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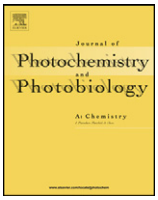

The synthesis and spectral properties of a stimuli-responsive D–π–A charge transfer dye based on indole donor and 2-cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran acceptor moieties

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ABSTRACT

A particular chromogenic and fluorophoric dye chemosensor was designed and synthesized, which was based on the stimuli-responsive D–π–A charge transfer system. Indole moiety as a donor unit and furan moiety as an acceptor unit were used. This prepared dye sensor showed the selective fluoride ion sensing effects in UV–vis absorption and fluorescence emission properties. Clear absorption changes and highly selective fluorescence quenching effects with fluoride ion were determined. Experimental data and images were collected and supported to provide a better understanding of this particular dye sensor.

1. Introduction

The research interests of chromogenic dye sensors or receptors toward anion detection have attracted great attentions due to their advantageous features and useful functions in chemical, biological and environmental processes. These interesting demands have led to many studies in the field of the recognition and the detection of anionic species [1–4]. Especially, the designs of dye sensor synthesis, which are capable of the recognizing target anions selectively, continue to attract a great deal of research interests. This structural dye sensor designs toward specific target anions have been still considered as a great challenge for dye chemists [5–7]. Among the various anions, fluoride is of great interests due to its well known role in dental care [8,9] and osteoporosis [10]. However, higher concentration of fluoride can result in considerable side effects, namely fluorosis, which causes nephrotoxic damages in human [1,2].

In this work, we have designed and introduced a particular chemosensor dye **3**, which can provide promising intermolecular proton transfer between a hydrogen atom on the indole N positions of the dye **3** and the fluoride anion. Thus, the feasibility of dye **3** as a chemosensor for fluoride is an interesting aim of this work [11–14].

We report herein the synthesis and binding properties of dye chemosensor **3**, which shows highly selective absorption and fluorescence changes with fluoride among the various anions. Dye **3** was structurally designed with push–pull molecular structure based on intramolecular charge transfer system. Prepared dye **3** was then studied with absorption/emission optical properties and anion recognizing effects. And the related details were discussed.

2. Experimental

Elemental analyses were recorded on a Carlo Elba Model 1106 analyzer. Mass spectra were recorded on a Shimadzu QP-1000. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Varian Inova 400 MHz FT-NMR spectrometer using TMS as internal standard. The UV–vis absorption spectra were measured on an Agilent 8453 spectrophotometer. Fluorescence spectra were measured on a Shimadzu RF-5301PC fluorescence spectrophotometer. Melting point was determined using an Electrothermal IA 900 and is uncorrected. The fluorescence quantum yields were determined by using fluorescein ($\Phi_F = 0.90$, acetonitrile as the solvent) as a reference.

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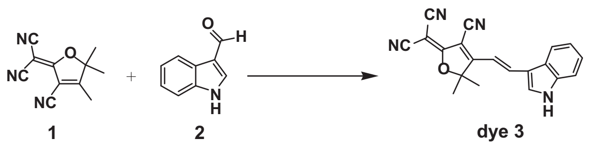


Fig. 1. Synthetic route for dye **3**.

2.1. Materials

Indole-3-carboxaldehyde, 3-hydroxy-3-methyl-2-butanone and malononitrile were purchased from Aldrich. The other chemicals were of the highest grade available and were used without further purification. All employed solvents were analytically pure and were employed without any further drying or purification. 2-Cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran **1** was made by condensation of 3-hydroxy-3-methyl-2-butanone with malononitrile [15,16].

2.2. Synthesis of dye 3

Compound **1** (1 mmol, 0.2 g) and indole-3-carboxaldehyde **2** (1 mmol, 0.15 g) were dissolved in 8 ml of ethanol and 2 ml of chloroform under a nitrogen atmosphere. Piperidine was added dropwise to the reaction mixture and refluxed for 3 h. The solids were filtered out using reduced pressure and dried.

Yield 70%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.81 (s, 6H), 6.93 (d, J = 15.92, 1H), 7.31–7.35 (m, 2H), 7.56–7.58 (m, 1H), 7.95–7.97 (m, 1H), 8.27 (d, J = 15.92, 1H), 8.41 (s, 1H), 12.60 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 26.20, 31.06, 51.22, 92.17, 98.47, 108.84, 112.41, 113.10, 113.83, 115.44, 120.76, 123.27, 124.51, 124.98, 138.57, 139.02, 144.76, 176.96, 177.74. EA: Anal. calcd. $C_{20}H_{14}N_4O$: C, 73.61; H, 4.32; N, 17.17. Found C, 73.26; H, 4.26; N, 17.17%. $M^+ = 326$. mp: >350 °C. Quantum yield: $\Phi_F = 0.14$, in CH_3CN. $\lambda_{max} = 524$ nm ($\varepsilon = 12{,}500$ M^{-1} cm^{-1}).

3. Results and discussion

As designed D–π–A structural system, dye chemosensor **3** consists of indole moiety as a donor part and furan moiety as an acceptor part in its structure. The indole part of dye **3** has NH fragment that can form intermolecular proton transfer complexes with the guest anions. For this aim, the dye **3** was readily synthesized by one-step reaction as shown in Fig. 1. Due to its well-defined intramolecular charge transfer system and NH hydrogen atom in donor part, dye **3** can act as very effective host molecules for the recognition of guest anions by intermolecular proton transfer. Especially, in this study, we have expected the dye **3** to be binded with fluoride ion. For this observation, the studies were conducted by adding the various anions (Cl^-, Br^-, NO_3^-, $CH_3CO_2^-$, ClO_4^-, $H_2PO_4^-$ and HSO_4^-) to acetonitrile solution of dye **3**.

The finding results for the UV–vis absorption and fluorescence emission changes in acetonitrile solution of dye **3** with anions can be proposed that fluoride has a higher negative charge and a better intermolecular proton transfer power compared to other anions [5]. When fluoride and NH proton of the indole part of dye **3** formed complex adducts, a considerable intramolecular charge transfer change, namely donor–acceptor electron stream, was occurred within the dye molecules. This could be a primary reason for the observed changes in UV–vis absorption and fluorescence emission properties. On the other hand, other anions led to negligible changes in optical spectra properties. The interaction effects of dye **3** with fluoride were shown in Fig. 2, which were performed by spectrophotometric titration experiments in acetonitrile solution.

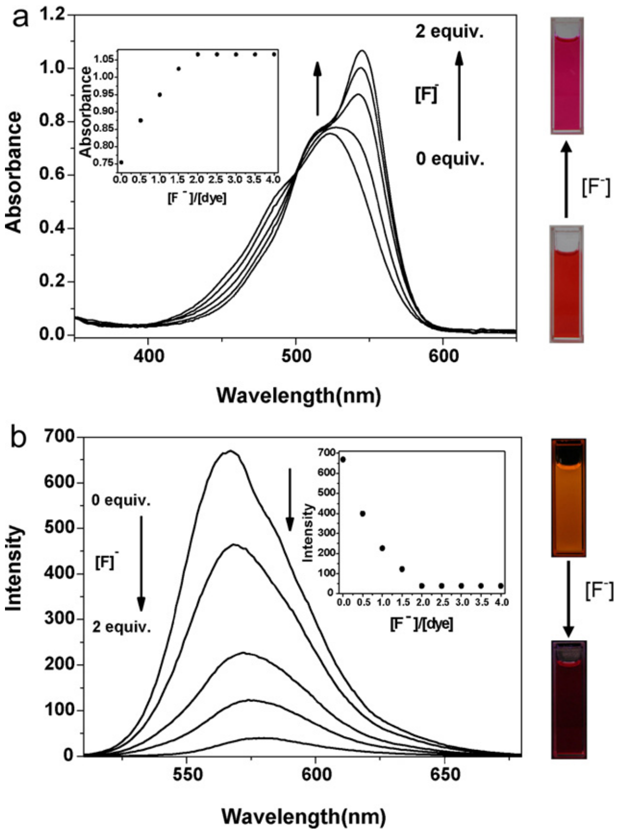


Fig. 2. Absorption (a) and emission (b) changes of dye **3** (1×10^{-5} mol) in CH_3CN with fluoride.

The optical changing behaviors with fluoride ions were evaluated by titrating (from 0.5 equiv. of fluoride ion aliquots to 2 equiv. into a solution of dye **3**) at regular intervals and determined by recording the changes in the absorption and emission spectra (Fig. 2). Upon addition of fluoride to dye sensor **3**, the absorption band at 523 nm progressively shifted in its intensity and a new peak at 545 nm appeared. Along with this observation, an isosbestic point at 495 nm was determined. The finding of this isosbestic point proposes that at least a stable dye molecular moiety is present and that a stable binding complex is formed between dye **3** and fluoride.

Observation of fluorescence emission behavior was also carried out to confirm the potential ability of dye **3** to utilize as a fluorescence anion sensor. Dramatic quenching behavior of the fluorescent emission was observed with the addition of fluoride ion (Fig. 2(b)). On the intermolecular proton transfer between fluoride and dye **3**, the intramolecular electron charge transfer system and the excited state were greatly modified, which led to decrease of fluorescence emission. Colorimetric changes due to the deprotonation of NH, which directly influenced the chromophore and the fluorophore system, have been greatly interested as a chemosensor for fluoride detection [17,18]. The corresponding photo-image of color changes with absorption and emission of dye **3** in acetonitrile after addition of fluoride ions was displayed in Fig. 2.

However, other anions such as Cl^-, Br^-, NO_3^-, $CH_3CO_2^-$, ClO_4^-, $H_2PO_4^-$ and HSO_4^- did not affect any color change in absorption properties. Fig. 3 shows these findings that the addition of other anions displays negligible effect to the sensing effects of dye sensor **3**. Absorption changes were barely observable after the addition of each anion. As expected selectivity functions with fluoride, other anions did not cause any color absorption changes.

To confirm the nature of the intermolecular proton transfer between dye **3** and F^-, the proton NMR spectrum of dye **3** was

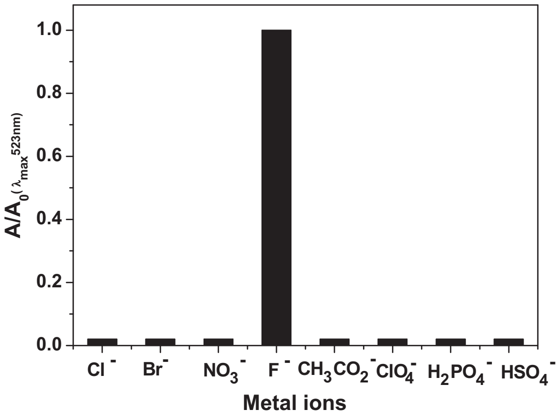


Fig. 3. Comparison of absorption ratio of dye **3** with various anion detections, where A and A_0 represent the absorbance in the presence and absence of anions, respectively.

recorded in the absence and presence of different concentrations of F^- (Fig. 4). It was noticed that original NH proton signal, appearing at 12.58 ppm, disappeared upon successive addition of $[Bu_4N]^+F^-$. With an increase in the addition of F^-, the olefinic and the aromatic protons showed a regular upfield shift due to the NH–F^- bond formation which increases the electron density of the phenyl ring and the olefinic moiety. These results indicate that an intermolecular proton transfer between dye **3** and F^- is formed. However, addition of the other anionic salts of $[Bu_4N]^+$ showed relatively negligible changes in their chemical shifts.

For interpretation of the intramolecular charge transfer system of dye **3**, the quantum chemical DMol^3 approach was considered. All theoretical calculations were performed by DMol^3 program of *Materials Studio 4.3* package, which has the quantum mechanical code using density functional theory. Perdew–Burke–Ernzerhof (PBE) function of generalized gradient approximation (GGA) level with double numeric polarization basis set was used to calculate the energy level of the frontier molecular orbital. Fig. 5 shows the electron distribution states in the frontier MOs. Electron distribution in HOMO was presented in indole moiety of donor and was moved to acceptor moiety in LUMO after energy excitation. This observation can be well agreed with a strong migration characteristic of electrons in dye **3**, namely intramolecular charge-transfer system. HOMO–LUMO excitation moves the electron distribution from indole moiety to the acceptor, which shows the charge migration of ICT character of dye **3**.

The potential function of molecular switching effects with pH stimulation of alkali–acid addition was investigated in acetonitrile, which was considered by deprotonation/protonation effects based on intramolecular charge-transfer system. Reversible absorption and fluorescence emission changes of dye **3** were displayed in Fig. 6. Upon the addition of tetrabutyl ammonium hydroxide to the dye **3** solution, the peak λ_{max} at 524 nm decreased and the new peak at 546 nm dramatically increased (Fig. 6(a)). And the addition of hydrochloric acid recovered completely back to the initial state. As shown in Fig. 6(a)), deprotonation shifted the absorption band bathochromically, the corresponding energy levels being: HOMO (−5.378 eV)/LUMO (−3.658 eV) in dye **3** and HOMO (−1.939 eV)/LUMO (−0.459 eV) in dye **3**$^-$. The low excitation energy gap of 1.480 eV for the dye **3**$^-$ fitted well with the observed maximum absorption wavelengths in terms of the decrease in the peak at 524 nm and the increase in the peak at 546 nm.

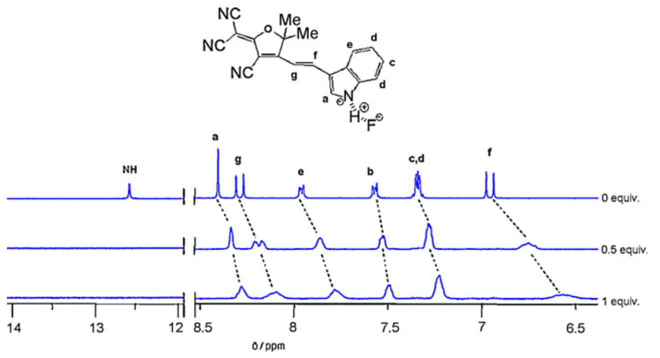


Fig. 4. ^1H NMR spectral change with strength of intermolecular proton transfer between NH fragment and fluoride.

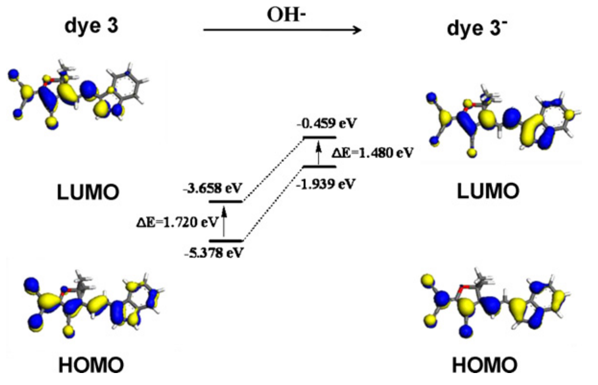


Fig. 5. Electron distribution of HOMO and LUMO energy levels of dye **3** and dye **3a**$^-$.

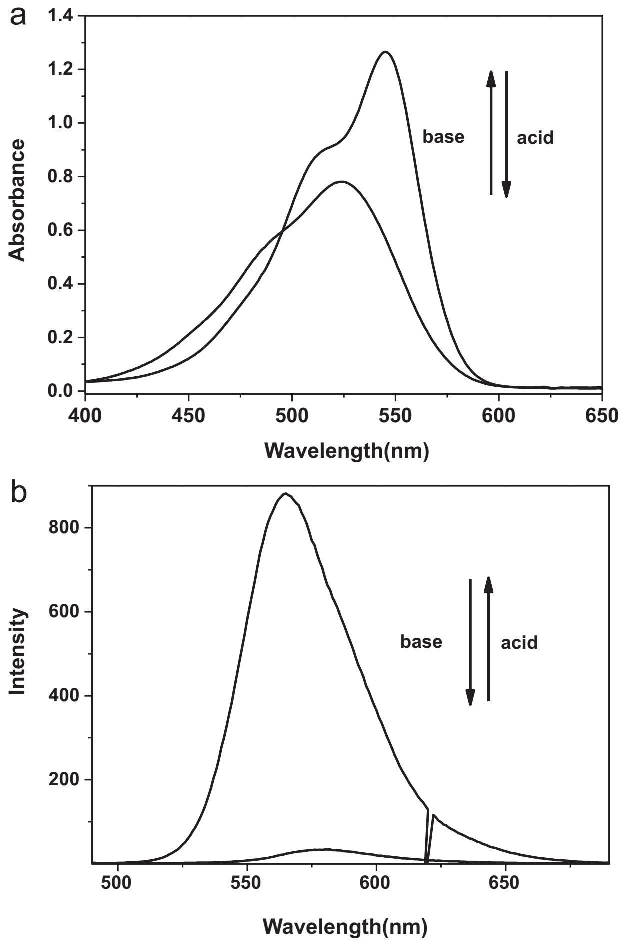
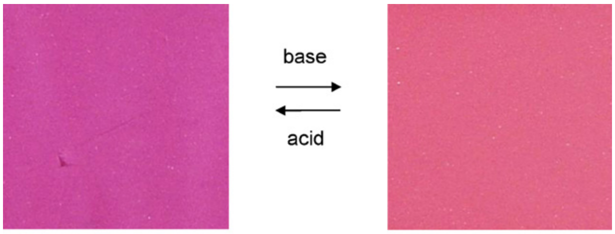
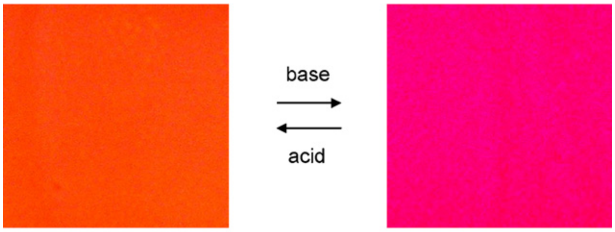


Fig. 6. UV–vis absorption (a) and fluorescence emission switching (b) of dye **3** (1×10^{-5} mol) in CH_3CN with deprotonation/protonation.



Absorption changes



Emission changes

Fig. 7. Color changes with absorption and emission of dye sensor casted on thin layer silica gel sheet in acid/amine VOCs exposure.

Fluorescence emission spectra (Fig. 6(b)) also showed similar results. Upon the addition of hydrochloric acid to colorless dye solution, the emission of dye **3** was sharply recovered and completely back to the initial emission state. Namely, the fluorescence intensity reversibly changed at 568 nm by alternate addition with tetrabutyl ammonium hydroxide and hydrochloric acid.

In addition, this dye was exposed to acid and amine vapor gases to confirm the volatile organic compounds (VOCs) detection. Adsorbed dye **3** on TLC plate was exposed to acetic acid and dimethylamine vapor conditions, where the resulting absorption and emission changing properties were clearly monitored. The findings imply that this designed dye chemosensor offers potential application for the development of optical signaling material for the detection of VOCs (Fig. 7).

4. Conclusions

We have designed and synthesized a particular dye chemosensor **3** based on indole moiety as a donor unit and furan moiety as an acceptor unit. This dye sensor **3** showed very effective detection behaviors of UV–vis absorption and fluorescence emission intensity with the addition of fluoride. As expected with selective recognition for fluoride, other anions did not cause any color change.

Acknowledgements

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