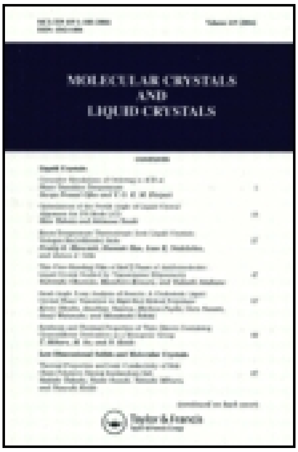

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pH Triggered Dye Chemosensor: Design, Synthesis and Optical Switching Properties

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pH Triggered Dye Chemosensor: Design, Synthesis and Optical Switching Properties

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A novel dye chemosensor based on indole as a donor unit and quinaldium as an acceptor unit have caused promising optical changes when used as a reversible, pH-induced, molecular switching in the presence of alkali/acid stimulus. The dye chemosensor also exhibited marked fluorescence quenching in the presence of alkali addition, which are based on intramolecular charge transfer (ICT) system.The level of energy potential and the electron flowing of this dye chemosensor such as HOMO and LUMO values were calculated by computational calculation approaches.

Keywords Dye chemosensor; Alkali addition; Anion recognition; Optical switching; Homo; Lumo

1. Introduction

The promising sensing function of alkali anions using dye chemosensor compound has been attracted great attention owing to its application importance in both chemical and environmental application [1–6]. The pH triggered potential sensing ability of dye chemosensor based on optical switching properties is also an interesting research topic. In addition, the molecular framework design of dye chemosensor that shows sensitive reaction behaviors towards a specific target anion, name OH^- is a great challenge for dye chemists and researchers [7].

This optical switching characteristics of dye chemosensor is importantly based on push unit-π conjugation-pull unit of intramolecular charge transfer (ICT) system through dye chromophore or fluorophore molecules and the resulting dye chemosensor can be utilized

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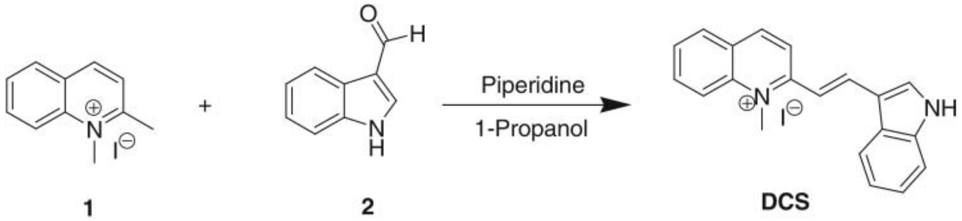

Figure 1. Synthetic route for dye chemosensor (**DCS**).

as useful sensing probes for checking, determining and monitoring subjecting target anion detection[1,2,8–13].

Of various types of push-π-pull charge transfer dye, indole moiety is a well-known, representative, which undergoes intramolecular charge transfer. This is the reason to design and choose the indole moiety as an electron-donation unit in the dye chemosensor molecular structure. As the designed dye chemosensor has NH segment within the molecular structure, it can act as H-bond donors for OH^- anions [7,14,15]. Thus, this indole moiety can be utilized as electron-donatingand H-bond unit.

In this context, this workreportsthe synthesis of a novel dye chemosensor for pH triggered optical switching effects based on a push-π-pull, ICT system. Hence, both the promising potential of dye chemosensor (**DCS**, Fig. 1) to recognize OH^-anions and the changes in its absorption/emission properties imparted by pH were discussed [16–20].

2. Experimental

All reagent and chemicals were purchased from Aldrich Chemical Co. and TCI. Solvents were purified by standard procedures and used under moisture free atmosphere. The other materials were commercial products and were used without further purification. Elemental analyses 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. ^{1}H NMR spectra were recorded using a Varian Inova 400 MHz FT-NMR spectrometer with TMS as internal standard. Melting point was determined using anTA Q600 thermal analyzer.

Quinaldiumsalt**1** (0.5g, 1.754 mmol) and indole-3-carboxaldehyde **2** moieties (0.26g, 1.175 mmol) were dissolved in 20 ml of 1-propanol. Piperidine was added dropwise and the ensuing mixture was refluxed for 7h. The desired solid was obtained with decreasing to room temperature and then filtration under reduced pressure and washing with hexane were carried out. The aimed dye chemosensor product (namely Dye ChemoSensor: **DCS**) was obtained in 78.8% yield (Fig. 1).

^{1}H NMR(400 MHz) DMSO-d$_6$: δ (ppm) 4.46 (s, 3H), 7.29 (m, 2H), 7.54 (m, 2H), 7.82 (t, $J = 7.48$, 1H), 8.06 (t, $J = 7.28$, 1H), 8.20(m, 1H), 8.23(d, $J = 9.08$, 1H), 8.39 (s, 1H), 8.43 (d, $J = 8.92$, 1H), 8.59 (s, $J = 9.24$, 1H), 8.63 (d, $J = 15.44$, 1H), 8.81 (d, $J = 9.16$, 1H), 12.31 (s, 1H). EA: anal. calcd. $C_{20}H_{17}IN_2$: C; 58.27, H; 4.16, N; 6.79. foundC; 58.25, H; 4.08, N; 6.64%. Ms = 285.2.mp: 275∼276°C

3. Results and Discussion

Indole moiety has been attracted as a useful donor component to design D-π-A system of dye chemosensor, which is capable of forming the host-guest complex by hydrogen-anion binding at NH segment [a]. Herein, the selected acceptor component, 1,2-dimethyl-qunaldium salt **1** was condensed with donor component, indole-3-carboxaldehyde **2** to produce the target dye chemosensor (**DCS**).With based on a typical D-π-A structural framework of dye chemosensor molecule, the intramolecular electron migration characteristics can be developed through **DCS** structure. The characteristics of pH triggered opto-switching/-chemosensing effects of **DCS** influenced by alkali/acid changes were observed in acetonitrile ($1\times10\text{–}^{5}$ M), where very promising opto-switching/-chemosensing behaviors were determined. These obtained results are caused by intramolucular charge transfer (ICT) system, which are structurally framed with push-π conjugation-pull structural design. Reversible UV-Vis. absorption and fluorescence emission changes of **DCS** with alkali/acid stimulus were represented in Figs 2 and 3.

The chemosensing potential of **DCS** imparted by pH stimulation was monitored by the addition ofalkali and acid to a 1×10^{-5} M solution of **DCS** in acetonitrile. The prominent reversible absorption and fluorescence emission changes are shown in Figs 2 and 3, from which it is clear that upon the addition of tetrabutylammonium hydroxide to a solution of **DCS** in acetonitrile, the peak λ_{max} at 461 nm decreased and a new peak at 526 nm appeared (Fig. 2); the addition of trifluoroacetic acid then resulted in the absorption peak at 461nm to re-appear. The fluorescence emission spectral behaviors (Fig. 3) also showed similar observation. The emission spectrum peak at 548 nm was dramatically quenched with the addition of tetrabutylammonium hydroxide to the **DCS** solution and the next step of addition using trifluoroacetic acid to a emission quenched colorless solution of **DCS** resulted in a return to the initial emission state. Therefore, very promising reversible chemosensing behaviors with UV-Vis absorption and fluorescence emission were accomplished by the alternate addition of tetrabutylammonium hydroxide and trifluoroacetic acid. There spectral changing behaviors of **DCS** could be caused by the deprotonation of NH segment at the

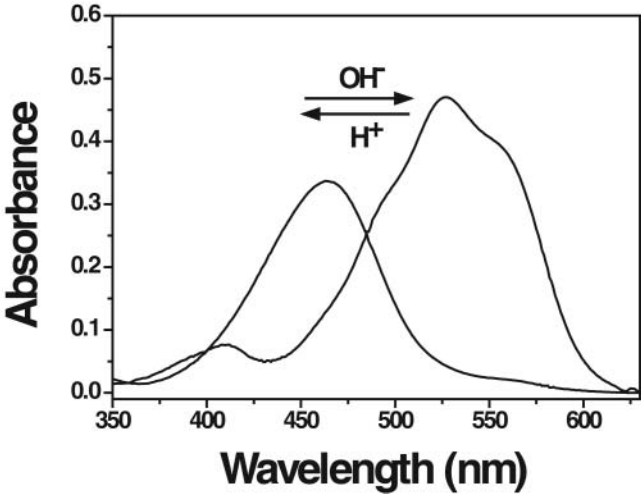

Figure 2. Effect of pH triggered deprotonation/protonation on UV–Vis absorptionswitching of 1×10^{-5} M solution of **DCS** in acetonitrile. [Bu_4NOH] and [CF_3COOH] are $1\times10\text{–}^{6}$ M.

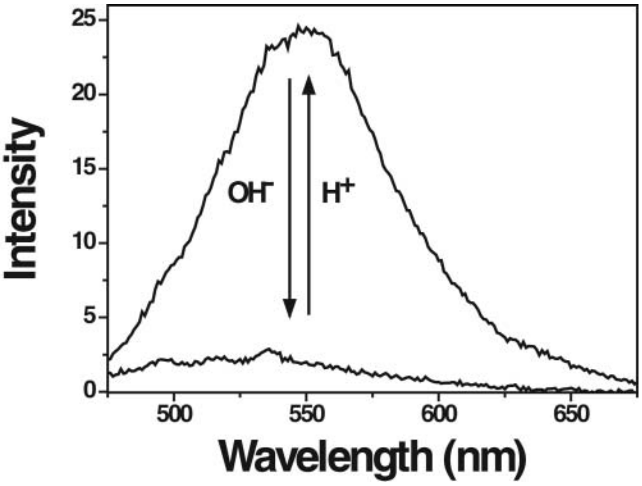

Figure 3. Effect of pH triggered deprotonation/protonation on fluorescence emissionswitching of 1×10^{-5} M solution of **DCS** in acetonitrile. [Bu_4NOH] and [CF_3COOH] are 1 × 10–^{6} M.

indole moiety of **DCS**, which directly influenced on chromogenic and fluorogenic system of **DCS** molecule. The distribution of electron density of **DCS** was rearranged by forming N^- at indole moiety (see Fig. 1), which greatly imparted intramolecular charge transfer of **DCS**. Owing to its well-explained, push and pull conjugation structure that includes (NH) hydrogen atom, it isexpected that **DCS** could function as a receptor molecule for the recognition of OH^-anions via H-bonding interaction.

pH stimuli-color switching image of **DCS** is shown in Fig. 4, which was measured by the addition of OH^- and H^+ with increasing molar equivalence. As shown in Fig. 4, **DCS** chromophore showed reversible color switching images according to the pH deprotonation and protonation stimuli-effects.

For modeling calculation of the electron density distribution of **DCS** (Fig. 5), the quantum chemical DMol^3 determination was conducted. All theoretical calculations were

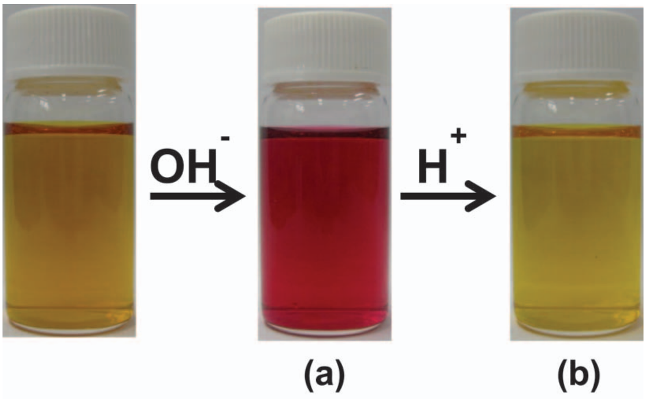

Figure 4. UV-Vis absorption image photographs of **DCS** in pH deprotonation (a) and protonation (b) reversible effects.

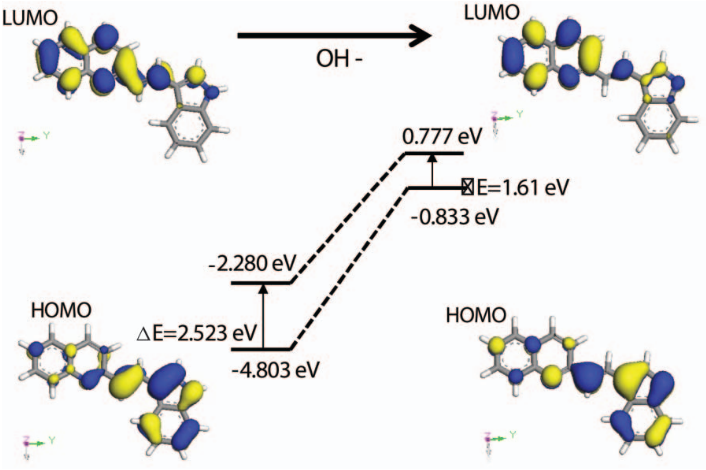

Figure 5. Electron distribution of HOMO and LUMO energy levels of **DCS**.

proceeded by DMol^3 program of *Materials Studio 4.3 package* [12,13], which has the quantum mechanical code using density functional theory. Perdew-Burke-Ernzerhof (PBE) function of generalized gradient approximation (GGA) level [14] with double numeric polarization basis set was used to calculate the energy level of the frontier molecular orbital. In this context, Fig. 5 displays HOMO and LUMO energy values and electron density distribution of **DCS.**

Figure 5 shows the electron distribution states in the frontier MOs. After OH$^-$addition reaction to **DCS** molecule, the electron density distribution was dramatically changed. The presence of electron clouds was shown in the indole donor part in HOMO state, but the electrons totally moved to the quinaldium acceptor part in LUMO state. In addition, the resulting energy gapbetween HOMO and LUMO with OH$^-$ addition was decreased from $\Delta E = 2.523$eV to $\Delta E = 1{,}610$eV: that of the reacted **DCS** is smaller than that of **DCS**. This means that the alkali reacted **DCS** is expected to exhibit the bathochromic absorption compared with that for **DCS**. This finding can be supported by Fig. 2. The OH$^-$ addition resulted in a decrease of the shorter absorption band and an increase of new peak in the longer wavelength region. Thus, this observation is well agreed with a strong electron flowing character of **DCS** caused by OH$^-$ nucleophilic addition reaction to the dye molecules, namely intramolecular charge transfer system (ICT).

4. Conclusions

In this work, we have synthesized the novelpush-π conjugation-pull ICT dye chemosensor having quinaldium salt as an electron-withdrawing unit and indole as an electron-donating unit. This dye chemosensor displayed marked changes in UV-Vis absorption and fluorescence emission intensity upon the pH stimulation. The dye exhibitedsizeable color changes when used as a reversible, pH-induced, molecular switching observation. And HOMO/LUMO energy potentials and electron density distribution were modeled and simulatedwith computational calculation.

Acknowledgement

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