Polymorphism, Photoluminescence, and Electroluminescence of Diaminodicyanopyrazine

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(Received November 8, 2004; CL-041329)

A diaminodicyanopyrazine derivative, having bulky substituents, was designed and synthesized. The synthesized dye exhibited an intense photoluminescence in the solid state. An electroluminescent device was prepared by using the dye. The dye exhibited polymorphism. Red and yellow single crystals of the dye were prepared by using a gas-phase sublimation growth procedure. The spectral shift due to the polymorphism is also discussed, and a candidate dye for red colored electroluminescent devices is proposed.

Organic electroluminescent (EL) devices have attracted much attention because of their possible application as light-emitting displays. Matsuoka and co-workers reported the absorption and photoluminescence spectra of 2,5-bis(dimethylamino)-3,6-dicyanopyrazine (**1**), 2,5-bis(1-pyrrolidinyl)-3,6-dicyanopyrazine (**2**), and 2,5-bis(piperidino)-3,6-dicyanopyrazine (**3**).[1] Those pyrazine derivatives have high electron affinity and intense orange and red photoluminescence. These characteristics are favorable to the light-emitting and electron-transporting layer for red colored EL devices. However, some properties should be improved to enable the pyrazine derivatives to be applied to EL devices of the vacuum deposition type. For example, the photoluminescence of dyes **1** and **2** were almost quenched on the evaporated thin films. These dyes are planar molecules, and showed large bathochromic shifts from solution to the solid state. The bathochromic shift and quenching of photoluminescence may be caused by intermolecular interactions due to the planar structure of the molecule. Dye **3** has an intense photoluminescence in the solid state. However, the melting point of dye **3**, 116 °C, was too low for EL devices. In order to apply the pyrazine framework to red colored EL devices, we tried to develop a derivative having both a high melting point and intense photoluminescence in the solid state.

We designed dye **4**, which has bulky substituents to prevent intermolecular interactions and the quenching of photoluminescence (Figure 1). The structure of the dye molecule was optimized by the AM1 method and the electronic state was calculated by the INDO/S method, implemented in the WinMOPAC 3.0 program.[2] The first electronic excitation of the dye was assigned as the HOMO–LUMO transition and the intra-molecular charge transfer transition from the amino groups to the cyano groups. As shown in Figure 1, the excitation is localized on the central pyrazine moiety, and the excited moiety can be protected from adjacent molecules by the use of bulky substituents. We synthesized dye **4**, with an improvement in melting point.[3] The absorption, photoexcitation, and photoemission bands of dye **4** in dichloromethane were 496, 507, and 564 nm, respectively. The synthesized powder of dye **4** was yellow, and the color was changed from yellow to orange by grinding. We assumed that the color change should be due to polymorphism. To study the relationship between the structure and the color, we prepared a single crystal of dye **4**. Red and yellow crystals were prepared from dye **4** by using a gas-phase sublimation growth procedure. Intense photoluminescences were observed from these two single crystals and powders of dye **4**. The excitation and emission spectra for these states of dye **4** are shown in Figure 2. Large spectral shifts were observed for both photoexcitation and photoemission bands.

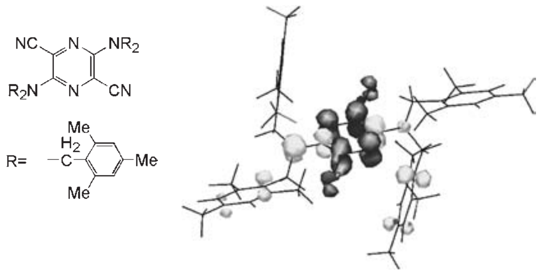


Figure 1. Structure and schematic representation of the first electronic excitation of dye **4**. The gray and black parts represent decrease and increase of electron density due to the first excitation, respectively.

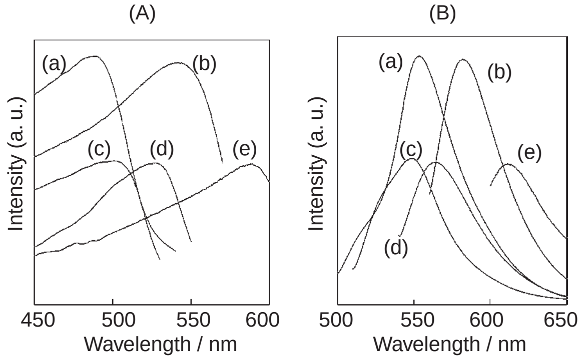


Figure 2. Photoexcitation, (A), and photoemission, (B), spectra of dye **4**: (a) yellow powder; (b) ground orange powder; (c) yellow crystal; (d) evaporated film; (e) red crystal.

The crystallographic structures[4] of the red and yellow crystals are shown in Figure 3. Usually, the spectral shift from solution to solid state can be explained by the intermolecular interactions in the solid state.[5] However, no close π–π contacts within 7.0 Å were observed between neighboring molecules in both crystals, suggesting that the intermolecular distances in both crystals are too large to cause a significant intermolecular interaction. The INDO/S calculations for the molecular structures of the crystals assigned the absorption bands at 382 and 354 nm to the red and yellow crystals, respectively. This calculation indicated that the blue shift of the yellow crystal was due to the molecular structure. The blue shift was explained by the use of the INDO/S calculation for 2,5-dicyanopyrazine. The first electron-

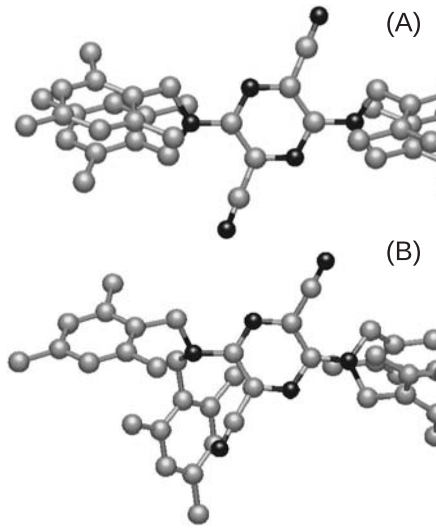


Figure 3. Crystallographic structures of red, (A), and yellow, (B), crystal of dye **4**. Representations of hydrogen atoms were ignored.

ic excitation was assigned as the HOMO–LUMO transition. The shapes of the HOMO and LUMO of 2,5-dicyanopyrazine are shown in Figure 4. The HOMO showed significant contributions at the 3- and 6-positions, although the LUMO had no contribution at these positions. This result suggests that the introduction of an electron-donating substituent at the 3- and 6-positions caused an elevation of the HOMO energy level, but caused no change to the LUMO energy level. Accordingly, the introduction of amino groups to the positions caused a narrower energy gap between HOMO and LUMO. As shown in Figure 3, the one amino group of the yellow crystal is twisted from the central pyrazine plane, and cannot contribute to elevation of the HOMO energy level. As a result, the yellow crystal had a larger HOMO–LUMO energy gap than the red crystal, and exhibited a blue shift in photoexcitation and photoemission spectra. The INDO/S calculations gave the HOMO energy levels of -7.31 and -7.59 eV to the red and yellow crystals, respectively, and gave the same LUMO energy level of -0.80 eV to both crystals. In other words, the angle between the amino group plane and pyrazine ring significantly contributes to the spectral shift, and the small angle should cause a bathochromic shift. The dihedral angle between the amino groups and pyrazine ring of the red crystal was about 27°. Those of the yellow crystal were about 53 and 15°. The calculated structure shown in Figure 1 was a candidate for the structure in solution. The dihedral angle for the structure shown in Figure 1 was about 40°. We estimated that: (A) the dihedral angles between amino groups and pyrazine ring of the orange powder and molecule in solution lie midway between 53 and 27°; (B) the color change of the yellow powder by grinding was due to the change of the dihedral angle.

The photoemission band, at 620 nm, of the red crystal is well suited to a red colored EL device. We fabricated an EL device of glass/ITO/4,4′-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (40 nm)/dye **4** (60 nm)/Al (100 nm) by vacuum deposition, and observed the luminance of 2000 cd/m^2 (1.0 cd/A at 23 V) and 1 cd/m^2 (0.4 cd/A at 8 V). This result supported the validity of our molecular design concept, although the EL emission band was at 575 nm, being closer to the photoemission band, 563 nm, of the evaporated film than that of the red crystal. No bathochromic shift of the band was achieved by variation of the vacuum deposition conditions.

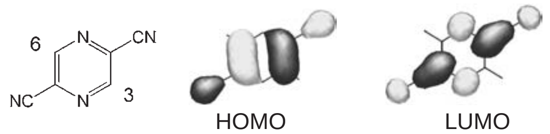
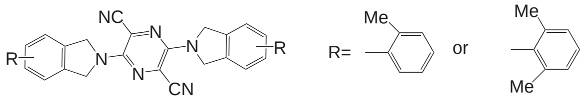


Figure 4. Schematic representation of HOMO and LUMO of 2,5-dicyanopyrazine calculated by the INDO/S method.

Our calculations and experimental results suggest that a pyrazine derivative, having both bulky substituents and small dihedral angle between amino groups and pyrazine ring, should be a good candidate for red colored EL devices. Introducing less bulky amino groups to dicyanopyrazine would be successful in achieving the small dihedral angle. We propose the following structure, having both less bulky amino groups and bulky peripheral substituents, as the dye for red colored EL devices.



In summary, we designed and synthesized dye **4**, and fabricated an EL device with the dye. Interestingly, the dye exhibited polymorphism. The spectral shift due to the polymorphism was explained by the molecular orbital calculations, and a candidate for red colored EL devices was proposed.

We thank Dr. H. Uekusa at the Tokyo Institute of Technology for performing the X-ray crystallographic analysis. We also thank the Nippon Soda Co. Ltd. for a gift sample of dye **4**. This research was supported by a Grant-in-Aid for Scientific Research (B) 15350083 by the Japan Society for the Promotion of Science (JSPS).

References and Notes

1 K. Shirai, A. Yanagisawa, H. Takahashi, K. Fukunishi, and M. Matsuoka, *Dyes Pigm.*, **39**, 49 (1998).

2 MOPAC2000 ver. 1.11, Fujitsu Ltd, Tokyo, Japan (1999).

3 Dye **4** was synthesized from 2,5-diamino-3,6-dicyanopyrazine and 1-bromomethyl-2,4,6-trimethylbenzene. Selected data for dye **4**: ^{1}H NMR (CDCl$_3$): δ 6.78 (8H, s), 4.42 (8H, s), 2.23 (12H, s), 1.90 (24H, s); Anal. Calcd. for $C_{46}H_{52}N_6$: C, 80.19; H, 7.61; N, 12.20%. Found: C, 79.94; H, 7.41; N, 12.18%: mp 234–235 °C: fluorescence quantum yield (Φ) in solution 0.5.

4 Crystallographic data for the red crystal of dye **4**: monoclinic, space group $P21/n$, $a = 8.7571(5)$, $b = 17.1976(14)$, $c = 12.9837(8)$ Å, $\alpha = 90$, $\beta = 102.889$, $\gamma = 90°$, $V = 1906.1(2)$ Å^3, $Z = 2$, R (wR_2) $= 0.03$ (0.12). Crystallographic data for the yellow crystal of dye **4**: triclinic, space group $P-1$, $a = 8.6525(1)$, $b = 15.2196(7)$, $c = 16.0458(5)$ Å, $\alpha = 99.865(1)$, $\beta = 101.917(3)$, $\gamma = 101.697(2)°$, $V = 1973.80(11)$ Å^3, $Z = 2$, R (wR_2) $= 0.04$ (0.13).

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