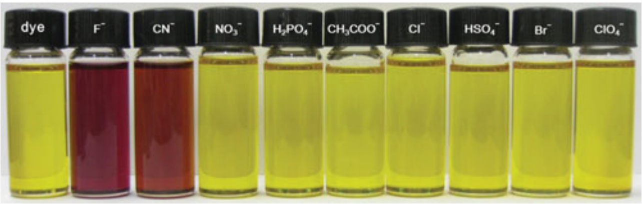


Figure 2. The photo image of color changes for chemosensor solutions with different anions in DMSO.

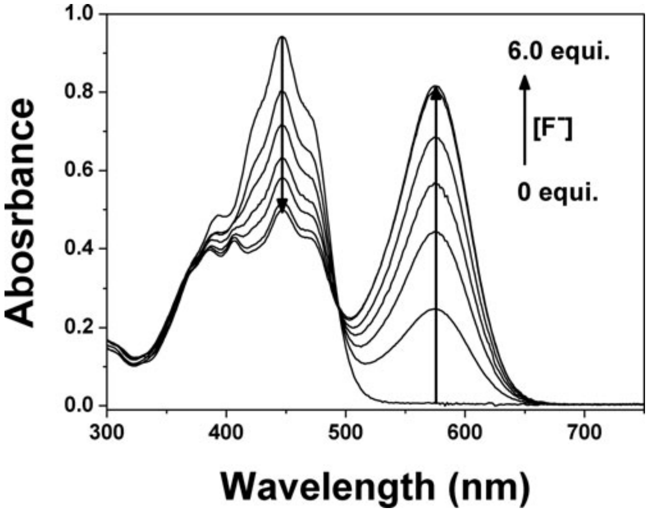


Figure 3. Absorption response of chemosensor (2×10^{-5} M) upon addition of different mole concentrations for F^- (0∼7equi.) in DMSO.

absorption band at 447 nm gradually decreased and new peak at 580 nm appeared. The similar change of absorption spectra was also investigated depending on the addition of different mole concentrations for CN^- ion to chemosensor in DMSO. At the same time, the isosbestic point at 480 nm was observed in both spectra. The isobastic point is the good evidence showing that stable complex formations between chemosensor and respective F^- and CN^- are present in solution [13].

As shown in Figs. 3 and 4, these absorption changes of chemosensor were caused by F^- and CN^- ions being induced complex formation. Especially, NH- fragment in molecular

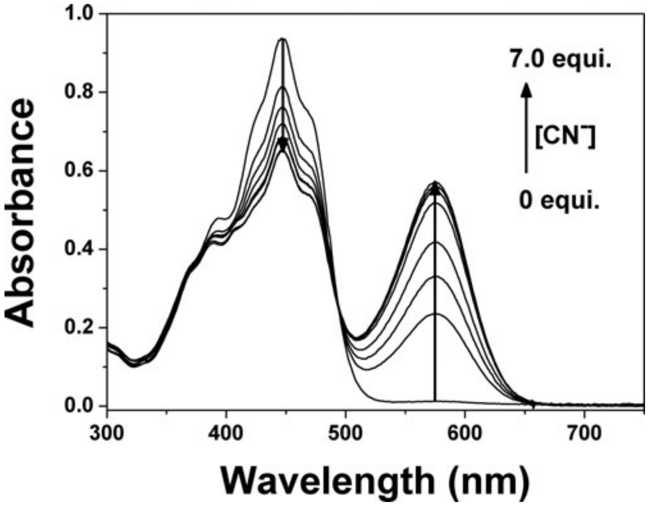


Figure 4. Absorption response of chemosensor (2×10^{-5} M) upon addition of different mole concentrations for CN^- (0∼6equi.) in DMOS.

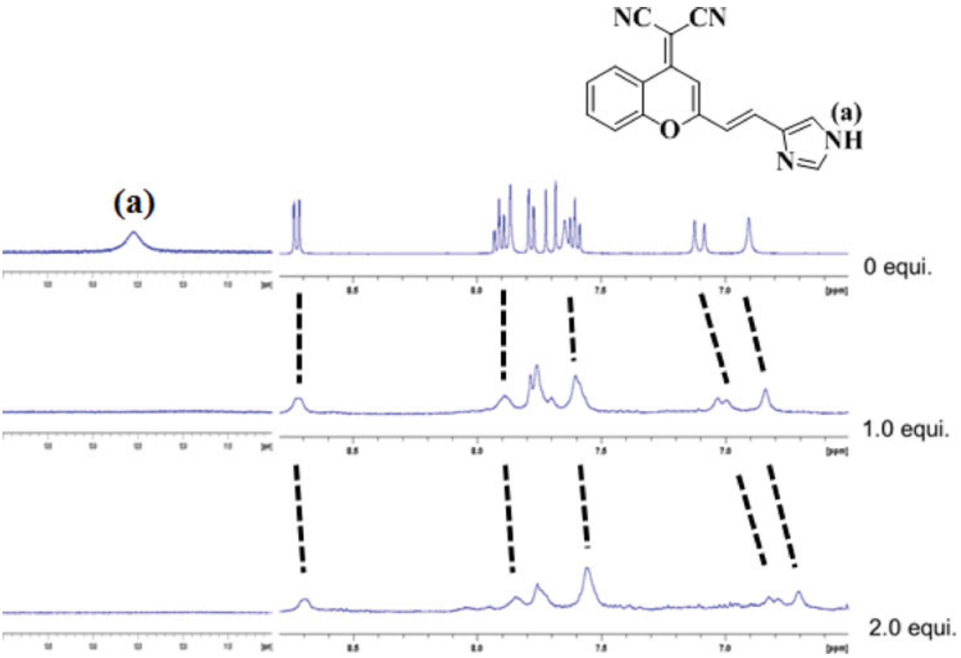


Figure 5. ^{1}H NMR spectra of chemosensor (2×10^{-2} M) with different mole conentrations of F^- (0, 1.0, 2.0equi.) (400MHz, DMOS-d_6).

structure has been studied due to its efficient to detect anion by deprotonation [14]. In this connection, ^{1}H NMR spectroscopy employed to gain a clear understanding of the complex structure for chemosensor (1.5×10^{-2} M) toward F^- (0∼2equi.) in DMSO-d_6. Figure 4 showed that ^{1}H NMR spectra of chemosensor upon the addition of F^- ion mole concentrations. For the present, proton of NH- fragment in imidazole moiety for chemosensor was observed at 12.54 ppm and the peak clearly disappeared as F^- ion was added. This indicated that deprotonation of NH- fragment was induced due to bind with F^- ion. Furthermore, the olefinic and aromatic proton signals also showed an upfiled, indicating that NH + F^- increased the electron density of the olefinic and aromatic ring [11]. The results supported binding process of chemosenesor as we expected that NH- fragment was deprotonated by the complexation with F^- ion.

In addition, pH sensing ability of the chemosensor was also determined by the addition of OH^- ion to chemosensor (2×10^{-5} M) in DMSO. In Figure 6, the measured absorption spectra was displayed that the band at 447 nm gradually decreased and new peak at 580 nm appeared. And it was also found that the isosbestic point was shown at 480 nm. The result is similar as shown in Figs. 3 and 4. This absorption response of chemosensor with OH^- also can be explained by the deprotonation effects of NH- fragment in imidazole moiety. Thus, the chemosensor can be a potential application probe as the role of pH sensor.

Modeling calculation of electron density distribution of chemosensor was finally studied using this chemosenor. All theoretical calculations were carried out by DMol^3 program of *Material Studio 4.3* package, having the quantum mechanical code using density functional theory [15–17]. Figure 7 showed that electron distributions of chemosensor for HOMO and LUMO states were depended on the presence OH^- ion. Electron in HOMO was distributed in imidazole moiety and was moved to chromene moiety in LUMO. After

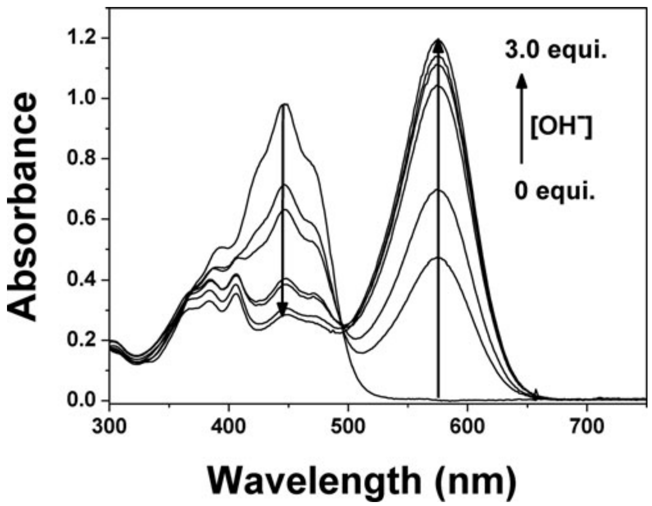


Figure 6. Absorption spectra of chemosenesor (2×10^{-5} M) upon the addition of OH^- (0∼3 equi.) in DMSO.

deprotonation effect was considered by OH^- ion in the molecular structure, the electron movement was opposed between HOMO and LUMO states. This finding can suggest the ICT system property: indicating a strong migration characteristic of electrons in chemosenor. In addition, the energy gap between HOMO and LUMO was also calculated

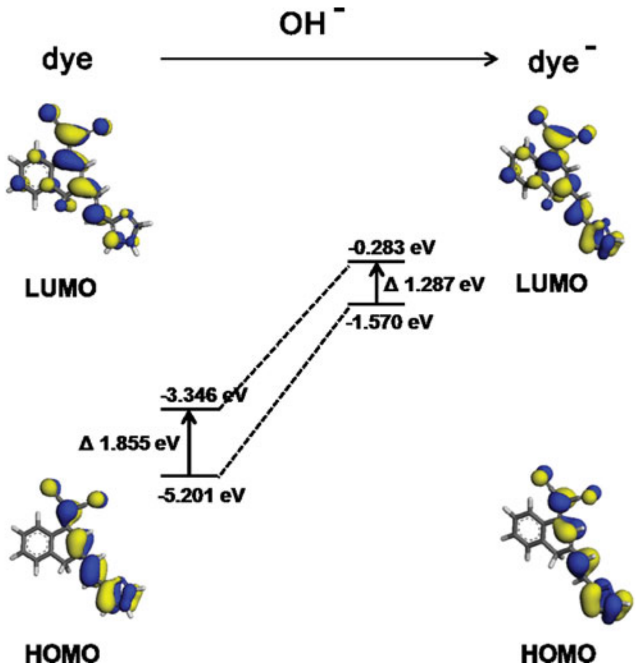


Figure 7. Electron distributions of HOMO and LUMO energy levels for chemosensor and chemosensor + OH^-, respectively.

in same qualification. The obtained value was decreased from $\Delta E = 1.855\text{eV}$ to 1.287eV. This change in values is well agreed with the observed absorption maximum wavelength change of chemosensor 'bathochromic shift' as shown in Figure 7.

4. Conclusions

In this work, we have synthesized the chemosensor through the reaction of of 2-(4H-chromen-4-yildene)malonitrile and 4-imidazolecarboxaldehyde. This chemosensor displayed that significant changes in absorption intensity upon the addition of F^- and CN^- ions were induced by the deprotonation of NH- fragment in imidazole moiety. In addition, potential ability as pH sensor was also determined by the deprotonation effect with the presence of OH^-. HOMO/LUMO energy levels and electron density distributions were also simulated and calculated by computational approach named as *Material Studio 4.3* package.

Acknowledgments

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