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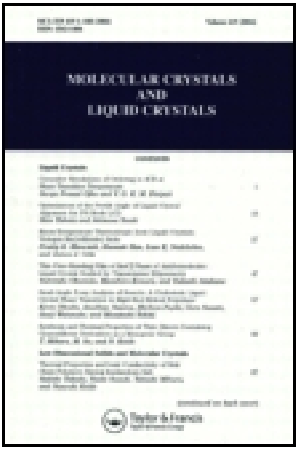

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Electro-Optical Properties and X-ray Crystal Structure of a New Bisazomethine Dye

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Electro-Optical Properties and X-ray Crystal Structure of a New Bisazomethine Dye

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The photoluminescence and electroluminescence properties of a new bisazomethine dye derived from diaminomaleonitrile were investigated. This dye was examined as red-light-emitting materials in organic EL devices. The crystal structure of a new bisazomethine dye has been determined by X-ray crystallography. The molecules were found to form J-aggregate-like molecular arrangement.

Keywords: azomethine dye; electroluminescent (EL); emitting materials; X-ray crystal structure

INTRODUCTION

Organic electroluminescent (EL) devices have received attention because of potential application to full color flat panel displays. The distinctive characteristics of organic ELs are that they utilize organic fluorescent or phosphorescent dyes as an emitter. Therefore, they can provide various emission colors in accordance with a wide selection of organic fluorescent dyes [1–3]. Since Tang and VanSlyke reported that

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a double layered organic EL device consisting of a hole injection layer and an emitting layer exhibited a luminance over 1000 cd m^{-2} at a relatively low driven voltage of 10 V, those have been extensive studies on layered organic EL devices with the aim of achieving high brightness and full color emission [4–6]. Since the first discovery of the double organic layer EL devices [4] consisting of diamine hole transport layer and a 8-hydroxyquinoline aluminium (Alq_3) complex emitting layer in 1987, EL devices has been studied due to their practical application as a full color flat panel displays. After Tang's research work, other 8-hydroxyquinoline derivatives metal complex were also used as an emitter [7]. A bisazomethine dye derived from diaminomaleonitrile together with 4-diethylaminobenzaldehyde [8] has been studied as a material for organic electroluminescent devices because of its red fluorescence in solution as well as in the solid state [9]. Recently, we also showed that azomethine dyes, which have bright red PL light, are promising materials for the red-light-emitting OLED [10]. In this paper, we report on the synthesis, EL properties and X-ray crystal structure of a new azomethine dye, in which the butoxy group enhances the steric hindrance of the molecule, as an emitting material.

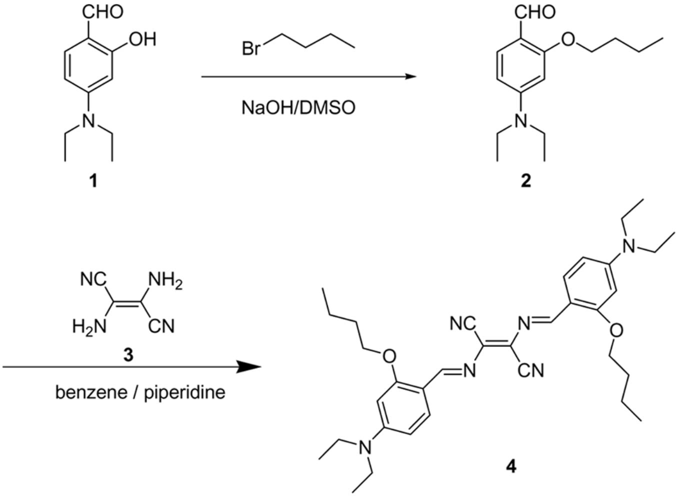
EXPERIMENTAL

Elemental analyses were recorded on a Carlo Elba Model 1106 analyzer. Mass spectra were recorded on a Shimadzu QP-1000 spectrometer using electron energy of 70 eV and the direct probe EI method. ^{1}H NMR spectra were recorded on a Varian Unity Inova 400 MHz FT-NMR spectrometer with TMS as internal standard. UV-visible spectra were recorded on a Shimadzu 2100 spectrometer. Melting points were determined using an Electro-thermal IA 900 apparatus and are uncorrected. The 4-(diethylamino)-2-butoxybenzaldehyde **2** was synthesized according to the literature method [11] with a high yield of 90%.

Bisazomethine Dye 4

Diaminomaleonitrile **3** (0.1 g, 0.6 mmol) and 4-(diethylamino)-2-butoxybenzaldehyde **2** (0.3 g, 1.2 mmol) were heated at 60°C for 7 h in benzene (10 ml) containing 1 ml of piperidine. Water was removed azeotropically using a Dean-Stark trap. The reaction mixture was cooled to room temperature. The precipitated crude product was separated by filtration, washed with methanol and recrystallized from chloroform.

21% yield; mp 128–130°C MS m/z M^+681; ^{1}H NMR (400M Hz, $CDCl_3$); δ 0.98(t, $J = 7.04$, 6H), 1.21(t, $J = 7$, 12H), 1.34(t, $J = 7.04$, 3H), 1.54(m, $J = 7.52$, 4H), 1.89(m, $J = 7.52$, 4H), 3.40(m, $J = 7$, 8H), 4.05(m, $J = 6.52$, 4H), 4.24(m, $J = 7$, 2H), 6.14(s, 2H), 6.28(d, $J = 8.8$, 2H), 6.59(s, 1H), 6.75(d, $J = 13.52$, 2H), 7.33(d, $J = 8.8$, 2H), 7.67(d, $J = 7.52$, 2H), 7.91(S, 1H); Anal. Cald for $C_{42}H_{55}N_3O_5$: C, 73.98; H, 8.13; N, 6.16. Found; C, 73.75; H, 8.39; N, 6.24.



Fabrication of EL Device

Bisazomethine dye **4** and α-NPD (N,N′-di-[(1-naphthalenyl)-N,N′-diphenyl]-1,1′-biphenyl)-4,4′-diamine) were used as an emitting layer and a hole transporting layer in EL devices. α-NPD has a high hole drift mobility and has been utilized as a hole transport layer in organic devices. The structure of organic EL devices was ITO/α-NPD/Azomethine dye/Alq_3/LiF/Al. In a device with Al cathode, dye, α-NPD, LiF and Alq_3 layer were deposited by vacuum thermal evaporation on a ITO under a vacuum of about 2×10^{-6} Torr. LiF was used for enhancing electron injection efficiency of OLEDs. The thickness of α-NPD,dye, Alq_3, LiF and Al cathode were about 40, 40, 20, 0.5 and 100 nm, respectively, which were measured by a quartz crystal thickness monitor placed near the substrate. The electron-injecting layer is tris(8-quinolinolato)aluminium complex (Alq_3), which has electron transport properties and has been used as a electron transport layer in EL device. The active area of devices is $3.0 \times 3.0\,mm^2$.

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The electrical and luminescent characteristics of EL devices were analyzed by using a source meter 2400 (Keithley) and optical power meter 1830 S (Newport). The EL spectrum and Commission Internationale De L'Eclairage (CIE) coordinates were measured with a Spectroradiometer (Minolta CS-1000).

X-ray Crystallographic Analysis

Single crystals of dye **4** were prepared by diffusion method using chloroform and cyclohexane as good and poor solvents, respectively. Crystal data: $C_{34}H_{46}N_6O_2$, $Mw = 570.78$, monoclinic, $P2_1/c$, $Z = 2$, $a = 8.624$ (3), $b = 22.712$ (6), $c = 8.511$ (2) Å, $\beta = 98.34$ (3)°, $D_{calc} = 1.149\,\mathrm{g/cm^3}$, 11646 reflections were collected, 2798 unique ($R_{int} = 0.057$), 690 observed ($I > 2\sigma(I)$), 213 parameters, $R_1 = 0.054$, $wR_2 = 0.2012$, GOF = 1.002, refinement on F^2. The data was collected on a Rigaku RAXIS RAPID imaging plate diffractometer with a graphite-monochromated Cu$K\alpha$ radiation (40 kV, 50 mA) to a maximum 2θ value of 136.5° at room temperature. A total of 24 ($\Delta\varphi = 30°$) images were measured using an oscillation technique. An absorption correction was applied. The structure was solved by the direct method (*SIR92* [12]) and refined by least-squares calculations using the *Crystal Structure* software package [13]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed on the calculated positions and refined by riding model.

RESULTS AND DISCUSSION

It is well known that the amino groups of diaminomaleonitrile **3** react with carbonyl groups to afford azomethine linkages. The condensation of compound **3** with arylaldehydes proceeded in the presence of piperidine in benzene, removing the generated water with Dean-Stark trap. We studied OLED using theazomethine dye **4**. Figure 1 shows the configuration of EL device fabricated in the present study and the structure of α-NPD. Recently, a thin layer of inorganic Li compounds, such as Li_2O and LiF, was reported to be useful in bilayer cathode systems. This cathode system is based on the assumption that the organic layer at the cathode interface is doped with a low-work-function metal, such as Li, when such a reactive metal is evaporated onto the organic layer. As a result, the barrier height for electron injection from the cathode to the organic layer is lowered. Comparison of the absorption spectra in solution and vapor deposited thin film of dye is illustrated in Figure 2.

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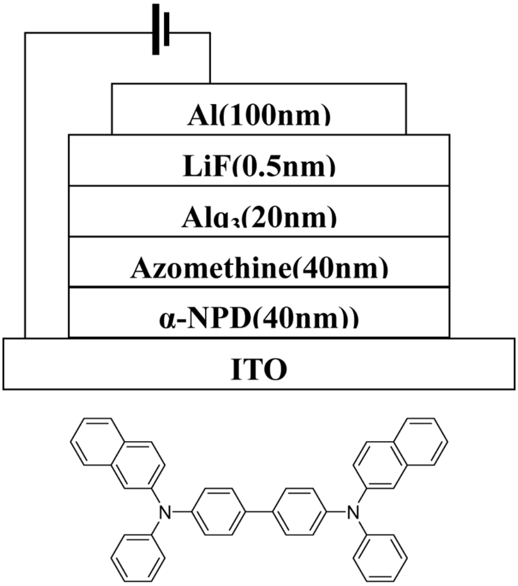

α-NPD

FIGURE 1 Device configuration of EL and molecular structure of α-NPD.

The $\lambda_{\max}$ of dye **4** was caused due to intramolecular charge transfer chromophore system in which the arylamine moiety is a donor and the central ethylene moiety is an acceptor. Dye **4** absorbed at 555 nm in chloroform, but the absorption maximum was found to shift to the longer wavelength in vapor deposited thin films. The fluorescence spectra also exhibit a bathochromic spectral shift. These bathochromic shifts would be caused by intermolecular interactions in the solid state.

Figure 3 shows the characteristics of applied voltage-current density of EL device with dye **4**. Turn-on voltage of the OLED with dye **1** is about 20 V. The current density of dye has 15 mA/cm^2 at 30 V. Red light emission was observed for the EL device under forward bias. Figure 4 shows the voltage-luminescence (*V-L*) characteristics of the EL devices. The luminescence intensity was exponentially increased with increasing voltage in dye **4**. The linear dependence of the luminescence intensity on the voltage is indicated that charge carriers are easily injected from both the electrodes by increasing the voltage or current density. The device with dyeshowed a maximum luminance of 24 cd/m^2 at a current density of 18 mA/cm^2 at 30 V. The light emitting property was confirmed from EL device. But the corresponding

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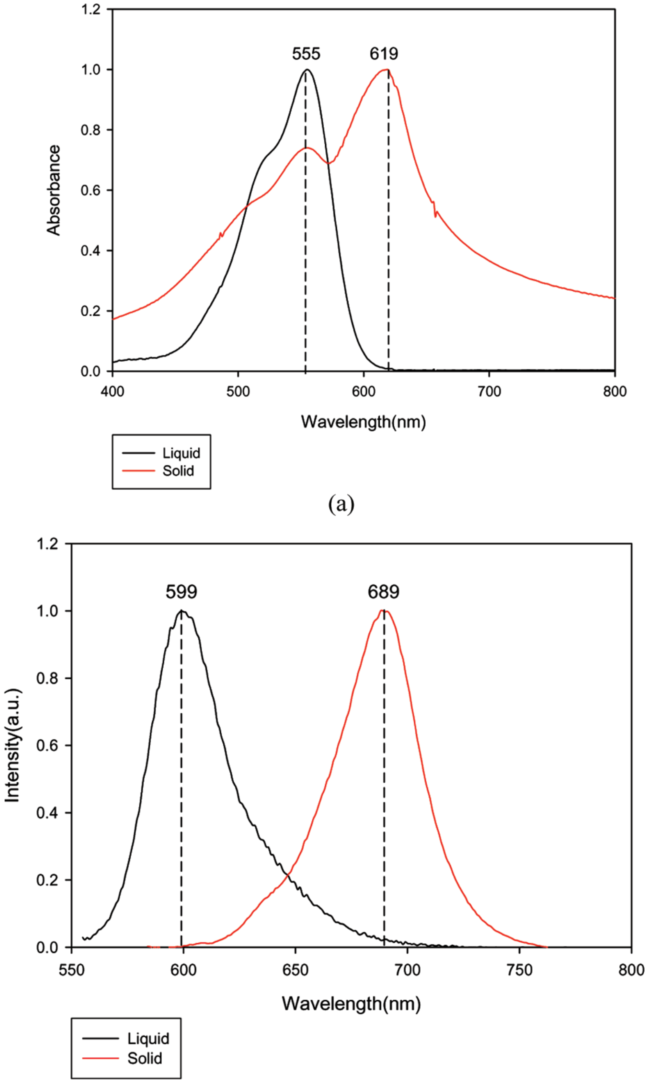

(a)

(b)

FIGURE 2 UV-vis (a) and photoluminescence (b) spectra of dye **4** in chloroform and in vapor deposited thin films.

luminescence and emitting efficiencies are not sufficient to use in practical purposes. Figure 5 shows the EL spectra of the device. EL spectra for the devices show a main peak at approximately 680 nm.

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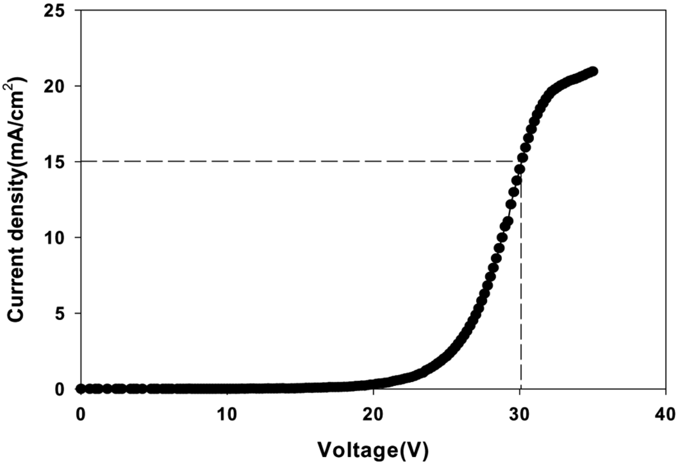

FIGURE 3 Voltage-current (V-I) density characteristics of the EL devices with dye **4**.

The CIE coordinates are x = 0.68, y = 0.29 which correspond to the red emission.

X-ray structural analysis indicated another important characteristic of dye **4**. The molecule was found to have an almost planar

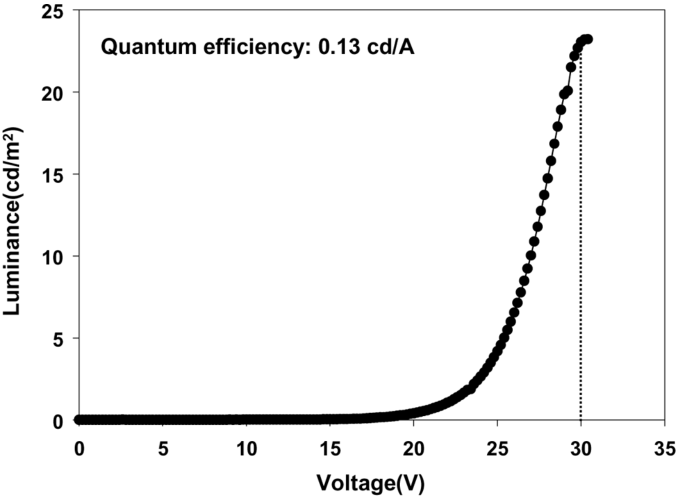

FIGURE 4 Voltage-luminescence (V-L) characteristics of EL device.

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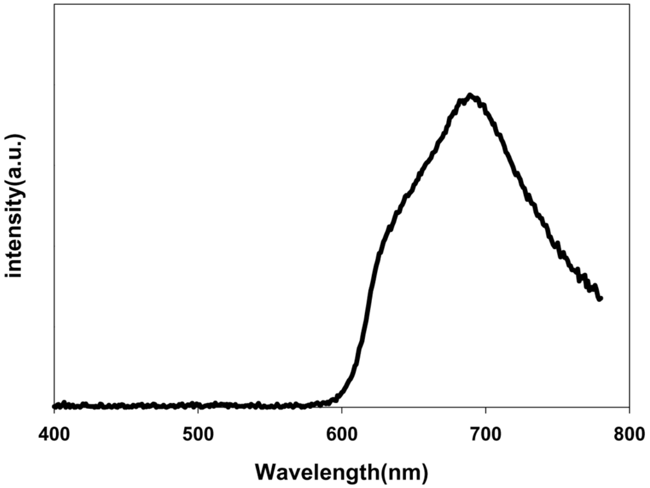

FIGURE 5 Electroluminescence (EL) spectra of the multilayer EL device.

conjugated system with trans conformation. As shown in Figure 6, molecules are arranged in a characteristic fashion which is reminiscent of the proposed molecular arrangement for J-aggregates [14–16]. Figure 6(a) depicts a two-dimensional stacking column on the *ac* plane. In this column, molecules are stacked along the (102) direction with the slip angles of about 16 and 24° with respect to the long molecular axis. This molecular arrangement is very similar to the "brick-stone" structure, which is one of the well-known structure for J-aggregates. These stacking columns are aligned along the *b*-axis by twofold screw symmetry to give three-dimensional crystal structure. Molecules were also found to form a two-dimensional molecular layer on the (102) plane through these stacking columns as shown in Figure 6(b). The "brick-stone" structure is also recognized in this layer, even though the molecules are not completely parallel. These characteristic molecular arrangements are considered to contribute to the observed bathochromic shift in both absorption and fluorescent spectra from solution to the solid state.

Bisazomethine dyes based on daminomaleonitrile are known to form characteristic J-aggregate-like molecular arrangements in single crystals [17,18] and several derivatives form J-aggregates in vacuum-deposited films [19,20]. The present X-ray analysis is thus considered to reveal the potential of dye **4** to form J-aggregates in an appropriate medium or in the solid state.

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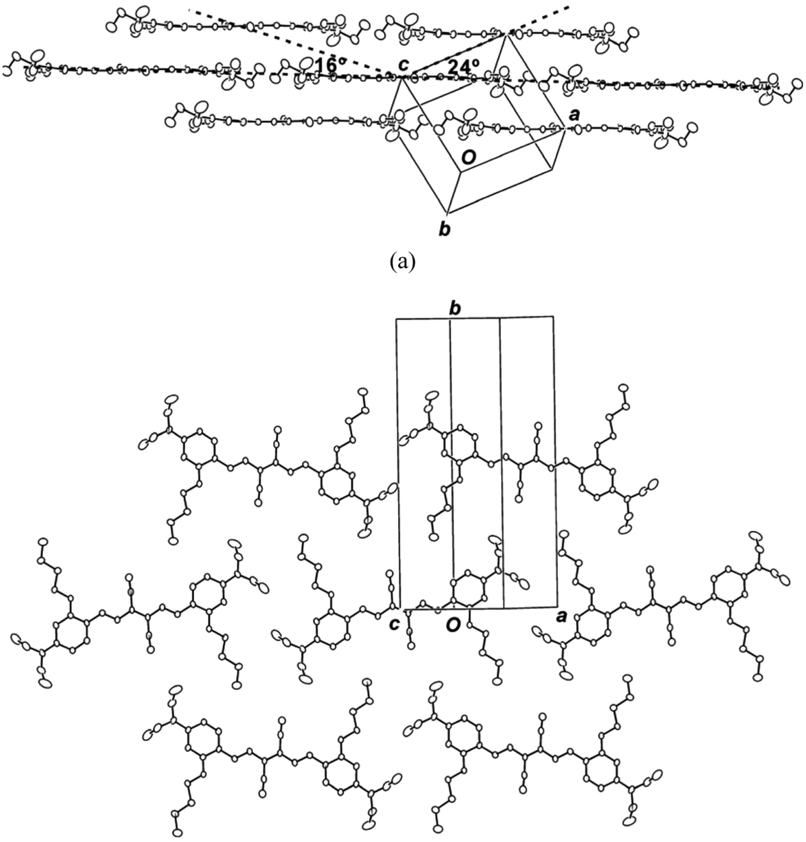

(a)

(b)

FIGURE 6 (a) Two-dimensional molecular stacking column on the *ac* plane and (b) two-dimensional molecular layer on the (102) plane.

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