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Yu Wang [a], Seon-Yeong Gwon [a], Young-A Son [b] & Sung-Hoon Kim [a]
[a] Department of Advanced Organic Materials Science and Engineering, Kyungpook National University, Daegu, 702-701, S. Korea
[b] Department of Advanced Organic Materials and Textile System Engineering, Chungnam National University, Daejeon, 305-764, S. Korea
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Spectroscopic Characterization of Heptamethine Cyanine Dyes for the Interaction with the CN^- and F^-

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

[1]Department of Advanced Organic Materials Science and Engineering, Kyungpook National University, Daegu 702-701, S. Korea
[2]Department of Advanced Organic Materials and Textile System Engineering, Chungnam National University, Daejeon 305-764, S. Korea

*The selectivity and sensitivity of a benzoindolium heptamethine cyanine dyes toward CN^- and F^- in DMSO are described. These anions interact with **Dye-1** and **Dye-2** forming anion-Dye adducts, the formation of which was supported by the Pariser-Parr-Pople molecular orbital (PPP MO) calculation. The different optical responses in **Dye-1** stimulated by addition of CN^- (blue to pale yellow) and F^- (blue to pink) allow simultaneous estimation of CN^- and F^-.*

Keywords Heptamethine cyanine dye; Anion recognition; Orbital calculation; Optical responses; Chemosensing; F^- and CN^-.

1. Introduction

Cyanine dyes absorb in a wide range of wavelengths. The color-structure relationships of cyanines and related dyes have been quantitatively evaluated by the Pariser-Parr-Pople molecular orbital method by Fabian and Hartmann [1]. The structural changes affecting the color of cyanine dyes have also been summarized by Griffiths [2]. Especially, indolenine cyanine dyes are expected from their superior solubility and their strong absorption in near infrared (NIR) region. The use of an ion binding dye with chromophore activity in the near NIR region has the advantage of greatly reduced background interference since most biomolecules do not have absorbance in this wavelength region [3–4]. A number of colorimetric and fluorescence-based chemosensors have been reported recently including heptamethine cyanine dyes [5]. Anions are key to many processes, both industrial and biological, playing crucial roles in both health and the environment. In particular, cyanide is a detrimental anion causing poisoning in biology and the environment [6]. As fluoride is the smallest anion and has unique biological and chemical properties, its recognition and detection are of great interest because of its well-known usage in dental care [7, 8] and

*Address correspondence to Prof. 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 Prof. Sung-Hoon Kim, Department of Advanced Organic Materials Science and Engineering, Kyungpook National University, Daegu 702-701, S. Korea. Tel: +82-53-950-5641; Fax : +83-53-950-6617. E-mail: shokim@knu.ac.kr

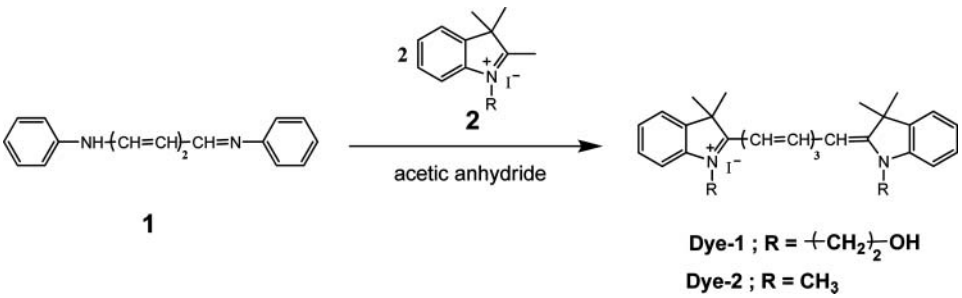
osteoporosis [9] as well as its potentially damaging nephrotoxic effect in humans that can result from overly high concentrations of fluoride [10]. The development of colorimetric signaling chemosensors for the selective recognition of anions has received considerable attention in recent decades owing to their key role in host-guest chemistry, especially from both biological and environmental perspectives [11]. The molecular design of chemosensing receptor system is an additional interesting area in anion recognition chemistry. The chemosensing effect involves binding a specific target anion (A^-) to receptor molecules (R) as a result of which, the chemosensor chromophore displays changes of optical signal (eg absorbance) owing to the formation of a receptor: sensing anion complex. Currently, colorimetric chemosensors are popular due to their capability to detect analytes by naked eye without resorting to any expensive instruments. Therefore, to develop simple-to-use and naked eye diagnostic tool for selective detection of anion is a hot and interesting topic. Our work aims to construct a heptamethine cyanine dye-based near infrared probes with colorimetric assay to specifically detect the presence of CN^- and F^-.

2. Experimental

All chemicals, including the tetrabutylammonium salts of various anions, namely CN^-, F^-, $H_2PO_4^-$, NO_3^-, HSO_4^-, ClO_4^-, Br^-, Cl^- and solvents were of the highest purity grade available and were used without further purification. Measurements of UV-Visible absorption were performed by the addition of anions to dye solutions. And then the samples were well mixed to test for 10 min using Vortex mixer. UV-Visible absorption spectra were measured on an Agilent 8453 spectrophotometer. **Dye-1** and **Dye-2** were synthesized according to the literature method [12]. The absorption maxima wavelengths of π-conjugated molecules were calculated by the Pariser-Parr-Pople molecular orbital (PPP-MO) method. Two center electron repulsion integrals were determined by the Nishimoto-Mataga relationship, and electronic excitation energies were refined by a limited configuration interaction (CI) treatment involving the first nine singly excited singlet configurations obtained by promoting an electron from the three highest occupied orbitals to the three lowest unoccupied orbitals. The calculated configuration interaction vectors indicate that in most cases the contribution of the HOMO-LUMO electron transition to the visible absorption band is about 95%.

3. Results and Discussion

The synthetic route of indolenine heptamethine cyanine dyes shown in Scheme 1.



Scheme 1. Synthesis of **Dye-1** and **Dye-2**.

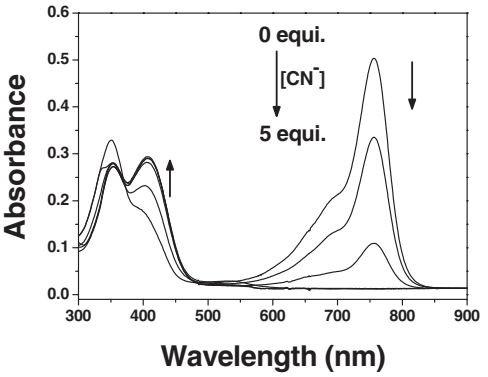


Figure 1. Effect of cyanide ion concentration on the absorbance of 1.0×10^{-5} M solution of **Dye-1** in DMSO.

The indolenine heptamethine cyanine dyes can be synthesized by the reaction of 2,3,3-trimethyl indolenine salt **2** with glutaconaldehyde **1**. These dyes also can be synthesized by a stepwise procedure as shown in Scheme 1. This present work is aimed at the interaction of **Dye-1** and **Dye-2** with the anions. In our present experiments, tetrabutylammonium salts of various anions, namely CN^-, F^-, $H_2PO_4^-$, NO_3^-, HSO_4^-, ClO_4^-, Br^-, Cl^- were gradually added to the solution of cyanine dyes in DMSO as anion source, and the interaction abilities of cyanine dyes with anions were invested by UV-Vis spectroscopy.

Figure 1 showed the absorption spectral changes of **Dye-1** as a function of the CN^- concentration in DMSO at room temperature; as the CN^- concentration increased, the absorbance of **Dye-1** at 756 nm progressively decreased in intensity and peak at 408 nm increased. An isobestic point at 560 nm also developed and the solution changing from blue to pale yellow. From the titration to a solution of **Dye-1**, we notice the stoichiometry of the Dye-1: CN^- is 1:5, in Fig. 1. The effect of F^- concentration on the absorbance of **Dye-1** is shown in Fig. 2. Likewise the addition of F^- to the solution of **Dye-1**, the absorption band at 756 nm abruptly decreased in intensity, while new bands with a peak at around 400 and 542 nm appeared. The color changed from blue to pink. However, addition of other anions such as, $H_2PO_4^-$, NO_3^-, HSO_4^-, ClO_4^-, Br^-, Cl^- under similar condition does not

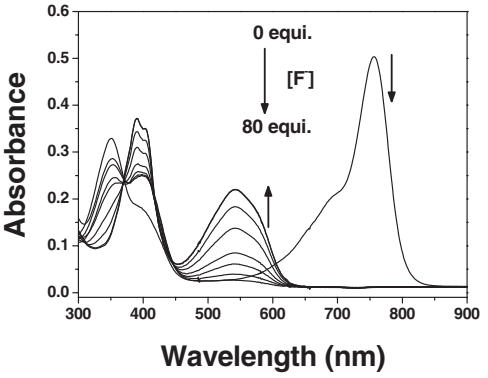
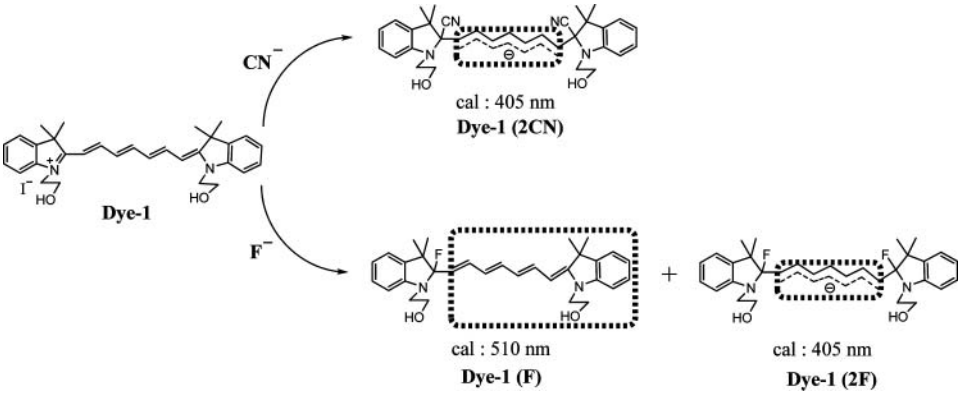


Figure 2. Effect of fluoride ion concentration on the absorbance of 1.0×10^{-5} M solution of **Dye-1** in DMSO.

have any significant effect on the absorption spectrum of **Dye-1**. The superior selectivity of **Dye-1** for CN^- and F^- in DMSO solution is evident from the absorbance response of the anions.

Strekowski and co-workers studied the addition reaction of hydroxide or ethoxide ion with benzindolium heptamethine cyanine dyes [13]. They reported that the simple reaction of heptamethine cyanine dye, *2-′7′-(3″-butyl)-1,1-dimethyl-2″,3″-dihydro-1″H-benz[e]indol-2″-ylidene)-4′-chloro-3′,5′-(propane-1‴,3‴-diyl)-1′,3′,5′-heptatrien-1′-yl]-3-butyl-1,1-dimethyl-1H-benz[e]indolium iodide*, in aqueous MeOH in the presence of KOH, which gave the hydroxyl adduct. The presence of the hydroxyl group in the adduct at the heterocyclic nuclei was established. For this reason, our results can be explained in terms of the addition reaction of nucleophiles such as CN^- and F^- with **Dye-1**. We propose that these spectral changes are due to the interaction of the anions such as CN^- and F^- with the **Dye-1** and the subsequent perturbation of the π system (Scheme 2).



Scheme 2. A possible structure and calculation results of **Dye-1** with CN^- and F^-.

Dye-1 absorbs at 756 nm and produces a new band at 408 nm by the introduction of a two CN^-. On the other hand, the introduction of a F^- to indole moiety of **Dye-1** produced a new band at 542 and 400 nm which correspond to the mono- and di-introduced adducts. We quantitatively evaluated the color-structure relationship before and after addition of

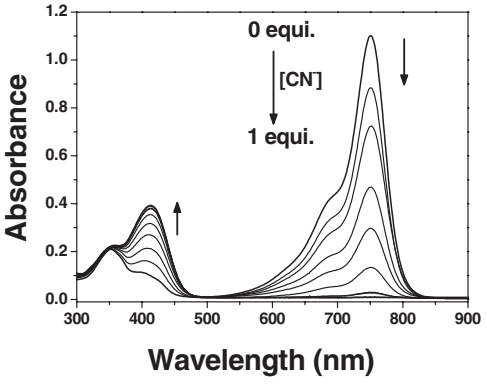


Figure 3. Effect of cyanide ion concentration on the absorbance of 1.0×10^{-5} M solution of **Dye-2** in DMSO.

CN^- and F^- to **Dye-1** by means of PPP MO method. The calculation result show that the absorption maximum wavelength of the compounds depend markedly on the number of anions such as CN^- and F^- (λ_{max}: 405 nm in **Dye-1(2CN)** and **Dye-1(2F)**, λ_{max}: 510 nm in **Dye-1(F)**). This result was in well agreement with theoretical calculation as shown in Scheme 2. The different optical responses in **Dye-1** stimulated by addition of CN^- (blue to pale yellow) and F^- (blue to pink) allow simultaneous estimation of CN^- and F^-. As Fig. 3 shows, upon the addition of CN^- to the DMSO solution of **Dye-2**, the absorption band at 751 nm decreased and a new peak at 413 nm appeared; an isobestic point at 500 nm also developed. The appearance of this isobestic point suggests that at least one stable **Dye-2**-CN^- species is present in solution and is indicative that a stable adduct formed between **Dye-2** and CN^-. However, none of the other anions investigated, namely F^-, $H_2PO_4^-$, NO_3^-, HSO_4^-, ClO_4^-, Br^- and Cl^- had any noticeable effect on absorption.

4. Conclusions

In conclusion, we synthesized and characterized new dyes which are **Dye-1** and **Dye-2** based on heptamethine cyanine dyes. **Dye-1** showed highly selective functions toward CN^- and F^- recognition in DMSO with compared to other examined anions. An obvious sensing effect for CN^- was also observed with **Dye-2**. Moreover, these dyes exhibited significant sensing responses accompanying color changes; CN^- (blue to pale yellow) and F^- (blue to pink).

Acknowledgments

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