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New solvatochromic merocyanine dyes based on Barbituric acid and Meldrum's acid

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ABSTRACT

Two new types of solvatochromic merocyanine dyes derived from either Meldrum's acid or Barbituric acid have been synthesized by the condensation of 4-((2-hydro xyethyl)(methyl)amino) benzaldehyde with 5-(2,6-dimethyl-4*H*-pyran-4-ylidene) Meldrum's acid and 5-(2,6-dimethyl-4*H*-pyran-4-ylidene) Barbituric acid, respectively. The solvatochromic responses of the merocyanine dyes in 22 solvents of widely different polarities were measured; positive solvatochromism, with a large absorption bathochromic shift, was observed on moving from xylene to DMSO, corresponding to their maximum fluorescence emission with a large bathochromic shift. The dyes have the potential for the development of efficient probes for the detection of volatile organic compounds.

1. Introduction

Solvatochromic dyes attract much attention because of their application suitable as probes for the determination of solvent polarity and potential applications for colorimetric sensor arrays for volatile organic compounds (VOC) [1,2]. Solvatochromism can be defined as the phenomenon whereby a compound changes color, either by a change in the absorption or emission spectra of the molecule, when dissolved in different solvents [3,4]. Recently, solvatochromic dyes such as pyridinim betaine [5], 2′,2-bithiophene [6], stilbazolium [7], and better known as Brooker's merocyanine have been synthesized and studied [8,9]. Among these solvatochromic dye molecules, merocyanine dyes have attracted increasing attention because of their potential application in a number of areas (i.e., as photographic sensitizers, for nonlinear optics, and in chemotherapy) [10–15]. Merocyanine dyes are heterocyclic chromophores that seem especially promising candidates as solvatochromic dyes owing to their electronic structure. The ground-state electronic structure of merocyanine dyes having a push–pull system which can be described in terms of a two-state valence-bond model. This model assumes resonance between neutral and zwitterionic molecular structures and provides a useful qualitative interpretation of their solvatochromism and bond-length alternation phenomena [16]. In general, condensation reaction of *N*,*N*-dimethylamino benzaldehyde derivatives with Meldrum's acid and Barbituric acid or their derivatives lead to the formation of merocyanine dyes with interesting spectroscopic properties. So, the Meldrum's acid and Barbituric acid can be envisaged as a potentially useful fragment in the design of solvatochromic merocyanine dyes [17,18]. In the present report, we designed and synthesized two new solvatochromic merocyanine dye analogous by condensation of 4-((2-hydro xyethyl)(methyl)amino) benzaldehyde with 5-(2,6-dimethyl-4*H*-pyran-4-ylidene) Meldrum's acid and 5-(2,6-dimethyl-4*H*-pyran-4-ylidene) Barbituric acid as shown in Scheme 1. We investigated their UV–vis absorption and fluorescent emission spectroscopic behaviors in 22 different solvents. The comparison of their solvatochromic behavior revealed some interesting color differences between these systems in various solvents. They have potential application for the development of efficient sensors for the detection of volatile organic compounds (VOCs) [19].

2. Experimental

Melting points were determined using an Electrothermal IA 900 apparatus and were uncorrected. Elemental analyses were recorded on a Carlo Elba Model 1106 analyzer. Mass spectra were recorded on a JMS-700 High resolution mass spectrometer using an FAB ion source. ^{1}H NMR spectra were recorded in $CDCl_3$ using a Varian Inova 400 MHz FT-NMR Spectrometer using TMS as

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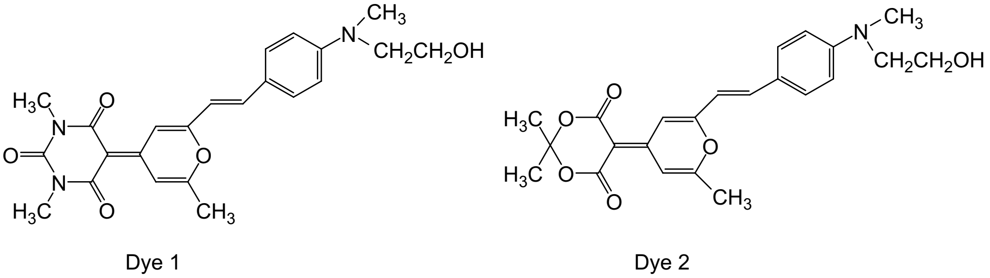


Scheme 1. Structures of the solvatochromic merocyanine dyes based on Barbituric acid (Dye **1**) and Meldrum's acid (Dye **2**).

internal standard. The UV–vis spectra and transmittance were obtained on an Agilent 8457 UV–vis spectrophotometer. Fluorescence spectra were measured on a SHMADZU RF-5301PC Fluorescence spectrophotometer.

2.1. Materials

1,3-Dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione, 2,2-dimethyl-1,3-dioxane-4,6-dione and 4-((2-hydroxyethyl)(methyl)amino) benzaldehyde 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. Compound **5** was synthesized according to the literature method [20,21].

2.2. Synthesis of the 5-(2,6-dimethyl-4H-pyran-4-ylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (4)

A mixture of 2,6-dimethyl-4*H*-pyran-4-one **1** (1.24 g, 0.01 mol) and 1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione **2** (1.56 g, 0.01 mol) in acetic anhydride (15 ml) was gently refluxed for 2 h. After cooling, the precipitated product was filtered and recrystallized in methanol to give 2.25 g yellow powder with 80% yield.

M.p. 264 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 6.67 (s, 2H, pyran-H), 3.30 (s, 6H, NCH_3), 1.56 (s, 6H, CH_3), EI-MS, $m/z = 262$ Elemental analysis: C, 59.49; H, 5.30; N, 10.59%. $C_{13}H_{14}N_2O_4$ requires: C, 59.54; H, 5.38; N, 10.68%.

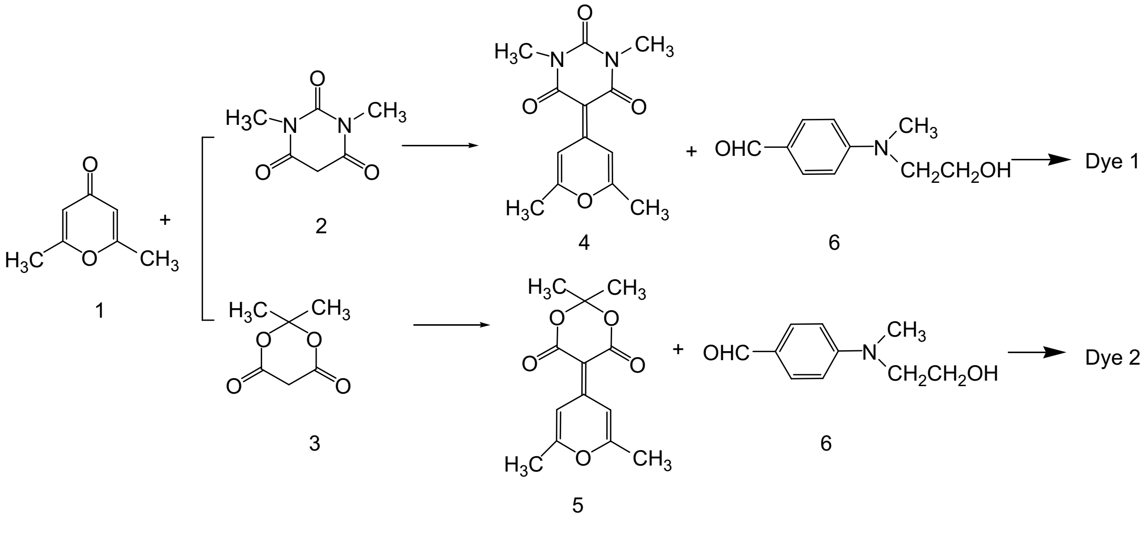
2.3. Synthesis of 5-(2,6-dimethyl-4H-pyran-4-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (5)

A mixture of 2,6-dimethyl-4*H*-pyran-4-one **1** (1.24 g, 0.01 mol) and 3,5-dimethyl-1,3,5-oxadiazinane-2,4,6-trione **3** (1.44 g, 0.01 mol) in acetic anhydride (10 ml) was gently refluxed for 2.5 h under nitrogen atmosphere. After cooling, the precipitated product was filtered and recrystallized in acetic acid to give 1.5 g straw yellow powder with a 55.9% yield.

M.p. 219–226 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 6.68 (s, 2H, pyran-H), 2.23 (s, 6H, $-NCH_3$), 1.58 (s, 6H, CH_3), EI-MS, $m/z = 250$. Elemental analysis: C, 62.20; H; 5.50%. $C_{13}H_{14}O_5$ requires: C, 62.39; H, 5.64%.

2.4. Synthesis of 5-(2-(4-((2-hydroxyethyl)(methyl)amino) styryl)-6-methyl-4H-pyran-4-ylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (dye 1)

A solution of 5-(2,6-dimethyl-4*H*-pyran-4-ylidene)-1,3-dimethylpyrimidine-2,4,6 (1*H*, 3*H*,5*H*)-trione **4** (5 mmol, 1.31 g), 4-((2-hydroxyethyl)(methyl)amino)benzaldehyde **6** (5 mmol, 0.88 g) and piperidine(0.45 ml) in acetonitrile (30 ml) was heated under reflux for 8 h using a Dean–Stark trap. The reaction solution was cooled to room temperature, and the solid crude product was isolated and dried. Then the crude product was purified by column chromatography (silica) using the mixture of chloroform and methanol (v/v = 50:1) as an eluent, followed by further recrystallization from ethanol to obtain the purified black red powder with a 35% yield.



Scheme 2. Synthetic routes of the Dye **1** and Dye **2**.

Table 1
λ_{max} and λ_{em} values of dyes **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} (nm)	$\Delta\nu^a$ (cm^{-1})	λ_{max} (nm)	λ_{em} (nm)	$\Delta\nu^a$ (cm^{-1})	
Xylene	495	584	3079	480	565	3134	33.1
Toluene	498	592	3188	481	569	3215	33.9
Benzene	497	598	3398	483	565	3005	34.3
1,2-Dichlorobenzene	506	646	4283	496	592	3211	38.0
Chloroform	501	644	4432	505	592	2910	39.1
Dichloromethane	500	651	4639	496	600	3495	40.7
1,2-Dichloroethane	502	652	4583	500	601	3361	41.3
Trichloroethylene	498	609	3660	511	527	594	35.9
Ethyl acetate	497	645	4617	492	594	3490	38.1
Acetone	501	648	4528	496	632	4339	42.2
Ethanol	508	654	4395	517	645	3838	51.9
Methanol	502	656	4676	510	649	4200	55.4
Propanol	506	653	4449	521	645	3690	50.7
n-Butanol	508	653	4371	528	645	3436	47.1
THF	503	647	4394	496	599	3467	37.4
DMF	510	657	4387	508	642	4109	43.8
DMSO	516	657	4159	513	646	4013	45.1
Pyridine	513	657	4272	508	633	3887	40.5
Formamide	511	664	4509	517	653	4028	56.6
Diethyl ether	494	612	3903	485	573	3167	34.5
1,4-Dioxane	496	611	3795	485	559	2729	36.0
Acetonitrile	493	654	4993	493	614	3997	45.6

[a] Stokes shift.

M.p. 284 °C. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ: 8.82 (d, 2H, Ar-H, $J = 7.8$ Hz), 7.46 (d, 1H, $J = 9.0$ Hz, Ar-H), 7.42 (d, 2H, $J = 9.0$ Hz, Ar-H), 6.77 (d, 1H, =CH), 6.75 (d, 1H, =CH), 6.67 (s, 1H, pyran-H), 6.62 (s, 1H, pyran-H), 4.54 (s, 1H, OH), 3.88 (m, 2H, –CH$_2$–O), 3.58 (m, 2H, –NCH$_2$–), 3.35 (s, 6H, –NCH$_3$), 3.0 (s, 3H, –NCH$_3$), 1.55 (s, 3H, –CH$_3$). EI-MS, $m/z = 423.0$. Elemental analysis: C, 65.20; H, 5.90; N, 9.90%. Chemical formula: $C_{23}H_{25}N_3O_5$ requires: C, 65.24; H, 5.95; N, 9.92%.

2.5. *Synthesis of 5-(2-(4-((2-hydroxyethyl)(methyl)amino)styryl)-6-methyl-4*H*-pyran-4-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (dye **2**)*

A solution of 5-(2,6-dimethyl-4*H*-pyran-4-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione **5** (5 mmol, 1.25 g), 4-((2-hydroxyethyl)(methyl)amino)benzaldehyde **6** (5 mmol, 0.88 g) and piperidine(0.45 ml) in acetonitrile (30 ml) was heated under reflux for 8 h using a Dean–Stark trap. The reaction solution was cooled to room temperature, and the solid crude product was isolated and dried. Then the crude product was purified by column chromatography (silica) using the mixture of chloroform and methanol (v/v = 100:1) as an eluent, followed by further recrystallization from ethanol to obtain the purified black red powder with a 30% yield.

M.p. 190 °C. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ: 8.89 (d, 1H, $J = 7.58$ Hz, Ar-H), 8.70 (d, 1H, $J = 7.48$ Hz, Ar-H), 7.74 (d, 1H, $J = 9.0$ Hz, Ar-H), 7.72 (d, 1H, $J = 8.48$ Hz, Ar-H), 7.42 (s, 1H, =CH), 6.69 (s, 1H, =CH), 6.67 (s, 1H, pyran-H), 6.66 (s, 1H, pyran-H), 4.88 (s, 1H, OH), 3.72 (m, 2H, –CH$_2$–O), 3.54 (m, 2H, –NCH$_2$–), 3.36 (s, 3H, –NCH$_3$), 2.48 (s, 6H, –NCH$_3$), 2.0 (s, 3H, –CH$_3$). EI-MS, $m/z = 411.0$. Elemental analysis: C, 67.0; H, 6.0; N, 3.35%. Chemical formula: $C_{23}H_{25}NO_6$ requires: C, 67.14; H, 6.12; N, 3.40%.

3. Results and discussion

In our design and synthesis strategy, we took the following points into consideration: At first, Meldrum's acid (2,2,-dimethyl-1,3-dioxane-4,6-dione) and Barbituric acid or their derivatives can be easily capable of condensing with a wide range of ketones to form all kinds of merocyanine dyes [22]. Secondly, these merocyanine dyes showed good spectral sensitivity, absorption in the

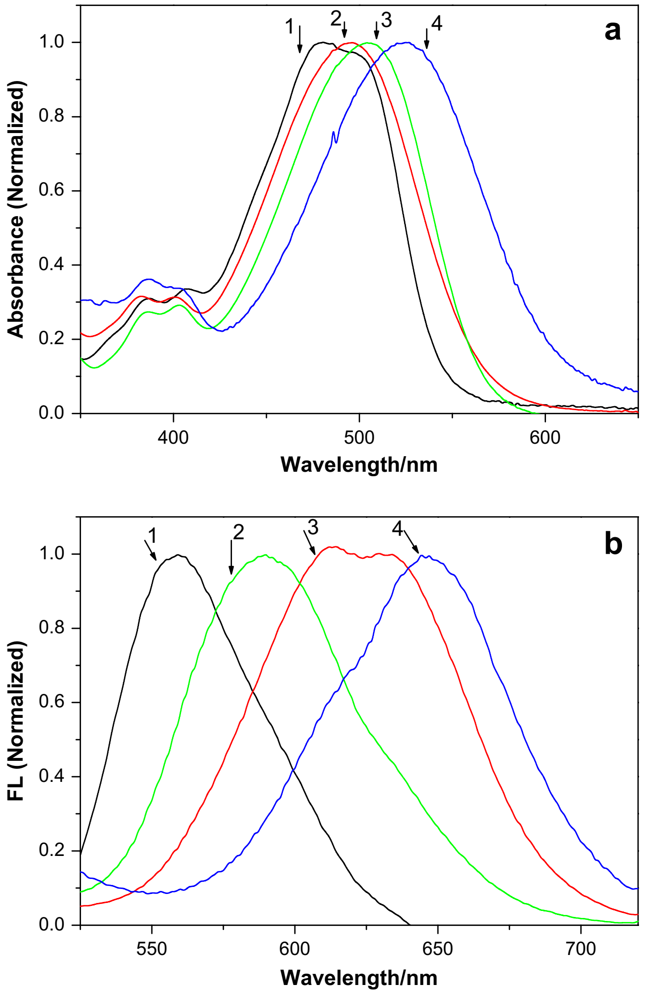


Fig. 1. The normalized UV–vis absorption (a) and fluorescence emission spectra (b) of dye **1** (ca. 10^{-5} mol L^{-1}) in xylene (1), acetone (2), CHCl$_3$ (3) and DMSO (4), respectively.

Fig. 2. The UV–vis absorption and fluorescence emission photographs of dye **1** in several solvents.

visible range in which all solvents are transparent, and good solubility in all organic solvents. These merocyanine dyes incorporated of distinct electron-donor and -acceptor moieties at both ends of conjugated π-systems have long been known to induce long-wavelength absorptions and emissions, both sensitive to the solvent environment. Thirdly, 2,6-dimethyl-4*H*-pyran type dyes are attractive from several points of view, such as their application as photo-(PL) and electroluminescent (EL) materials in the fields of dye laser [23], fluorescent sensor and logic memory [24,25], and organic light-emitting device (OLED) [26,27]. The synthesis of the dyes **1** and **2** was performed by condensation reaction as shown in Scheme 2, the key intermediates 5-(2,6-dimethyl-4*H*-pyran-4-ylidene) Barbituric acid **4** and 5-(2,6-dimethyl-4*H*-pyran-4-ylidene) Meldrum's acid **5** were synthesized by reacting Barbituric acid **2** and Meldrum's acid (2,2,-dimethyl-1,3-dioxane-4,6-dione) **3** condensated with 2,6-dimethyl-4*H*-pyran-4-one, respectively. These key intermediates were subsequently reacted with 4-((2-hydroxyethyl)(methyl)amino)benzaldehyde by condensation reaction. The chemical structures of all the intermediates, dyes **1** and **2** are characterized by ^{1}H NMR, MS and elemental analysis.

The λ_{max} and λ_{em} values of the solvent-dependent absorption and fluorescent emission of dyes **1** and **2** in various solvents and

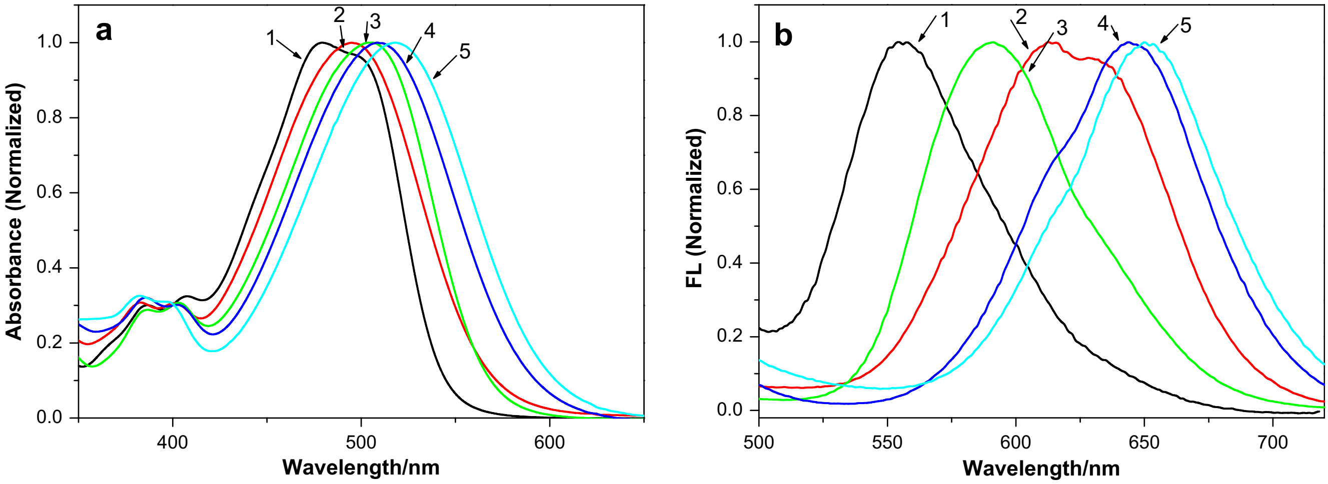


Fig. 3. The normalized UV–vis absorption (a) and fluorescence emission spectra (b) of dye **2** (ca. 10^{-5} mol L^{-1}) in in xylene (1), acetone (2), $CHCl_3$ (3), ethanol (4) and DMSO (5), respectively.

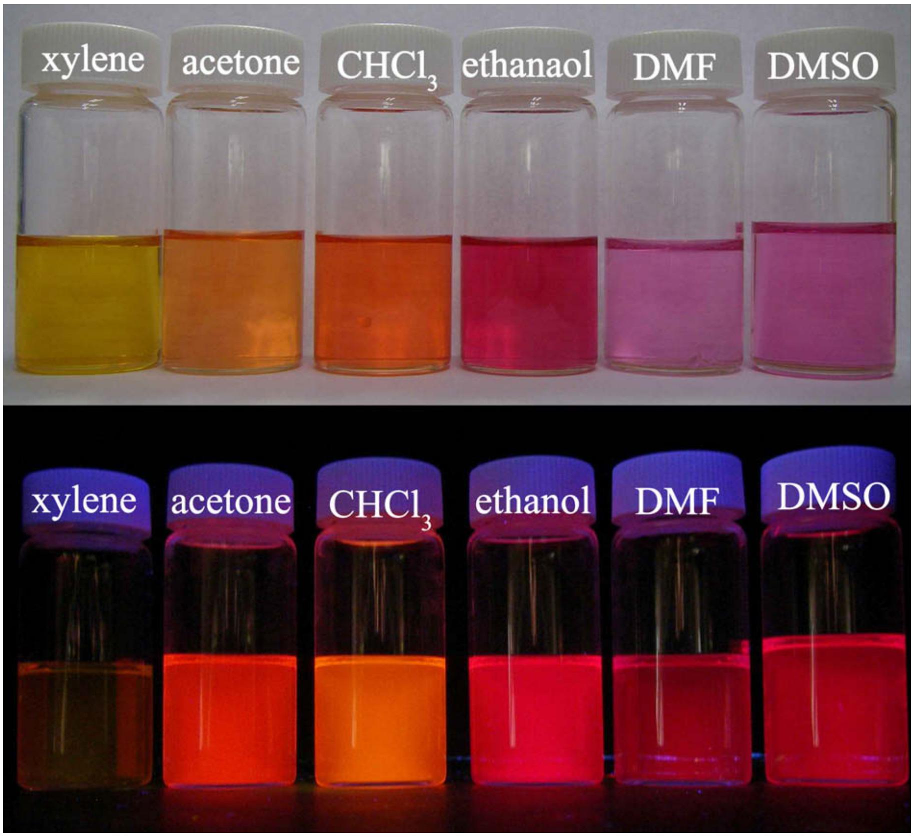


Fig. 4. The UV–vis absorption and fluorescence emission photographs of dye **2** in several solvents.

$E_T(30)$ values are listed in Table 1. As can be seen from Table 1, the dyes **1** and **2** are readily soluble in various solvents, including benzene as a nonpolar solvent. The dyes **1** and **2** exhibited the evidently solvatochromic properties.

The normalized absorption and emission spectra of dye **1** in several solvents having different polarities are shown in Fig. 1. The highly intense long-wavelength absorption band of dye **1** undergoes large red shifts with increasing solvent polarity (ca. 21 nm on going from xylene to DMSO). These features indicate a strongly allowed π–π^* transition with charge-transfer characters. The intramolecular charge-transfer (ICT) interaction, that is from the 2-(methylamino)ethanol group to the Barbituric acid fragment is strongly enhanced upon excitation as evidence from the extreme bathochromic shift of the fluorescence maximum in polar solvents. The emission maximum of dye **1** is bathchromically shifted by 73 nm changing the solvent from xylene to DMSO. Such a behavior indicates stabilization of the highly dipolar excited state in polar solvents. The maximum Stokes Shift is 161 nm ($\Delta\nu = 4993\ \text{cm}^{-1}$) in the acetontrile solution. Fig. 2 shows the UV–vis absorption and fluorescence emission photographs of dye **1** in various solvents, the dye **1** in several solvents with different colors and fluorescent emission can be easily observed by naked eyes.

We also investigated solvatochromic properties of the dye **2** in various solvents. Fig. 3 shows the normalized absorption and emission spectra of dye **2** in similar range of solvents. Dye **2** also exhibited a large red shift in both absorption and emission spectra as solvent polarity increases, indicating a large change in the dipole moment of molecules upon excitation due to an intramolecular charge–transfer interaction. The maximum absorption band of dye **2** undergoes a large red-shift with increasing solvent polarity (ca. 48 nm on going from exylene to *n*-butanol). The emission maximum of dye **2** is 81 nm shifted to the red end of the spectrum. The maximum Stokes Shift is 139 nm ($\Delta\nu = 4200\ \text{cm}^{-1}$) in the methanol solution. Fig. 4 shows the UV–vis absorption and fluorescence emission photographs of dye **2** in several representative solvents, the dye **2** in these solvents with different colors and fluorescent emission.

Compared with the dyes **1** and **2**, we inferred that the merocyanine dyes based on Barbituric acid dye **1** exhibited consistently smaller transition energies (larger λ_{max} value) than the merocyanine dyes based on Meldrum's acid dye **2** in the same solvent.

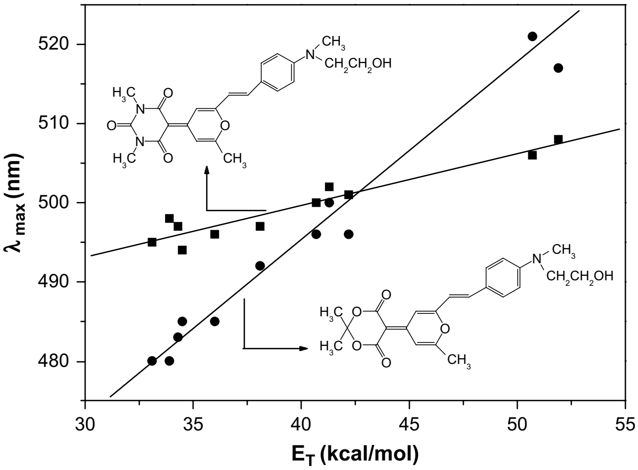


Fig. 5. The liner plots on plotting λ_{max} (the maxima of absorption) versus the solvent parameter E_T of dye **1** and dye **2**.

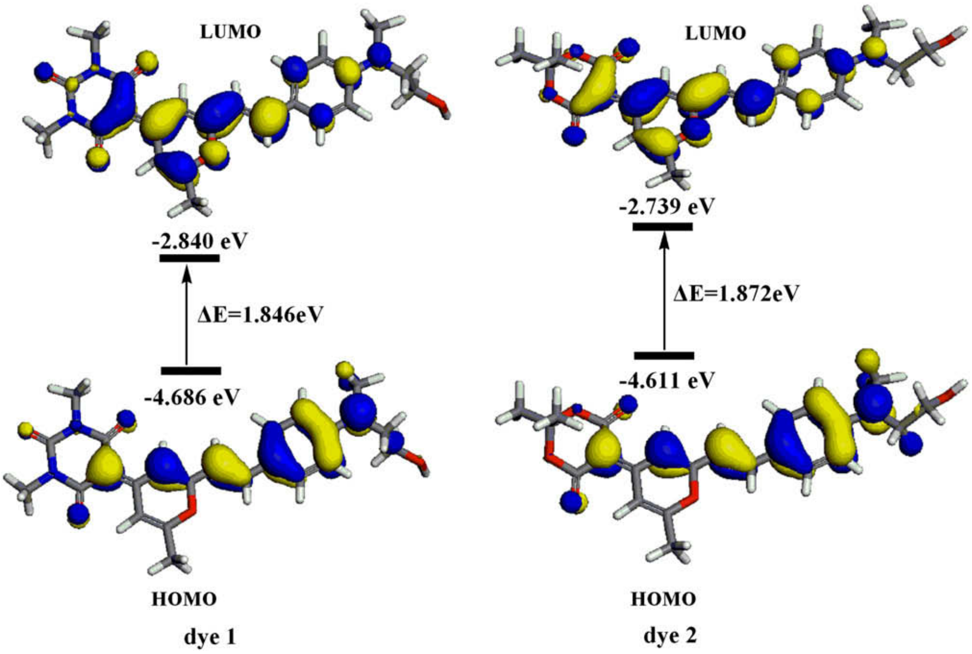


Fig. 6. Electron distribution of the HOMO and LUMO energy levels of dyes **1** and **2**.

From their molecular structure, it can be seen that the dyes **1** and **2** share the same donor group, similarly conjugated to two different acceptor fragments. Their relative transition energies should depend on the relative electron affinities of the acceptor fragments. The pyrimidinetrione moiety of dye **1** should accommodate a negative charge more easily than the dioxanedione fragment in dye **2**. The larger transition energies of dye **2** are in line with these expections. If the dye molecules possess a strong dipole, when the excited state is more polar than the ground state, its stabilization is favoured by more polar solvents. There is a decrease in transition energy and a bathochromic shift in the spectrum (positive solvatochromic). Dimroth et al. have suggested that the transition energy for pyridinium-*N*-phenoxide betain dye, expressed in kcal mol^{-1}, be used as a polarity parameter [3]. This quantity is referred to as the E_T value. Table 1 listed all UV–vis spectra data of the dye **1**, dye **2** and the E_T value of the solvents. The reasonable linear plots of the dye **1** and dye **2** were obtained on plotting λ_{max} versus the solvent parameter E_T as shown in Fig. 5. As the solvent polarity increased, a bathochromic shift of the dye **1** and dye **2** were observed (i.e., positive solvatochromic).

This result was in agreement with theoretical calculation as shown in Fig. 6. The theoretical calculations were performed by $DMol^3$ program in the Materials Studio 4.2 package [28,29] which is the quantum mechanical code using density functional theory. Perdew–Burke–Ernzerhof (PBE) function of generalized gradient approximation (GGA) level [30] with double numeric polarization basis set was used to calculate the energy level of the frontier molecular orbits. Fig. 6 shows the calculated molecular structure and the electron distribution of its HOMO and LUMO of the dye **1** and dye **2**. Comparison of the electron distribution in the frontier molecular orbits (MOs) reveals that HOMO–LUMO excitation moved the electron distribution from aminobenzene moiety to the Barbituric/Meldrum and pyran moieties, which show a strong migration of intramolecular charge-transfer character of dyes. The redistribution of the electron density during the HOMO–LUMO electron transition determines the influence on the color properties of dyes of factors such as the effect of substituents, interaction of dye molecules with its environments such as solvent and polymer substrate.

4. Conclusion

In conclusion, two new solvatochromic merocyanine dyes based on Barbituric and Meldrum's acids have been prepared. They exhibited the evidently positive solvatochromic properties in various solvents. Of the two new solvatochromic merocyanine dyes, dye **2** showed a greater sensitivity to this effect. They exhibit potential and useful application for the development of efficient sensors for the detection of volatile organic compounds (VOCs).

Acknowledgements

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