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Topochemically photoreacted fluorescent dimers of 2,3-dicyanopyrazines

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ABSTRACT

Novel fluorescent materials derived from 2,3-dicyanopyrazine were synthesized and subjected to photodimerization reaction. Styryl substituents were attached by Wittig reaction, and the [2+2] photocycloaddition of the 2,3-dicyanopyrazine, either in solution or as a thin film, was studied with irradiation under a high-pressure Hg lamp. The resulting compounds were characterized by ¹H NMR, FT-IR and elemental analysis. Spectral changes of UV–visible absorption intensity and fluorescent intensity were examined at specific exposure intervals. While the cyclobutane ring of dimers induced a discrete π conjugation with aryl substituents to show a hypsochromic shift of absorption and emission spectra, the fluorescence intensity was increased and the specific lowest unoccupied molecular orbital (LUMO) levels were formed compared to monomers.

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PIGMENTS

1. Introduction

Since the importance of functional dyes has increased with the rapid progress of information and communication industries, a variety of functional dye molecules have been reported and many synthetic methods, mechanisms, and specific properties have been demonstrated [1–3].

We are interested in the 2,3-dicyanopyrazine chromophores because of their wide range of applications, such as biological active materials, nonlinear optical materials, and emitters for electroluminescence (EL) devices. A great deal of interest has been focused on the synthesis and characteristics for functional materials based on 2,3-dicyanopyrazine chromophore because they have strong electron-withdrawing ability due to the nitrile group on the pyrazine ring, and they show a strong fluorescence even in solid state [4–7].

Electromagnetic radiation induces a chemical change in a molecule due to the absorption of a photon, which transforms the state of molecular orbitals [8–11]. The photochemical [2+2] cycloaddition reactions have been the subject of extensive investigations and have played an important role in the development of mechanistic organic photochemistry [12–16]. Stilbene has been extensively studied as it has an absorption band in the near ultraviolet (UV) region and only on the photochemical reactive site, which yields simple reaction products.

Our efforts in this study were focused on the new fluorescence materials resulting from the 2,3-dicyanopyrazine system undergoing a photocycloaddition reaction. The resulting compound has advantages in terms of thermal and chemical stability. Specifically, the introduction of a *t*-butyl unit to 2,3-dicyanopyrazine was studied and tested to verify the improvement in structure stability and solubility. The resulting photochemical properties were studied for application as an optical waveguide and photoresist.

2. Experimental

Compounds were identified and their properties were measured using the following techniques. Flash chromatography was performed by using Merck-EM type 60 (230–400 mesh) silica gel (flash). Melting points were obtained with a capillary melting point apparatus and were uncorrected. Elemental analysis was checked by using Flash EA-1112 analyzer. ¹H NMR spectra were recorded on a VARIAN UnityInova 300 MHz FT-NMR spectrometer. UV–visible and fluorescence spectra were measured using SCINCO S-4100 and SHIMADZU RF-5301PC spectrophotometers.

The fluorescence quantum yield (Φ) was determined by optically dilute measurement with Rhodamine B ($\Phi_{\rm f} = 0.69$ in ethanol) as a reference and using the following net equation [17].

$$\Phi_{A} = \Phi_{ref} \left(\frac{\text{PL}_{A}}{\text{UV}_{A}} \right) \left(\frac{\text{UV}_{ref}}{\text{PL}_{ref}} \right) \left(\frac{n_{A}^{2}}{n_{ref}^{2}} \right)$$



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In this equation, PL is the integrated area under the corrected emission spectrum, and UV is the absorbance of the solution at the excitation wavelength λ . Subscripts *A* and *ref* refer to the unknown and reference solutions, respectively, and *n* is the refractive index of the corresponding solutions. Cyclic voltammetry (CV) experiments were performed by BAS-100 electrochemical analyzer with a three-electrode configuration consisting of a Pt disk working electrode, Ag/AgCl reference electrode and Pt wire counter electrode. All measurements were in acetonitrile with 0.1 M tetra-*n*-buty-lammonium tetrafluroroborate (TBABF₄) as a supporting electrolyte. Their electronic level was calculated from the difference between their onset redox potential and the half-wave potential of ferrocene.

2.1. General procedure to synthesize 2

Br₂ (89.47 g, 0.559 mol) was added dropwise to a solution of 1-(4-*tert*-butylphenyl)propan-1-one **1** (152.0 g, 0.799 mol) in 300 ml of CHCl₃ with stirring at 10 °C. After 2 h at room temperature, the mixture was diluted with ice water and extracted with 500 ml of CHCl₃. The organic layer was washed with water and dried with anhydrous sodium sulfate. The mixture was concentrated under reduced pressure and the crude product was purified by column chromatography over silica gel with EA:*n*-hexane = 1:3 as the eluent to form **2** (yellow liquid, 94%); ¹H NMR (300 MHz, CDCl₃) δ 7.92 (d, *J* = 8.7 Hz, Ar–H, 2H), 7.48 (d, *J* = 8.7 Hz, Ar–H, 2H), 5.20 (q, Br–C–H, 1H), 2.11 (d, *J* = 6.8 Hz, –CH₃, 3H), 1.40 (s, *t*-Bu, 9H); Elemental Anal. Calcd. For C₁₃H₁₇BrO: C, 58.01; H, 6.37. Found: C, 58.19; H, 6.41; GC–MS(*m*/*z*) 269.04 Calcd. 269.18.

2.2. General procedure to synthesize 3

Brominated precursor **2** (202 g, 0.75 mol) and potassium acetate (257.6 g, 2.62 mol) in 500 ml of acetone were refluxed for 12 h. The solution was filtered and the filtrate was evaporated using a rotary evaporator. The acetoxy group-substituted precursor was hydrolyzed in 300 ml of 10% NaOH methanolic solution under reflux condition for 1 h. After extracting with 500 ml ethyl acetate (EA) and 600 ml of water, the organic layer was dried with sodium sulfate and evaporated *in vacuo*. The crude product was purified by column chromatography over silica gel with EA:*n*-hexane = 1:3 as the eluent to form **3** (yellow liquid, 86%); ¹H NMR (300 MHz, CDCl₃) δ 7.86 (d, *J* = 9.0 Hz, Ar–H, 2H), 7.51 (d, *J* = 8.7 Hz, Ar–H, 2H), 5.16 (m, 1H), 3.81 (s, -OH, 1H), 1.35 (s, -t-Bu, 9H), 0.90 (d, *J* = 6.8 Hz, -CH₃, 3H); Elemental Anal. Calcd. For C₁₃H₁₈O₂: C, 75.69; H, 8.80. Found: C, 75.36; H, 9.01; GC–MS(*m*/*z*) 206.19 Calcd. 206.28.

2.3. General procedure to synthesize 4

1-(4-*tert*-Butylphenyl)-2-hydroxypropan-1-one **3** (128 g, 0.62 mol) was added to a mixture of $CuSO_4 \cdot 5H_2O(334 \text{ g}, 1.33 \text{ mol})$ in 79 ml of pyridine and 18 ml of water. The mixture was refluxed and the reaction progress was monitored using thin-layer chromatography (silica gel and EA:*n*-hexane = 1:3). Then, the mixture was extracted with 500 ml EA and 600 ml water. The organic layer was dried with sodium sulfate and evaporated *in vacuo*. The crude product was purified by column chromatography over silica gel with EA:*n*-hexane = 1:3 as the eluent to form **4** (yellow liquid, 75%); ¹H NMR (300 MHz, CDCl₃) δ 7.92 (d, *J* = 9.0 Hz, Ar–H, 2H), 7.51 (d, *J* = 8.7 Hz, Ar–H, 2H), 1.34 (s, -*t*-Bu, 9H), 0.90 (s, –CH₃, 3H); Elemental Anal. Calcd. For C₁₃H₁₆O₂: C, 76.44; H, 7.90. Found: C, 76.64; H, 8.09; GC–MS(*m*/*z*) 204.04 Calcd. 204.26.

2.4. General procedure to synthesize 5

Br₂ (10.97 g, 0.07 mol) was added dropwise to a solution of 1-(4*tert*-butylphenyl)propane-1,2-dione **4** (20.0 g, 0.01 mol) in 100 ml CHCl₃ with stirring at 10 °C. After 2 h at room temperature, the mixture was diluted with ice water and extracted with 300 ml of CHCl₃. The organic layer was washed with water and dried with anhydrous sodium sulfate. The mixture was concentrated under reduced pressure and the crude product was purified by column chromatography over silica gel with EA:*n*-hexane = 1:3 as the eluent to form **5** (yellow liquid, 94%); ¹H NMR (300 MHz, CDCl₃) δ 7.85 (d, *J* = 8.7 Hz, Ar–H, 2H), 7.49 (d, *J* = 8.7 Hz, Ar–H, 2H), 3.72 (s, Br–C–H, 2H), 1.35 (s, -*t*-Bu, 9H); Elemental Anal. Calcd. For C₁₃H₁₅BrO₂: C, 55.14; H, 5.34. Found: C, 55.71; H, 5.66; GC–MS(*m*/*z*) 283.06 Calcd. 283.16.

2.5. General procedure to synthesize 6

A solution of 3-bromo-1-(4-*tert*-butylphenyl)propane-1,2-dione (40 g, 0.14 mol), 2,3-diaminomaleonitrile (15.2 g, 0.14 mol) and a small amount of *p*-toluenesulfonic acid as a catalyst in methanol (200 ml) were refluxed for 2 h. After the reaction was complete, the mixture was cooled to room temperature. Methanol was added into the mixture, which was then stirred for 1 h at room temperature. The generated precipitate was filtered and washed with methanol. The crude product was purified by column chromatography over silica gel with EA:*n*-hexane = 1:3 as the eluent to form **6** (white solid, 76%); mp 134 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.63 (d, *J* = 8.7 Hz, Ar–H, 2H), 7.59 (d, *J* = 8.7 Hz, Ar–H, 2H), 3.81 (s, Br–C–H, 2H), 1.38 (s, -*t*-Bu, 9H); Elemental Anal. Calcd. For C₁₇H₁₅BrN₄: C, 57.48; H, 4.26; N, 15.77. Found: C, 57.14; H, 4.76; N. 15.39; GC–MS(*m*/*z*) 355.07 Calcd. 355.23.

2.6. General procedure to synthesize 7

A solution of triphenylphosphine 44.3 g (0.16 mol) in toluene (150 ml) was added dropwise into the mixture of **6** 40 g (0.11 mol) in toluene 200 ml at 10 °C and the mixture was stirred for 1 h at room temperature and refluxed for 5 h. After the reaction was completed, the mixture was hot-filtered and washed by toluene. The filtered cake was recrystallized by *n*-hexane. 7 (organic solid 57%): m.p. 207 °C; ¹H NMR (DMSO-*d*₆) δ 7.65 (m, PPh₃, 15H), 7.63 (d, *J* = 8.7 Hz, Ar–H, 2H), 7.59 (d, *J* = 8.7 Hz, Ar–H, 2H), 4.02 (s, CH₂, 2H), 1.38 (s, *-t*-Bu, 9H); Elemental Anal. Calcd. For C₃₅H₃₀BrN₄P: C, 68.07; H, 4.90; N, 9.07. Found: C, 68.49; H, 5.37; N. 9.38; MALDI-TOF-Ms (*m*/*z*) 617.34 Calcd. 617.52.

2.7. General procedure to synthesize 8

A solution of [(3-(4-tert-butylphenyl)-5,6-dicyanopyrazin-2-yl) methyl]triphenyl phosphonium bromide (4.8 g, 7.77 mmol) in anhydrous N,N-dimethylformamide (DMF, 10 ml) under N₂ atmosphere was added dropwise for 30 min to sodium hydride (0.40 g, 9.32 mmol) in anhydrous DMF (7 ml) at 0-5 °C and the mixture was stirred for 1 h at room temperature. When the reaction was completed, the same equivalent of benzaldehydes was slowly added. The reaction mixture was refluxed under N₂ atmosphere. After the reaction was completed, the mixture was cooled and methanol was added. The mixture was then filtered and washed with methanol. The residue was chromatographed on silica gel using EA:*n*-hexane = 1:3 as the eluent to form **8a** (yellow solid, 51%); m.p. 104 °C; IR (KBr pellet): ν(cm⁻¹) 2231 (C=N), 1616 (C=C), 1498, 1376; ¹H NMR (300 MHz, CDCl₃) δ 8.19 (d, 1H, J = 15.6 Hz), 7.70 (d, 2H, J = 8.7 Hz), 7.61 (d, 2H, J = 8.7 Hz), 7.58 (m, 2H), 7.43 (m, 3H), 7.35 (d, 1H, J = 15.6 Hz), 1.41 (s, t-Bu, 9H); ¹³C NMR(300 MHz. CDCl3) δ 155.1, 154.6, 151.3, 137.5, 133.0, 130.7, 131.5, 131.2, 128.6, 128.5, 127.9, 125.5, 125.4, 123.5, 117.1, 34.2, 31.3; $\Phi_{\rm f}$ 0.011; Elemental Anal. Calcd. For C₂₄H₂₀N₄: C, 79.10; H, 5.53; N, 15.37. Found: C, 78.62; H, 5.88; N. 15.63; GC-MS(*m*/*z*) 364.12 Calcd. 364.44.

8b (yellow solid, 54%) m.p. 108 °C; IR (KBr pellet): $\nu(\text{cm}^{-1})$ 2227 (C=N), 1619, 1604 (C=C), 1498, 1375; ¹H NMR (300 MHz, CDCl₃) δ 8.16 (d, 1H, *J* = 15.3 Hz), 7.70 (d, 2H, *J* = 8.4 Hz), 7.61 (d, 2H, *J* = 8.4 Hz), 7.48 (d, 2H, *J* = 8.4 Hz), 7.33 (d, 1H, *J* = 15.6 Hz), 7.27 (d, 2H, *J* = 8.4 Hz), 2.4 (s, 3H), 1.41 (s, *t*-Bu, 9H); ¹³C NMR(300 MHz, CDCl₃) δ 155.0, 154.0, 150.9, 138.4, 137.6, 136.5, 133.0, 131.2, 130.7, 128.6, 128.5, 126.6, 127.4, 127.0, 123.5, 122.5, 117.4, 34.2, 31.6, 21.3; $\Phi_{\rm f}$ 0.021; Elemental Anal. Calcd. For C₂₅H₂₂N₄: C, 79.34; H, 5.86; N, 14.80. Found: C, 78.94; H, 5.94; N. 14.65; GC-MS(*m*/*z*) 378.18 Calcd. 378.47.

8c (yellow solid, 52%) m.p. 102 °C; IR (KBr pellet): ν (cm⁻¹) 2237 (C=N), 1621, 1604 (C=C), 1500, 1375; ¹H NMR (300 MHz, CDCl₃) δ 8.15 (d, 1H, *J* = 15.6 Hz), 7.70 (d, 2H, *J* = 8.4 Hz), 7.61 (d, 2H, *J* = 8.4 Hz), 7.5 (d, 2H, *J* = 8.4 Hz), 7.46 (d, 2H, *J* = 8.4 Hz), 7.27 (d, 1H, *J* = 15.6 Hz), 1.41 (s, 9H), 1.34 (s, *t*-Bu, 9H); ¹³C NMR(300 MHz, CDCl₃) δ 155.6, 154.6, 151.3, 150.5, 139.0, 133.0, 131.2, 131.5, 130.7, 128.2, 125.5, 124.9, 123.5, 117.1, 34.6, 30.8; Φ_f 0.017; Elemental Anal. Calcd. For C₂₈H₂₈N₄: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.43; H, 6.86; N. 13.48; GC-MS(*m*/*z*) 420.28 Calcd. 420.55.

8d (yellow solid, 51%) m.p. 113 °C; IR (KBr pellet): ν (cm⁻¹) 2239 (C=N), 1598 (C=C), 1494, 1257 (C–O), 1172; ¹H NMR (300 MHz, CDCl₃) δ 8.16 (d, 1H, *J* = 15.6 Hz), 7.70 (d, 2H, *J* = 8.4 Hz), 7.61 (d, 2H, *J* = 8.4 Hz), 7.52 (d, 2H, *J* = 8.4 Hz), 7.27 (d, 1H, *J* = 15.6 Hz), 6.95 (d, 2H, *J* = 8.4 Hz), 3.86 (s, 3H), 1.41 (s, *t*-Bu, 9H); ¹³C NMR(300 MHz, CDCl₃) δ 159.8, 155.1, 154.6, 151.3, 133.0, 130.7, 131.5, 131.2, 130.2, 129.8, 125.5, 125.4, 123.5, 117.1, 114.2, 34.7, 31.3; ϕ f 0.018; Elemental Anal. Calcd. For C₂₅H₂₂N₄O: C, 76.12; H, 5.62; N, 14.20; Found: C, 76.01; H, 5.75; N. 14.33; GC–MS(*m*/*z*) 394.16 Calcd. 394.47.

2.8. General procedure to synthesize photodimer 9

Compounds 8a-8d (1 mmol) were dissolved in benzene (40 ml) and solutions were irradiated with 365 nm light emitted from a high-pressure Hg lamp (450 W of strength at 365 nm) at room temperature for 7 h. The mixture was evaporated under reduced pressure, and the product was purified by column chromatography over silica gel with EA:*n*-hexane = 1:5 as the eluent to form **9a**: m.p.; $180 \,^{\circ}\text{C}$; ¹H NMR(300 MHz, CDCl₃) δ 7.60 (d, Ar–H, 4H, $J = 8.4 \,\text{Hz}$), 7.45 (d, Ar-H, 4H, J = 8.4 Hz), 7.26 (m, Ar-H, 6H), 7.18 (m, Ar-H, 4H), 5.23 $(dd, J_1 = 10.1 Hz, J_2 = 7.2 Hz, 2H), 4.86 (dd, J_1 = 10.1 Hz, J_2 = 7.2 Hz, 2H),$ 1.41 (s, *t*-Bu, 18H); ¹³C NMR (300 MHz, CDCl₃) δ 161.2, 159.1, 151.3, 136.5, 134.0, 131.7, 129.9, 128.9, 128.1, 125.9, 125.5, 125.3, 117.8, 46.4, 45.3, 34.5, 31.5; $\Phi_{\rm f}$ 0.39; Elemental Anal. Calcd. For C₄₈H₄₀N₈: C, 79.10; H, 5.53; N, 15.37. Found: C, 78.94; H, 5.64; N. 15.51; MALDI-TOF-Ms spectra (m/z) 728.31 Calcd. 728.88 **9b**: m.p.; 187 °C; ¹H NMR(300 MHz, CDCl₃) δ 8.32 (d, Ar-H, 2H, I = 8.4 Hz), 7.54 (d, Ar-H, 4H), 7.25 (m, Ar-H, 2H, J = 8.4 Hz), 7.05 (d, Ar-H, 4H, J = 8.4 Hz), 6.89 $(d, Ar-H, 4H, J = 8.4 Hz), 4.50 (dd, J_1 = 10.1 Hz, J_2 = 7.2 Hz, 2H), 3.58$ (dd, *J*₁ = 10.1 Hz, *J*₂ = 7.2 Hz, 2H), 2.29 (s, -CH₃, 6H), 1.30 (s, *t*-Bu, 18H); ^{13}C NMR(300 MHz, CDCl₃) δ 161.2, 159.1, 151.3, 135.6, 133.5, 133.1, 130.0, 129.9, 128.8, 128.0, 125.5, 125.4, 117.1, 46.7, 45.1, 34.2, 31.3, 21.3; $\Phi_{\rm f}$ 0.43; Elemental Anal. Calcd. For C₅₀H₄₄N₈: C, 79.34; H, 5.86; N, 14.80. Found: C, 79.03; H, 5.95; N. 14.87 MALDI-TOF-Ms spectra (m/z) 756.71 Calcd. 756.94.

9c: m.p.; 186 °C; ¹H NMR(300 MHz, CDCl₃) δ 8.31 (d, Ar–H, 2H, *J* = 8.4 Hz), 7.52 (d, Ar–H, 2H, *J* = 8.4 Hz), 7.26 (d, Ar–H, 8H, *J* = 8.4 Hz), 6.91 (d, Ar–H, 4H, *J* = 8.4 Hz), 4.50 (dd, *J*₁ = 10.0 Hz, *J*₂ = 7.1 Hz, 2H), 3.56 (dd, *J*₁ = 10.0 Hz, *J*₂ = 7.1 Hz, 2H), 1.27 (d, *t*-Bu, 36H); ¹³C NMR(300 MHz, CDCl₃) δ 161.6, 159.1, 151.3, 148.5, 133.8, 133.3, 130.2, 129.4, 127.7, 125.4, 125.3, 124.8, 117.6, 48.3, 46.7, 34.2, 31.3; Φ_{f} 0.78; Elemental Anal. Calcd. For C₅₆H₅₆N₈: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.46; H, 6.95; N. 13.58 MALDI-TOF-Ms spectra (*m*/*z*) 840.68 Calcd. 841.10.

9d: m.p.; 194 °C; ¹H NMR(300 MHz, CDCl₃) δ 8.31 (d, Ar–H, 2H, *J* = 8.4 Hz), 7.51 (d, Ar–H, 4H, *J* = 8.4 Hz), 7.27 (d, Ar–H, 2H, *J* = 8.4 Hz), 7.18 (d, Ar–H, 4H, *J* = 8.4 Hz), 6.90 (d, Ar–H, 4H, *J* = 8.4 Hz), 5.01 (dd, *J*₁ = 10.0 Hz, *J*₂ = 6.9 Hz, 2H), 4.52 (dd, *J*₁ = 10.0 Hz, *J*₂ = 6.9 Hz, 2H), 3.86 (s, O–CH₃, 6H), 1.41 (s, t-Bu, 18H); ¹³C NMR(300 MHz, CDCl₃) δ 160.0, 158.7, 157.3, 151.3, 133.4, 130.4, 129.9, 128.8, 127.6, 125.5, 125.4, 117.1, 114.1, 55.8, 46.7, 45.1, 34.8, 32.9; $\Phi_{\rm f}$ 0.76; Elemental Anal. Calcd. For C₅₀H₄₄N₈O₂: C, 76.12; H, 5.62; N, 14.20; Found: C, 75.97; H, 5.83; N. 14.44 MALDI-TOF-Ms spectra (*m*/*z*) 788.45 Calcd. 788.94.

3. Results and discussion

3.1. Synthesis

1-(4-tert-butylphenyl)propan-1-one 1 was synthesized using a previously described method [18]. It was treated with one equivalent of bromine in chloroform to produce an 85% yield of α brominated 4-(*tert*-butyl)alkyl phenone **2**. The reaction of α brominated ketone with an excess (3.5 equiv.) of anhydrous potassium acetate in acetone afforded α -acetoxylated 4-(*tert*-butyl) alkyl phenone [19,20]. This compound was reacted with 10% methanolic NaOH under reflux condition to produce the corresponding compound of 1-(4-tert-butylphenyl)-2-hydroxypropan-1-one **3**. α -Diketone **4** was obtained through the oxidation of α hydroxyketone **3** with copper sulfate in aqueous pyridine solution. The 1-(4-tert-butylphenyl)propane-1,2-dione **4** was treated with one equivalent of bromine in chloroform at room temperature to produce an 89–95% yield of α -brominated 1-(4-*tert*-butylphenyl) propane-1,2-dione 5. 2,3-Dicyanopyrazine 6 was synthesized from the condensation of α -brominated 1-(4-tert-butylphenyl)propane-1,2-dione 5 and diaminomaleonitrile (DAMN) in the presence of a catalytic amount of *p*-toluenesulfonic acid in methanol. Treatment of 6 with 1.5 equiv. of triphenylphosphine in toluene afforded a good yield of {[3-(4-*tert*-butylphenyl)-5,6-dicyanopyrazin-2-yl] methyl}triphenylphosphonium bromide 7 (70%).

Reactions of **7** with one equivalent of aryl aldehyde in the presence of 1.2 equivalent of sodium ethoxide under reflux conditions produced styryl derivatives **8a–d**. The synthetic route of this study is summarized in Schemes 1 and 2. The new compounds were characterized by FT-IR, UV–visible spectroscopy and ¹H NMR spectroscopy. From the FT-IR spectra of compounds **8a–d**, absorption bands were observed at 2227–2237 and 1604–1621 cm⁻¹. The medium intensity band in the 2227–2237 cm⁻¹ region was due to stretching vibration of the CN groups. The strong intensity band at the 1604–1621 cm⁻¹ region was due to stretching vibration of the C=C groups.

The ¹H NMR spectra of the 2,3-dicyanopyrazine compounds **8a–d** showed a doublet peak at 8.1–8.2 ppm, indicating the presence of the typical *trans* (J = 15.6 Hz) confirmation of the proton in the olefinic moiety. Additionally, the singlet proton peak appeared at 1.40–1.34 ppm, corresponding to the terminal *t*-butyl group.

3.2. Photoreaction of 2,3-dicyanopyrazines

Compound **8a** in benzene solution was irradiated by UV light at 365 nm for 7 h to produce the photodimer **9a** with a 40% yield. This reaction route is summarized in Scheme 3. The product was isolated by column chromatography using EA:*n*-hexane = 1:5 as the eluent. The configuration of dimerized structure of **9a** was confirmed by ¹H NMR.

Fig. 1 shows the ¹H NMR spectra of **8c** and **9c**. The assignment of **8c** was conducted by the ¹H NMR spectrum, which showed typical *trans* (J = 15.6 Hz) confirmation of the proton in the olefinic moiety



Scheme 1. Synthetic routes of 2,3-dicyanopyrazine precursor 7.

with respect to that of the *cis* (J = 12 Hz) [21,22]. Compared to **8c**, a common feature of chemical shifts for protons on the cyclobutane ring in **9c** is shown in Fig. 1. Two sets of doublet of doublets for the two paired protons on the cyclobutane ring were observed at 4.50 and 3.56 ppm ($J_1 = 10.2$ Hz, $J_2 = 7.2$ Hz). The cyclobutane ring must have received a steric hindrance between the aromatic substituents, and we can assume that the conformation during the cycloaddition reaction progressed to a more stable form. Two conformation models, which were determined from the coupling tendency with adjacent protons, were introduced in Fig. S1 (see the Supplementary materials), and it was concluded that the NMR spectrum was mainly determined by the head-to-tail structure in the case of **9c** [22,23]. The ¹H NMR spectra of the cyclobutane ring in **9a**, **9b** and **9d** showed a pattern similar to that of **9c**, and were assigned to a head-to-tail configuration.

On the other hand, compounds **8a–8d** were dissolved in benzene and the solutions were irradiated with 365 nm light



Scheme 2. Synthetic routes of 2,3-dicyanopyrazine derivatives (8a-8d).

emitted from the high-pressure Hg lamp (450 W of strength at 365 nm) at room temperature for 0 s, 30 s, 1 min, 5 min, 10 min, 20 min, and 30 min under a N₂ atmosphere. During irradiation, the changes of **8a**–**8d** were observed by UV–visible and fluorescence spectroscopy (Fig. 2). During irradiation using 365 nm UV light, the absorption maximum intensity at 375 nm of **8a** decreased and the new absorption maximum of 351 nm increased. The isosbestic points were observed at 324 nm, 341 nm and 362 nm, and equilibrium mixtures will be included in benzene. The fluorescence intensity at 445 nm increased and the wavelength was blue-shifted to 410 nm during irradiation using 365 nm UV light.

3.3. Optical and electrochemical properties

Strong intramolecular charge-transfer chromophoric systems were observed for compounds **8** and **9**, with absorption and emission maxima at 318–408 nm and 388–459 nm, respectively. The electron-donating character of the substituents in compounds **8** and **9** strongly reflected their absorption spectra in producing bathochromic shifts depending on their electron-donating ability. While the cyclobutane ring of dimers induced a discrete π -conjugation with aryl substituents to show a hypsochromic shift of absorption and emission spectra, the fluorescence intensity was increased and the specific LUMO levels were formed compared to monomers, as shown in Fig. 2. The Stoke's shift (SS) indicates the difference between F_{max} and λ_{max} and corresponds to energy loss in the first excited singlet state. The SS increased gradually with increasing electron-donating ability of substituents.



Scheme 3. Synthetic route of photodimerization.



Fig. 1. ¹H NMR spectra of 8c and 9c in CDCl₃.

CV was used to investigate the electrochemical redox behaviors of these compounds. The electrochemical properties of compounds **8** and **9** were recorded in acetonitrile using 0.1 M Bu₄NBF₄ as a supporting electrolyte. The calculated HOMO energy levels were obtained from the oxidation potentials using the following equation and the estimated bandgap (E_g) and LUMO levels from the UV edge in the electronic absorption spectra are listed in Table 1 [24,25].



Fig. 2. Changes in the absorption and fluorescence spectra of 8a in solution under irradiation.

 Table 1
 Optical and electrochemical properties of compounds 8a-8d and 9a-9d.

	$^{a}\lambda_{abs}^{max}(nm)$	$\lambda_{em}^{max}(nm)$		^b SS (nm)	LUMO (eV)	^c HOMO (eV)	$^{d}E_{g}(eV)$
		CHCl ₃	Film				
8a	358	425	472	67	-3.54	-6.32	2.78
8b	386	454	478	68	-3.45	-6.2	2.75
8c	389	459	478	70	-3.45	-6.29	2.84
8d	408	502	532	94	-3.21	-5.81	2.60
9a	318	388	465	70	-2.83	6.07	3.24
9b	343	414	467	71	-2.78	-6.0	3.22
9c	348	420	467	72	-2.74	-6.04	3.30
9d	365	458	525	93	-2.58	-5.68	3.00

^a In chloroform.

^b Stoke's shift (SS).

^c Calculated data from cyclic voltammograms.

^d Estimated data from UV edge.

$$HOMO(eV) = -4.8 - (E_{onset} - E_{1/2}(Ferrocene))$$

In this equation, E_{onset} is the onset oxidation potential (V) and $E_{1/2}$ (ferrocene) is the half-wave potential (V) of ferrocene in the solution. As the oxidation potentials decreased with increasing electron-donating ability, the HOMO level was estimated in more positive positions and narrow band gaps were simultaneously exhibited in the optical results.

The spin-coated thin film containing 8c was irradiated by UV light at 365 nm and the changes in the fluorescence spectra are shown in Fig. 3. Solutions of compounds 8a-8d (5%) in benzene were filtered through a polytetrafluoroethylene syringe filter (0.45- μ m pore size) prior to application to the glass substrate. Resist films were prepared by spin coating on a glass substrate. The coating speed was maintained for 20 s at 1000 rpm. The coated layer was exposed under the high-pressure Hg lamp using a paper mask over 1 h. During irradiation, the changes of 8 to 9 were observed by UV-visible and fluorescence spectroscopy. The irradiated film was immersed in EA:n-hexane(1:5) as the eluent for 20 s. The film was dried at room temperature for 24 h and further dried at 50 °C in a vacuum oven for 3 h. The fluorescence maximum at 478 nm was blue-shifted to 467 nm during the irradiation. The irradiated film comprised of 8 and 9 showed behavior typical of a negative-type photoresist, as shown in Fig. 4. Compound 9 had different solubility in common organic solvents compared to compounds 8a-d. Compounds 8 and 9 were very soluble in common solvents such as acetone, chloroform and ethyl acetate, but they were insoluble in nhexane. We approached miscible co-solvents to control solubility



Fig. 3. Procedure of the spin-casting process and changes in the fluorescence spectra of 8c in a thin film under irradiation.



Fig. 4. Film comprised of **8c** and **9c** by irradiated using a high-pressure Hg lamp (450 W of strength at 365 nm) in contact printing mode.

which could cut only the monomer compound **8** during the immersion. Compound **8** was very soluble in EA:*n*-hexane(1:5) but **9** was insoluble. This was the reason to use the co-solvent as the immersing solvent.

The fluorescence after UV light irradiation showed much higher intensity than before. The new fluorescent 2,3-dicyanopyrazine containing dimers may be applied to light switching devices, optical information storage, and EL materials.

4. Conclusions

In this study, novel fluorescent materials derived from 2,3dicyanopyrazine by controlling the electron density were designed and synthesized via various reactions. The resulting compounds were primarily characterized by ¹H NMR, FT-IR and EA.

The photoreactions of 2,3-dicyanopyrazine were studied as a thin film or in solution with irradiation under a high-pressure Hg lamp, and the spectral changes in the UV absorption intensity were examined at specific exposure intervals. During UV light irradiation at 365 nm, the absorption maximum intensity of **8a** at 375 nm decreased and the new absorption maximum at 351 nm increased. The isosbestic point was observed at 360 nm. The spin-coated thin film comprised of **8c** was irradiated by UV light at 365 nm and changes in the fluorescence spectra were assessed. During UV light irradiation at 365 nm, the fluorescence after UV light irradiation was blue-shifted to 467 nm. The fluorescence after UV light irradiation was brighter than before.

The photodimer exhibited the behavior of a negative-type photoresist. After irradiation, the photodimer became insoluble in EA:*n*-hexane = 1:5 due to the [2+2] cycloaddition of 2,3-dicyanopyrazine moieties.

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Appendix. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.dyepig.2011.10.015.

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