Dyes and Pigments 92 (2012) 1069–1074

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Synthesis of 6-(4-diethylamino)phenyl-2-oxo-2*H*-pyran-3-carbonitorile derivatives and their fluorescence in solid state and in solutions

Masayori Hagimori[a], Naoko Mizuyama[b], Kenichirou Yokota[c], Yasuhisa Nishimura[c], Mika Suzuta[c], Chen-Kuen Tai[d], Bo-Cheng Wang[d,*], San-Lang Wang[d], Tzenge-Lien Shih[d], Kuen-Da Wu[d], Zhi-Shuan Huang[d], Shih-Chun Tseng[d], Chieh-Yu Chen[d], Jian-Wei Lu[d], Ho-Hsiang Wei[d], Keisuke Kawashima[e], Shinich Kawashima[e], Yoshinori Tominaga[c,d,**]

[a] *Faculty of Pharmaceutical Sciences, Nagasaki International University, 2825-7 Huis Ten Bosch, Sasebo 859-3298, Japan*
[b] *Department of Pharmacy, Saga University Hospital, 5-1-1 Nabeshima, Saga 849-8521, Japan*
[c] *Faculty of Environmental Studies, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan*
[d] *Department of Chemistry, Tamkang University, Tamsui 251, Taiwan*
[e] *Harima Chemical, Inc., 671-4 Noguchi-machi, Kakogawa 675-0019, Japan*

ARTICLE INFO

Article history:
Received 4 March 2011
Received in revised form
12 May 2011
Accepted 17 May 2011
Available online 12 July 2011

Keywords:
2-Pyrone dyes
One-pot synthesis
Ketene dithioacetal
Fluorescence
Solvatochromism
Solid state

ABSTRACT

One-pot synthesis of a new 2-pyrone dye (**3a**) by the reaction of 4-diethylamino-acetophenone (**1**) with methyl 2-cyano-3,3-bis(methylsulfanyl)acrylate (**2**) in the presence of sodium hydroxide as the base was carried out in DMSO. Compound **4a** was synthesized by the replacement of methylsulfanyl group of **3a** with dimethylamine at 4-position of pyrone ring. Similarly, compound **5a** was prepared via the reaction of **3a** with diethyl malonate. Compounds **3a**–**5a** exhibited the following fluorescence in the solid state: red (**3a**), green (**4a**), and orange (**5a**). In addition, it was revealed that 2-pyrone dyes exhibit fluorescence in various solvents and show positive solvatochromism. Compounds **3a** and **5a** exhibited intense fluorescence in chloroform and dichloromethane (fluorescence quantum yield Φ: 0.94–0.95). In contrast, compound **4a** exhibited intense fluorescence in polar solvents (methanol: $\Phi = 0.92$). These 2-pyrone dyes have the potential for applications in various fields.

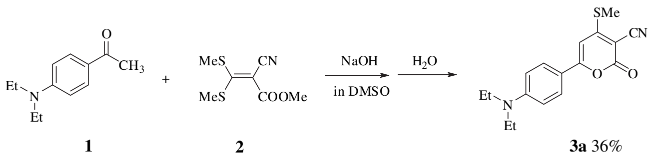
1. Introduction

Fluorescent dyes are currently attracting considerable interest owing to their wide range of applications in various fields, e.g., for preparing emitters for electroluminescence devices in copy-preventing, materials for collecting solar energy, fluorescent films for greenhouses, and fluorescent colorants [1–8]. Recently, we have reported that 2-pyrone-type compounds having very strong fluorescence properties can be synthesized using sulfonyl ketene dithioacetals [9–12] and active methyl compounds in the presence of an appropriate base [13–15]. There are very few dyes that exhibit fluorescence both in the solid state and in solutions because generally the molecular aggregation in the solid state causes fluorescence quenching. The 2-pyrone derivatives synthesized previously showed almost no fluorescence in solution; however we recently reported the synthesis of 2-pyrone derivatives that exhibited light emission in the range of 400–626 nm in the solid state and 511–516 nm when dissolved in $CHCl_3$ [13–15]. The pattern of substitution of the groups in the pyrone ring has a considerable influence on the fluorescence properties of these 2-pyrone derivatives. In particular, the presence of aryl groups such as the phenyl group at the 6-position of the pyrone ring has a significant effect on the fluorescence properties. Furthermore, the introduction of electron-donating groups such as a diethylamino moiety in the aryl group affects the fluorescence and emission, and can cause a bathochromic shift. The presence of electron-withdrawing substituents such as cyano, ester, and sulfonyl groups are necessary at the 3-position of the pyrone ring [13–15]. It has been observed that in the solid state, 2-pyrone derivatives synthesized using ketene dithioacetals emit light. The strongest fluorescence properties were observed in the case of 2-pyrones having a 4-diethylaminophenyl

---

* Corresponding author. Tel.: +886 2 26215656.
** Corresponding author. Faculty of Environmental Studies, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan. Tel.: +81 958192713; fax: +81 958192716.
E-mail addresses: mhagimori@niu.ac.jp (M. Hagimori), bcw@mail.tku.edu.tw (B.-C. Wang), ytomi@nagasaki-u.ac.jp (Y. Tominaga).

0143-7208/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2011.05.014



Scheme 1.

group at the 6-position of the 2-pyrone ring. We continue our previous studies on heterocyclic compounds, and in this study, we synthesize 6-(4-diethylamino)-phenyl-2-oxo-2*H*-pyran-3-carbonitorile derivatives (**3a**–**5a**) using 4-diethylaminoaceto-phenone (**1**) and ketene dithioacetal (**2**) [16–18] in the presence of an appropriate base. These novel 2-pyrone derivative compounds have a diethylamino group, instead of a dimethylamino group, as the electron-donating group. It is expected that because of the diethylamino group, the molecular aggregation is lower and that as a result, strong fluorescence emission is induced. We compare the fluorescence properties of these derivatives with those of dimethylamino derivatives (**3b**–**5b)** [13] in solid state and in solutions. In addition, we investigated the solvatochromic behavior of **3a**–**5a** in various solvents.

2. Experimental

Synthesis and characterization of compounds were carried out using general procedures employing the following equipment. All melting points were determined using a Mitamura Riken Kogyo Mel-Temp apparatus or a Laboratory Devices Mel-Temp II apparatus and were uncorrected. IR spectra were recorded in potassium bromide pellets on a Jasco 810 or Shimadzu IR-460 spectrometer. UV absorption spectra were determined in 95% ethanol on a Hitachi 323 spectrometer. Fluorescence spectra were recorded on a Shimadzu RF-5300pc. NMR spectra were obtained on Gemini 300NMR (300 MHz), Varian Unityplus 500NMR (500 MHz), and Bruker (600 MHz) spectrometers using tetramethylsilane as the internal standard. Mass spectroscopy was performed using JEOL DX-303 mass spectrometers. Microanalyses were performed by K. Tsuda on a Perkin–Elmer instrument at Nagasaki University. All compounds were reagent grade and used without further purification unless otherwise specified.

2.1. Materials

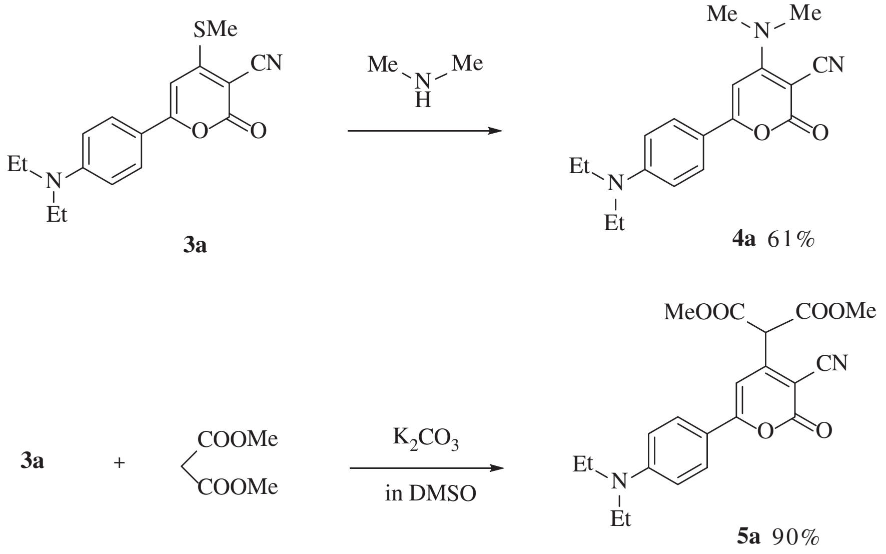
All chemicals were reagent grade and used without further purification unless otherwise specified. All the solvents were of analytic grade and used as received.

*2.2. Synthesis of 6-(4-diethylamino)phenyl-4-methylsulfanyl-2-oxo-2H-pyran-3-carbonitrile (**3a**)*

A mixture of 4-(diethylamino)phenylacetophenone (**1**) (0.96 g, 5.0 mmol), methyl 2-cyano-3,3-bis(methylsulfanyl)acrylate (**2**) (1.01 g, 5.0 mmol), a powdered sodium hydroxide (0.8 g, 2.0 mmol) and 20 ml of DMSO and this solution was maintained at 10–15 °C. This mixture was stirred for 5 h at the same temperature. The reaction mixture was poured into 300 ml of ice-water and then allowed to stand for 30 min. The resulting precipitate was collected by filtration and washed several times with water. After air-drying, the product was recrystallized from toluene to give red needles (0.56 g, 1.78 mmol, 36% yield), mp 245–246 °C. The pure compound was recrystallized from toluene to give red needles, mp 246–247 °C. IR (KBr, cm^{-1}) ν: 2969, 2924, 2366 (CN), 1697, 1572, 1469, 1346. UV (EtOH) λ_{max} nm (log ε): 469(4,33). ^1H-NMR ($CDCl_3$, 400 MHz) δ: 1.23 (6H, t, $J = 7.3$ Hz, CH_2–CH_3), 2.65 (3H, s, SMe), 3.45 (4H, q, $J = 7.3$ Hz, 2 × N–CH_2–), 6.47 (1H, s, 5H), 6.67 (2H, d, $J = 9.3$ Hz, 3′, 5′-H), 7.74 (2H, d, $J = 9.3$ Hz, 2′, 6′-H). ^{13}C-NMR ($CDCl_6$, 100 MHz) δ: 12.51 (2), 14.63, 44.70 (2), 94.14, 111.29 (3), 114.33, 115.16, 129.05 (2), 151.23, 158.31, 163.39, 168.89. Ms (Bruker, TOF/TOF) m/z: 313.164 ($M^+ - 1$). Anal. Calcd for $C_{17}H_{18}NSO_2 = 314.1089$: C, 64.94; H, 5.77; N, 8.91%. Found: C, 64.92; H, 5.71; N, 8.92%.

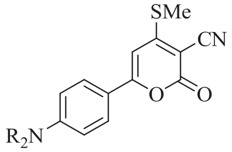
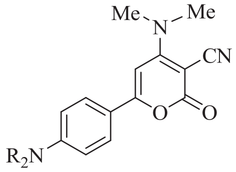
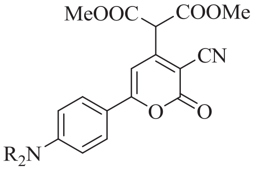
*2.3. Synthesis of 6-(4-diethylamino)phenyl-4-dimethylamino-2-oxo-2H-pyran-3-carbonitrile (**4a**)*

A mixture of **3a** (0.63 g, 2.0 mmol), 50% dimethylamine (2.50 g, 27.8 mmol), and 30 ml of methanol was refluxed for 2 h. The excess dimethylamine and methanol were completely removed under reduced pressure on a rotary evaporator. The residue was recrystallized from methanol to give yellow leaflets (**4a**) (0.38 g,



Scheme 2.

Table 1
UV and fluorescence data for 2-pyrones in $CHCl_3$ and solid state.

Compounds				Dissolved in $CHCl_3$			Solid	
				λ_{max} (nm)[a]	Em_{max} (nm)[b]	Φ[c]	Em_{max} (nm)[b]	Φ[c]
3	**3**		**a**: R = Et	474	540	0.95	624	0.34
			b: R = Me	466	534	0.60	675	0.11
4	**4**		**a**: R = Et	406	490	0.47	525	0.22
			b: R = Me	398	486	0.17	525	0.58
5	**5**		**a**: R = Et	498	542	0.94	606	0.05
			b: R = Me	490	536	0.84	643	0.06

[a] Concentration: 10−5 M.
[b] Each emission was measured using excitation wavelengths.
[c] This quantum yields were determined by using Absolute PL Quantum Yield Measurement System (C9920-01) of Hamamastu Photonics.

1.22 mmol, 61% yield), mp 257–258 °C. IR (KBr, cm^{-1}) ν: 2972, 2930, 2198 (CN), 1686 (C=O), 1597, 1547, 1519, 1473, 1204, 793. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.19 (6H, t, J = 7.1 Hz, $-CH_2-CH_3$), 3.32 (6H, s, NMe_2), 3.40 (4H, q, J = 7.1 Hz, 2 × $N-CH_2-$), 6.19 (1H, s, 5-H), 6.66 (2H, br s, 3′, 5′-H), 7.66 (2H, d, J = 8.4 Hz, 2′, 6′-H). ^{13}C-NMR (DMSO-d_6, 100 MHz) δ: 12.35 (2), 42.38 (2), 44.58 (2), 69.80, 89.67, 111.08, 118.44, 128.08 (4), 161.16, 163.05. Ms m/z: 312 ($M^+ + 1$, 17), 311 (M^+, 81), 297 (20), 296 (100), 176 (22), 132 (7). Anal. Calcd for $C_{18}H_{21}N_3O_2$ = 311.1634: C, 69.43; H, 6.80; N, 13.49%. Found: C, 69.13; H, 6.90; N, 13.41%.

2.4. Synthesis of dimethyl 3-cyano-6-(4-diethylamino)phenyl-2-oxo-2H-pyran-4-ylmalonate (5a)

A mixture of of **3a (**0.31 g,1.0 mmol), dimethyl malonate (0.53 g, 4.0 mmol), potassium carbonate (1.38 g, 10.0 mmol), and 15 ml of DMSO was stirred for 1 h at room temperature. After the reaction, the reaction mixture was poured into 100 ml of water and then acidified with 10% hydrochricacid. The resulting precipitate that appeared was collected by filtration and washed with water. After air-drying, the product was recrystallized from methanol to give red needles (0.37 g, 0.90 mmol, 90% yield), mp 209–210 °C. IR (KBr, cm^{-1}) ν: 2974, 2956, 2216 (CN), 1748 (C=O), 1731 (C=O), 1607, 1598, 1507, 1211, 1200. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.23 (6H, t, J = 7.1 Hz, $N-CH_2-CH_3$), 3.45 (4H, q, J = 7.1 Hz, $N-CH_2-$), 3.84 (6H, s, OMe), 4.98 (1H, s, −CH−), 6.66 (2H, d, J = 9.3 Hz, 3′, 5′-H), 6.86 (1H, s, 5-H), 7.76 (2H, d, J = 9.3 Hz, 2′, 6′-H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 12.46, 12.55, 44.74 (2), 53.69, 53.77, 55.23, 55.46, 93.91, 98.56, 111.31 (2), 114.11, 115.33, 129.39, 129.48, 151.42, 156.31, 158.97, 165.51, 165.77. Ms m/z: 399 ($M^+ + 1$, 24), 398 (M^+, 99), 384 (23), 383 (100), 351 (11), 296 (12), 176 (15), 132 (10). Anal. Calcd for $C_{21}H_{23}N_2O_4$ = 398.4092: C, 63.31; H, 5.57; N, 7.03%. Found: C, 63.39; H, 5.58; N, 7.09%.

2.5. Fluorescence measurements

(a) Solid state: A powder sample of the subject compound was heaped on a tray. After covering the sample with a quartz plate, the tray was fixed in the fluorescence spectrometer. After setting the fluorescence wavelength, the excitation spectrum was determined by scanning at the fluorescence wavelength. Similarly, the fluorescence spectrum was obtained by scanning at the excitation wavelength. The excitation wavelength was determined and the fluorescence spectrum was measured.

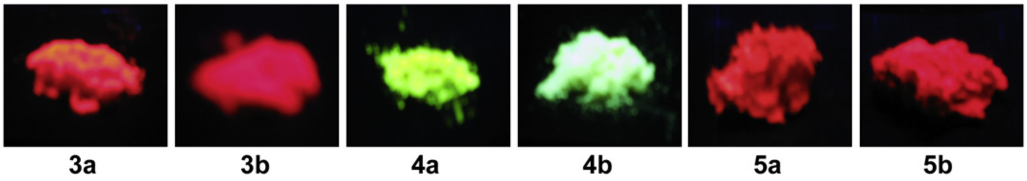

3a 3b 4a 4b 5a 5b

Fig. 1. Solid-state fluorescence of 2-pyrones irradiated with black light (365 nm).

Table 2
UV–Vis absorption properties of **3a**–**5b** in various solvents.[a]

Solvent	Absorption maximum (nm) (log e)					
	3a	**3b**	**4a**	**4b**	**5a**	**5b**
benzenze	466 (4.75)	460 (4.73)	398 (4.63)	394 (4.61)	490 (4.75)	482 (4.65)
diethyl ether	462 (4.79)	454 (4.67)	396 (4.67)	392 (4.65)	482 (4.77)	474 (4.66)
chloroform	474 (4.79)	466 (4.69)	406 (4.68)	398 (4.64)	498 (4.83)	490 (4.73)
dichloromethane	472 (4.83)	464 (4.74)	400 (4.71)	400 (4.71)	496 (4.89)	486 (4.79)
acetone	466 (4.73)	458 (4.66)	398 (4.65)	396 (4.67)	488 (4.64)	480 (4.72)
acetonitrile	466 (4.79)	460 (4.67)	398 (4.67)	394 (4.62)	382 (4.75)	376 (4.69)
DMSO	476 (4.75)	470 (4.67)	400 (4.64)	398 (4.61)	388 (4.72)	382 (4.66)
ethanol	470 (4.75)	465 (4.65)	400 (4.64)	396 (4.62)	392 (4.72)	484 (4.68)

[a] Measured 1×10^{-5} mol/L.

Quantum yields were obtained by using Absolute PL Quantum Yield Measurement System (C9920-01) of Hamamastu Photonics.

(b) Solution state: Quantum yields were obtained by using Absolute PL Quantum Yield Measurement System (C9920-01) of Hamamastu Photonics. The concentrations of the measured samples in the excitation wavelength region were adjusted using a molar absorption coefficient of 0.05. The solution fluorescence spectra were obtained in a manner similar to that described for measurement in the solid state. The emissions were measured using each excitation wavelength.

3. Results and discussion

Scheme 1 shows the synthesis of compound (**3a**). Reaction of **1** with **2** in the presence of powdered sodium hydroxide in dimethyl sulfoxide (DMSO) for 10 h at room temperature and subsequent treatment with cold water yields **3a** (mp: 245–246 °C) and the yield was 36%.

Dramatic changes in the fluorescence colors can be observed when the methylsulfanyl group at the 4-position of the pyrone ring is substituted with either an amino moiety or a malonyl substituent. Then, if the abovementioned substitutions can be achieved, it would be possible to prepare a compound possessing the desired color fluorescence color property. The synthesis of 4-amino-6-aryl-2-oxo-2*H*-pyran-3-carbonitriles by a displacement reaction of 4-methylsulfanyl-2*H*-pyran- 3-carbonitriles with various amines in methanol under reflux has been reported. Therefore, **3a** was reacted with amines to yield 6-(4-diethylamino)phenyl-4-dimethylamino-2-oxo-2*H*-pyran-3-carbonitrile (**4a**). As shown in Scheme 2, compound **4a** in the form of yellow needles was formed by the reaction of **3a** with dimethylamine in refluxing methanol (mp 257–258 °C), and the yield was 61%. Compound **5a** was synthesized by the reaction of **3a** with dimethyl malonate in the presence of sodium hydroxide (base) in DMSO at room temperature. This compound was obtained in the form of red needles with 90% yield and mp of 209–210 °C.

The development of materials with high quantum efficiency and fluorescence quantum yield (Φ) is important in order to assess the potential applications of these fluorescent compounds. Recently, the synthesis of fluorescent 2-pyrone derivatives that emit fluorescence (red, green, and blue) in the solid state has been reported. We previously reported the synthesis of *N*-methyl compounds, 6-(4-dimethylamino)phenyl-2-oxo-2*H*-pyran-3-carbonitriles (**3b**–**5b**) by a convenient one-pot reaction involving ketene dithioacetals [14]. We analyzed the room-temperature fluorescence emission spectra of *N*-ethyl compounds (**3a**–**5a**) and *N*-methyl compounds (**3b**–**5b**) in their solid states (the analysis results are listed in Table 1). The fluorescence maximum of **3a** in $CHCl_3$ was observed at 543 nm and of solid **3a** was observed at 624 nm. The fluorescence maximum wavelength of **3a** was slightly longer than that of **3b**, however **3a** dissolved in $CHCl_3$ exhibited intense fluorescence ($\Phi = 0.95$), which was higher than that of **3b** ($\Phi = 0.60$). The fluorescence of solid **3a** exhibited a hypsochromic shift of 51 nm compared to that of **3b**, and red fluorescence was observed (Fig. 1). The Φ value of solid **3a** was about 3 times higher than that of solid **3b**. We speculated that the molecular stacking might weaken in the presence of an ethyl group and result in increased fluorescence intensity. The compounds **4a** and **4b** exhibited highly hypsochromic shift compared to **3a** and **3b** in solution and solid state. The fluorescence maximum wavelength of **4a** was longer than that of **4b** in $CHCl_3$ and the Φ value of **4a** in $CHCl_3$ was 2.8 times higher than that of **4b**. These phenomena in $CHCl_3$ were similar to the results for **3a** and **3b**. However, it is interesting to note that compound **4b** exhibited strong green fluorescence in solid state ($\Phi = 0.58$) (Fig. 1), the Φ value of **4b** was 2.6 times higher than that of **4a** and was considerably higher than that of other 2-pyrone derivatives. It was considered that the molecular arrangement and orientation in the solid sate resulted in the high fluorescence intensity of **4b**. In a previous study, X-ray crystallographic analysis revealed that compound **4b** was almost plane with small torsion angles (15°) and that this small torsional angles caused strong molecular stacking; the molecular packing diagram of **4b** clearly showed short molecular distances (ca 3.12 Å)

Table 3
Fluorescence properties of **3a**–**5b** in various solvents.

Solvent	Emission maximum (nm) (Φ)					
	3a	**3b**	**4a**	**4b**	**5a**	**5b**
benzene	524 (0.50)	522 (0.28)	482 (0.04)	478 (0.02)	524 (0.75)	522 (0.48)
diethyl ether	532 (0.13)	532 (0.23)	490 (0.03)	488 (0.01)	534 (0.78)	532 (0.39)
chloroform	540 (0.95)	534 (0.60)	490 (0.47)	486 (0.17)	542 (0.94)	538 (0.84)
dichloromethane	540 (0.95)	536 (0.63)	494 (0.66)	492 (0.28)	548 (0.93)	546 (0.69)
acetone	540 (0.39)	542 (0.16)	500 (0.38)	500 (0.16)	556 (0.32)	556 (0.16)
acetonitrile	546 (0.09)	544 (0.04)	504 (0.68)	504 (0.35)	–[a]	–[a]
DMSO	552 (0.13)	554 (0.04)	512 (0.89)	514 (0.69)	–[a]	–[a]
ethanol	548 (0.01)	546 (0.04)	504 (0.92)	504 (0.63)	–[a]	–[a]

[a] No fluorescence was observed.

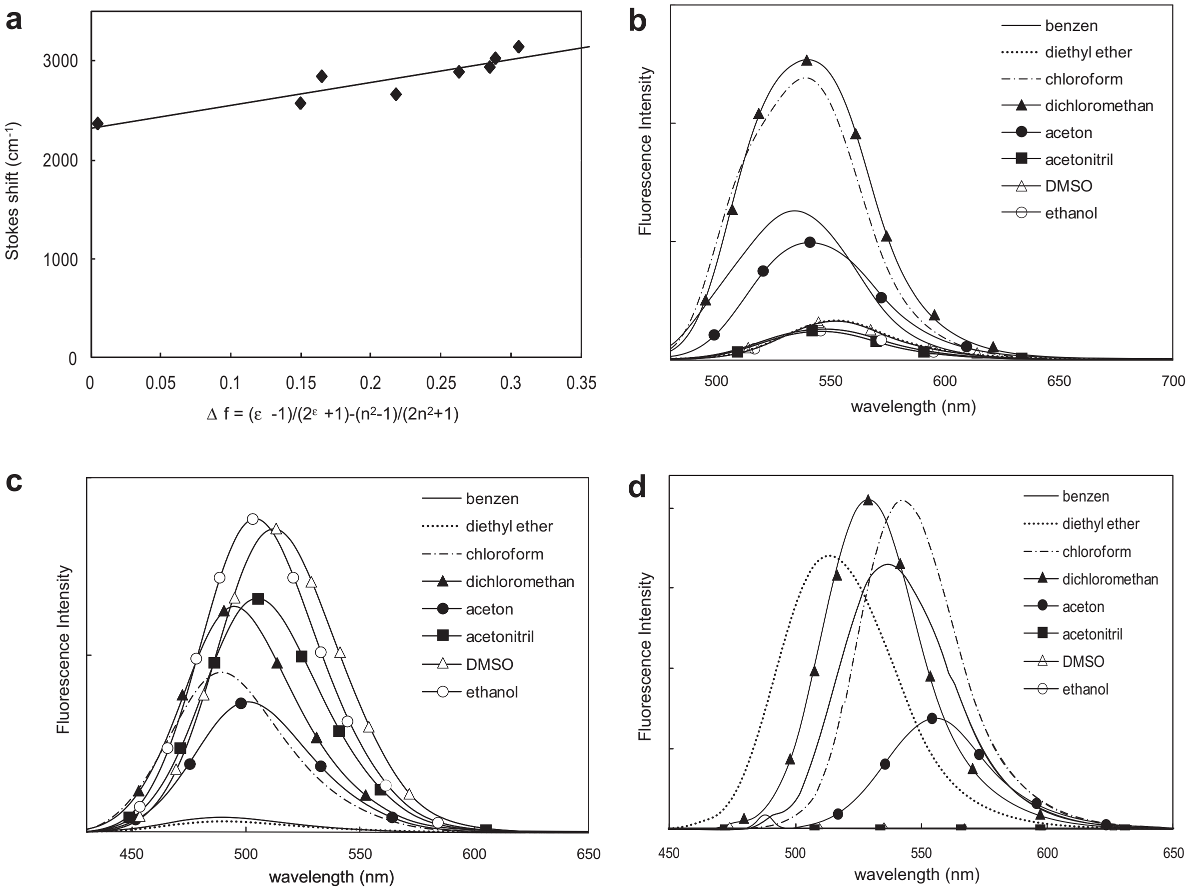


Fig. 2. (a) Lippert-Mataga plot of **3a** in benzene, chloroform, diethylether, dichloromethane, DMSO, acetone, ethanol, acetonitril (1×10^{-5} M). ε: dielectric constant, n: refractive index. (b) Fluorescence spectra of **3a** in various solvents. (c) Fluorescence spectra of **4a** in various solvents. (d) Fluorescence spectra of **5a** in various solvents.

[13]. The properties of compounds **5a** and **5b** in $CHCl_3$ were similar; the fluorescence maximum wavelength of **5a** was longer than that of **5b**, and the intensity of the fluorescence of **5a** in $CHCl_3$ was higher than that of **5b** in $CHCL_3$. The absorption data for **5a** and **5b** indicated that the absorption of these compounds bathochromically shifted from the absorption of **3b** by 24–32 nm. The Φ values of **5a** and **5b** were 0.94 and 0.84, respectively. The compounds **5a** and **5b** in the solid state exhibited weak orange–red fluorescence, and the Φ values of **5a** and **5b** were 0.05 and 0.06, respectively (Fig. 1).

It was observed that the new 2-pyrone derivatives **3a**–**5a** that have a diethylamino group at 4-position of the phenyl group showed a bathochromic shift of absorption and fluorescence and also showed a high fluorescence quantum yield when dissolved in $CHCl_3$. Therefore, we also investigated the solvatochromic properties of **3**–**5** in various solvents. Table 2 lists the absorption data, and Table 3 lists the fluorescence data for **3**–**5**. The replacement of a dimethylamino group with a diethylamino group induced a bathochromic shift in the absorption, while a slight bathochromic shift in the fluorescence of **3**–**5** was observed by the replacement of a dimethylamino group with a diethylamino group. The emission maximum of **3**–**5** was dependent on the dielectric constant of the solvent, and as a result the Stokes shift became larger with an increase in the polarity of the solvent used. Quenching of the fluorescence of **5a** and **5b** was observed in high-permittivity solvents (ethanol, DMSO, acetonitril). However, the bathochromic shift in the case of acetone was larger than the bathochromic shift in the case of benzene. These results suggest that the malonic ester group present at the 4-position of pyrone ring have a significant effect on fluorescent properties. The solvatochromic effect has been estimated by using a Lippert-Mataga plot (Fig. 2a) [19–21]. The plot of Stokes shifts versus the polarity function Δf of compound 3a shows the good correlation between Stokes shifts and solvent polarity. This result indicated that the dipole moment of molecules changes upon excitation due to intramolecular charge transfer.

In addition, it was observed that the fluorescence quantum yield significantly depend on the solvent molecules. The polarity of a solvent will generally influence the fluorescence-emission spectra of fluorophores. The Φ values of **3a** and **3b** in non-polar solvents was high; in particular, fluorescence quantum yields of 3a in chloroform (Φ: 0.95) and dichloromethane (Φ: 0.95) were very high (Fig. 2b). In contrast, 4a and 4b emitted both in polar and non-polar solvents except for benzene and diethyl ether (Φ: 0.17–0.92). In DMSO and ethanol, the fluorescence quantum yield of 4a was very high (Fig. 2c). Compounds 5a and 5b, like **3a** and **3b**, showed strong fluorescence in non-polar solvents (Fig. 2d). The fluorescence quantum yield of the synthesized 2-pyrone derivatives increased when the amino group of 4-position of phenyl group and 4-position of pyrone ring in solution was changed; this suggest that it is possible to use fluorophores for various purposes.

4. Conclusion

The strongly fluorescent dye **3a** with an electron-donating 6-(4-diethylamino)phenyl group and an electron-withdrawing cyano group was synthesized by a convenient one-pot reaction of ketene dithioacetal (**2**) with 4-diethylaminoacetophenone (**1**) in the presence of sodium hydroxide as the base in DMSO. The compounds **4a** and **5a** were synthesized by replacing of the methylsulfanyl group of **3a** in good yield. The novel 2*H*-pyrone derivatives (**3a**–**5a**) exhibited fluorescence in the solid state (red (**3a**), green (**4a**), and orange (**5a**)), and they also exhibited positive solvatochromism in various solvents. The fluorescence of **3a**–**5a** in solutions showed a bathochromic shift and intense fluorescence from the fluorescence of the previously reported 2*H*-pyrone derivatives (**3b**–**5b**) in solution. It is anticipated that these materials will find applications in various fields.

References

[1] Tang CW. Organic electroluminescent diodes. Appl Phys Lett 1987;51:913–5.

[2] Kido J, Izumi Y. Efficient electroluminescence from tris(4-methyl-8-quinolinolato) aluminum (III). Chem Lett; 1997:963–4.

[3] Hamada Y, Sano T, Shibata K, Kuroki K. Influence of the emission site on the running durability of organic electroluminescent devices. Jpn J Appl Phys 1995;34:L824–6.

[4] Tang CW, Van Slyke SA, Chen CH. Electroluminescence of doped thin films. J Appl Phys 1989;65:3610–6.

[5] Friend RH, Gymer RW, Holmes AB, Burroughes JH, Marks RN, Taliani C, et al. Electroluminescence in conjugated polymers. Nature 1999;397:121–8.

[6] Odaka H, Okimoto Y, Yamada H, Okimoto H, Kawasaki M, Tokuda Y. Control of magnetic-field effect on electroluminescence in Alq_3-based organic light emitting diodes. Appl Phys Lett 2006;88:123501–3.

[7] Hoshi T, Kumagai K, Inoue K, Enomoto S, Nobe Y, Kobayashi M. Electronic absorption and emission spectra of Alq_3 in solution with special attention to a delayed fluorescence. J Luminescence 2008;128:1353–8.

[8] Hagimori M, Mizuyama N, Tominaga Y. Synthesis of pyrano[4,3-*b*]quinolizine derivatives from 6-aryl or styryl-4-methylsulfanyl-2-oxo-2*H*-pyrans and their fluorescence. ARKIVOC 2008;13:16–27.

[9] Tominaga Y, Matsuda Y. Synthesis of heterocyclic compounds using nitro ketene dithioacetal. J Heterocycl Chem 1985;22:937–49.

[10] Tominaga Y, Matsuda Y. Synthesis of indolizine derivatives and their related compounds using ketene dithioacetals. J Synth Org Chem Jpn 1985;43:669–79.

[11] Tominaga Y. Synthesis of 2-pyrone and 2-pyridone derivatives using ketene dithioacetals. J Synth Org Chem Jpn 1989;47:413–24.

[12] Tominaga Y. Synthesis of heterocyclic compounds using ketene dithioacetals. In: Menon J, editor. In trends in heterocyclic chemistry, vol. 2. Trivandrum: Council of Scientific Research Integration, Research Trends; 1991. p. 43–83.

[13] Mizuyama N, Murakami Y, Nagaoka J, Kohra S, Ueda K, Hiraoka K, et al. Synthesis and fluorescence of 6-(4-dimethylaminophenyl)- and 6-[2-(4-*N*,*N*-disubstituted aminophenyl)vinyl]-4-methylthio-2-oxo-2*H*-pyran-3-carbonitriles in solution and in the solid states. Heterocycle 2006;68:1105–6.

[14] Mizuyama N, Murakami Y, Nakatani T, Kuronita K, Kohra S, Ueda K, et al. Reaction of 6-aryl- or styryl-4-methylsulfanyl-2-oxo-2H-pyrans with active methylene compounds and fluorescence properties of the products. J Heterocycl Chem 2008;45:265–77.

[15] Hagimori M, Mizuyama N, Shigemitsu Y, Wang BC, Tominaga Y. Development of fluorescent 2-pyrone derivatives using ketene dithioacetals for organic EL devices. Heterocyces 2009;78:555–70.

[16] Hidaki S, Tominaga Y, Matsuda Y, Kobayashi G, Sakemi K. Sulfonyl ketenethioacetal. III. Reaction of sulfonyl ketenethioacetal with active methylene compounds. Yakugaku Zasshi 1979;99:1234–9.

[17] Kashima K, Hidaki S, Tominaga Y, Matsuda Y, Kobayashi G, Sakemi K. Sulfonyl ketenethioacetal. 1 Synthesis and reaction of sulfonyl ketenethioacetals. Yakugaku Zasshi 1979;99:38–44.

[18] Hagimori M, Matsui S, Mizuyama N, Yokota K, Nagaoka J, Tominaga Y. Novel synthesis of 4*H*-quinolizine derivatives using sulfonyl ketene dithioacetals. Eur J Org Chem 2009;33:5847–53.

[19] Lippert E. Dipolmoment und elektronenstruktur von angeregten molekulen. Z Naturforsch A 1955;10:541–5.

[20] Mataga N, Kaifu Y, Koizumi M. Solvent effects upon fuorescence spectra and the dipolemoments of excited molecules. Bull Chem Soc Jpn 1955;29:465–70.

[21] Ito F, Nagai T, Ono Y, Yamaguchi K, Furuta H, Nagamnra T. Photophysical properties of 2-picolinoylpyrrole boron complex in solutions. Chem Phys Lett 2007;435:283–8.