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Proton-induced fluorescent switching of a new 2D- π -A type vinylcyanoacetate-pyran dye

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1. Introduction

The design and creation of molecular systems that show chemical and physical changes in responses to external stimuli is a topic of current interest because of their potential application as sensing and switching devices [1–5]. In particular, multifunctional dyes that are sensitive toward both external physical and chemical triggers provide a versatile basis for the construction of sophisticated switches that communicate, for instance, through changes in fluorescence, refractive index, polarizability, electrical conductivity, and magnetism properties. Of particular interest is the design of fluorescent molecular switches, as they can precisely control and detect the fluorescence signal by simple chemical input, even down to the level of single molecules or ions under ambient conditions. Various fluorescent molecular switches have been proposed based on systems whose emission properties can be modulated by external inputs, such as temperature [6], light [7], redox potential [8], and ions [9]. Protons are often used as input chemicals because the proton binding often triggers several photoinduced processes, such as electron transfer [10-11], charge transfer [12-13], and energy transfer [14], thus enabling the modulation of emission properties. In principle, fluorescent molecule construction with photoinduced electron transfer (PET) [15] or intramolecular charge

ABSTRACT

A new 2D- π -A type vinylcyanoacetate-pyran dye, ethyl 2-(2,6-bis(2-butoxy-4-(diethylamino)styryl)-4Hpyran-4-ylidene)-2-cyanoacetate (BDPC) was prepared by condensation reaction. The chemical structures of all the intermediates and the BDPC dye are characterized by ¹H NMR, MS. It showed interestingly solvatochromic and solvatofluorchromic properties in various solvents. Its LUMO and HOMO values were obtained by the theoretical calculation. The fluorescent intensity of BDPC dye can be reversibly selected by protonation/deprotonation of the amine moiety via control of intramolecular charge transfer (ICT), leading to a fluorescent molecular switch with two distinguished "on" and "off" states.

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transfer (ICT) [16] between fluorophore and receptor systems is one of the most frequently used pathways for building useful sensors and switches. Aromatic amines are typical examples of pH fluorescent sensors and switches because their fluorescent spectra can be changed reversibly by protonation/deprotonation [17–18]. Meanwhile, it is a challenge to design new molecules that switch with modulation of intramolecular charge transfer (ICT). Here, we reported a new proton induced fluorescent molecular switch based on 2D– π -A type vinylcyanoacetate-pyran dye, named thyl 2-(2,6-bis(2-butoxy-4-(diethylamino)styryl)-4Hpyran-4-ylidene)-2-cyanoacetate (BDPC) as shown in Scheme 1. The fluorescent intensity of BDPC dye can be reversibly selected by protonation/deprotonation of the amine moiety via control of intramolecular charge transfer (ICT), leading to a fluorescent molecular switch with two distinguished "on" and "off" states.

2. Experiment

2.1. Materials and methods

Most of chemicals were purchased from Aldrich Chemical Co. and TCI. Solvents were purified by normal procedures and handled under moisture free atmosphere. The other materials were commercial products and were used without further purification. The intermediates 2-butoxy-4-(diethylamino) benzaldehyde **4** was synthesized according to the literature method with a high yield of 90% [19].



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Scheme 1. The chemical switching process and proton modulation mechanism of $2D-\pi$ -A vinylcyanoacetate-pyran BDPC dye.

2.2. Instruments and spectral measurements

Melting points were determined using an Electrothermal IA 900 and are uncorrected. UV–visible absorption spectra were measured on an Agilent 8453 spectrophotometer. Fluorescence spectra were measured on a Shimadzu RF-5301PC Fluorescence spectrophotometer. Mass spectra were recorded on a Shimadzu QP-1000 spectrometer using electron energy of 70 eV and the direct probe El method. ¹H NMR spectra were recorded using a Varian Inova 400 MHz FT-NMR spectrometer with TMS as internal standard. Spectrophotometric titrations were performed on 2.0×10^{-5} mol/L solutions of $2D-\pi$ -A type vinylcyanoacetate-pyran BDPC dye in C_2H_5OH . The different concentration of acid and base standard solution of the required protonation/deprotonation were added, respectively. The UV–vis absorption and fluorescence spectra of the samples were recorded.

2.3. Synthesis of ethyl

2-cyano-2-(2,6-dimethyl-4H-pyran-4-ylidene)acetate

A mixture of 2,6-dimethylpyran-4-pyrone **1** (3.1 g, 25 mmol), ethyl cyanoacetate **2** (2.7 ml, 25 mmol), and acetic acid (12.5 ml) was refluxed for 6 h. The pale, yellow solid obtained was filtered, washed with methanol, and recrystallized from methanol.

Yield: 58%, m.p.: 184–186 °C; mass (m/z) 219(M⁺); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.81 (s, 1H), 6.59 (s, 1H), 4.14 (m, 2H), 2.33 (s, 6H), 1.22 (t, *J* = 7.52, 3H); Anal. Cald. for C₁₂H₁₃NO₃: C, 65.74; H, 5.98; N, 6.39. Found; C, 65.61; H, 6.12; N, 6.20%.

2.4. Synthesis of ethyl 2-(2,6-bis(2-butoxy-4-(diethylamino)styryl)-4H-pyran-4-ylidene)-2-cyanoacetate dye (BDPC)

A solution of 2-cyano-2-(2,6-dimethyl-4*H*-pyran-4ylidene)acetate **3** (1 g,4.6 mmol), 2-butoxy-4-(diethylamino)benzal dehyde **4** (2.3 g, 9.1 mmol,) and piperidine (0.45 ml) in 1-propane (30 ml) was refluxed for 8 h using a Dean–Stark trap. The reaction solution was cooled to room temperature, and the solid product was isolated and washed well with n-propanol, and dried. The crude product was recrystallized from methanol.

Yield: 21%, m.p.: $128-130 \degree C$; Ms (*m*/*z*) $681(M^+)$; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 0.98 (t, *J* = 7.04, 6H), 1.21 (t, *J* = 7.0, 12H), 1.34 (t, *J* = 7.04, 3H), 1.54 (m, *J* = 7.52, 4H), 1.89 (m, *J* = 7.52, 4H), 3.40 (m, *J* = 7.0, 8H), 4.05 (m, *J* = 6.52, 4H), 4.24 (m, *J* = 7.0, 2H), 6.14 (s, 2H), 6.28 (d, *J* = 8.8, 2H), 6.59 (s, 1H), 6.75 (d, *J* = 13.52, 2H), 7.67(d, *J* = 7.52, 2H), 7.91 (s, 1H). Anal. Cald. for C₄₂H₅₅N₃O₅: C, 73.98; H, 8.13; N, 6.16 Found; C, 73.75; H, 8.39; N, 6.24%.

3. Results and discussion

3.1. The design and synthesis of $2D-\pi$ -A type vinylcyanoacetate-pyran BDPC dye

In our synthesis strategy, a 2D- π -A type vinylcyanoacetatepyran dye was prepared by condensation reaction as showed in Scheme 2. The vinyl-dicyano-pyran dye is the typical electron donor- π -conjugate-electron acceptor (2D- π -A) compounds,



Scheme 2. Synthesis of vinylcyanoacetate-pyran BDPC dye.



Fig. 1. The Normalized UV-vis absorption and fluorescence emission spectra of vinylcyanoacetat-pyran BDPC dye in hexane (1), toluene (2), ethyl acetate (3), acetone (4) and DMSO (5), respectively (1–5; absorption, 1'–5'; emission).

which showed interesting photochemical and photophysical properties due to their intrinsic intramolecular charge transfer (ICT) character [20]. In addition, pyran dye is highly charge-separated at a photoexcited state and shows a remarkably large Stokes shift. The dicyano-pyran based dyes have been intensively developed for applications using as photo- (PL) and electroluminescent (EL) materials in the fields of dye laser [21], fluorescent sensor and logic memory [22-23], and organic light-emitting device (OLED) [24]. At first, the intermediates ethyl 2-cyano-2-(2,6-dimethyl-4H-pyran-4-ylidene)acetate **3** was synthesized by reacting 2,6-dimethylpyran-4-pyrone 1 and ethyl cyanoacetate 2 in acetic anhydride solution refluxed for 6 h. Then $2D-\pi$ -A type vinylcyanoacetate-pyran BDPC dye was obtained by condensation reaction with the ethyl 2-cyano-2-(2,6-dimethyl-4Hpyran-4-ylidene)acetate **3** and compound **4** using piperidine as catalyst. The chemical structures of all the intermediate 3, 4 and the

Table 1

Photophysical properties of vinylcyanoacetate-pyran BDPC dye.

Solvent	$\lambda_{max} \left(nm \right)$	$\lambda_{em} \left(nm \right)$	Δv^{a} (cm ⁻¹)	E_T (kcal mol ⁻¹)
Hexane	460	524	2655	30.1
Toluene	474	562	3303	33.9
THF	486	600	3909	37.4
Ethyl acetate	482	596	4768	38.1
CHCl₃	488	605	3963	39.1
CH_2Cl_2	485	614	4332	40.7
Acetone	490	635	4660	42.2
Acetonitrile	486	647	5120	45.6
DMF	496	650	4777	43.8
DMSO	500	653	4686	45.1
C ₂ H₅OH	492	645	4821	51.9
CH₃OH	486	648	5144	55.4

^a Stokes shift

2D-π-A type vinylcyanoacetate-pyran BDPC dye are characterized by ¹H NMR, MS. Elementary analysis.

3.2. Photophysical properties of vinylcyanoacetate-pyran BDPC dye

The normalized UV-vis spectra, fluorescence emission of vinylcyanoacetate-pyran BDPC dye in several solvents having different polarity are shown in Fig. 1. The highly intense long-wavelength absorption band of BDPC dye undergoes evident red-shifts with increasing solvent polarity (ca. 40 nm on going from hexane to DMSO). These features indicate a strongly allowed $\pi - \pi^*$ transition with charge transfer characters. The intramolecular charge transfer (ICT) interaction, that is from the diethylaminobenzene group to 2-cyanoacetate fragment is strongly enhanced upon excitation as evidence from the extreme bathochromic shift of the fluorescence maximum in polar solvents. The solvent dependence of fluorescence spectra has sometimes called solvatofluorchromism. We found that the BDPC dye showed the interesting solvatofluorchromic property in various solvents. The emission maximum



Fig. 2. Electron distribution of the HOMO and LUMO energy level of BDPC dye and BDPC + H⁺.



Fig. 3. The UV-vis absorption spectra changes of vinylcyanoacetate-pyran BDPC dye in $C_2H_5OH~(2.0\times10^{-5}mol\,L^{-1})$ solution upon addition of protonation/deprotonation.

of BDPC dye is bathochromic shifted 129 nm changing the solvent from hexane to DMSO. Such a behavior indicates stabilization of the highly dipolar excited state in polar solvents. The maxmium Stokes shift is $5120 \,\mathrm{cm}^{-1}$ in the acetontrile solution. The photophysical data of BDPC dye are also summarized in Table 1.

3.3. Theoretical calculation of vinylcyanoacetate-pyran BDPC dye

In order to gain a deeper insight into the intramolecular charge transfer process of BDPC dye, we performed by theory calculation based on DMol³ program in the Materials Studio 4.2 package [25–26]. Fig. 2 shows the electron distribution of the HOMO and LUMO energy level of BDPC dye and its bonding the proton. Accordingly, the HOMO and LUMO energy level of BDPC dye before and after protonation were calculated to be -4.466, -2.541 eV and -4.826, -2.601 eV, respectively. Comparison of the electron distribution in the frontier MOs reveals the HOMO–LUMO excitation moved the electron distribution from diethylaminobenzene moiety to the 2-cyanoacetate moiety, which showed a strong migration of ICT character of BDPC dye.



Fig. 4. The fluorescence emission spectra changes of vinylcyanoacetate-pyran BDPC dye in $C_2H_5OH~(2.0 \times 10^{-5} \text{mol L}^{-1})$ solution upon addition of protonation/deprotonation ($\lambda_{ex} = 410 \text{ nm}$).



Fig. 5. The fluorescent monitoring of cycles on and off (by alternate titration with acid and base) conversion of vinylcyanoacetate-pyran BDPC dye in C₂H₅OH $(2.0 \times 10^{-5} \text{mol L}^{-1})$ solution (λ_{em} = 645 nm; λ_{ex} = 410 nm).

3.4. Absorption spectra titration of vinylcyanoacetate-pyran BDPC dye with protonation/deprotonation

The interaction of the 2D- π -A type vinylcyanoacetate-pyran BDPC dye with acid/base was investigated in C₂H₅OH solution through spectrophotometric titration experiments. In particular, a standard solution of HCl was added stepwise to a $(2.5\times10^{-4}\,\text{M})$ solution of BDPC dye at room temperature. Fig. 3 showed the UV-vis absorption spectra changes of BDPC dye in C₂H₅OH solution with protonation/deprotonation. Upon addition of proton, the band at 492 nm progressively decreases, while a new band with a peak at 410 nm forms and develops. The presence of an isosbestic points at 445 nm indicates that only two species coexist at the equilibrium. Upon addition of base, the above yellow solution of BDPC dye became gradually red and recovered the initial state. The character absorption shifts hypsochromically by 80 nm. As demonstrated above, the absorption at 410 nm is slight 'switched on' upon gradual addition of proton for BDPC dve. and the 492 nm absorption is 'switched off'.

3.5. Fluorescence switching of vinylcyanoacetate-pyran BDPC dye with protonnation/deprotonation

Corresponding to the difference between the Uv-vis absorption with protonation and deprotonation, the fluorescent response of BDPC dye was also shown as Fig. 4. The BDPC dye produced strong fluorescence emission at 650 nm (excitation at 410 nm) at room temperature. Upon addition of proton, the fluorescent emission peak at 650 nm progressively decreases and absolutely quenched. Upon addition of base, the fluorescent intensity gradually recovered the initial state. The switching signal transduction mechanism here is based on modulation of intramolecular charge transfer (ICT) by the interaction of the proton and the electron of nitrogen atom of the aminobenzene moiety. The modulation in the electron-donating capabilities of the amide group in the presence and absence of proton directly influences the ICT from donor to acceptor moiety. In the presence of proton, a positively charged aminobenzene moiety of BDPC dye was formed, which causes a significant decrease in the charge density on the aminobenzene nitrogen, with associated reducing in the push-pull effect of the ICT transition. However, in the absence of proton, the extent of ICT from the donor amide moiety to the acceptor moiety is enhanced, so the fluorescent intensity gradually increased and recovered the initial state. In addition, the Fig. 5 showed that the fluorescence intensity reversibly changed at 650 nm by alternate addition with acid and



Fig. 6. The color change and fluorescence emission response photographs of vinylcyanoacetate-pyran BDPC dye in C₂H₅OH on addition of 10 equiv. HCl. Left to right: BDPC dye, BDPC dye and HCl, the emission of BDPC dye, and emission of BDPC dye and HCl.

base and this cycle could be repeated more than 5 times, which is an excellent proton induced fluorescence switch. Fig. 6 shows the UV–vis absorption and fluorescence emission photographs of BDPC dye in C_2H_5OH on addition of 10 equiv. proton.

4. Conclusions

In conclusion, we designed and synthesized a new new $2D-\pi$ -A type vinylcyanoacetate-pyran dye. It exhibited the evidently positive solvatochromic and solvatofluorchromic properties in different polarity solvents. An acid-induced fluorescent molecular switch was demonstrated by modulation of intramolecular charge transfer with protonation/deprotonation. This fluorescent molecular switch system showed promising application in the fields of optonic and electronic smart materials, logic gate, nanomachines, fluorescence sensors and other molecular photonic devices.

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