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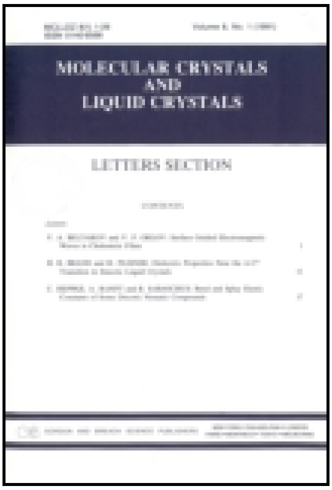

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Young-A Son[a], Seon-Yeong Gwon[b] & Sung-Hoon Kim[b]

[a] BK21, Department of Advanced Organic Materials Engineering, Chungnam National University, Daejeon, South Korea

[b] Department of Advanced Organic Materials Science and Engineering, Kyungpook National University, Daegu, South Korea

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Characteristics of Guajazulene Based Chemosensor Toward CN^- and F^- Anions

YOUNG-A SON,[1,*] SEON-YEONG GWON,[2]
AND SUNG-HOON KIM[2,*]

[1]BK21, Department of Advanced Organic Materials Engineering, Chungnam National University, Daejeon, South Korea
[2]Department of Advanced Organic Materials Science and Engineering, Kyungpook National University, Daegu, South Korea

*A chemosensor having electron pushing donor and pulling acceptor material based on conjugation bridges, namely D-π-A structural chemosensor, was herein designed and synthesized. This chemosensor **3** contained guajazulene and indole moieties, which was synthesized through a one-step condensation reaction. The synthesized material showed very selective sensing properties towards anions. Upon the addition of CN- and F-, the remarkable changes in absorption spectra were monitored. However, each of others did not show any noticeable optical changes. The original intramolecular charge transfer system of chemosensor **3** was altered by the formation of N- at iindole moiety with anion reaction: caused by the deprotonation of NH at the indole moiety of chemosensor. With intermolecular charge transfer system between chemosensor **3** and anions, the electron density and distribution were determined by frontier calculation method.*

Keywords Guajazulene; indole; anion; chemosensor; D-π-A

1. Introduction

Anion probe and receptor have been enjoyed great attention in recent years due to their substantially potential application in chemical, biological, medical, and environmental process [1–3]. The N- contained heterocycles derivatives are very important in this research area due to binding complex using host-guest ligand with some anions [4, 5]. Linking these components to electron acceptor-substituted conjugation systems can establish D-π-A framework, which can render colormetric properties to chemosensor driving the detection observed by naked eye [6–8]. Azulene is an interesting hydrocarbon consisting of a five- and a seven-membered ring fused to form an unsaturated bicyclic system. One critical characteristic of azulene derivatives is their polar functions via contributions of two inverse charge exhibited aromatic structures, namely cyclopentadienyl anion and tropylium cation

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[*] Address correspondence to Young-A Son, Department of Advanced Organic Materials and Textile System Engineering, Chungnam National University, Daejeon, 305-764, S. Korea. Tel.: +82 42 821 6620; Fax: +82 42 823 3736. E-mail: yason@cnu.ac.kr

[*] Address correspondence to Sung-Hoon Kim, Department of Textile System Engineering, Kyungpook National University, Daegu, 702-701, S. Korea. Tel.: +82 53 950 5641; Fax: +82 53 950 6617. E-mail: shokim@knu.ac.kr

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[9–12]. We report herein the synthesis and the properties of anion chemosensor **3** based on guaiazulene and indole derivatives, which shows higher sensitivity to target anions. Structurally chemosensor **3** involves a planner form containing large conjugated area, which can provide chemosensor **3** with spectral changing properties by better electron migration between the electron donor part and acceptor part. In this context, it is elucidated with the synthesis, spectral properties and binding complex of chemosensor **3**. And the related details were discussed.

2. Experimental

2.1 Measurement

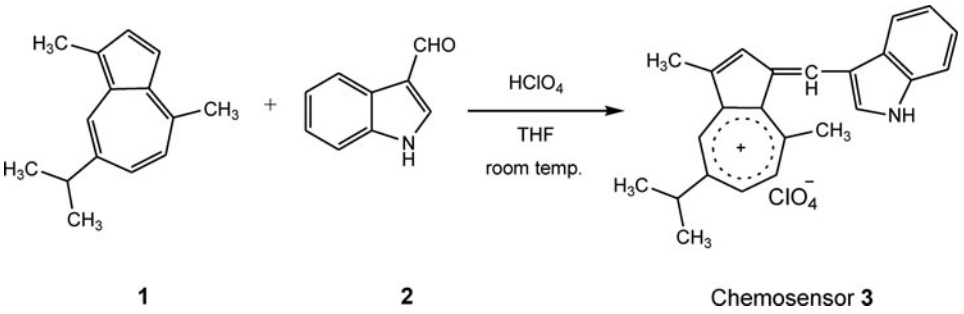
1,4-Dimethyl-7-isopropylazulene (Guaiazulene) and indole-3-carboxaldehyde was purchased from TCI and Aldrich, respectively. Normal methods were employed to ensure purification of all solvents and moisture free laboratorial condition. Other chemicals were commercially available with high grade and were used without further purification. Absorption and fluorescence spectra of the prepared chemosensor **3** were measured with an Agilent 8453 spectrophotometer and a Shimadzu RF-5301PC fluorescent spectrophotometer, respectively. ^{1}H NMR spectra and elemental analyses were recorded with JNM-AL400 spectrometer operated at 400 MHz NMR and a Carlo Elba Model 1106 analyzer, respectively. Mass spectra were recorded on a JEOL MStation [JMS-700]. HOMO/LUMO calculation and modeling simulation proceed with DMol^3 of *Material Studio 4.3*.

2.2 Synthesis

To 25 ml of a mixture of 1,4-dimethyl-7-isopropylazulene 1 (0.5 g, 2.52 mmol) and indole-3-carboxaldehyde 2 (0.366g, 2.52 mmol), 10 ml of tetrahydrofuran and 15 drops of perchloric acid was added. The mélange solution was then stirred vigorously for 12 hours at room temperature under protection of nitrogen atmosphere. After reaction ended, the mixture was filtered, washed with ether and then dried. The product (chemosensor **3**) was gained as green colored solid. Yield 25% (0.268g). EA: anal. calcd. $C_{24}H_{24}ClNO_4$: C, 67.68; H, 5.68; N, 3.29. found C, 67.30; H, 5.65; N,3.30%. FAB $[M]^+ = 326.3$. mp: 246°C.

3. Results and Discussion

In this study, Guaiazulene, 1,4-dimethyl-7-isopropylazulene, is a typical derivative of azulene which involves 10-π electron system having cyclopentadiene and cycloheptatriene rings. The aromatic stability of each ring was supported by one electron transfer from seven-membered ring to five-membered ring, resulting in stable aromatic sextet based on Hückel's Rule. In this regards, the five-membered ring is readily attracted by electrophilic reagent. In addition, guaiazulene can react with some acids to from stable tropylium cation, which can be utilized as a good electron-accepting group [13–15]. Thus, we designed to employ a one step reaction connecting an electron-donating part (indole moiety) to guaiazulene (Scheme 1). Indole moiety being enjoyed to recognize target ions by the formation of macrocyclic dyes is herein used as single host-guest ligand with anions via deprotonation of NH part. The double bonds within carbon bridges can provide a pathway of intramolecular charge transfer between two conjugated parts. Thus, chemosensor **3** towards anions based on the D-π-A framework can be established. From this designed dye chemosensor **3**, we expect sensitivity and selectivity functions toward CN- and F$^-$.



Scheme 1. Synthetic scheme of chemosensor **3**.

Upon the addition of CN^- and F^-, chemosensor **3** represented interesting optical and spectral changes (Figure 1).

The initial spectrum of chemosensor **3** was observed at 585 nm. Upon the addition of CN^- and F^- anions, new absorption bands arose around 509 nm accompanied with decreasing original absorbance at 585 nm. Accordingly, the color of solutions turned gradually from purple to pink. This observation suggested that the formation of complex may undergo the single host-guest ligand with anions via deprotonation of NH part in indole moiety. Gradual

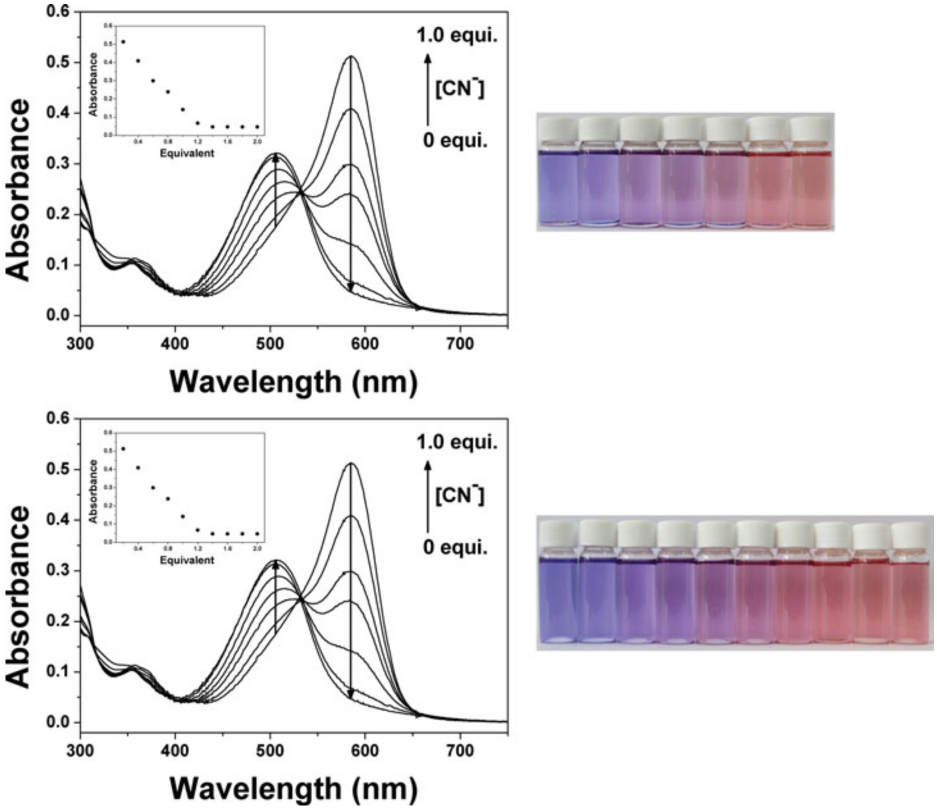


Figure 1. Absorption changes of chemosensor **3** by the addition of (a)CN^-, (b)F^-.

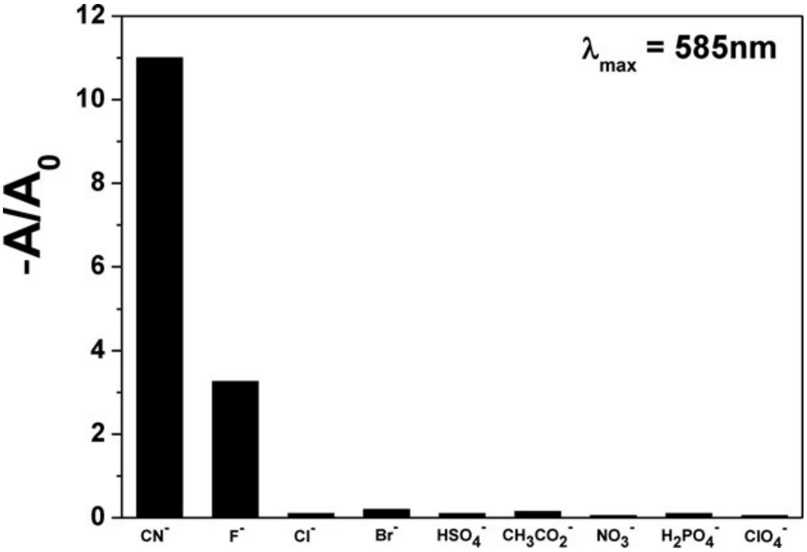


Figure 2. Absorbance response of chemosensor **3** (1×10^{-5} M) to 0.2 equiv of various anions in DMSO.

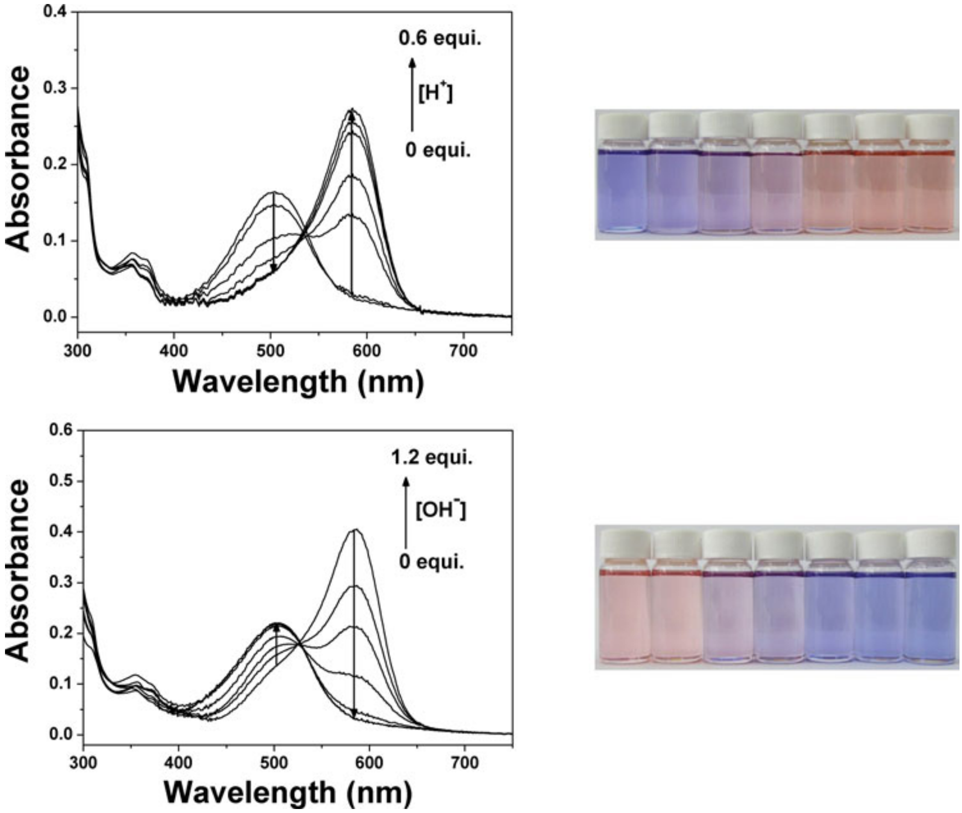


Figure 3. Switching effects of deprotonation/protonation on UV–Vis absorption of 1×10^{-5} M solution of chemosensor **3** in DMSO.

color changes of absorption spectra ended differently with addition of different amount of each anion: 1.2 equiv for CN^- and 1.5 equiv for F^-. In addition, observed isosbestic points indicated that each complex possessed stable molecular configuration in response to the interaction between chemosensor molecules **3** and each anion. These spectral changes may refer to intermolecular charge transfer caused by coordination between NH segment and anions, also being understood as hydrogen donating-accepting effect of chemosensor **3**. Comparison of absorbance rates for various anions was shown in Figure 2. This finding can be considered as quantitative analysis approach to the sensing functions for anions. Compared other anions showed negligible sensing effects to react with chemosensor **3**.

The characteristics of opto-switching/-chemosensing sensor influenced by alkali/acid environmental changes were monitored in DMSO, where the prominent opto-switching/-chemosensing effects were observed. These findings are caused by ICT system based on push-π conjugation-pull molecular structure. Reversible UV-Vis. absorption and fluorescence emission changes of chemosensor **3** with alkali/acid stimulus in DMSO were displayed in Figure 3.

The chemosensing potential of chemosensor **3** to undergo molecular switching imparted by pH stimulation was determined by the addition of alkali and acid to a 1×10^{-5} M solution of chemosensor **3** in DMSO. The reversible absorption changes are represented in Figure 3, from which it is clear that upon the addition of tetrabutylammonium hydroxide to a solution of chemosensor **3** in DMSO, the peak λ_{max} at 585 nm decreased and a new

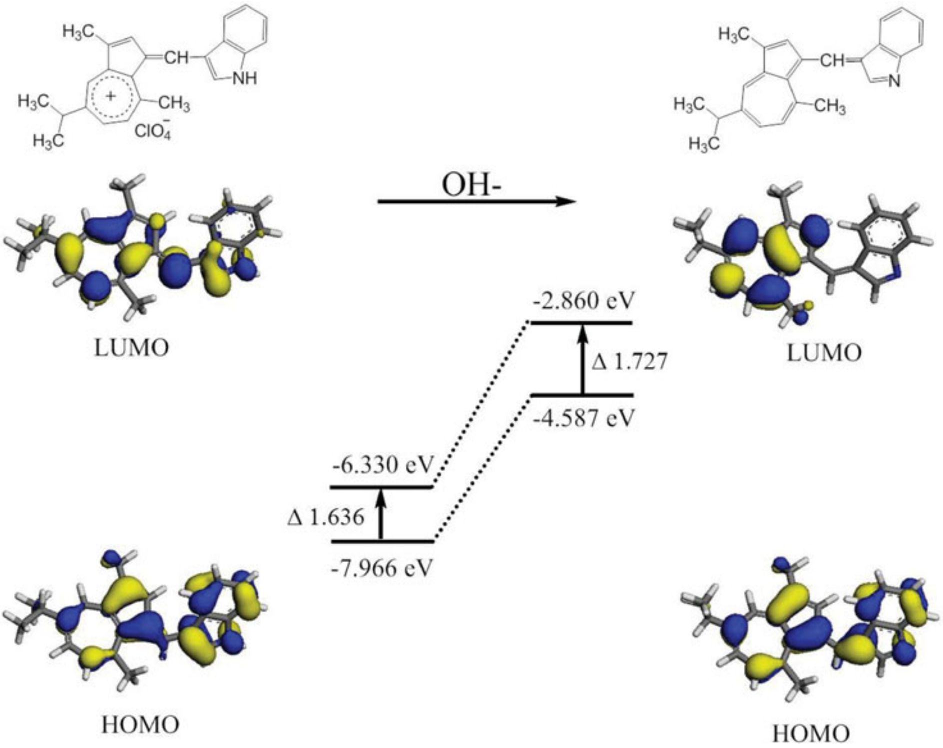


Figure 4. Electron distribution of HOMO and LUMO energy levels using computational simulation with chemosensor **3**.

peak at 506 nm appeared; the addition of trifluoroacetic acid then resulted in the absorption peak at 585 nm to re-appear.

Figure 4 shows the electron distribution states in the frontier MOs [16–18]. Electron distribution in HOMO was presented in indole moiety of donor and was moved to acceptor moiety in LUMO after energy excitation. However, some electrons still remain at NH segment in LUMO state. Anion sensing reaction underwent in electron poor LUMO states. After anion binding with NH segments, all electron density at NH segment within indole moiety disappeared. This observation can be well agreed with a strong migration characteristic of electrons within chemosensor **3**, namely intramolecular charge transfer system.

4. Conclusions

The sensing mechanism of interaction between chemosensor **3** and anions was precisely designed and the resulting sensor was synthesized. The association of chemosensor **3** with anions underwent an intermolecular charge transfer course to form 1:1 complex, wherein the initial intramolecular charge transfer system of chemosensor **3** are greatly altered by the formation of N- at indole moiety arising from the intermolecular electron transfer from anions to chemosensor **3**. The spectral changes of chemosensor **3** may be caused by the deprotonation of NH at the indole moiety, which straightly impacts on chromogenic system of chemosensor **3**.

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