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D–π–A solvatochromic charge transfer dyes containing a 2-cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran acceptor

Sung-Hoon Kim [a,*], Sue-Yoen Lee [b], Seon-Yeong Gwon [a], Young-A Son [c], Jin-Seok Bae [a]

[a] *Department of Textile System Engineering, Kyungpook National University, Daegu 702-701, South Korea*
[b] *Department of Advanced Organic Materials Science and Engineering, Kyungpook National University, Daegu 702-701, South Korea*
[c] *School of Chemical and Biological Engineering, Chungnam National University, Daejeon 305-764, South Korea*

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ABSTRACT

The preparation and solvatochromic behavior of novel, intramolecular charge transfer dyes obtained by the condensation of 2-cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran with 4-dimethylamino benzaldehyde and 9-formyljulolidine are described. The absorption and fluorescence emission spectra of the dyes were studied in solvents of differing polarity. The dyes exhibited positive solvatochromism and their solvatochromic properties are discussed with the aid of semiempirical calculations. The HOMO and LUMO values of the dyes were obtained using both cyclic voltammetry and theoretical calculations; the electrochemical results were in agreement with both observed values and theoretical calculations. pH molecular switching was achieved by modulation of intramolecular charge transfer by means of protonation/deprotonation in DMSO solution.

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1. Introduction

Solvatochromic D–π–A charge transfer dyes attract much attention because of their applicability as probes for the determination of solvent polarity as well as their potential application as colorimetric chemosensors for volatile organic compounds (VOC) [1,2]. Charge transfer dyes have also been developed for use as photo- (PL) and electroluminescent (EL) materials in dye lasers [3,4], sensors [5], dye-sensitized solar cells [6,7], switchable viscosity probes [8], dual-ion-switched molecular brakes [9] and optical light emitting diodes (OLED's) [10]. Solvatochromism can be defined as the phenomenon whereby a compound changes colour, either by a change in the absorption or emission spectra of the molecule, when dissolved in different solvents [11,12]. Recently, solvatochromic dyes such as pyridinium betain [13] and stilbazolium [14] have been synthesized and studied. We have been concerned with the solvatochromic behavior of Barbituric acid and Meldrum's acid based merocyanine dyes and on the structural features responsible for relative changes in the magnitude of their spectral shifts [15]. 2-Cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran **1** was well adopted as a strong electron acceptor that induces significantly high dipole moment, first-order molecular hyperpolarizability [16,17]. In this present report, we designed the synthesis and the solvatochromic properties of the D–π–A charge transfer dyes containing 2-cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran **1** as shown in Scheme 1. The organic functional dyes with D–π–A molecular structure have attracted much attention because of their inherent nonlinear optical characteristics, which are highly sensitive to changes in the external environment such as polarity and pH of media, due to their intrinsic character [5]. We have previously reported the synthesis and pH-induced molecular switching of D–π–A type solvatochromic charge transfer dyes [18,19]. In this work, pH-induced changes in absorption and fluorescence spectra of these dyes were also examined.

2. Experimental

Melting points were determined using an Electrothermal IA900 apparatus and were uncorrected. Elemental analyses were recorded on a Carlo Elba Model 1106 analyzer. Mass spectra were recorded on a Shimadzu QP-1000 spectrometer using electron energy of 70 eV and direct probe EI method. ^{1}H NMR spectra were recorded in DMSO-d_6 using a Varian Inova 400 MHz FT-NMR using TMS as internal standard. The UV–Vis absorption spectra were measured on an Agilent 8453 spectrophotometer. Fluorescence

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[*] Corresponding author. Tel.: +82 53 950 5641; fax: +82 53 950 6617.
E-mail address: shokim@knu.ac.kr (S.-H. Kim).

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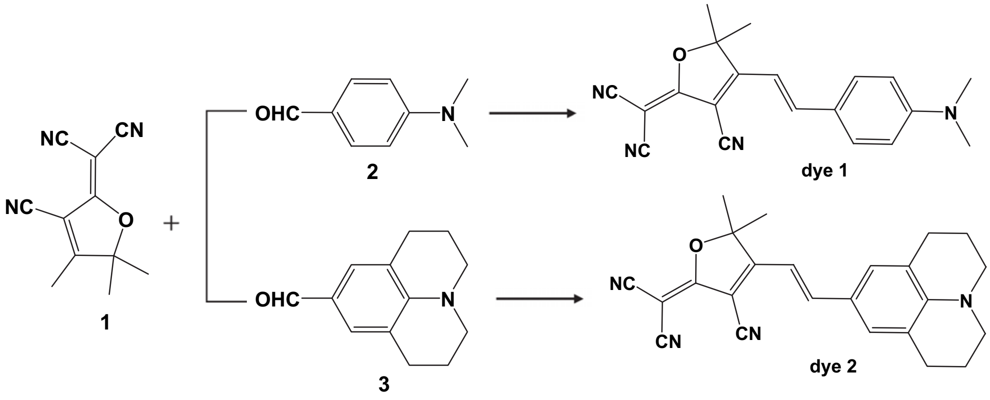

Fig. 1. Synthetic routes of dye **1** and dye **2**.

spectra were measured on a Shimadzu RF-5301PC Fluorescence spectrophotometer.

2.1. Materials

4-Dimethylaminobenzaldehyde, julolidine, 3-hydroxy-3-methyl-2-butanone and malononitrile were purchased from Aldrich. Thr 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-Cyanomrthylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran **1** was made by condensation of 3-hydroxy-3-methyl-2-butanone with malononitrile [20]. 9-Formyljulolidine **3** was synthesized according to the literature [21]. Dye **1**–**2** were prepared by the literature procedure [22–24].

2.2. Electrochemical measurement

The redox potentials were measured by cyclic voltammetry on an *VersaSTAT3* model. Cyclic voltammetry experiment was run in an acetonitrile solution containing tetrabutylammonium hexafluorophosphate electrolyte. The reference electrode, Ag/Ag^+ was directly immersed in the reaction cell. The working electrode was a glassy carbon. The counter electrode was a platinum wire. The scan rate was commonly 50 mV/s. HPLC grade acetonitrile was used as purchased and used in the electrochemical redox potential measurements of these dyes.

2.3. Synthesis of dye **1** and **2**

Dye **1** and **2** were prepared from the similar method described in previous work [22–24]. Structures were confirmed by the following.

2.3.1. Dye **1**

Yield 13% : mp 290–292 °C.

^1H NMR (DMSO-d_6, 400 MHz): δ 1.76 (s, 6H), 3.12 (s, 6H), 6.84 (d, $J = 9.08$ Hz, 2H), 6.91 (d, $J = 15.84$ Hz, 1H), 7.80 (d, $J = 9.01$ Hz, 2H), 7.95 (d, $J = 15.84$ Hz, 1H). EI-MS, $m/z = 330$ Anal. Calcd. for $C_{20}H_{18}N_4O$: C, 72.71; H, 5.49; N, 16.96. Found; C, 72.16; H, 5.57; N, 17.08%.

2.3.2. Dye **2**

Yield 24%: mp 238–240 °C.

^1H NMR (DMSO-d_6, 400 MHz): δ 1.71 (s, 6H), 1.88 (q, $J = 5.24$ Hz, 4H), 2.71 (t, $J = 6.00$ Hz, 4H), 3.40 (t, $J = 5.56$ Hz, 4H), 6.76 (d, $J = 15.48$ Hz, 2H), 7.39 (s, 2H), 7.86 (d, $J = 15.44$ Hz, 2H). EI-MS, $m/z = 382$. Anal. Calcd. for $C_{24}H_{22}N_4O$: C, 75.37; H, 5.80; N, 14.65. Found; C, 74.41; H, 5.92; N, 14.41%.

3. Results and discussion

3.1. Solvatofluorchromism

The synthesis of dye **1** and **2** is depicted in Fig. 1.

The target compound dye **1** (with dimethylaminobenzene) and dye **2**(with julolidine moiety) on the terminal phenyl ring of aminophenyl donor were successfully obtained by condensing aldehydes 4-dimethylaminobenzaldehyde **2** and 9-formyljulolidine **3** with a strong electron acceptor 2-cyanomrthylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran **1** in ethanol/chloroform (4:1 v/v). The chemical structures of all the intermediates and dyes were characterized by ^1H NMR, MS and elemental analysis. The $\lambda_{max,\ abs}$ and $\lambda_{max,em}$ values of the solvent-dependent absorption and fluorescent emission of dye **1** and **2** in various solvents and $E_T(30)$ values are listed in Table 1.

The results show that dye **1** and **2** exhibited strong solvatochromic properties. The absorption and emission spectra of dye **1** in several solvents having different polarities are shown in Fig. 2. As the solvent polarity is increased, a bathochromic shift is observed (i.e., positive solvatochromism), (Fig. 2a). The absorption maximum showed a shift with solvent polarity, which extended from 527 nm for xylene to 584 nm for ethanol. The fluorescence spectra also exhibited a solvent effect (Fig. 2b). The emission maximum showed shifts with solvent polarity, which extended from 597 nm for xylene (excited at 510 nm) to 647 nm for DMF (excited at 510 nm).

These photophysical properties of dye **1** show a close similarity to that observed for solvatochromic merocyanine dyes based on Barbituric acid and Meldrum's acid [15]. These features indicate

Table 1
$\lambda_{max,\ abs}$ and $\lambda_{max,\ em}$ values of dye **1** and **2** in various solvents and $E_T(30)$ values of solvents.

Solvent	dye **1**		dye **2**		$E_T(30)$ (kcal mol^{-1})
	λ_{max} (nm)	λ_{em}^a (nm)	λ_{max} (nm)	λ_{em}^a (nm)	
Xylene	527	597	593	632	33.1
Toluene	551	602	594	634	33.9
THF	558	630	606	655	37.4
Chloroform	576	614	617	650	39.1
Acetone	565	638	616	658	42.2
DMF	581	647	629	668	43.8
Acetonitrile	577	638	620	660	45.6
Ethanol	584	639	629	660	51.9

[a] Excited at 510 nm.

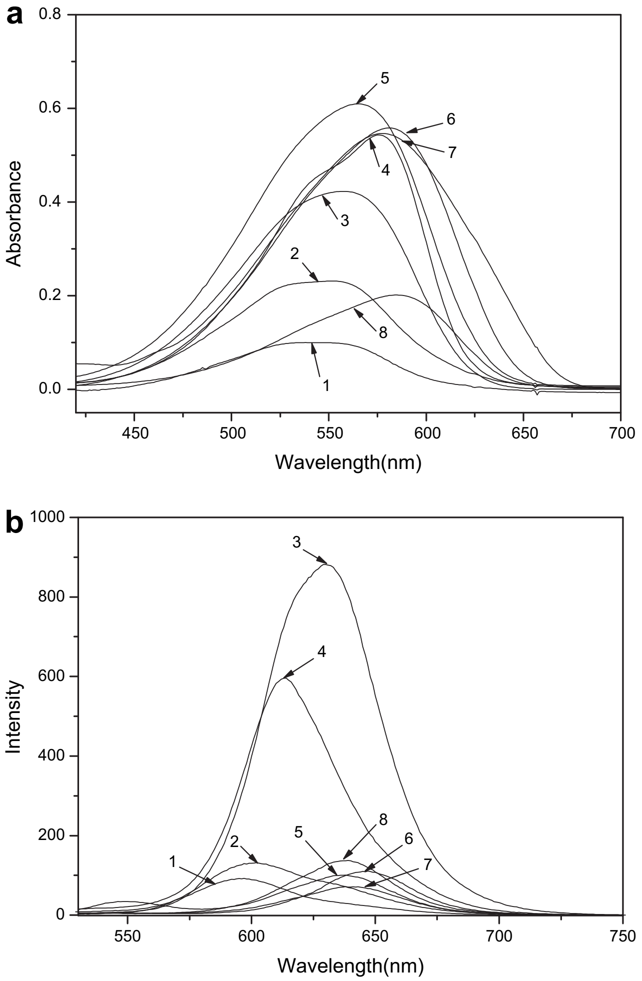

Fig. 2. The UV–vis absorption (a) and fluorescence emission spectra (b) of dye **1** (1×10^{-5} mol L^{-1}) in xylene (1), toluene (2), THF (3), $CHCl_3$ (4), acetone (5), DMF (6), acetonitrile (7), ethanol (8), respectively.

a strongly allowed π–π* transition with charge transfer characters. The intramolecular charge transfer (ICT) interaction, that is from aminobenzene moiety to the acceptor fragment is strongly enhanced upon excitation as evidence from the extreme bathochromic shift of the fluorescence maximum in polar solvents. The positive solvatochromism indicated that dye **1** has a large dipole moment in the excited state rather than in the ground state.

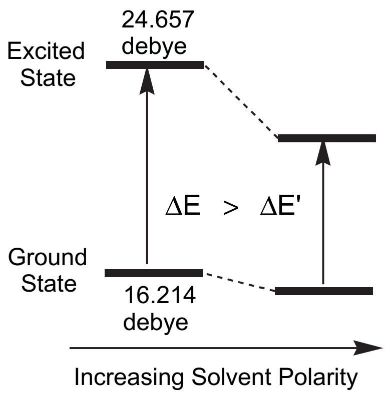

Fig. 3. Effect of solvent polarity on the transition energy of dye **1–2**.

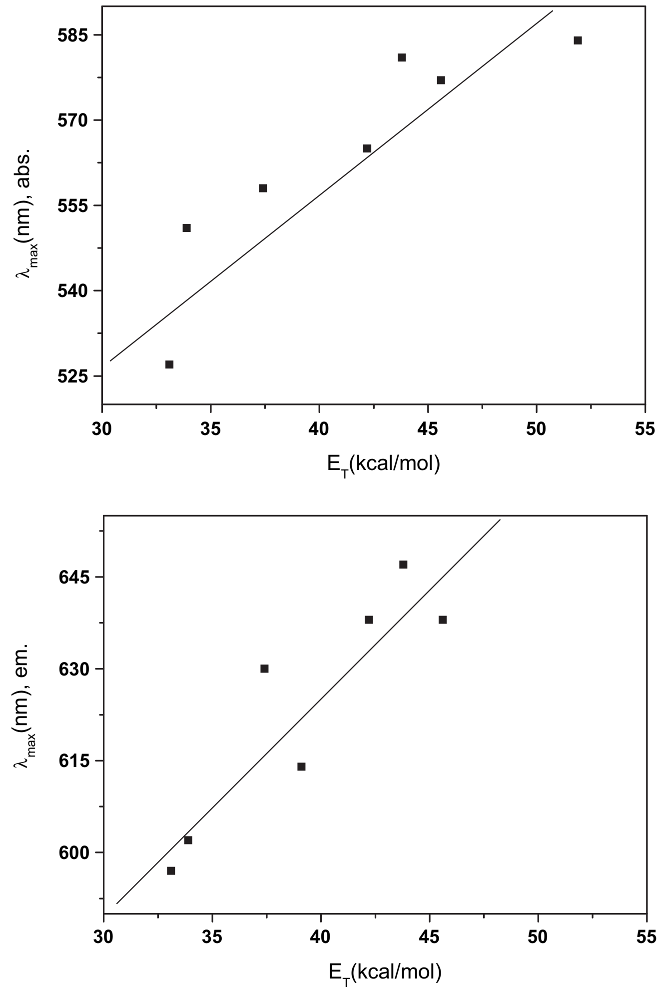

Fig. 4. Plot of absorption and emission maxima of dye 1 of a function of solvent polarity parameter E_T.

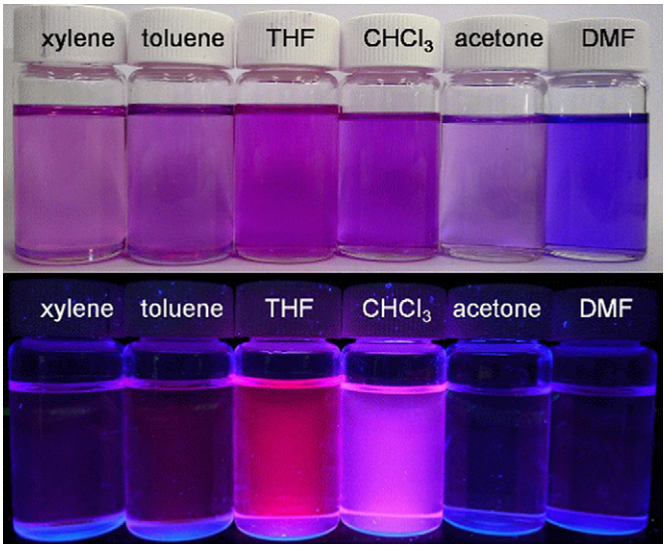

Fig. 5. The UV–vis absorption and fluorescence emission photographs of dye **1** in several solvents.

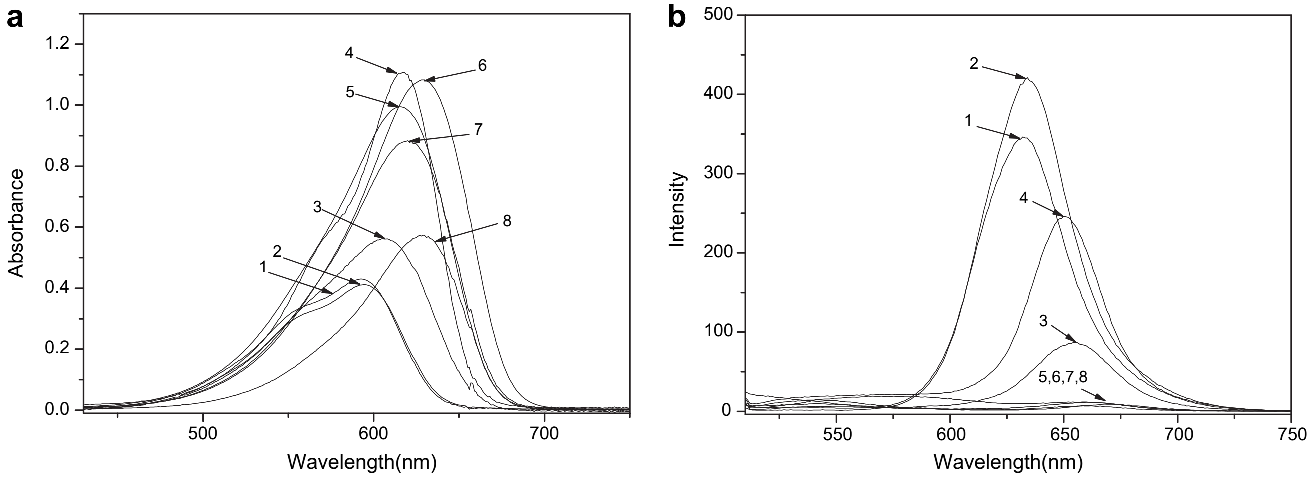

Fig. 6. The UV–vis absorption (a) and fluorescence emission spectra (b) of dye **2** (1×10^{-5} mol L^{-1}) in xylene (1), toluene (2), THF (3), $CHCl_3$ (4), acetone (5), DMF (6), acetonitrile (7), ethanol (8), respectively.

Pariser-Parr Pople(PPP)-calculated dipole moment (μ, Debye) in the ground state and first excited singlet states of dye **1** are presented in Fig. 3.

The dependence of the absorption and emission maximum of dye **1** on $E_T(30)$ solvent polarity parameter can be fitted to almost linear function (Fig. 4). As the solvent polarity increased, a bathochromic shift observed (i.e., positive solvatochromism).

Fig. 5 shows the UV–Vis absorption and fluorescence emission photographs of dye **1** in various solvents, dye **1**, in several solvents with different colours and fluorescent emission, can be easily observed by the naked eyes.

We also investigated solvatochromic properties of dye **2** in various solvents. Fig. 6 shows the absorption and emission spectra of dye **2** in a similar range of solvents. Dye **2** shows one solvent-dependent absorption band in the visible (around 590–630 nm), with a bathochromic shift of 40 nm, when going from xylene to ethanol (Fig. 6a). Dye **2** also exhibited a large red shift in emission spectra as solvent polarity increases. (Fig. 6b)

Fig. 7 shows that there is a fairly good relationship between $\lambda_{\max,\ \mathrm{abs}}$, $\lambda_{\max,\ \mathrm{em}}$ and the solvent polarity parameter $E_T(30)$.

Fig. 8 shows the UV–Vis absorption and fluorescence emission photographs of dye **2** in several solvents (Fig. 9).

3.2. Theoretical calculation and electrochemical properties of dye 1–2

For the interpretation of the intramolecular charge transfer process of dye **1** and **2**, the quantum chemical $DMol^3$ approach was used. All the theoretical calculations were performed by $DMol^3$ program in the Materials Studio 4.4 package [25,26] which is the quantum mechanical code using density functional theory. Perdew-Burke-Ernzerhof (PBE) function of generalized gradient approximation (GGA) level [27] with double numeric polarization basis set was used to calculate the energy level of the frontier molecular orbital. Fig. 9 shows the electron distribution of the HOMO and LUMO energy level of dye **1** and **2**.

Comparison of the electron distribution in the frontier MOs reveals that the HOMO-LUMO excitation moves the electron distribution from aminobenzene moiety to the acceptor, which showed a strong migration of ICT character of dye **1** and **2**.

The electrochemical reduction/oxidation behaviors of these dyes were determined by cyclic voltammetry (CV) in dry CH_3CN. Using this measurement [28], the potentials of the highest oxidation peak and the lowest reduction peak can be used to calculate

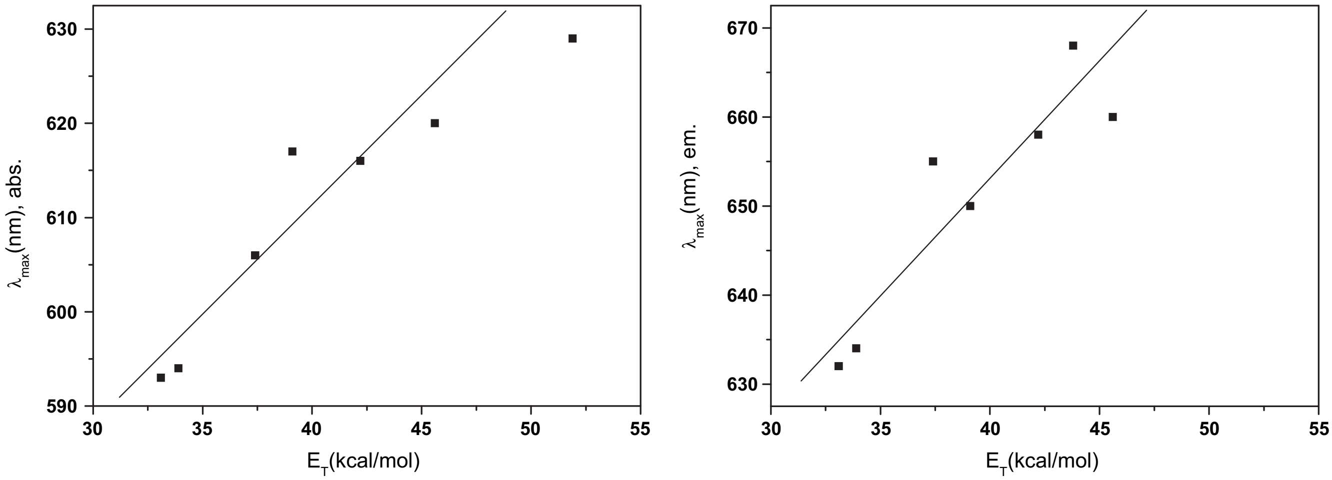

Fig. 7. Plot of absorption and emission maxima of dye **2** of a function of solvent polarity parameter E_T.

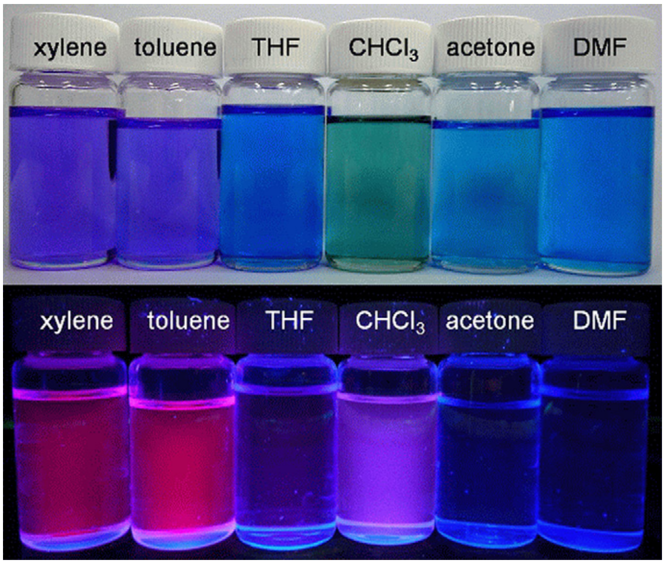

Fig. 8. The UV–vis absorption and fluorescence emission photographs of dye **2** in several solvents.

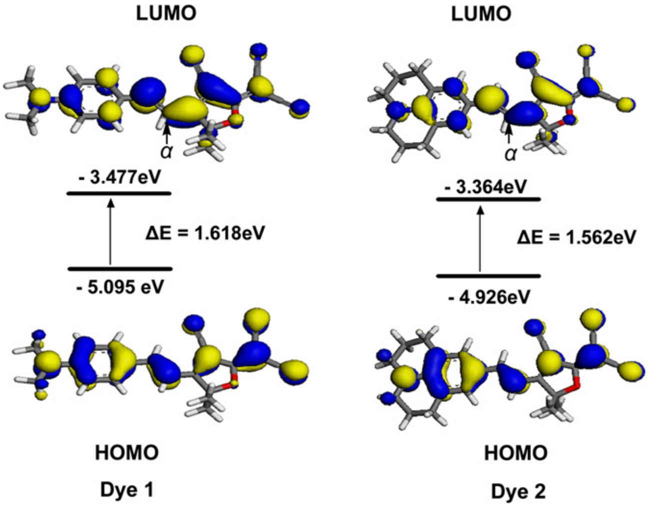

Fig. 9. Electron distribution of the HOMO and LUMO energy levels of dye **1** and **2**.

the HOMO/LUMO energy levels. The following equation (1) can be used at this determination.

$$\text{HOMO(orLUMO)} \times (\text{eV}) = -4.8 - [E_{\text{oxidationorreductionpeak}} - E_{1/2}(\text{Ferrocene})] \quad (1)$$

The electronic states (HOMO/LUMO) of dye **1** and dye **2** were investigated by cyclic voltammetry (CV). As shown in Fig. 10, both of the dyes; **1** and **2** exhibited oxidation and reduction peaks. The estimated electron affinity (LUMO level) values for dye **1** and dye **2** were −3.78 eV and −4.03 eV, respectively. The ionization potential (HOMO level) of dye **1** and dye **2** were −5.78 eV and −4.79 eV, respectively. As the first visible absorption of dye **1** and dye **2** caused by the intramolecular charge transfer character of the transition, the introduction of julolidine moiety to the D–π–A system produced a bathochromic shift of 60 nm. Electrochemical results were in agreement with observed values and theoretical calculation.

3.3. pH-induced switching in electronic absorption and fluorescence spectra

The interaction of the dye **1** and **2** with acid (CF_3COOH)/base ($(Bu)_4N(OH)$) was investigated in DMSO solution through spectrophotometric titration experiments. Fig. 11 showed the UV–Vis absorption and fluorescence spectral changes of dye **1** and **2** in DMSO solution with acid/base.

Upon addition of acid and base to the dye **1** solution, the band at 600 nm progressively decreases. Addition of base results in an obviously decreased absorbance at 600 nm, while acid induce much smaller. The color changed from red to colorless. Fluorescence spectra (Fig. 11b) also showed a similar result, which is consistent with that of UV–Vis spectra. On the other hand, no changes were observed in the absorption and fluorescence spectra of dye **2** upon addition of acid. While upon addition of base to the solution of dye **2**, absorption and fluorescence intensity decreased drastically. Upon addition of acid or base, the colorless solution of dye **1** and **2** became gradually red and recovered completely back to the initial state. We propose that these spectral changes, with proton in dye **1**, are due to the interaction of the proton and the electrons of nitrogen atom of the alkylamino moiety. As a result, the protonation reduces the electron density in the nitrogen atom, thus the ICT process is not possible any more and absorption and emission intensity decreased. The addition of OH^- to dye **1** and **2** could conceivably lead to carbanion adducts. Actually, the α-carbon

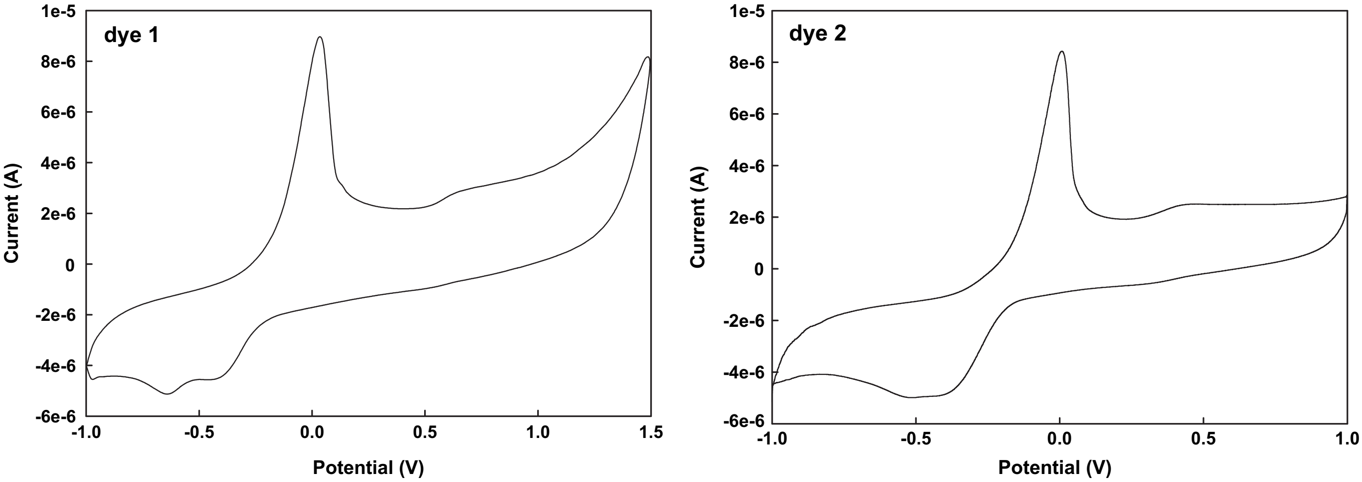

Fig. 10. Cyclic voltammetry (CV) of dye **1** and **2** in CH_3CN solution: scan rate = 50 mV/s.

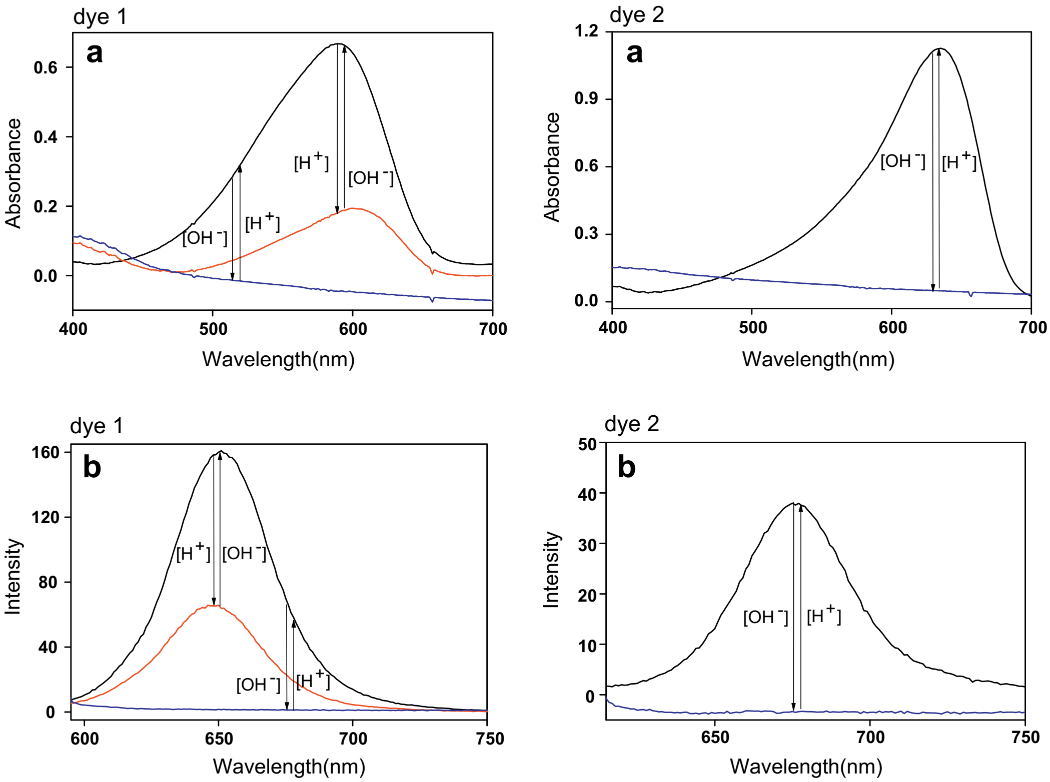

Fig. 11. The UV–Vis absorption (a) and fluorescence spectral switching (b) of dye **1** and **2** in DMSO solution with protonation/deprotonation.

which has lower electron density in LUMO can interact with OH^- as a nucleophile (LUMO of dye **1** and **2** in Fig. 9).

4. Conclusions

Owing to the presence of a julolidine moiety as a strong donor, dye **2** exhibited ~60 nm red-shifted absorption compared to that of dye **1**. As both dyes exhibited positive solvatofluorchromic properties in various solvents, the solvatochromic behavior of the dyes offers application in volatile organic compound (VOCs) detection. The HOMO and LUMO values obtained using theoretical calculations were in agreement with those secured from electrochemical measurement. pH-Induced molecular switching was demonstrated by modulation of intramolecular charge transfer via protonation/deprotonation.

Acknowledgements

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