Fluorescence Spectra of 6-Substituted 2,3-Dicyano-5-[4-(diethylamino)styryl]-7-methyl-6*H*-1,4-diazepines in Solid State

Emi Horiguchi, Shinya Matsumoto,[†] Kazumasa Funabiki, and Masaki Matsui*
Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193
[†]*Faculty of Education and Human Sciences, Yokohama National University, 79-2 Tokiwadai, Hodogaya-ku, Yokohama 240-8501*

(Received November 20, 2003; CL-031127)

Intense fluorescence of 2,3-dicyano-5-[4-(diethylamino)-styryl]-7-methyl-6*H*-1,4-diazepines in solid state could be successful in improving interference in cofacial molecular stacking between the chromophores by the bulky 6-substituent.

Solid fluorescent materials have potential applications to emitters in electroluminescence devices. The introduction of substituents into fluorescent molecules can affect the intermolecular interactions to change the emission maximum and fluorescence intensity in the solid state.[1] 2,3-Dicyano-6*H*-1,4-diazepines are non-planar fluorophores having a methylene group located out of conjugated π-plane.[2] Less paper concerning the non-doped red emitters in organic electroluminescence have been reported so far. We report herein the fluorescence spectra of 6-substituted 2,3-dicyano-5-[4-(diethylamino)styryl]-7-methyl-6*H*-1,4-diazepines **1**–**3** in solution and solid state and the correlation between the crystal structures and solid state fluorescence. The structures of **1**–**3** are shown in Figure 1.[3]

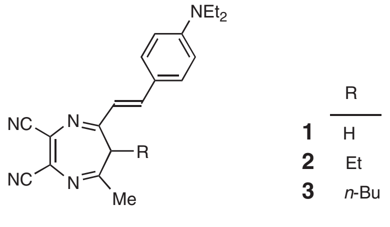

Figure 1. Structure of 6-substituted 2,3-dicyano-5-[4-(diethylamino)styryl]-7-methyl-6*H*-1,4-diazepines **1**–**3**.

The UV–vis absorption and fluorescence spectra of **1**–**3** in chloroform are shown in Figure 2. The compounds **1**–**3** showed the absorption maxima (λ_{max}) around 491–500 nm with molar absorption coefficients (ε) 40400–43400. The emission maxima (λ_{em}) were observed around 595–608 nm with half-width 80 nm, indicating brilliant red emitting. The relative fluorescence intensity was in the following order: **1** $\gg$ **2** and **3**. Flexible alkyl groups could accelerate the internal conversion to reduce the fluorescence intensity in solution.[4]

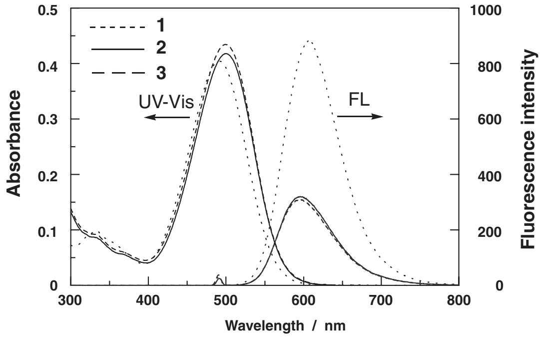

Figure 2. UV–vis absorption and fluorescence spectra of **1**–**3** (1×10^{-5} mol dm^{-3}) in chloroform.

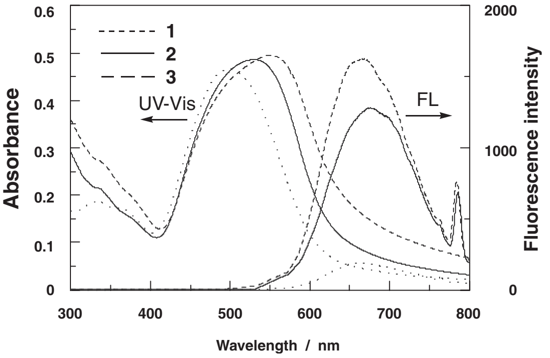

Figure 3. UV–vis absorption and fluorescence spectra of **1**–**3** on vapor deposited thin film.

The UV–vis absorption and fluorescence spectra of **1**–**3** in vapor deposited thin films are shown in Figure 3. The λ_{max} were observed around 499–551 nm, being slightly bathochromic compared with those in chloroform. The film thickness was 40–44 nm. The absorbance of films were similar, being 0.47–0.50. The λ_{em} were observed in the range of 663–676 nm, being more bathochromic compared with those in chloroform. Interestingly, the fluorescence intensity in solid state was in the following order: **3** > **2** $\gg$ **1**. This is quite different from that in solution. The UV–vis absorption and fluorescence spectra of **1**–**3** in solution and vapor deposited thin film were observed as racemic compounds.

To examine the fluorescence intensity of **1**–**3** in the solid state, the crystal structure analysis was performed.[5] All compounds were crystallized by solvent diffusion method using hexane and chloroform as racemic crystals. As shown in Figures 4–6, three kinds of characteristic molecular pairs were found by a detailed examination of the crystal structures.

Figure 4 shows the stacking pairs of **1**–**3** between the phenylene rings. Two molecules were found to stack in a tail-to-tail fashion. The interplanar distance between the phenylene rings were calculated to be 3.636, 3.832, and 3.415 Å for **1**, **2**, and **3**, respectively. The longest distance of the pair of **2** is ascribed to the different conformation of the diethylamino group compared to those of **1** and **3**.

Stacking pairs between the dicyanodiazepine moieties of **1**–**3** are depicted in Figure 5. The interplanar distance between the planes composed of the dicyanoethylene moiety in the above group are close: 3.389, 3.325, and 3.400 Å for **1**, **2** and **3**, respec-

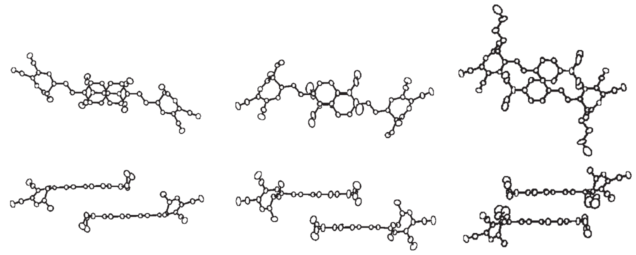

Figure 4. Stacking of **1**–**3** between phenylene rings.

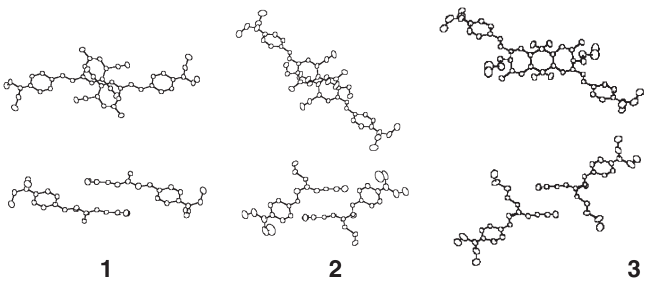

Figure 5. Stacking pairs of **1**–**3** between dicyanodiazepine moieties.

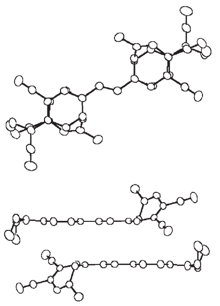

Figure 6. Stacking pair of **1** between whole chromophores.

tively, but no significant difference was observed among them.

Figure 6 shows a molecular pair of **1** cofacially stacked between the chromophores. The chromophores were completely overlapped each other. The interplanar distance was very short, being 3.257 Å. This type of pair was not observed for **2** and **3**. As the methylene groups at the 6-position in the diazepine ring are directed to another molecule, the alkyl group at the 6-position in **2** and **3** must inhibit this type of stacking. The fluorescence intensity of **1** in vapor deposited films was considerably weak as compared to those of **2** and **3**. From a structural point of view, this molecular pair is considered to have a great influence on the fluorescent intensity in the solid state.

Molecular stacking between π-planes, e.g. chromophores, is known to play a significant role in fluorescence properties in the solid state.[1] However the influence of the interactions between molecules on the fluorescence properties has not been fully understood. The complete overlap between π-conjugated chromophores would be a key structure for evaluating fluorescence properties in the solid state.

In conclusion, the fluorescence intensity of non-planar 6-substituted 2,3-dicyano-5-[4-(diethylamino)styryl]-7-methyl-6*H*-1,4-diazepines in solid state could be increased by introducing a bulky alkyl substituent at the 6-position due to prevention of the cofacial molecular stacking between the chromophores.

The authors are grateful to Miss K. Kobayashi of Riken (The institute of Physical and Chemical Research) for diffraction measurement of **3**.

References and Notes

1 a) K. T. Wong, Y. Y. Chien, R. T. Chen, C. F. Wang, Y. T. Lin, H. H. Chang, P. Y. Hsieh, C. C. Wu, C. H. Chou, Y. O. Su, G. H. Lee, and S. M. Peng, *J. Am. Chem. Soc.*, **124**, 11576 (2002). b) K. Shirai, M. Matsuoka, and K. Fukunishi, *Dyes Pigm.*, **42**, 95 (1999). c) K. Yoshida, Y. Ooyama, H. Miyazaki, and S. Watanabe, *J. Chem. Soc., Perkin Trans. 2*, **2002**, 700.

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3 Typical procedure for the synthesis of **3**: To a benzene solution (15 mL) of 6-butyl-2,3-dicyano-5,7-dimethyl-6*H*-1,4-diazepine (1 mmol) were added piperidine (5 drops) and 4-(dietylamino)benzaldehyde (1 mmol). The mixture was refluxed for 6 h. After evaporating the solvent, the product was isolated by column chromatography (SiO_2, toluene:ethyl acetate = 10:1) and recrystallized from cyclohexane. Yield 16%; mp 132–134 °C; ^1H NMR ($CDCl_3$) δ 1.00 (t, $J = 7.0$ Hz, 3H), 1.21 (t, $J = 7.0$ Hz, 6H), 1.27 (br s, 1H), 1.42–1.48 (m, 4H), 2.04 (s, 3H), 2.21–2.33 (m, 2H), 3.42 (q, $J = 7.0$ Hz, 4H), 6.30 (d, $J = 15.0$ Hz, 1H), 6.64 (d, $J = 8.8$ Hz, 2H), 7.42 (d, $J = 8.8$ Hz, 2H), 7.67 (d, $J = 15.0$ Hz, 1H); EIMS (70 eV) m/z (rel intensity) 387 (M^+; 52), 372 (100). Anal. Found: C, 74.44; H, 7.56; N, 18.08%. Calcd for $C_{24}H_{29}N_5$: C, 74.38; H, 7.54; N, 18.07%.

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5 X-ray crystallographic data for **1**: $C_{20}H_{21}N_5$, $Mw = 331.42$, monoclinic, $P2_1/a$, $Z = 4$, $a = 11.010(4)$, $b = 14.470(4)$, $c = 11.503(4)$ Å, $\beta = 94.21(3)^\circ$, $D_{calcd} = 1.204$ g/cm^3, $T = 298$ K, $F000 = 704$, μ(Mo Kα) $= 0.75$ cm^{-1}, Rigaku AFC7R, Mo Kα ($\lambda = 0.71069$ Å), 5785 reflections were collected, 5328 unique ($R_{int} = 0.024$), 3827 observed ($I > 2\sigma(I)$), 290 parameters, $R_1 = 0.052$ ($I > 2\sigma(I)$), $wR_2 = 0.091$(all data), GOF = 1.24, refinement on F, H atoms were found in the difference Fourier map and only the positional parameters were refined. **2**: $C_{22}H_{25}N_5$, $Mw = 359.47$, monoclinic, $P2_1/c$, $Z = 4$, $a = 13.067(3)$, $b = 11.276(2)$, $c = 14.816(2)$ Å, $\beta = 106.23(1)^\circ$, $D_{calcd} = 1.139$ g/cm^3, $T = 298$ K, $F000 = 768$, μ(Mo Kα) $= 0.70$ cm^{-1}, Rigaku AFC7R, Mo Kα ($\lambda = 0.71069$ Å), 6652 reflections were collected, 6112 unique($R_{int} = 0.033$), 5084 observed ($I > 2\sigma(I)$), 244 parameters, $R_1 = 0.067$ ($I > 2\sigma(I)$), $wR_2 = 0.208$(all data), GOF = 1.70, refinement on F, H atoms were found in the difference Fourier map and not refined. **3**: $C_{24}H_{29}N_5$, $Mw = 387.53$, monoclinic, $P2_1/n$, $Z = 4$, $a = 11.266(1)$, $b = 12.881(2)$, $c = 16.815(1)$ Å, $\beta = 109.301(7)^\circ$, $D_{calcd} = 1.118$ g/cm^3, $T = 298$ K, $F000 = 832$, μ(Cu Kα) $= 5.28$ cm^{-1}, Enraf Nonius CAD4, Cu Kα ($\lambda = 1.54178$ Å), 5066 reflections were collected, 4677 unique($R_{int} = 0.026$), 2016 observed ($I > 2\sigma(I)$), 262 parameters, $R_1 = 0.076$ ($I > 2\sigma(I)$), $wR_2 = 0.113$(all data), GOF = 1.60, refinement on F, H atoms were located on the calculated positions and not refined.