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Synthesis and Optical Chromic Properties of New Barbituric Acid based Dye Molecules Having Push- π -Pull System

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Since the molecular structures based on donor- π -acceptor dye shows good optical absorption and emission properties by push-pull chromophore system, donor- π -acceptor dyes have been intensively studied as functional key materials. In this study, the new donor- π acceptor dyes were designed, synthesized and characterized. The absorption and fluorescence emission spectra of these dyes, being related with chromic color changes, were determined with the several solvents of widely different polarities. The electron energy states of dyes were also characterized by theoretical calculations.

Keywords donor- π -acceptor; chromic properties; HOMO/LUMO; energy transfer; push- π -pull; electron energy

Introduction

Recently, considerable efforts have been focused on the study of donor- π -acceptor dye system. Donor- π -acceptor dyes have attracted great attentions in opto-electronic applications [1–3]. The power conversion efficiency, photo-stability and absorption/emission properties are greatly influenced by donor- π -acceptor dye structural system. In order to obtain higher opto-chromic efficiency of organic dye materials, the design of dye molecular structures such as strong donor and acceptor substituent, is very of importance in the area of dye synthesis and chemistry. If the π -conjugated chromophores contain strong terminal donor and acceptor groups, it is more effective for elucidating the enhancement of absorption and emission intensity.

In this context, barbituric acid has been greatly enjoyed as a useful fragment in donor-acceptor dye structural system, because barbiturate group has been considered as strong electron-withdrawing moiety. Furthermore, the conjugation system within the barbituric acid is also effective between carbonyl groups and nitrogen atoms [4–5]. As a donor unit, triphenylamine and carbazole moieties are widely considered to be electron rich groups [6–7] and selected in this experimental work.

In this study, we have also designed and synthesized new chromic dye materials, having donor- π -acceptor system. Barbituric acid is used as a strong electron-withdrawing

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group, and triphenylamine and carbazole moiety are considered as strong electron-donating groups. The corresponding absorption and fluorescence emission behaviors with chromic effects were determined with several solvent media having different polarities.

Experimental

Analysis and Measurement

^1H -NMR spectra were recorded on an NMR spectrometer JEOL-AL400 operating at 400 MHz. Chemical shifts were referenced to internal Me_4Si (TMS). The absorption and fluorescence spectra were measured with an Agilent 8453 spectrophotometer and a Shimadzu RF-5301PC fluorescence spectrophotometer, respectively. The elemental analyses were measured on a Thermo Fisher Scientific-Flash EA 1112 Automatic elemental analyzer. Electron distributions and energy potentials were calculated with *Material Studio 4.3*. Cyclic voltammograms were examined with a *Versa STAT3* using three-electrode conventional electro chemical cell. Cyclic voltammetry test was conducted in an CH_2Cl_2 solution containing tetrabutylammonium hexafluorophosphate electrolyte. The working electrode was a glassy carbon. The counter electrode was a platinum wire. The scan rate was commonly 100 mV/s.

Synthesis

Aldehyde intermediates such as 4-(diphenylamino) benzaldehyde (**2**) and 4-(9H-carbazol-9-yl) benzaldehyde (**3**) were synthesized according to previously described method [8–11]. The synthetic procedure of dye **1** and **2** is illustrated in Figure 1.

Dye 1

A mixture of barbituric acid (**1**) (0.31 g, 0.002 mol) and 4-(diphenylamino)-benzaldehyde (**2**) (0.54 g, 0.002 mol) in acetic anhydride (5 ml) was refluxed for 3 h. The reaction was cooled to room temperature and the solid particles were filtered. The product was then purified by recrystallization with acetic acid to give 0.48g with 59% yield. ^1H NMR (CDCl_3) : 8.43 (s, 1H); 8.24–8.22 (d, 2H); 7.38–7.34 (t, 4H); 7.29–7.19 (d, 6H); 6.95–6.92 (t, 2H); 3.40 (s, 6H). MS m/z : 411 (M^+). Anal. Calcd. For $\text{C}_{25}\text{H}_{21}\text{N}_3\text{O}_3$: C, 72.98; H, 5.14; N, 10.21; Found: C, 73.06; H, 4.65; N, 10.06.

Dye 2

A mixture of barbituric acid (**1**) (0.31 g, 0.002 mol) and 4-(9H-carbazol-9-yl)benzaldehyde (**3**) (0.54 g, 0.002 mol) in acetic anhydride (15 ml) was refluxed for 3h. The reaction was cooled to room temperature and the solid particles were filtered. The product was then purified by recrystallization with acetic acid to give 0.46 g with 57% yield. ^1H NMR (CDCl_3) : 8.64 (s, 1H); 8.42–8.39 (d, 2H); 8.15–8.13 (d, 2H); 7.75–7.73 (d, 2H); 7.58–7.56 (t, 2H); 7.45–7.44 (t, 2H); 7.34–7.26 (t, 2H); 3.42 (s, 6H). MS m/z : 409 (M^+). Anal. Calcd. For $\text{C}_{25}\text{H}_{19}\text{N}_3\text{O}_3$: C, 73.34; H, 4.68; N, 10.26; Found: C, 72.84; H, 4.64; N, 9.90.

Results and Discussion

The synthetic procedure of dye **1** and **2** is illustrated in Figure 1. Optical chromic properties of the donor- π -acceptor dyes were prepared, using strong electron-withdrawing unit (**1**) and strong electron-donating units (**2**, **3**).

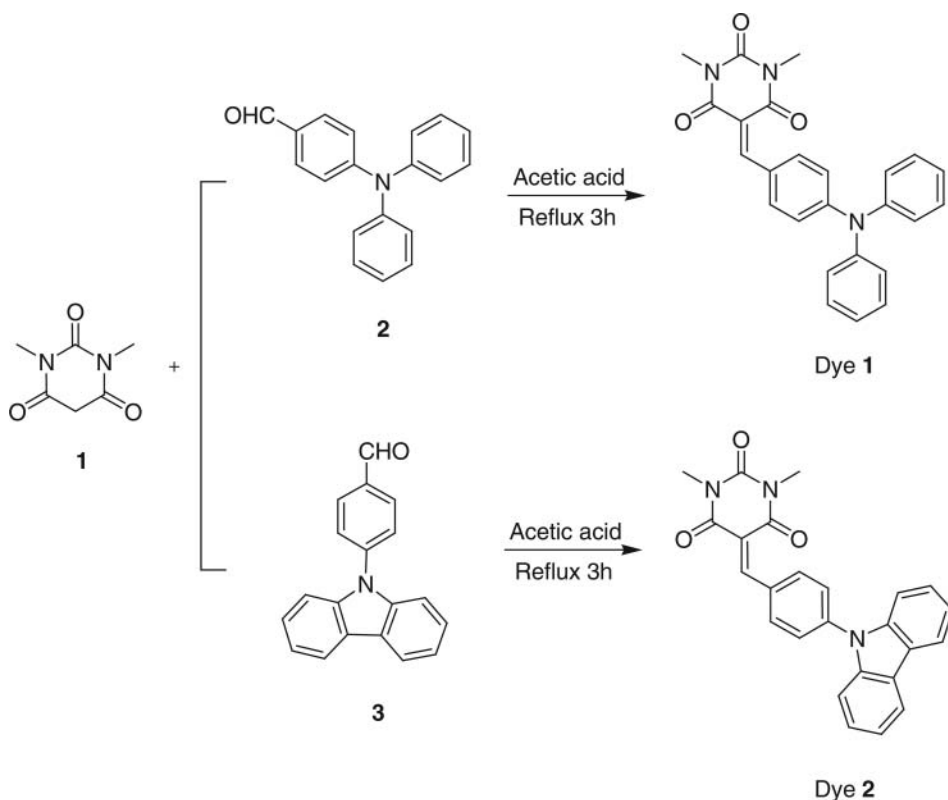


Figure 1. Synthetic routes of the dye 1 and 2.

The $\lambda_{\max, \text{abs}}$ and $\lambda_{\max, \text{em}}$ values of dye 1 and 2 in various solvents and $E_T(30)$ values are listed in Table 1. $E_T(30)$ is an empirical parameter of solvent polarity. Namely, the transition energy for pyridinium-*N*-phenoxide betain dye, expressed in kcal mol^{-1} , is used as a polarity parameter. It is possible to determine the chromic effects using nearly 362 different solvents [12–13].

Absorption spectra in various solvents with dye 1 and 2 are shown in Figure 2. All synthesized donor- π -acceptor dyes showed good solubility with CCl_4 , toluene, CH_2Cl_2 ,

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

Solvent	Dye 1		Dye 2		$E_T(30)$ (kcal mol^{-1})
	λ_{\max}	λ_{em}	λ_{\max}	λ_{em}	
CCl_4	466	540	430	485	32.4
Toluene	463	557	428	509	33.9
THF	458	575	413	559	37.4
EA	457	570	411	559	38.1
CH_2Cl_2	471	579	426	569	40.7
1,2-dichloroethane	469	579	423	569	41.3

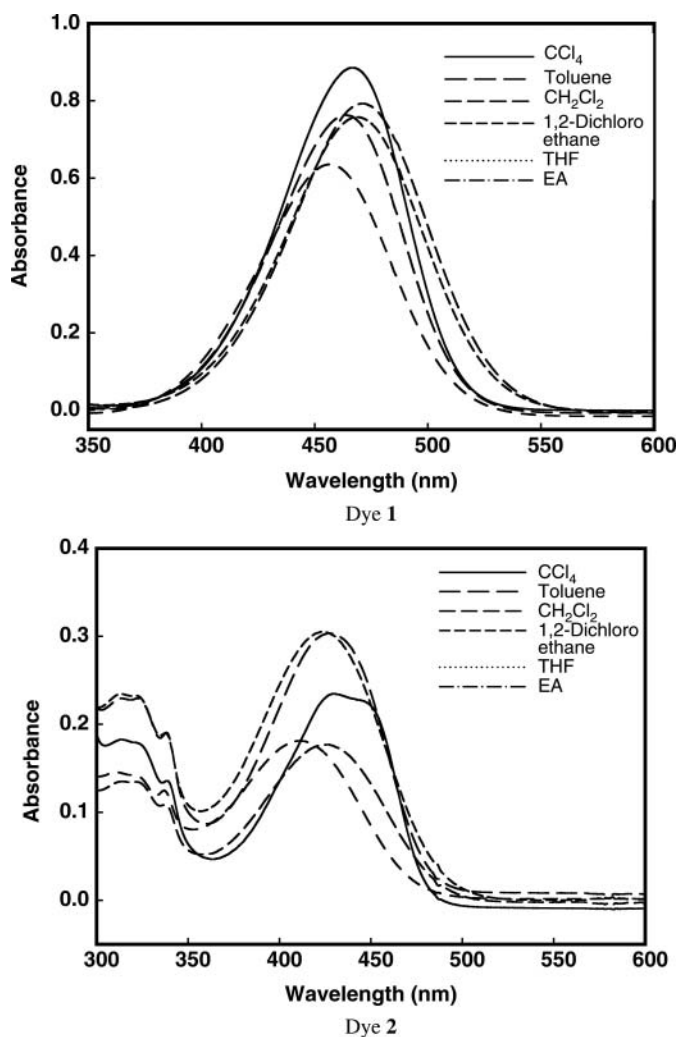
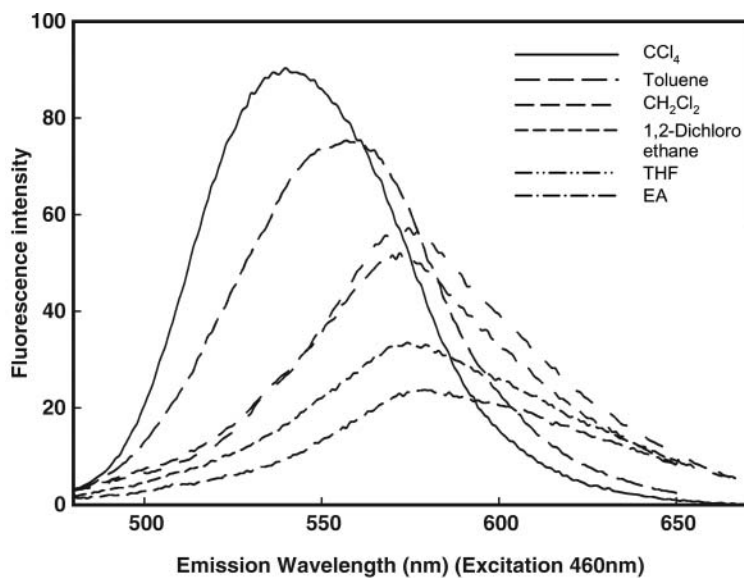


Figure 2. Absorption spectra of dye **1** and **2**.

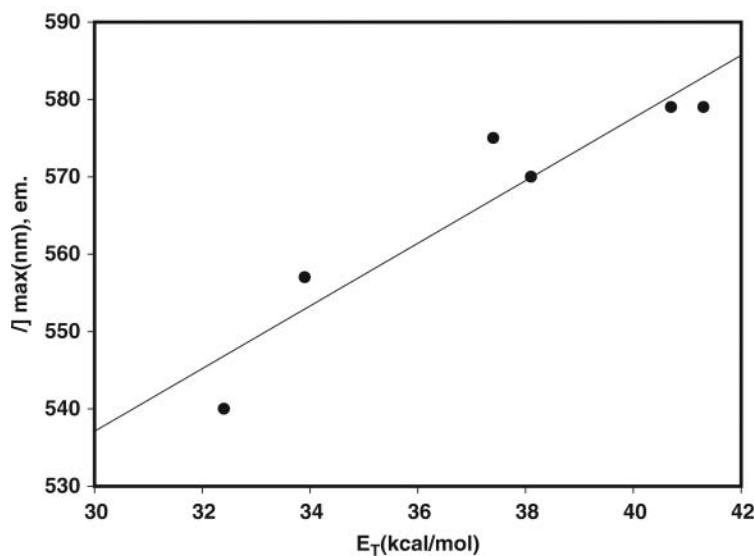
1,2-dichloroethane, ethyl acetate and THF. None of any noticeable effect on absorption has been monitored in various solvent polarities, being shifted within the range of 15 nm.

The fluorescence spectra and emission maximum of dye **1** on $E_T(30)$ solvent polarity parameters are shown in Figure 3. The dependence of emission maximum of dye **1** on $E_T(30)$ solvent polarity parameters was exhibited to almost linear function. From dye **1**, this result indicates the positive fluorescence solvatochromism with increasing solvent polarity. We also investigated fluorescence solvatochromic properties of dye **2** in similar method with dye **1**. From the findings of dye **2**, very similar fluorescence solvatochromic effects were observed as indicated in dye **1** (Figure 4). All prepared donor- π -acceptor dyes can be proposed to show the positive fluorescence solvatochromism with the increasing solvent polarity.

The corresponding results of fluorescence solvatochromism are reflected by large bathochromic shift of their fluorescence emission maxima with increasing solvent polarity.



(a)

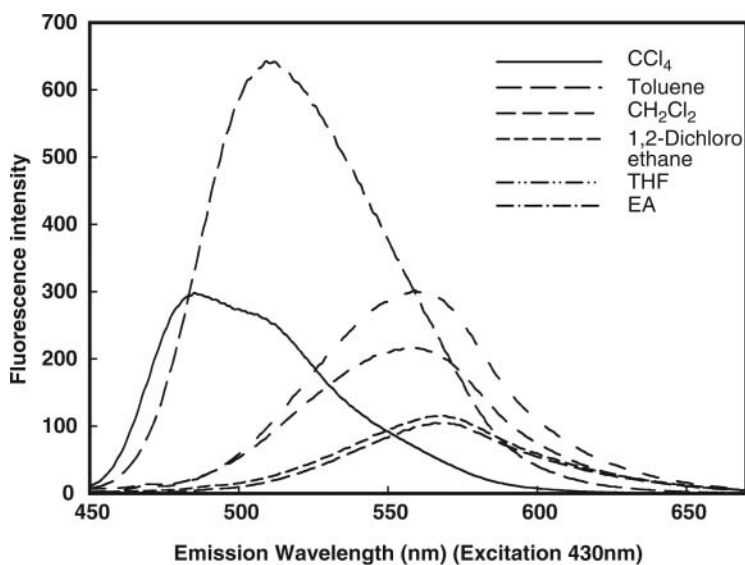


(b)

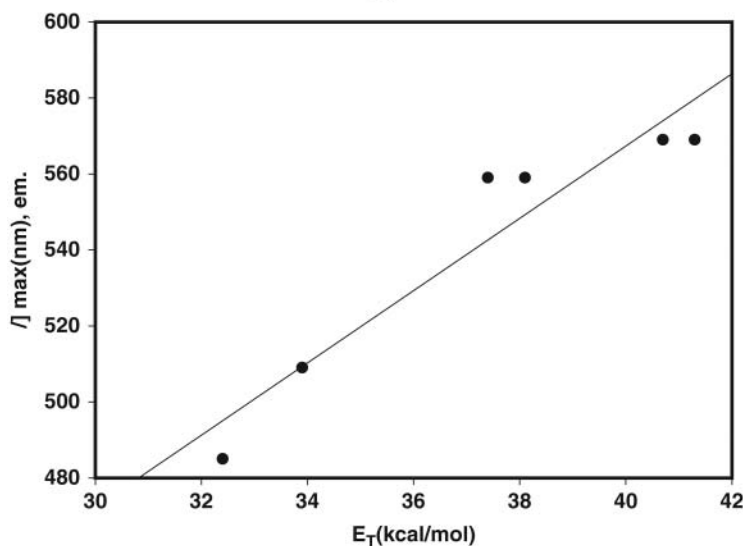
Dye 1

Figure 3. Fluorescence emission spectra of dye **1** in various solvents (a) and plot of emission maxima of dye **1** versus solvent polarity parameter $E_T(30)$ (b).

From results of Figure 3 and Figure 4, it is proposed that all dyes showed the positive fluorescence solvatochromism effect, being stable emitting state in polar solvent media. In particular, dye **2** showed higher intensity of emission in non-polar solvent such as CCl_4 and toluene. However, the emission intensity of dye **1** and **2** decreased with increasing solvent polarity, because the fluorescence quenching behavior of some aromatic hydrocarbons can be occurred when they have radical ion formation with solvent polarity [14–15].



(a)



(b)

Dye 2

Figure 4. Fluorescence emission spectra of dye **2** in various solvents (a) and plot of emission maxima of dye **2** versus solvent polarity parameter $E_T(30)$ (b).

To gain further insight into the geometrical shape and HOMO/LUMO energy levels of dye **1** and **2**, the geometrical structure and molecular orbital calculations were performed using a Material Studio 4.3 suite. All the theoretical calculation was based on DMol³ program. Figure 5 shows the electron distributions and the HOMO/LUMO energy level of dye **1** and **2**. A strong migration of intramolecular charge transfer (ICT) for all dyes is observed from donor units (triphenylamine and carbazole moieties) to acceptor unit (barbituric acid).

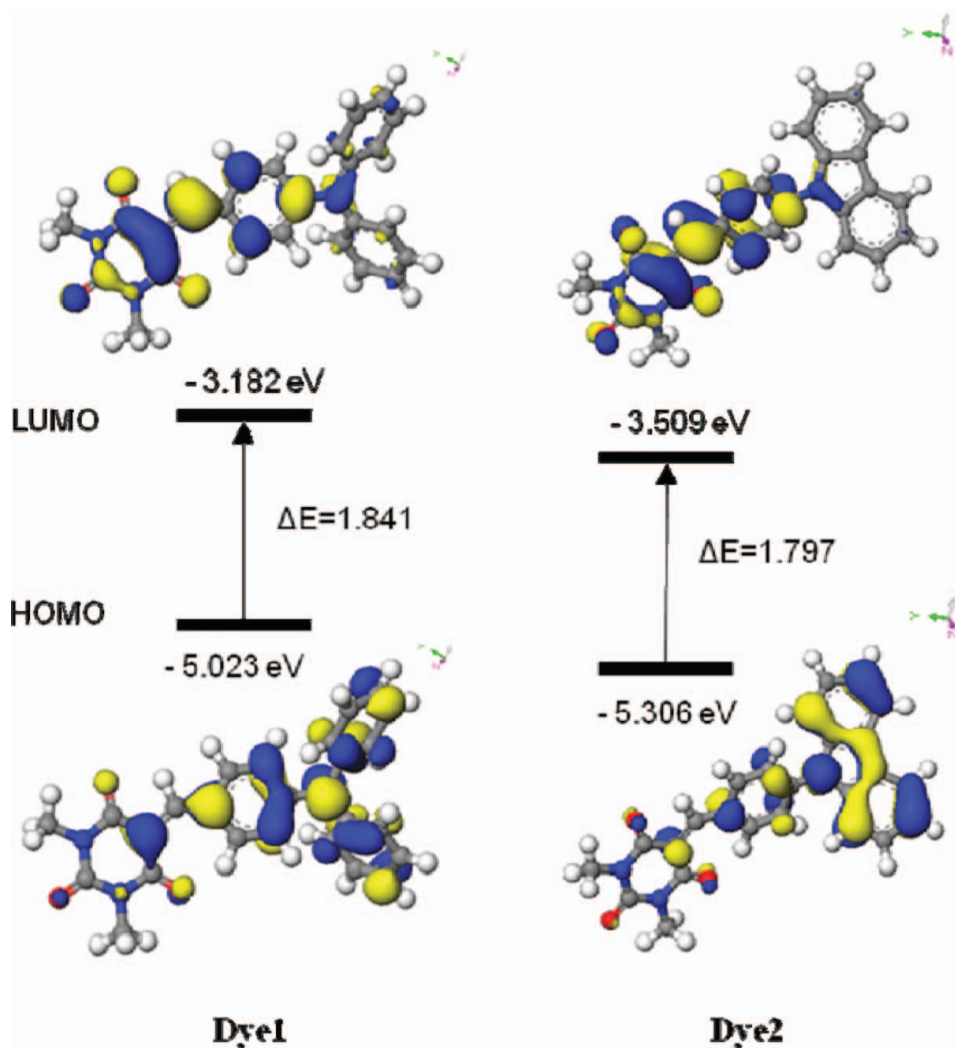


Figure 5. Electron distributions and HOMO/LUMO energy levels of dye **1** and **2**.

From the findings, the fluorescence emission intensity of dye **1** showed weak values in various solvents with compared to dye **2**. It can be explained that due to geometrically twisted molecular shape of dye **1**, the intramolecular repulsion effect increased and loss of π -conjugation and fluorescence intensity then occurred. Thus, the carbazole donor compound of dye **2** is more effective than triphenylamine donor compound of dye **1**. Fluorescence emission images of dye **1** and **2** in various solvents were shown in Figure 6. Especially, dye **2** showed evident fluorescence solvatochromic effects, which are well agreed with the previous finding and explanation.

Further electrochemical properties were calculated with cyclicvoltammetry (CV) measurement. Using CV measurement, we found the oxidation peak at 0.85 V(onset, dye **1**) and 0.87 V(peak, dye **2**). The resulting cyclicvoltammogram was summarized in Figure 7.

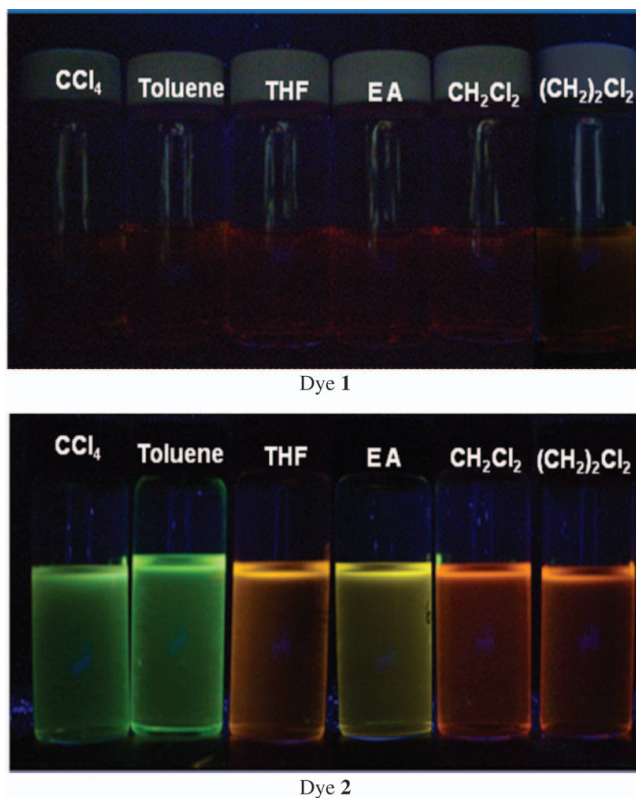


Figure 6. The Fluorescence emission photographs of dye **1** and **2** in several solvents.

In addition, the energy potentials of oxidation onset peak and absorption band gap were used to calculate empirical HOMO/LUMO energy levels. The following equation was used [16].

$$\text{HOMO (or LUMO) (eV)} = -4.8 - (E_{\text{peak or onset}} - E_{1/2}(\text{Ferrocene}))$$

The HOMO and LUMO levels were calculated to be -5.23 eV and -3.06 eV respectively for dye **1**, and -5.25 eV and -2.72 eV respectively for dye **2**. The HOMO/LUMO values that are computationally calculated and Determined with cyclic voltammograms of dye **1** and **2** are listed in Table 2. The potential energy levels of dye **1** and **2** showed the similar

Table 2. HOMO/LUMO values of dye **1** and **2**

Dye	Computationally calculated			Determined with cyclic voltammograms		
	HOMO	LUMO	ΔE	HOMO	LUMO	ΔE
1	-5.023	-3.182	1.84	-5.23	-2.92	2.31
2	-5.306	-3.509	1.79	-5.25	-2.72	2.53

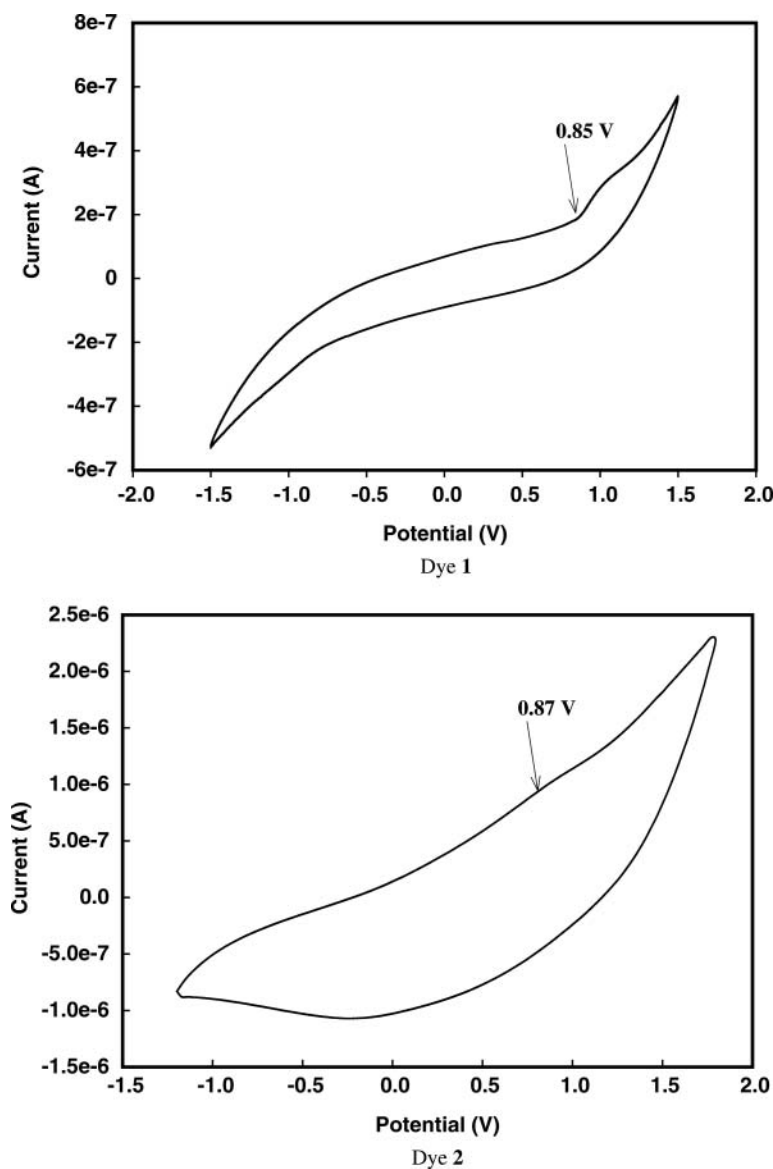


Figure 7. Cyclic voltammograms of dye **1** and **2** measured in CH_2Cl_2 .

characteristic patterns from the values of computational calculation and electrochemical measurement.

Conclusions

In this study, we have synthesized new D- π -A type dyes based on barbituric acid as an acceptor unit and triphenylamine and carboazole as donor units. Dye **1** and **2** indicated the positive fluorescence solvatochromism with increasing solvent polarity. However the fluorescence emission intensity of dye **1** showed weak values in various solvents with

compared to dye **2**. It can be explained that due to geometrically twisted molecular shape, the intramolecular repulsion effect increased and loss of π -conjugation and fluorescence intensity then occurred. The Dye **2** in several solvents with different colors and fluorescent emission can be easily observed by the naked eyes.

Acknowledgment

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