Substituent Effect of 2,3-Dicyanopyrazine Dyes on Solid-State Fluorescence

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Some pyrazine dyes based on the same chromophoric system with different steric nature were synthesized to evaluate the correlation between solid-state fluorescence and molecular arrangement. It was confirmed that the solid-state fluorescence is significantly correlated with the prevention of complete stacking between chromophoric systems in the crystalline state. This result suggests that the introduction of bulky substituents to fluorescent dyes should be made on substantial positions for preventing the complete stacking between the chromophoric systems on the basis of the crystal structure.

Organic fluorescent dyes are one of the most exciting subjects in functional dye chemistry in recent decades. Many studies on fluorescent dyes have been particularly dedicated to develop the characteristics of an organic electroluminescence (EL) device, which is the basic technology towards the forthcoming EL displays.[1] The most serious problem in the application of organic dyes to the emitter materials is fluorescence quenching in both condensed and crystalline states. The incorporation of bulky substituents to a fluorophore is a well-known strategy to gain intensive fluorescence in both states to prevent molecular stacking between π-conjugated systems. The molecular stacking between π-conjugated systems has been considered as a major cause for fluorescence quenching due to intermolecular interactions. However, the actual influence of molecular stacking on the fluorescent properties is not understood well. Furthermore, especially in the solid state, a well-defined explanation of the role of intermolecular interactions (so-called π–π interaction) by experiment has not been given so far. In fact, in order to obtain the intense fluorescence in organic solids, modification of molecular structure has been performed by trial and error. The substantial direction of the design of dye molecules for fluorescent solid materials has been required. Hence, many attempts have been made for organic fluorescent compounds in single crystals,[2] inclusion crystals,[3] and condensed states[4] to clarify the solid correlation among molecular structure, crystal structure, and fluorescent properties in the solid state.

We have developed a new fluorophore for red emitters based on a nonplanar dicyanodiazepine skeleton[5] and investigated the correlation among molecular structure, crystal structure, and solid-state fluorescence.[6] Among the three kinds of emitters for primary colors, red, green, and blue, for full-colored EL devices, red emitters have usually been prepared with dopants. Only lesser kinds of red emitters without dopants are known,[7] since fluorescence quenching is usually observed in the solid state in many fluorescent dyes for red emitters. In the course of our studies on dicyanodiazepine dyes, the solid-state fluorescence was found to be significantly correlated with the prevention of complete stacking between the chromophoric systems in the crystalline state.[6] The theoretical treatment of the electronic states of a parallel dimer, corresponding to a complete stacking pair of molecules, reveals that the dimer formation causes fluorescence quenching due to symmetrical limitation.[8] For example, non-fluorescent H-aggregates and concentration-dependent fluorescence quenching are interpreted on this basis. However, practical correlation between molecular aggregates in a given system and their fluorescence quenching have not been reported so far. Our result suggested that the effective introduction of bulky substituents should be made on fluorescent dyes for preventing the complete stacking. We then made an attempt to verify this result with the expansion of the fluorophore into the relative 2,3-dicyanopyrazine skeleton. Pyrazine dyes were intensively developed in the 1990's as a novel dye chromophore by Matsuoka's group.[9] These dyes have attracted attention as a new functional dye because of their strong fluorescence. The dyes with large substituents show strong fluorescence even in single crystals and vacuum deposited films. However, in the cases of the dyes with small substituents, fluorescence quenching generally occurs in the solid state.[2b] In this paper, the substituent effect on the solid-state fluorescence was examined in some new red-fluorescent 2,3-dicyanopyrazine dyes. Fluorescent properties in the crystalline state are discussed on the basis of the crystal structure and intermolecular interactions.

Results and Discussion

Synthesis of 5,6-Disubstituted 2,3-Dicyanopyrazine Dyes. The chromophore in the present study is closely related to the dicyanodiazepine chromophoric system. The cyano groups in a pyrazine ring work as an acceptor and the amino group conju-

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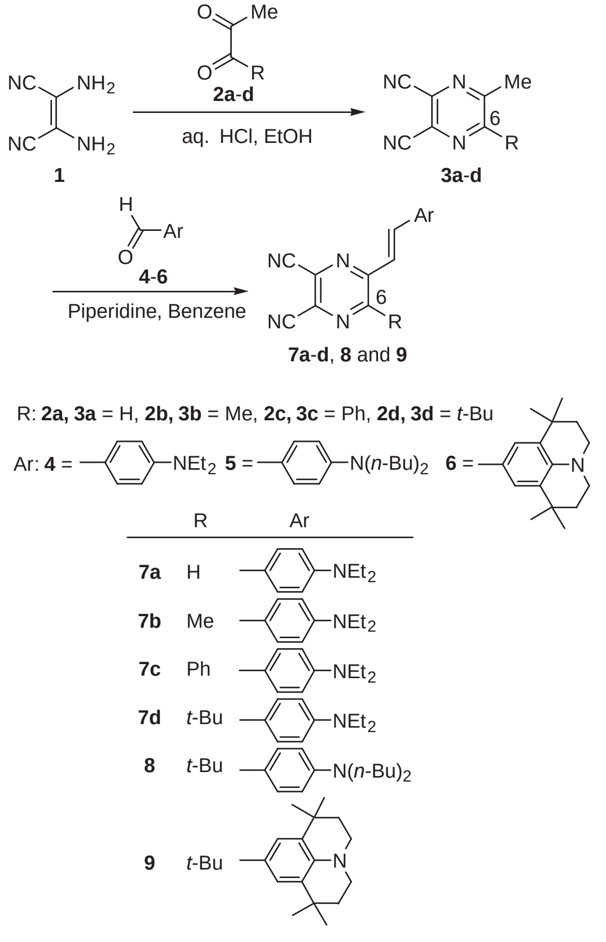
gated to the pyrazine ring through a styryl moiety acts as a donor. From the previous study on dicyanodiazepine dyes, the introduction of substituents around both the donor and the acceptor moieties can prevent the complete stacking of molecules.[6] Substituent effects were thus examined by two positions in the present chromophoric system, on the amino group and on the pyrazine ring at the 6-position. The 5,6-disubstituted 2,3-dicyanopyrazines **7a–7d**, **8**, and **9** were prepared as shown in Scheme 1. Diaminomaleonitrile (DAMN, **1**) reacted with the diones **2a–2d** in the presence of aqueous hydrochloric acid (3 mol dm^{-3}) to give the 6-substituted 2,3-dicyano-5-methylpyrazines **3a–3d** in 74–89% yields. Then, the condensation of **3a–3d** with the aromatic aldehydes **4–6** gave the 5,6-disubstituted 2,3-dicyanopyrazines **7a–7d**, **8**, and **9** in low to moderate yields.



Scheme 1.

Optical Properties of 5,6-Disubstituted 2,3-Dicyanopyrazine Dyes in Solution and in the Solid State. The UV–vis absorption and fluorescence spectra of **7a–7d** in toluene are shown in Fig. 1 and their characteristics are summarized in Table 1. No significant difference was observed in the absorption ($\lambda_{\max}$) and fluorescence maxima ($F_{\max}$) among **7a–7d**, since the electronic structure is influenced little by the substitu-

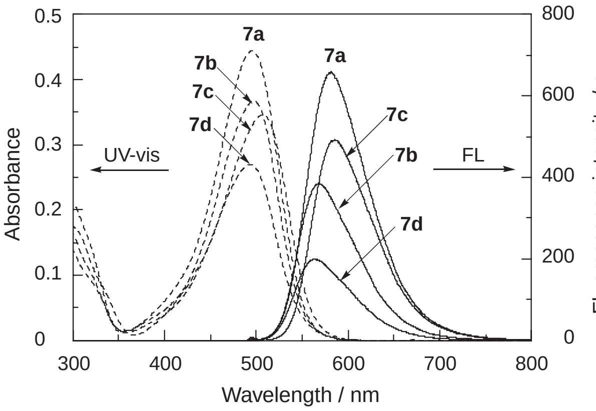
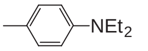
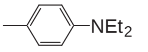
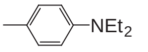
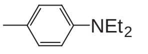
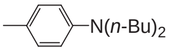
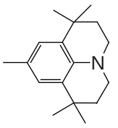


Fig. 1. UV–vis absorption and fluorescence spectra of **7a–7d** (1×10^{-5} mol dm^{-3}) in toluene.

Table 1. UV–Vis Absorption and Fluorescence Properties of **7–9**

Compd	R	Ar	Toluene[a]				Powder[b]			
			$\lambda_{\max}$ ($\varepsilon_{\max}$)/nm	$F_{\max}$[c]/nm	Φ_f[d]	SS[e]	$\lambda_{\max}$[f]/nm	$F_{\max}$[c]/nm	RFI[g]	SS[e]
7a	H		495 (43300)	582	0.94	87	527	—[h]	—[h]	—[h]
7b	Me		497 (37300)	568	0.43	71	526	660	5	134
7c	Ph		497 (34600)	585	0.82	88	543	—[h]	—[h]	—[h]
7d	t-Bu		493 (27000)	563	0.22	71	519	634	100	115
8	t-Bu		496 (33300)	565	0.25	69	522	625	31	103
9	t-Bu		521 (26400)	591	0.33	70	561	—[h]	—[h]	—[h]

a) Measured at the concentration of 1.0×10^{-5} mol dm^{-3} at 25 °C. b) Ground crystals. c) Excited with the absorption maximum. d) The fluorescence quantum yields were determined using quinine sulfate in 0.1 mol dm^{-3} sulfuric acid ($\Phi_f = 0.55$, $\lambda_{ex} = 366$ nm) as the standard. e) Stokes shift. f) Diffuse reflectance spectra (given in Kubelka–Monk units). g) The relative fluorescence intensity was determined by considering the fluorescence intensity of **7d** to be 100. h) Too weak to be measured.

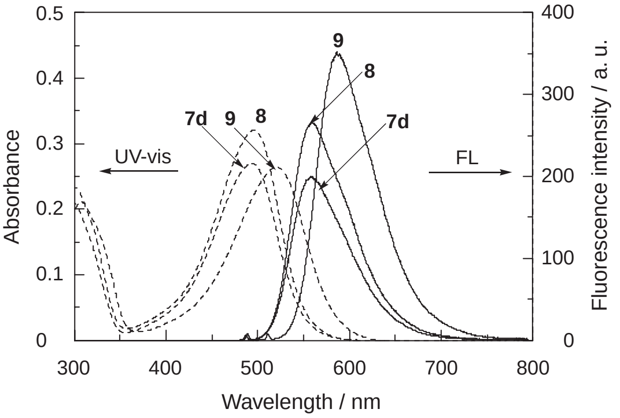


Fig. 2. UV–vis absorption and fluorescence spectra of **7d**, **8**, and **9** (1×10^{-5} mol dm^{-3}) in toluene.

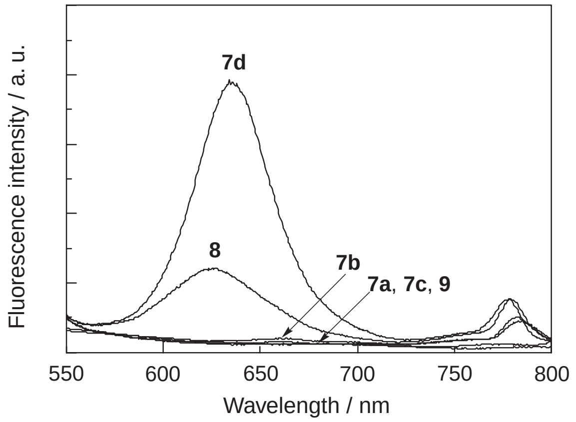


Fig. 3. Fluorescence spectra of **7**–**9** in powdered form.

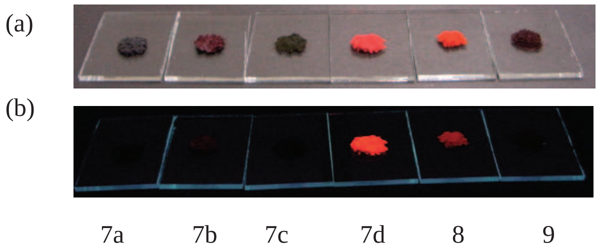


Fig. 4. Photographs of ground crystals of dyes **7**–**9** under (a) room light and (b) 254 nm light.

ent R. The dyes **7a**–**7d** showed their λ_{max} around 493–497 nm and the F_{max} were observed around 563–585 nm. The molar absorption coefficients (ε_{max}) were found to depend slightly on the substituent R. The ε_{max} value decreased in the order of dyes: **7a** (43300) > **7b** (37300) > **7c** (34600) > **7d** (27000) as the size increased of the substituent R. The present effect of the substituent on ε_{max} is in good accordance with the calculated result by semi-empirical molecular orbital calculations (Table S1). The dyes **7a**–**7d** exhibit relatively high fluorescence quantum yields (Φ_f) of 0.22–0.94. The dyes with flexible substituents **7b** and **7d** were found to show smaller Φ_f values than **7a** and **7c**. This result reflects the influence of substituents on fluorescent quantum yields. Flexible substituents are considered to promote the non-radiative relaxation to reduce the fluorescent quantum yield.[10] The UV–vis absorption and fluorescence spectra of **7d**, **8**, and **9** in toluene are shown in Fig. 2 and their characteristics are summarized in Table 1. The λ_{max} of **9** was observed at 521 nm, being much more bathochromic than the diethylamino **7d** and dibutylamino **8** derivatives. This is caused by the strong electro-donating property of the 9-julolidinyl group because the donor character of the amino nitrogen is improved by ring closure as compared with flexible dialkylamino derivatives. The F_{max} also showed a bathochromic shift from 563 to 591 nm. The relatively low Φ_f of these derivatives is probably attributed to the effect of the flexible *t*-butyl group at the 6-position. The similar Stokes shifts of **7**–**9** imply that there is no considerable difference in their excited electronic states. These results also indicate that **7**–**9** can be used as a red-emitting dopant.

The optical properties of **7**–**9** in the solid state are of great importance and interest. Table 1 also lists the diffuse reflectance and the fluorescence properties of **7**–**9** in powdered form. The solid-state fluorescence spectra of **7**–**9** in ground crystals and their photographs are shown in Figs. 3 and 4, respectively. The λ_{max} were observed around 519–561 nm. Though no remarkable difference was observed in the F_{max} among **7b**, **7d**, and **8**, the relative fluorescent intensities were found to be significantly different. The dye that exhibits the strongest fluorescence in powdered form, **7d**, also showed the smallest fluorescent quantum yield in a toluene solution. The next brightest dye was **8**, followed by **7b**. Surprisingly, the fluorescence intensities of **7a**, **7c**, and **9** were too weak to determine the maximum wavelength or relative intensity. The F_{max} of **7b**, **7d**, and **8** were also found to shift bathochromically as compared with those in toluene.[11] This remarkable change in the relative fluorescence intensity must be affected by intermolecular interactions in the solid state. Therefore, an attempt to analyze their crystal structures was made to investigate the difference in fluorescence intensity between in solution and in the solid state.

Crystal Structure Analysis. Crystal structure analysis was successfully carried out on **7a**, **7c**, **7d**, and **8**. Unfortunately, good single crystals for structure analysis were not obtained for **7b** or **9**.

The molecules of **7a**, **7c**, **7d**, and **8** were found to have a planar π-conjugated system. Dihedral angles between the pyrazine and the phenyl rings are 0.68, 5.58, 12.2, and 4.67° for **7a**, **7c**, **7d**, and **8**, respectively. The planarity of the chromophoric system composed of a dicyanopyrazine ring with an amino styryl moiety was also estimated by mean deviation from the least-squares plane. The calculated mean deviations were 0.001, 0.056, 0.094, and 0.056 Å for **7a**, **7c**, **7d**, and **8**, respectively. In addition, all of them showed small bond alteration and there is no significant difference in bond lengths. The electronic structure of a molecule in single crystals for these dyes is therefore considered to be almost the same. This is confirmed by means of molecular orbital calculations using the fractional coordinates as given in the Supporting Information (Table S2).

However, the molecular arrangement is quite different. Figures 5a–5d illustrate the observed stacking motifs for each dye. All dyes have two types of stacking structures between the chromophoric systems. In **7a**, molecules are stacked along the *c*-axis. The two molecules surrounded by a circle in Fig. 5a are completely stacked on each other in a head-to-tail fashion.

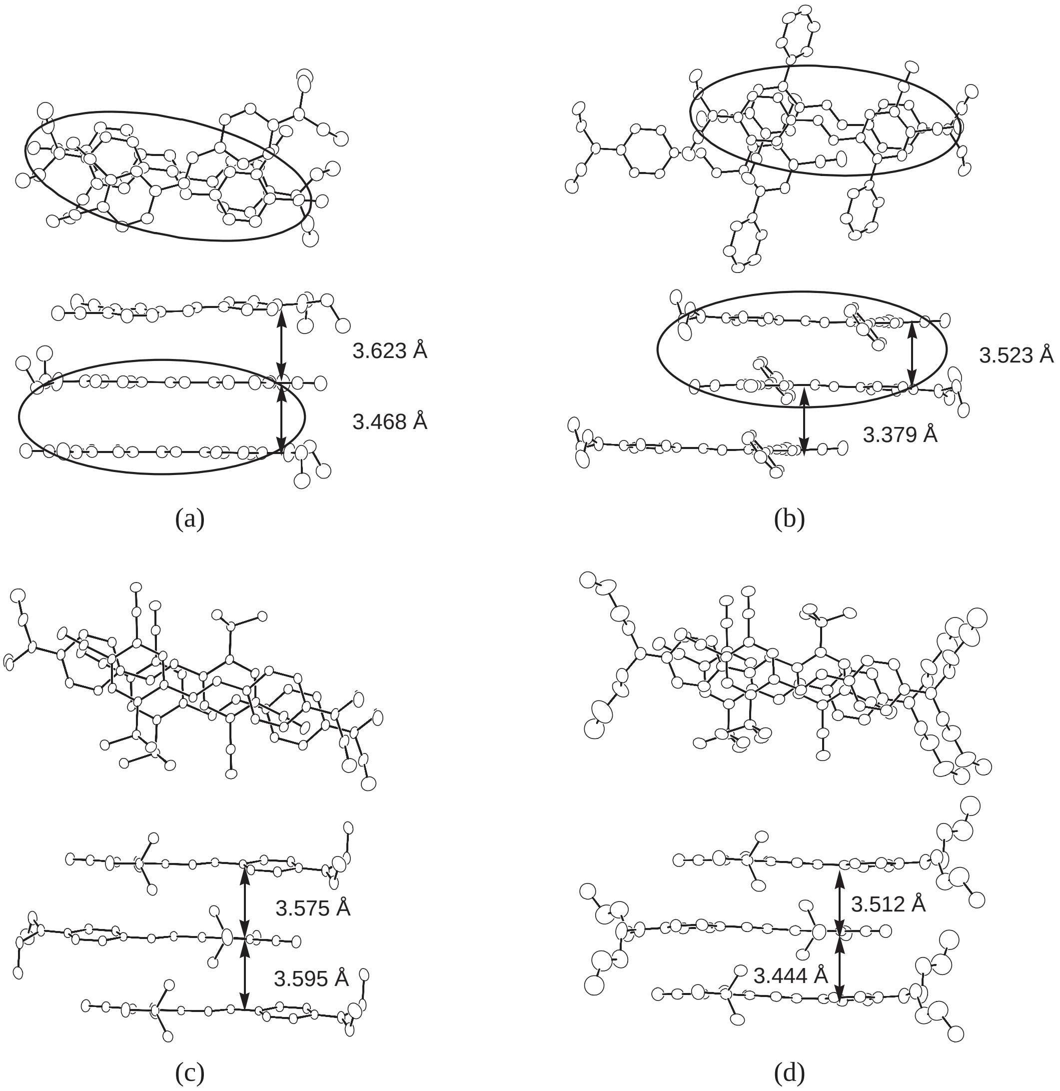


Fig. 5. Stacking motifs for (a) **7a**, (b) **7c**, (c) **7d**, and (d) **8**.

The upper molecule is also stacked in parallel and in a head-to-tail fashion, but it is twisted along the long molecular axis by about 34°. Hence, one-dimensional molecular columns form along the *c*-axis in which the complete stack pairs are stacked alternatively twisted along their long axis by about 34° (Fig. S1). Interplanar distances between the chromophoric systems are calculated to be about 3.468 and 3.623 Å for the complete and twisted stack pairs, respectively.

The molecules are arranged in a herring-bone fashion in **7c** (Fig. S2), but two types of molecular stacking are also recognized. The molecules are stacked along the direction normal to the (213) plane. Two molecules surrounded by a circle in Fig. 5b form a completely stacked pair in a head-to-tail fashion. The lower molecule is also stacked in parallel but less overlapped than the upper one. Interplanar distances between the chromophoric systems are calculated to be about 3.523 and 3.379 Å for the complete stack and less-overlapped pairs, respectively. The very short distance of the lower pair may be due to the small repulsion between the planes because of the small overlap of molecules.

Dyes with a *t*-butyl group on a pyrazine ring, **7d** and **8**, have a similar pattern of molecular stacking, as shown in Figs. 5c and 5d, respectively. In both dyes, molecules are stacked along the *a*-axis (Figs. S3 and S4). The molecules are inserted to the molecular arrangement of the inverted fragment along the *a*-axis. Each molecule is found to be well overlapped, but the overlaps are slightly shifted. Interplanar distances between the chromophoric systems are calculated to be about 3.575 and 3.595 Å for **7d**, and 3.512 and 3.444 Å for **8**, respectively.

In these dyes, significant structural differences were observed in the degree of overlap of the chromophoric systems and their interplanar distances. These structural features should be related to the fluorescent properties in the solid state.[2a,2g,2j,2l] A large overlap as well as a short interplanar distance can be correlated with the decrease in fluorescence intensity in the solid state. The complete overlap of a chromophoric system is considered to be a parallel dimer. The most typical example of a parallel dimer is H-aggregates, which are generally known to be non-fluorescent. This characteristic is successfully interpreted by theoretical description:[8] the optical transition for the lower energy state of a parallel dimer, in which the transition dipoles are packed in a head-to-tail fashion, is forbidden due to the out-of-phase symmetry and gives no fluorescence. In the case of single crystals, there are many molecules around a given molecule, thus, we have to consider the whole interaction between many molecule pairs in order to examine the electronic energy levels of molecular crystals. However, our previous study clearly showed that only the complete overlap of chromophoric systems should dominate the fluorescence quenching.[6] The fluorescence quenching of **7a** and **7c** is thus considered to be caused by forming a complete overlapped pair in the crystalline state. The fluorescence of **9** was found to be quenched in the solid state. We have no crystal structure of **9**, but the complete overlapped pair might also be formed in the crystalline state to deactivate excitation energies. Actually, two diffraction peaks were observed around 3.4 Å by powder X-ray diffraction of **9**. This result suggests the existence of two stacking pairs of molecules. On the other hand, in compounds **7d** and **8**, there is no complete overlap of chromophoric systems, so that they emit even in the crystalline state. The difference in their relative fluorescence intensity could be correlated with the interplanar distance of the stacking pairs. The larger the interplanar distances, the more intense the solid-state fluorescence. We also have no crystal structure of **7b**, which exhibits very weak fluorescence in the solid state. Compound **7b** has a relatively small substituent on the pyrazine ring compared with **7d** and **8**. The interplanar distance between the chromophoric systems can be considered to be shortened to give weak fluorescence.

Conclusion

The substituent effect of some new 2,3-dicyanopyrazine dyes on solid-state fluorescence was investigated on the basis of the crystal structures. The complete overlap between the chromophoric systems was found to dominate fluorescence quenching in the solid state. The fluorescence intensity in the solid state was also found to be influenced by an interplanar distance between chormophoric systems. Our results indicate that organic molecules for solid-state fluorescent materials should be designed to prevent complete stacking by the effective incorporation of bulky substituents to the chromophoric systems.

Experimental

Instruments. Melting points were measured with a Yanagimoto MP-S2 micro-melting-point apparatus. NMR spectra were obtained with a Varian Inova 500 spectrometer. EIMS spectra were recorded on a JEOL MS-700 spectrometer. IR spectra were recorded on a Perkin-Elmer spectrum BX FT-IR system for samples in KBr pellet form. Elemental analysis was performed with a Yanaco MT-6 CHN corder. UV–vis absorption and fluorescence spectra were taken on Hitachi U-3500 and F-4500 spectrophotometers, respectively. Diffuse reflectance spectra were taken on a Perkin-Elmer Lambda-20 UV–vis spectrometer. Samples were diluted with magnesium oxide. Solid-state fluorescence spectra of ground crystals were determined with the front surface accessory from a Perkin-Elmer LS-45 Luminescence spectrometer. The fluorescence quantum yield was determined using quinine sulfate in 0.1 mol dm^{-3} sulfuric acid as a reference ($\Phi_f = 0.55$, $\lambda_{em} = 366$ nm).

Materials. DAMN (**1**), methyl glyoxal 40% aqueous solution (**2a**), and 4-(dibutylamino)benzaldehyde (**5**) were purchased from Sigma-Aldrich. 1-Phenyl-1,2-propanedione (**2c**) and 4-(diethylamino)benzaldehyde (**4**) were purchased from Tokyo Kasei Co., Ltd. Diacetyl (**2b**) was purchased from Nakalai Tesque. 4,4-Dimethyl-2,3-pentanedione (**2d**),[12] 2,3-dicyano-5-methylpyrazine (**3a**),[13] 2,3-dicyano-5,6-dimethylpyrazine (**3b**),[13] and 1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizine-9-carbaldehyde (**6**)[14] were prepared as described in the literature.

Synthesis of 2,3-Dicyanopyrazines (3c and 3d). To an ethanol solution (20 mL) of DAMN (**1**) (1.08 g, 10 mmol) were added 3 mol dm^{-3} of aqueous hydrochloric acid (6 mL) and the diones **2** (10 mmol). The mixture was refluxed for 30 min. After the reaction was completed, the mixture was cooled to room temperature. The solvent was partially removed in vacuo. The residue was poured into water, filtered, washed with water, and then dried. The product was recrystallized (**3c**: ethanol; **3d**: hexane). The physical and spectral data are shown below.

2,3-Dicyano-5-methyl-6-phenylpyrazine (3c): Yield 82%; mp 135–137 °C; IR (KBr)/cm^{-1} 2244 (CN); ^{1}H NMR (CDCl$_3$) δ 2.84 (s, 3H), 7.55–7.61 (m, 3H), 7.66–7.68 (m, 2H); EIMS (70 eV) m/z (rel intensity) 220 (M$^+$; 69), 219 (100), 117 (13), 103 (48), 76 (16). Anal. Found: C, 70.81; H, 3.87; N, 25.52%. Calcd for $C_{13}H_8N_4$: C, 70.90; H, 3.66; N, 25.44%.

5-*t*-Butyl-2,3-dicyano-6-methylpyrazine (3d): Yield 74%; mp 90–93 °C; IR (KBr)/cm^{-1} 2232 (CN); ^{1}H NMR (CDCl$_3$) δ 1.49 (s, 9H), 2.90 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 25.5, 28.7, 39.4, 113.1, 113.3, 128.8, 129.3, 157.2, 166.3; EIMS (70 eV) m/z (rel intensity) 200 (M$^+$; 19), 185 (100), 158 (19), 57 (17). Anal. Found: C, 66.02; H, 6.04; N, 28.24%. Calcd for $C_{11}H_{12}N_4$: C, 65.98; H, 6.04; N, 27.98%.

Synthesis of 5,6-Disubstituted 2,3-Dicyanopyrazine Dyes (7a–7d, 8, and 9). To a benzene solution (15 mL) of **3a**–**3d** (1 mmol) were added piperidine (5 drops) and the aromatic aldehydes **4**–**6** (1 mmol). The mixture was refluxed (**7a**: 50 h, **7b**: 51 h, **7c**: 71 h, **7d**: 47 h, **8**: 88 h, and **9**: 69 h). After the reaction was completed, the mixture was cooled to room temperature. After removing the solvent, the product was isolated by silica-gel column chromatography (dichloromethane) and recrystallized (**7a**–**7d**: benzene, **8**: hexane, and **9**: ethyl acetate). The physical and spectral data are shown below.

2,3-Dicyano-5-[4-(diethylamino)styryl]pyrazine (7a): Yield 36%; mp 207–210 °C; IR (KBr)/cm^{-1} 2228 (CN); ^{1}H NMR (CDCl$_3$) δ 1.23 (t, $J = 7.1$ Hz, 6H), 3.45 (q, $J = 7.1$ Hz, 4H), 6.67 (d, $J = 9.0$ Hz, 2H), 6.83 (d, $J = 15.4$ Hz, 1H), 7.49 (d, $J = 9.0$ Hz, 2H), 7.92 (d, $J = 15.4$ Hz, 1H), 8.61 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 12.7, 44.7, 111.6, 113.5, 114.1, 114.5, 121.9, 127.3, 131.0, 133.5, 143.7, 145.3, 150.2, 155.0; EIMS (70 eV) m/z (rel intensity) 303 (M$^+$; 39), 289 (20), 288 (100). Anal. Found: C, 71.55; H, 5.72; N, 23.06%. Calcd for $C_{18}H_{17}N_5$: C, 71.27; H, 5.65; N, 23.09%.

2,3-Dicyano-5-[4-(diethylamino)styryl]-6-methylpyrazine (7b): Yield 31%; mp 216–219 °C; IR (KBr)/cm^{-1} 2228 (CN); ^{1}H NMR (CDCl$_3$) δ 1.20 (t, $J = 7.1$ Hz, 6H), 2.73 (s, 3H), 3.40 (q, $J = 7.1$ Hz, 4H), 6.71 (d, $J = 9.0$ Hz, 2H), 6.94 (d, $J = 15.1$ Hz, 1H), 7.55 (d, $J = 9.0$ Hz, 2H), 8.08 (d, $J = 15.1$ Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 12.7, 22.4, 44.7, 111.5, 112.3, 113.9, 114.3, 122.3, 126.5, 130.9, 131.0, 144.4, 150.1, 153.6, 154.4; EIMS (70 eV) m/z (rel intensity) 317 (M$^+$; 41), 303 (22), 302 (100). Anal. Found: C, 71.63; H, 6.13; N, 21.76%. Calcd for $C_{19}H_{19}N_5$: C, 71.90; H, 6.03; N, 22.07%.

2,3-Dicyano-5-[4-(diethylamino)styryl]-6-phenylpyrazine (7c): Yield 60%; mp 193–195 °C; IR (KBr)/cm^{-1} 2229 (CN); ^{1}H NMR (CDCl$_3$) δ 1.20 (t, $J = 7.1$ Hz, 6H), 3.42 (q, $J = 7.1$

Hz, 4H), 6.63 (d, $J = 9.0$ Hz, 2H), 7.00 (d, $J = 15.1$ Hz, 1H), 7.38 (d, $J = 9.0$ Hz, 2H), 7.54–7.58 (m, 3H), 7.70–7.72 (m, 2H), 8.07 (d, $J = 15.1$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 12.6, 44.6, 111.4, 113.8, 114.1, 114.4, 122.3, 126.6, 128.9, 129.5, 130.7, 130.8, 135.4, 143.7, 149.9, 152.5, 154.1; EIMS (70 eV) m/z (rel intensity) 379 (M^+; 68), 365 (31), 364 (100). Anal. Found: C, 76.16; H, 5.71; N, 18.49%. Calcd for $C_{24}H_{21}N_5$: C, 75.97; H, 5.58; N, 18.46%.

5-*t*-Butyl-2,3-dicyano-6-[4-(diethylamino)styryl]pyrazine (7d): Yield 55%; mp 226–229 °C; IR (KBr)/cm^{-1} 2232 (CN); ^{1}H NMR ($CDCl_3$) δ 1.22 (t, $J = 7.1$ Hz, 6H), 1.51 (s, 9H), 3.44 (q, $J = 7.1$ Hz, 4H), 6.85 (d, $J = 9.0$ Hz, 2H), 7.26 (d, $J = 14.9$ Hz, 1H), 7.48 (d, $J = 9.0$ Hz, 2H), 7.98 (d, $J = 14.9$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 12.7, 29.3, 39.2, 44.7, 111.6, 113.8, 114.4, 115.7, 122.6, 125.6, 130.0, 130.6, 143.0, 149.8, 153.0, 162.6; EIMS (70 eV) m/z (rel intensity) 359 (M^+; 59), 345 (32), 344 (100). Anal. Found: C, 73.68; H, 7.05; N, 19.44%. Calcd for $C_{22}H_{25}N_5$: C, 73.51; H, 7.01; N, 19.48%.

5-*t*-Butyl-2,3-dicyano-6-[4-(dibutylamino)styryl]pyrazine (8): Yield 16%; mp 155–158 °C; IR (KBr)/cm^{-1} 2230 (CN); ^{1}H NMR ($CDCl_3$) δ 0.98 (t, $J = 7.6$ Hz, 6H), 1.38 (sext, $J = 7.6$ Hz, 4H), 1.51 (s, 9H), 1.61 (quint, $J = 7.6$ Hz, 4H), 3.35 (t, $J = 7.6$ Hz, 4H), 6.66 (d, $J = 9.0$ Hz, 2H), 7.23 (d, $J = 14.9$ Hz, 1H), 7.49 (d, $J = 9.0$ Hz, 2H), 8.00 (d, $J = 14.9$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0, 20.3, 29.3, 29.5, 39.2, 50.9, 111.6, 113.8, 114.4, 115.6, 122.5, 125.5, 130.0, 130.5, 143.0, 150.2, 152.9, 162.6; EIMS (70 eV) m/z (rel intensity) 415 (M^+; 40), 372 (100), 330 (29). Anal. Found: C, 75.19; H, 8.03; N, 16.77%. Calcd for $C_{26}H_{33}N_5$: C, 75.14; H, 8.00; N, 16.85%.

5-*t*-Butyl-2,3-dicyano-6-[2-(1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizin-9-yl)ethenyl]pyrazine (9): Yield 33%; mp > 300 °C; IR (KBr)/cm^{-1} 2228 (CN); ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 12H), 1.52 (s, 9H), 1.77 (t, $J = 6.1$ Hz, 4H), 3.32 (t, $J = 6.1$ Hz, 4H), 7.18 (d, $J = 14.9$ Hz, 1H), 7.34 (s, 2H), 8.00 (d, $J = 14.9$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 29.3, 30.3, 32.1, 35.8, 39.1, 46.7, 113.8, 114.5, 114.8, 122.1, 124.7, 125.1, 130.3, 143.1, 143.9, 153.0, 162.3; EIMS (70 eV) m/z (rel intensity) 439 (M^+; 100), 424 (42). Anal. Found: C, 76.09; H, 7.65; N, 15.76%. Calcd for $C_{28}H_{33}N_5$: C, 76.50; H, 7.57; N, 15.93%.

X-ray Crystallography. Single crystals of **7a**, **7c**, and **8** were obtained by slow evaporation of benzene, toluene, and hexane solutions, respectively. Those of **7d** were grown by a solvent diffusion method using hexane and dichloromethane. The diffraction data were collected by a Rigaku Raxis RAPID-F imaging-plate area detector using graphite-monochromated Cu Kα radiation ($\lambda = 1.54178$ Å, 2.0 kW). The structure was solved by a direct method, *SIR92*[15] for **7a** and **7c** and *SHELX97*[16] for **7d** and **8**, respectively, and refined by fill-matrix least-squares calculations. H-atoms were located at the calculated positions and treated using the riding model. Structural disorder was found at the terminal alkyl groups in **7a** and **8**. In **7a**, one of the ethyl groups was disordered. The disordered group was refined on the assumption that the ethyl moiety is disordered in four conformations with equivalent occupancy and bond lengths for N–C and C–C were restrained to 1.50 and 1.54 Å, respectively. Both methyl groups of the terminal butyl groups in **8** were also found to be disordered. The disordered methyl groups were refined on the assumption that the methyl groups are disordered in three positions with equivalent occupancy, and bond lengths were restrained to 1.54 Å. All calculations were performed by *Crystal Structure* 3.10[17] program package. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk), by quoting the publication citation and the deposition numbers for **7a** (CCDC-263456), **7c** (CCDC-263457), **7d** (CCDC-263458), and **8** (CCDC-263459), respectively. Crystal data for **7a**: $C_{18}H_{17}N_5$, MW = 303.37, monoclinic, $C2/c$, $Z = 8$, $a = 21.462(4)$, $b = 13.629(2)$, $c = 14.463(3)$ Å, $\beta = 127.71(1)°$, $D_{\text{calcd}} = 1.204\ \text{g cm}^{-3}$, $T = 296$ K, 12871 reflections were collected, 2858 unique ($R_{\text{int}} = 0.053$), 1906 observed ($I > 2\sigma(I)$), 227 parameters, $R_1 = 0.071$, $wR_2 = 0.114$, GOF = 1.05, refinement on F, **7c**: $C_{24}H_{21}N_5$, MW = 379.46, monoclinic, $P2_1/n$, $Z = 4$, $a = 8.926(3)$, $b = 10.589(3)$, $c = 22.116(7)$ Å, $\beta = 95.69(3)°$, $D_{\text{calcd}} = 1.212\ \text{g cm}^{-3}$, $T = 296$ K, 15256 reflections were collected, 3451 unique ($R_{\text{int}} = 0.063$), 1391 observed ($I > 2\sigma(I)$), 283 parameters, $R_1 = 0.046$, $wR_2 = 0.154$, GOF = 1.08, refinement on F^2, **7d**: $C_{22}H_{25}N_5$, MW = 359.47, triclinic, $P\bar{1}$, $Z = 2$, $a = 7.324(2)$, $b = 9.621(2)$, $c = 15.176(3)$ Å, $\alpha = 107.84(1)$, $\beta = 95.69(3)$, $\gamma = 99.64(2)°$, $D_{\text{calcd}} = 1.190\ \text{g cm}^{-3}$, $T = 296$ K, 8019 reflections were collected, 3159 unique ($R_{\text{int}} = 0.061$), 2519 observed ($I > 2\sigma(I)$), 270 parameters, $R_1 = 0.054$, $wR_2 = 0.166$, GOF = 0.97, refinement on F^2, **8**: $C_{26}H_{33}N_5$, MW = 415.58, triclinic, $P\bar{1}$, $Z = 2$, $a = 7.022(1)$, $b = 9.586(2)$, $c = 19.272(3)$ Å, $\alpha = 96.34(2)$, $\beta = 101.85(2)$, $\gamma = 93.64(2)°$, $D_{\text{calcd}} = 1.098\ \text{g cm}^{-3}$, $T = 296$ K, 10044 reflections were collected, 3943 unique ($R_{\text{int}} = 0.047$), 1853 observed ($I > 2\sigma(I)$), 310 parameters, $R_1 = 0.066$, $wR_2 = 0.181$, GOF = 1.05, refinement on F^2.

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Supporting Information

The calculated UV–vis absorption band for the optimized structure of **7a–7d**, **8**, and **9** (Table S1), calculated UV–vis absorption band for **7a**, **7c**, **7d**, and **8** using the fractional coordinate sets of X-ray analysis (Table S2), crystal structure of **7a** (Fig. S1), crystal structure of **7c** (Fig. S2), crystal structure of **7d** (Fig. S3), and crystal structure of **8** (Fig. S4). This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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