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2D−π−A type pyran-based dye derivatives: Photophysical properties related to intramolecular charge transfer and their electroluminescence application

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Abstract

Five different types of 2D−π−A (vinylcyanoacetate)pyran derivatives, each having two donor (2D) and one acceptor (A) groups showed significantly large Stokes shifts. Their fluorescence bands shifted to longer wavelengths with an increase in solvent dielectric constant. The π-conjugated moiety, such as a carbazolyl group, as an electron donor did not impart red-emission saturation. A locked ring structure of the electron donor group led to narrowing of the full width at half maximum (fwhm) and to increased dipole moment in the ground state; in addition, bulky donor groups resulted in molecular stability and restrained electronic perturbation on the excited state. An EL device based on the dyes displayed bright and saturated red light with a high luminance of about 2000 cd/m^2 at a current density of 160 mA/cm^2 at 16 V.

Keywords: Fluorescence; Pyran-based dye; Electron donor; Electron acceptor; Charge transfer; Electroluminescence

1. Introduction

Electron donor−π-conjugate−electron acceptor (D−π−A) compounds are interesting due to their nonlinear optical properties, which are highly sensitive to changes in the external environment such as polarity and pH of media, due to their intrinsic intramolecular charge transfer (ICT) character [1]. Among many of the related compounds synthesized up to date, the pyran-based dyes have been intensively developed for applications using as photo- (PL) and electroluminescent (EL) materials in the fields of dye laser [2], sensor [1e,3], dye-sensitized solar cell [4], and organic light-emitting device (OLED) [5]. The 4-(dicyanomethylene)-2-methyl-6-(*p*(dimethylamino)styryl)-4*H*-pyran (DCM) is the representative compound, which produces the ultrafast process of ICT [6]. As well, the excited-state dipole moment (26.3 D) is higher than that in the ground state (6.1 D) [7]. Thus, DCM is highly charge-separated at a photoexcited state and shows a remarkably large Stokes shift leading to red-emission color saturation. Fundamental studies on the photophysical properties of its derivatives are still crucial for the exploration of new functions and applications in dye chemistry.

Since Tang and VanSlyke reported that a double layered organic EL device consisting of a hole injection layer and an emitting layer exhibited a luminance over 1000 cd/m^2 at a relatively low driving voltage of 10 V, there have been extensive studies

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on layered organic EL devices with the aim of achieving high brightness and full color emission [8,5c]. In order to obtain the high performance organic EL, organic materials are required to have good thermal stability and the ability to form amorphous thin films. There are two methods for tuning the color emitted from organic EL devices: an appropriate selection of the emitting materials with bright luminescence of desired colors or doping dyes into the host material. The former method is the most feasible for producing blue-light-emitting EL devices [9], and the latter is useful for the fabrication of the bright red-light-emitting organic EL devices [10]. DCM derivatives are well-known as low molecular weight red-emitting materials, which can be synthesized by a relatively simple method [11].

In this work, we synthesized five different types of 2D–π–A pyran-based dyes, (vinylcyanoacetate)pyran derivatives, having two donors (2D) and one acceptor (A) groups, as shown in Chart 1. Their fundamental, photophysical properties related to ICT character were investigated in various dilute solutions. Furthermore, EL property of one of these compounds was described in detail.

2. Experimental section

2.1. Synthesis of ethyl 2-cyano-2-(2,6-dimethyl-4H-pyran-4-ylidene)acetate, **8** [12]

A mixture of 2,6-dimethylpyran-4-pyrone, **6** (25 mmol, 3.1 g), ethyl cyanoacetate, **7** (25 mmol, 2.7 ml), 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 several times.

Yield: 43%, m.p. 184–186 °C; mass (*m/z*) 219 (M^+); ^{1}H NMR (400 MHz, $CDCl_3$): 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 $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.61; H, 6.12; N, 6.20%.

2.2. Synthesis of (vinylcyanoacetate) pyran derivatives, **1–5**

A solution of 2-cyano-2-(2,6-dimethyl-4*H*-pyran-4-ylidene)acetate, **8** (4.6 mmol, 1 g), 4-dimethylamino benzaldehyde **1′** (10.1 mmol, 1.5 g) 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 1-propanol, and dried. The crude product was recrystallized from methanol several times. Compounds **2–5** were obtained by a similar procedure using **2′**, **3′**, **4′** and **5′**, respectively.

Compound **1**: Yield: 23%, m.p. 254 °C; mass (*m/z*) 481 (M^+); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.98 (s, 1H), 7.45 (d, $J = 9.04$, 4H), 7.42 (d, $J = 4.04$, 1H), 7.38 (d, $J = 4.00$, 1H), 6.70 (d, $J = 9.04$, 4H), 6.65 (s, 1H), 6.55 (m, 2H), 4.25 (m, 2H), 3.05 (s, 12H), 1.35 (t, $J = 7.04$, 3H); Anal. Cald. for $C_{30}H_{31}N_3O_3$: C, 74.82; H, 6.49; N, 8.73. Found: C, 74.07; H, 6.50; N, 8.65%.

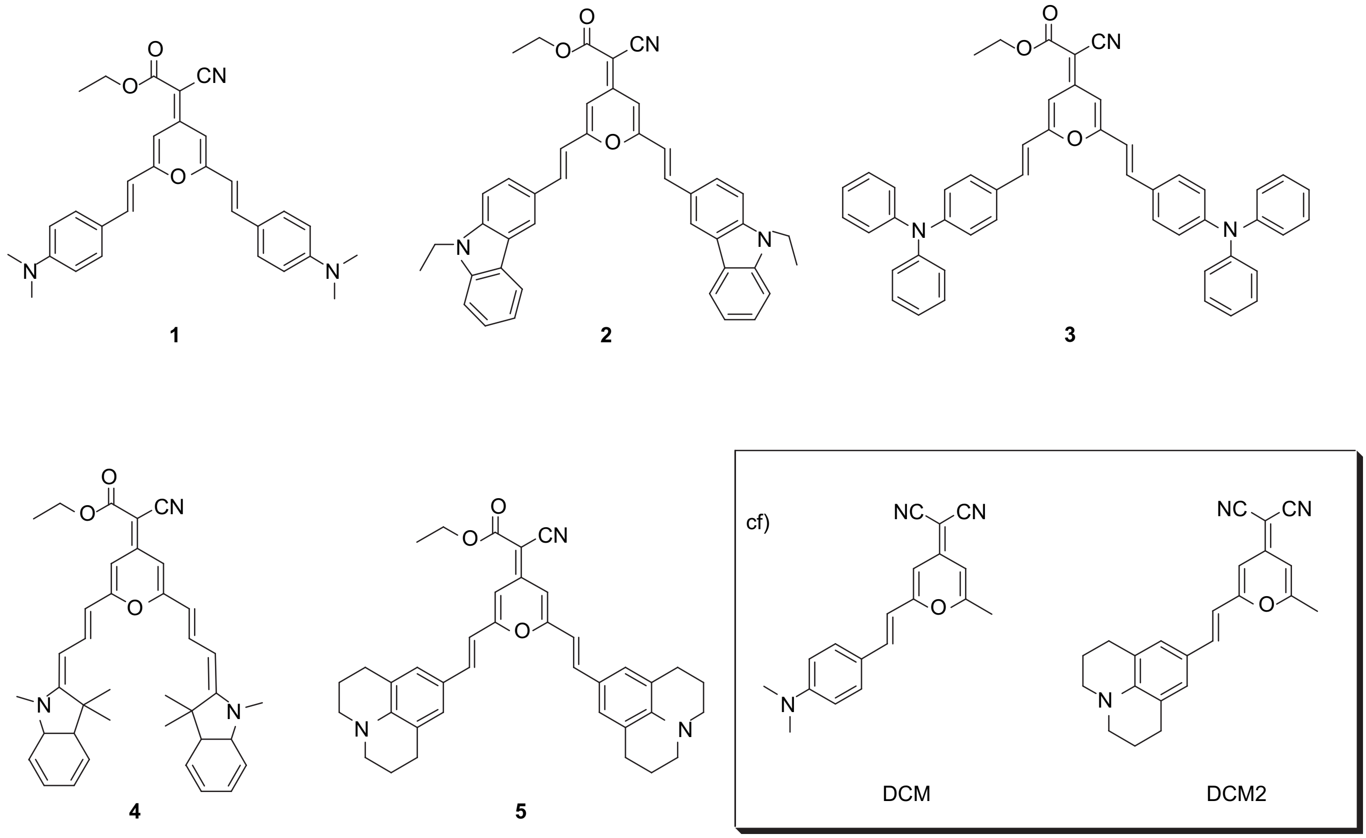


Chart 1. Chemical structures of (vinylcyanoacetate)pyran derivatives, **1–5**.

Compound **2**: Yield: 14%, m.p. 295–297 °C; mass (*m/z*) 629 (M^+) ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.29 (s, 2H), 8.15 (m, 2H), 8.04 (s, 1H), 7.70 (m. 4H), 7.52 (t, *J* = 7.52, 2H), 7.43 (m, 4H), 7.30 (t, *J* = 7.04, 2H), 6.79 (m, 2H), 6.71 (s, 1H), 4.37 (m, 4H), 4.26 (m, 2H), 1.46 (t, *J* = 7.56, 6H), 1.36 (t, *J* = 7.00, 3H); Anal. Cald. for $C_{42}H_{35}N_3O_3$: C, 80.10; H, 5.60; N, 6.67. Found: C, 79.11; H, 5.63; N, 6.67%.

Compound **3**: Yield: 36%, m.p. 214–216 °C; mass (*m/z*) 729 (M^+), ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.04 (s, 1H), 7.39 (m, 6H), 7.30 (t, *J* = 7.52, 8H), 7.14 (d, *J* = 8.52, 8H), 7.10 (t, *J* = 7.52, 4H), 7.03 (d, *J* = 8.52, 4H), 6.72 (s, 1H), 6.65 (d, *J* = 8.52, 1H), 6.61 (d, *J* = 8.56, 1H), 4.25 (m, 2H), 1.34 (t, *J* = 7.04, 3H); Anal. Cald. for $C_{50}H_{39}N_3O_3$: C, 82.28; H, 5.39; N, 5.76. Found: C, 81.64; H, 5.34; N, 5.75%.

Compound **4**: Yield: 63%, m.p. 263 °C; mass (*m/z*) 585 (M^+); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.79 (s, 1H), 7.67 (t, *J* = 13.28, 2H), 7.22 (d, *J* = 8.04, 4H), 6.94 (t, *J* = 7, 2H), 6.73 (d, *J* = 7.52, 2H), 6.48 (s, 1H), 5.94 (t, *J* = 13.4, 2H), 5.47 (d, *J* = 12.04, 2H), 4.23 (m, *J* = 7.04, 2H), 3.23 (s, 6H), 1.71 (s, 12H), 1.34 (t, *J* = 7, 3H); Anal. Cald. for $C_{38}H_{39}N_3O_3$: C, 77.92; H, 6.71; N, 7.17. Found: C, 77.33; H, 6.93; N, 7.14%.

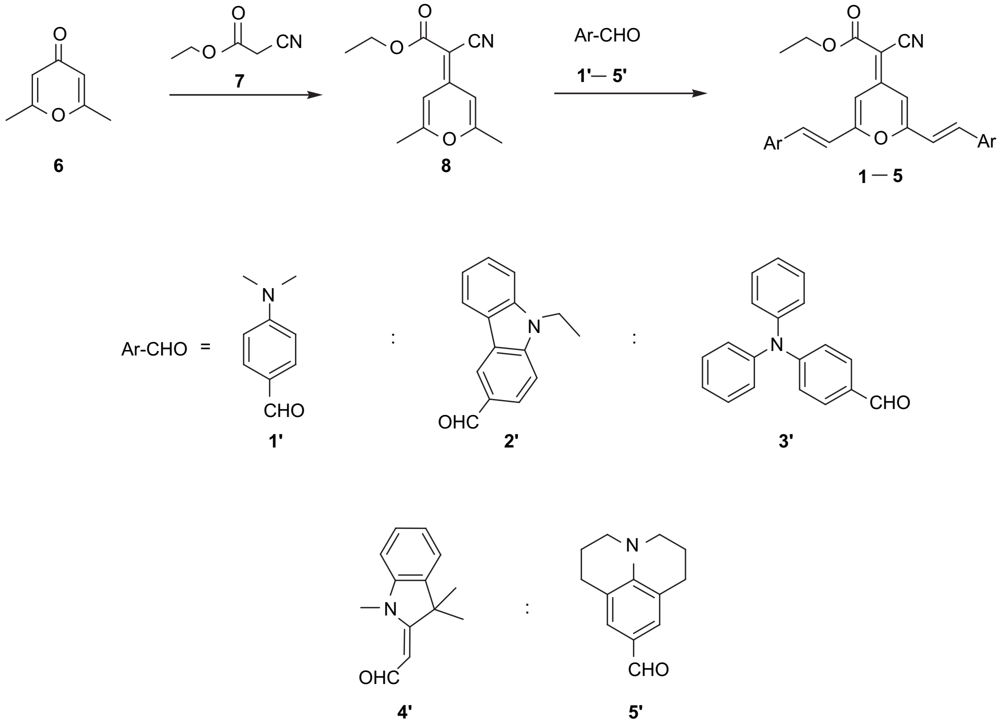
Compound **5**: Yield: 52%, m.p. 258 °C; mass (*m/z*) 585 (M^+); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.94 (s, 1H), 7.32 (d, *J* = 3.52, 2H), 7.02 (s, 4H), 6.61 (s, 1H), 6.46 (d, *J* = 9.56, 2H), 4.24 (m, *J* = 7.52, 2H), 3.25 (t, *J* = 5.04, 8H), 2.77 (t, *J* = 5.52, 8H), 1.99 (m, *J* = 5.52, 8H), 1.34 (t, *J* = 7, 3H); Anal. Cald. for $C_{38}H_{39}N_3O_3$: C, 77.92; H, 6.71; N, 7.17. Found: C, 77.78; H, 6.54; N, 7.12%.

2.3. Measurements

The UV–vis absorption spectra were measured on a *JASCO* UV-550 spectrophotometer, and the photoluminescence spectra were recorded on a *JASCO* FP6500 spectrofluorometer. The ^{1}H NMR spectra were measured in $CDCl_3$ containing tetramethylsilane as the internal standard using a *Bruker* Advance Digital 400 (400 MHz). Emission quantum yields were determined relative to quinine sulfate in 1 N H_2SO_4 assuming a quantum yield of 0.546 at an excitation wavelength of 365 nm [13]. The electrical and luminescent characteristics of EL devices were analyzed by using a source meter 2400 (Keithley) and optical power meter 1830S (Newport). The EL spectrum and Commission Internationale De L'Eclairage (CIE) coordinates were measured with a Spectroradiometer (Minolta CS-1000).

2.4. Fabrication of EL device

Compound **1** and α-NPD (*N*,*N*′-di-[(1-naphthalenyl)-*N*,*N*′-diphenyl]-1,1′biphenyl)-4,4′-diamine) were used as an emitting layer and a hole transporting layer, respectively. The structure of organic EL device was ITO/α-NPD/**1**/LiF/Al. In a device with Al cathode and **1**, α-NPD and **1** were deposited by vacuum thermal evaporation on an ITO under a vacuum of about 2×10^{-6} Torr. LiF was used for enhancing electron injection efficiency of OLEDs. The thickness of α-NPD, **1**, LiF and Al cathode were about 50, 40, 0.5 and 100 nm, respectively, which were measured by a quartz crystal thickness monitor placed near the substrate. The active area of devices is 3.0×3.0 mm^2.



Scheme 1. Syntheses of (vinylcyanoacetate)pyran derivatives, **1**–**5**.

3. Results and discussion

As illustrated in Scheme 1, the (vinylcyanoacetate)pyran derivatives, **1**–**5**, were synthesized by two-step processes including the synthesis of an aldehyde. Aldehydes **1′**–**5′** were prepared through Vilsmeier reaction [14]. Ester group incorporated compound **8** was synthesized from 2,6-dimethylpyran-4-pyrone, **6** and ethyl cyanoacetate, **7** in 43% yield. The reaction of compound **8** with aldehydes **1′**–**5′** gave **1**–**5** by the Knoevenagel condensation, respectively [15]. The chemical structures of **1**–**5** were confirmed by NMR, mass spectroscopy, and elemental analysis.

Chart 1 shows the chemical structures of 2D–π–A type pyran-based dyes, compounds **1**–**5**. Table 1 describes the dielectric constants and dipole moments of the solvents used in this study. The dielectric constants (ε) of ethanol, acetonitrile, acetone, THF, and 1,4-dioxane are 25.3 (dipole moment, $\mu = 1.69$), 36.6 (3.92), 21.0 (2.88), 5.66 (1.74), and 2.22 (0), respectively [16]. As estimated from these ε values, the solvent polarity is in the order acetonitrile > ethanol > acetone > THF > 1,4-dioxane. At first, we examined how well our dyes dissolved in these solvents. All compounds dissolved well in acetone, THF, and 1,4-dioxane. Compound **1** dissolved considerably in ethanol, whereas others absolutely did not. Compound **2** was partly insoluble in acetonitrile and also compound **3** was hardly soluble while others dissolved well in this polar solvent. This hints that compounds **2** and **3** are less polar than others.

Table 2 summarizes the UV–vis absorption maximum wavelengths ($\lambda_{\text{max,abs}}$) and fluorescence maximum wavelengths ($\lambda_{\text{max,em}}$) of compounds **1**–**5** in the solvents mentioned above. All compounds showed the shortest $\lambda_{\text{max,abs}}$ in 1,4-dioxane. However, they did not exhibit significantly different $\lambda_{\text{max,abs}}$ in solvents other than 1,4-dioxane. On the other hand, the fluorescence band significantly shifted to a longer wavelength with an increase in the dielectric constant of the solvent. Actually, the change in fluorescence color along with solvent polarity was also clearly recognized by naked eye. Fig. 1 shows the photographs of compounds **1**–**5** in the solvents when excited at 365 nm. This indicates that charge separation occurs within the molecules and that these compounds are highly polar in excited states rather than in ground states. The quantum yields of these emission of compounds **1**–**5** in THF were 15.8, 3.0, 14.3, 7.1, and 5.8%, respectively. The values of the quantum yields of the dyes were significantly dependent on the solvent. For example, the quantum yields of the emission of compound **1** in ethanol, acetone, and THF, were 0.5, 0.8, and 15.8 %, respectively. It was found that the fluorescence intensity of all dyes decreased by orders of magnitude with increasing solvent polarity. These results are consistent with the expected effects of ICT on fluorescence quantum yield; i.e., fluorescence efficiency should decrease with increasing strength of intramolecular charge transfer [1].

Table 1
Properties of solvents used in this study

	Ethanol	Acetonitrile	Acetone	THF	1,4-Dioxane
Dielectric constant	25.3	36.6	21.0	5.66	2.22
Dipole moment	1.69	3.92	2.88	1.74	0

Figs. 2 and 3 show the UV–vis absorption and fluorescence spectra of **1**–**5** in acetonitrile, respectively. Compound **4**, having (indolinylidene)propenyl group as a donor, shows the longest $\lambda_{\text{max,abs}}$ and $\lambda_{\text{max,em}}$ of 506 and 684 nm, respectively, while, compound **2**, having (carbazolyl)vinyl group as a donor, shows the shortest ones of 446 and 601 nm, respectively. This indicates that π-conjugated moiety such as the carbazolyl group cannot sufficiently increase the ICT character of the 2D–π–A system, and hence, such molecular design is not preferable to red-emission color saturation in PL and EL applications. As also shown in Fig. 1, the emission color of **2** is far from the red color saturation even in the most polar solvent of acetonitrile. The comparison of **1** and **5** identifies the molecularly rocking effect on a photophysical property. Compound **5** in acetonitrile shows an absorption maximum at 498 nm which is longer than that of **1** (475 nm) by 11 nm. Whereas, both **1**

Table 2
UV–vis absorption maxima wavelengths ($\lambda_{\text{max,abs}}$), fluorescence maxima wavelengths ($\lambda_{\text{max,em}}$)[a], and quantum yields of compounds **1**–**5** in various solvents

		Ethanol	Acetonitrile	Acetone	THF	1,4-Dioxane
1	$\lambda_{\text{max,abs}}$, $\lambda_{\text{max,em}}$ (nm)	476, 640[b]	475, 644	N/A[c]	475, 626	460, 577
	Quantum yield (%)	0.5	N/A	0.8	15.8	N/A
2	$\lambda_{\text{max,abs}}$, $\lambda_{\text{max,em}}$ (nm)	N/A[d]	446, 601[b]	448, 589	450, 566	448, 534
	Quantum yield (%)	N/A	N/A	N/A	3.0	N/A
3	$\lambda_{\text{max,abs}}$, $\lambda_{\text{max,em}}$ (nm)	N/A[d]	N/A[d]	462, 637	465, 618	462, 566
	Quantum yield (%)	N/A	N/A	N/A	14.3	N/A
4	$\lambda_{\text{max,abs}}$, $\lambda_{\text{max,em}}$ (nm)	N/A[d]	506, 684	N/A[c]	508, 654	501, 617
	Quantum yield (%)	N/A	N/A	N/A	7.1	N/A
5	$\lambda_{\text{max,abs}}$, $\lambda_{\text{max,em}}$ (nm)	N/A[d]	498, 645	N/A[c]	498, 629	488, 608
	Quantum yield (%)	N/A	N/A	N/A	5.8	N/A

[a] Excited at $\lambda_{\text{max,abs}}$.

[b] Measured in soluble part.

[c] Well dissolved, but merely spectroscopic analysis was not performed.

[d] Hardly soluble.

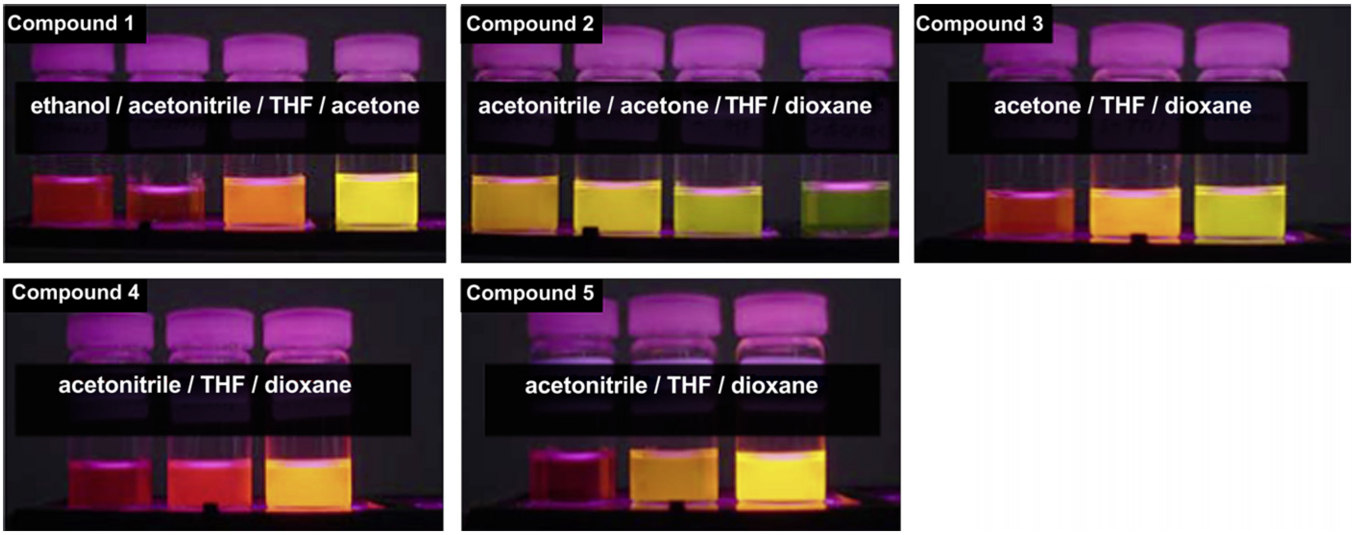


Fig. 1. Photographs of compounds **1**–**5** in various solvents (excited at 365 nm).

and **5** show the same fluorescence maximum at 645 nm although a significant difference of the full width at half maximum (fwhm) is seen, e.g., 130 nm for **1** and 83 nm for **5**. The narrower fwhm of **5**, compared to **1**, means that its photoexcited species is closer to a single species. The structure relationship between **1** and **5** is very similar to that between DCM and DCM2 as shown in Chart 1. DCM2 has a locked ring structure of an electron-donating alkylamino group, unlike DCM. The dipole moment of DCM2 in the ground state is 11 D [17] which is greater than that of DCM (6.1 D) [7]. This implies that DCM2 is polar in the ground state rather than DCM. Similar to DCM2, the electron donor moiety in **5** is locked by a ring structure. The locked structure may lead to effective restriction of molecular perturbation in order to narrow the fwhm and to increase the electron-donating property. This idea agrees well with the fact that the dipole moment of DCM2 in the ground state is greater than that of DCM.

Fig. 4 shows the variation of fluorescence spectra of **1** along with excitation wavelengths in various solvents. The excitation wavelength significantly affected $\lambda_{\mathrm{max,em}}$ in polar solvent, whereas it does not in non-polar solvent. The fluorescence band shifts to a longer wavelength in acetonitrile by 25 nm with an increase in the excitation wavelength from 430 to 520 nm, whereas it never does in 1,4-dioxane. This means that the fluorescence in non-polar solution comes from a certain, fixed, single photoexcited species, whereas fluorescence in polar solutions comes from transient, plural, photoexcited species on a very short life time scale. This was confirmed by the excitation spectra, as shown in Fig. 5. The shape of

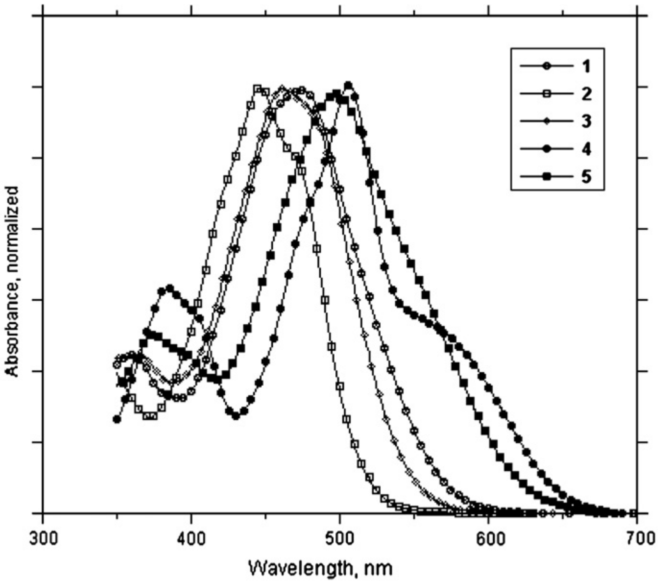


Fig. 2. UV–vis absorption spectra of compounds **1**–**5** in acetonitrile ($c < 1.0 \times 10^{-6}$ M). As for **3**, acetone was used instead of acetonitrile.

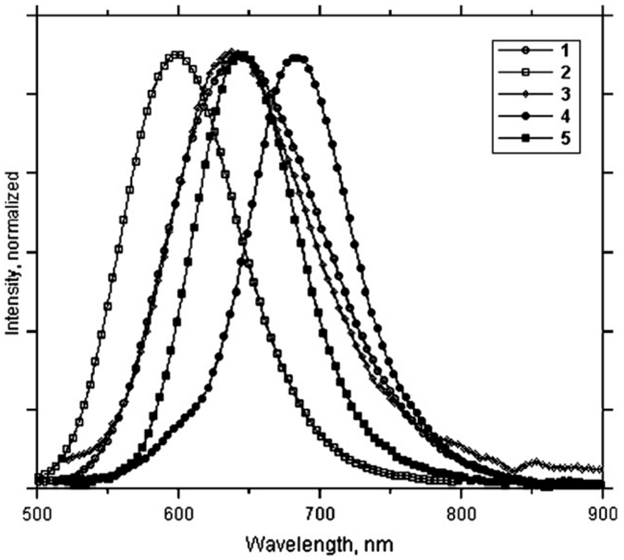


Fig. 3. Fluorescence spectra of compounds **1**–**5** in acetonitrile ($c < 1.0 \times 10^{-6}$ M). All compounds were excited at their $\lambda_{\mathrm{max,abs}}$. As for **3**, acetone was used instead of acetonitrile.

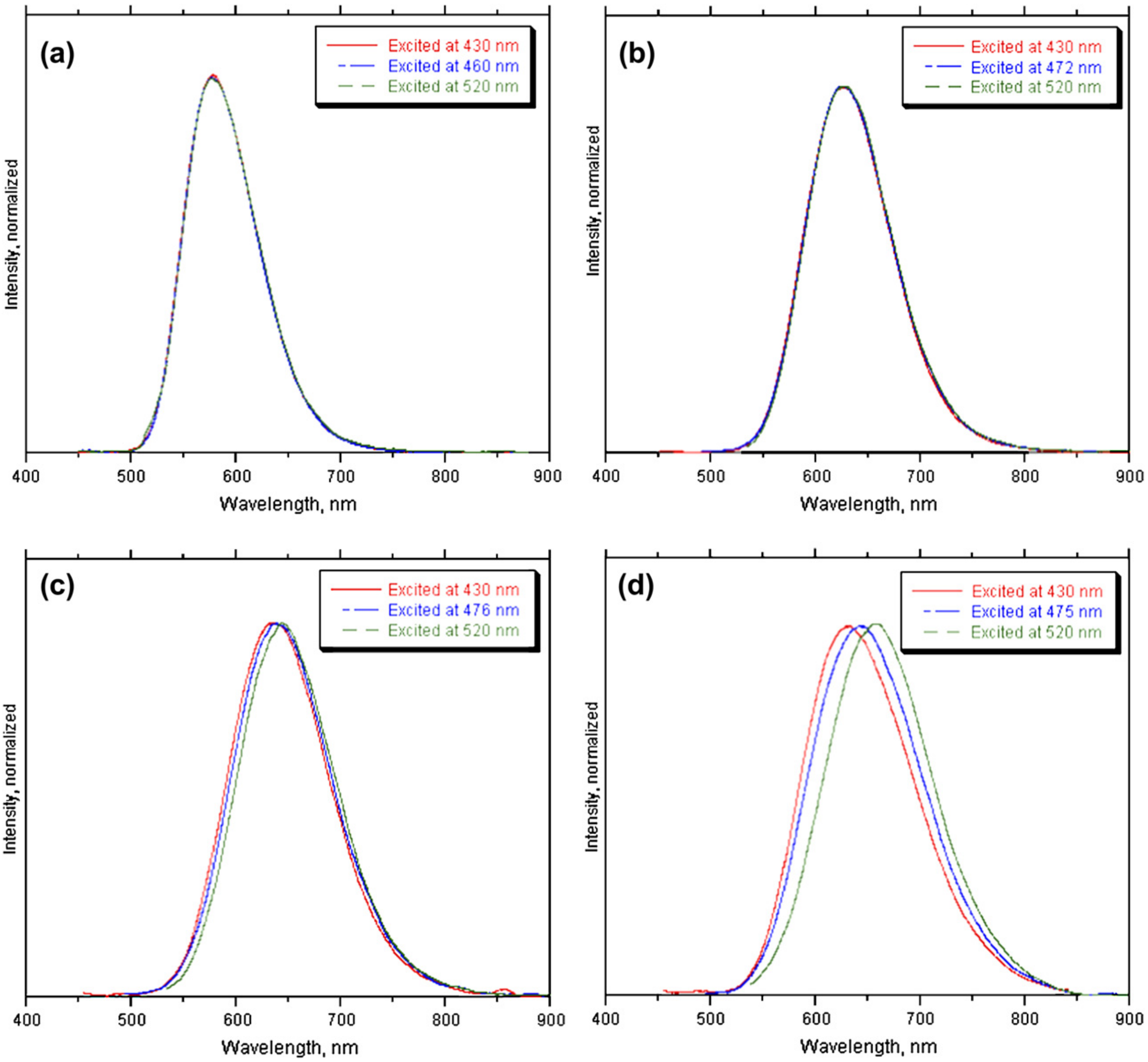


Fig. 4. Variation of fluorescence spectra of **1** in (a) 1,4-dioxane, (b) THF, (c) ethanol, and (d) acetonitrile along with excitation wavelengths ($c < 1.0 \times 10^{-6}$ M).

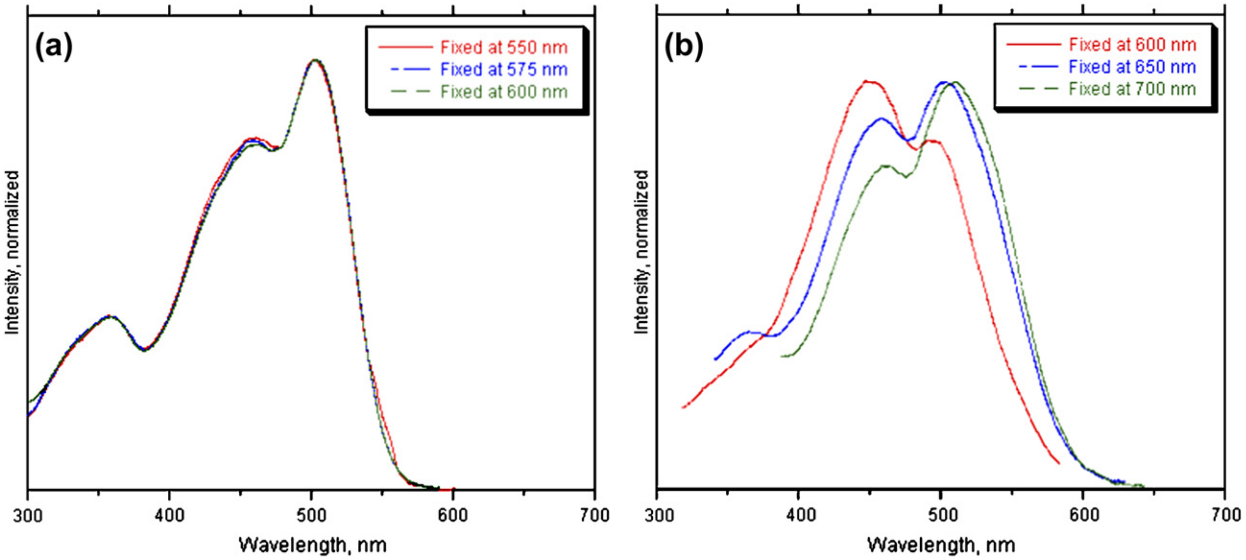


Fig. 5. Excitation spectra of **1** in (a) 1,4-dioxane and (b) acetonitrile ($c < 1.0 \times 10^{-6}$ M).

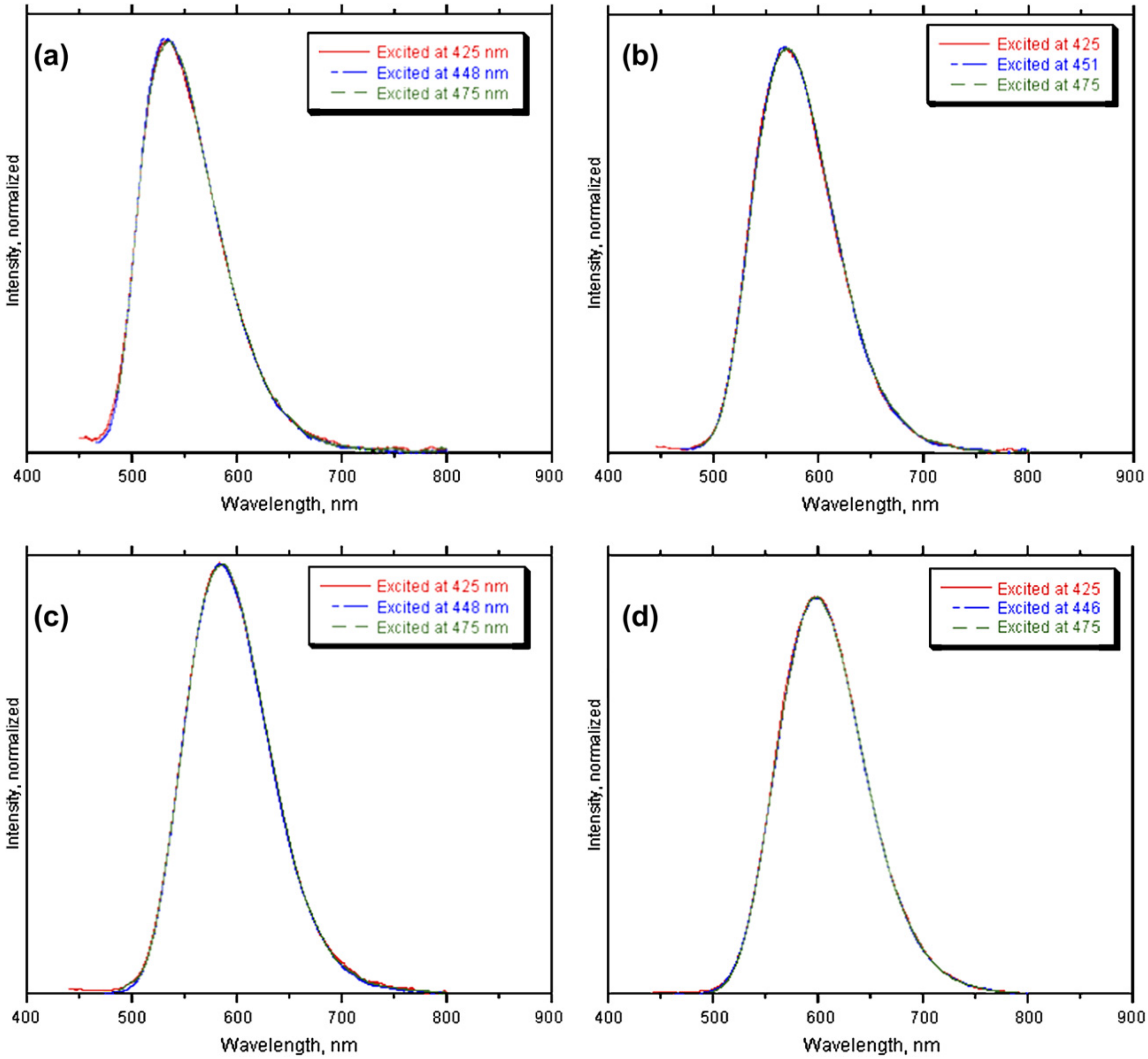


Fig. 6. Variation of fluorescence spectra of **2** in (a) 1,4-dioxane, (b) THF, (c) acetone, and (d) acetonitrile along with excitation wavelength ($c < 1.0 \times 10^{-6}$ M).

the excitation spectrum hardly changed in 1,4-dioxane even though the emission wavelength was shifted in the range of 550–600 nm. In contrast, the shape of excitation spectra appreciably changed in acetonitrile when the emission wavelength was shifted in the range of 600–700 nm; i.e., when the emission was monitored at 600 nm, the excitation spectrum showed an excitation maximum at 450 nm together with a shoulder at 493 nm. The excitation spectrum, however, showed an excitation maximum at 510 nm together with a shoulder at 460 nm when the emission was fixed at 650 or 700 nm.

We also investigated the variation of fluorescence of **2**–**5** along with excitation wavelengths in various solvents. These compounds showed a different tendency from **1**. For example, Fig. 6 shows the fluorescence spectra of **2**. The fluorescence band never shifted in any solvent even if the excitation wavelength changed from 425 to 475 nm. This indicates that compound **2** emits from a fixed, single, photoexcited species regardless of the kind of solvent. This is probably due to the fact that compounds other than **1** have bulky donor groups as compared to **1**. The bulky groups would lead the molecular stability to restrain formation of any other transient species in an excited state and to fix a single photoexcited species.

Fig. 7 shows the voltage–current (V–I) density and voltage–luminescence (V–L) characteristics of the EL device with **1**. The inset figure shows the configuration of EL device fabricated in the present study and the structure of α-NPD. Recently, a thin layer of inorganic Li compounds, such as Li_2O and LiF, was reported to be useful in bilayer cathode systems. This cathode system is based on the assumption that the organic layer at the cathode interface is doped with a low-work-function metal, such as Li, when such a reactive metal is evaporated onto the organic layer. As a result, the barrier height for electron injection from the cathode to the organic layer is lowered. The forward current was obtained when the ITO electrode was biased positively and Al electrode

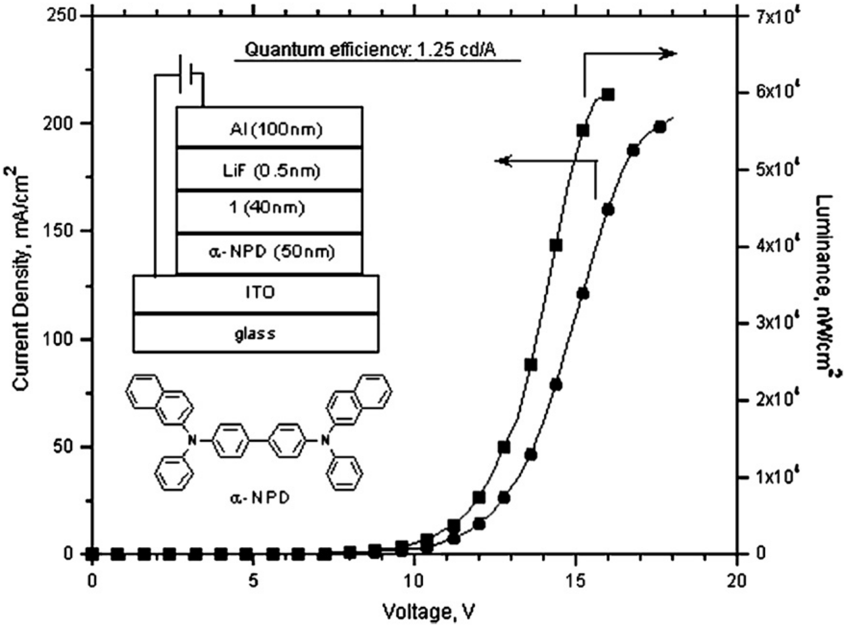


Fig. 7. Voltage–current (V–I) density and voltage–luminescence (V–L) characteristics of the EL device with **1**. Inset: Device configuration and chemical structure of α-NDP.

negatively. The forward current increased with increasing forward bias voltage for EL device. Red-light emission was observed for the EL devices under forward bias.

The luminescence intensity exponentially increased with increase of the voltage. The linear dependence of the luminescence intensity on the voltage indicates that charge carriers are easily injected from both the electrodes by increasing the voltage or current density. The turn-on voltage of the device with **1** is approximately 10 V. The device with **1** showed a maximum luminance of about 2000 cd/m^2 at a current density of 160 mA/cm^2 at 16 V. Such high luminescence intensity indicates an easy recombination of holes and electrons in the emitting layer. The EL spectrum of the present device showed a main peak at approximately 692 nm. The CIE coordinate (x, y) was (0.71, 0.29), which corresponds to the red emission.

4. Conclusions

We successfully synthesized a new class of 2D–π–A type pyran-based dyes, **1**–**5**, by two-step processes including Vilsmeier and Knoevenagel reactions. Their ICT characters were clearly verified at a steady state in solution. All compounds studied in this work, showed a significantly large Stokes shift. Their fluorescence bands significantly shifted to longer wavelengths with an increase in the dielectric constant of the solvent.

The π-conjugated moiety such as the carbazolyl group was not preferable to an electron donor group for efficient red-emission color saturation. The molecular structures of the electron-donating group significantly influenced the fluorescence property. Molecular locking of the electron donor group led to narrowing the fwhm and to increasing the dipole moment at a ground state. Bulky donor groups also led molecular stability to restrain the electronic perturbation at an excited state. Bright and saturated red light was observed from EL device based on the present dye, indicating its potential use as a red emitter in EL application. Further optimizations of EL device via multi-layer structure and doping or blending system for better EL performance are in progress. These types of dyes are also applicable to volatile organic compound (VOC) sensors [18], due to its variable fluorescence color and intensity, according to solvent polarity. Based on the fundamental knowledge about the photophysical property of these dyes, the optimization of such optical devices plus processability will be accelerated by polymer synthetic technology. Thus, it is a challenging subject to synthesize polymers having these dyes in a side chain. The related experiments are currently underway in our laboratory.

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