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Red electroluminescent azomethine dyes derived from diaminomaleonitrile

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Abstract

The photoluminescence (PL) and electroluminescence (EL) properties of azomethine dyes derived from diaminomaleonitrile were investigated. These dyes were examined as red-light-emitting materials in organic EL devices.

Keywords: Azomethine dye; Electroluminescence (EL); Photoluminescence (PL); Red emission

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1. Introduction

An appreciable amount of research has been carried out in the field of organic electroluminescence (EL) based optoelectronic devices during the last decade. The distinctive characteristics of organic light-emitting diodes (LEDs) are that they utilize organic fluorescent or phosphorescent dyes as emitters. Therefore, they can produce various emission colors in accordance with a wide selection of organic fluorescent dyes [1–3]. Since the proposal by Tang and VanSlyke on the use of the multilayer structures for high-performance EL devices, there has been significant progress in the development of design concepts of multilayer structures as well as in molecular design of fluorescent dyes and charge transport dyes [4–6]. There are two methods for tuning the color emitted from organic EL devices: an appropriate selection of the emitting materials with bright luminescence of desired colors or doping dyes into the host dye. The former method is the most feasible for producing blue-light-emitting EL devices [7], and the latter is useful for the fabrication of the bright red-light-emitting organic EL devices [8]. In this paper, our objective is to design and synthesize novel bisazomethine fluorescent dyes that can be used as red emitters in organic EL devices.

2. Experimental

2.1. Materials and equipment

Elemental analysis was 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. UV–vis spectra were recorded on a Shimadzu 2100 spectrometer. Melting points were determined using an Electro-thermal IA 900 apparatus and are uncorrected. Diaminomaleonitrile, triphenylamine and *N*-ethylcarbazole-3-carboxaldehyde were obtained from Aldrich. The procedure of preparation and characterization data of dye **5** have been reported earlier [9]. Structures were confirmed from data described in the literature and from data shown below.

2.1.1. Dye 5

Yield: 17%, m.p. >300 °C, mass (m/z): 518 (M^+), Anal. Calcd. for $C_{34}H_{26}N_6$: C 78.74, H 5.05, N 16.21%; found C 77.75, H 5.23, N 16.07%.

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2.1.2. *p-N,N-diphenylaminobenzaldehyde* **2**

Yield: 22.3%, m.p. 137–138 °C, mass (*m*/*z*): 273 (M^+), Anal. Calcd. for $C_{19}H_{15}NO$: C 83.49, H 5.53, N 5.12%; found C 83.49, H 5.62, N 4.9 5%.

2.2. *Synthesis of dye* **4**

Diaminomaleonitrile **1** (0.2 g, 1.8 mmol) and *p*-*N*,*N*-diphenylaminobenzaldehyde **2** (1 g, 3.6 mmol) were heated at 75 °C for 3 h in benzene (20 ml) containing 2 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 benzene and recrystallized from chloroform.

Yield: 25%, m.p. 286–287 °C, mass (*m*/*z*): 618 (M^+), Anal. Calcd. for $C_{42}H_{30}N_6$: C 81.53, H 4.89, N 13.58%; found C 81.47, H 5.24, N 12.12% (see Scheme 1).

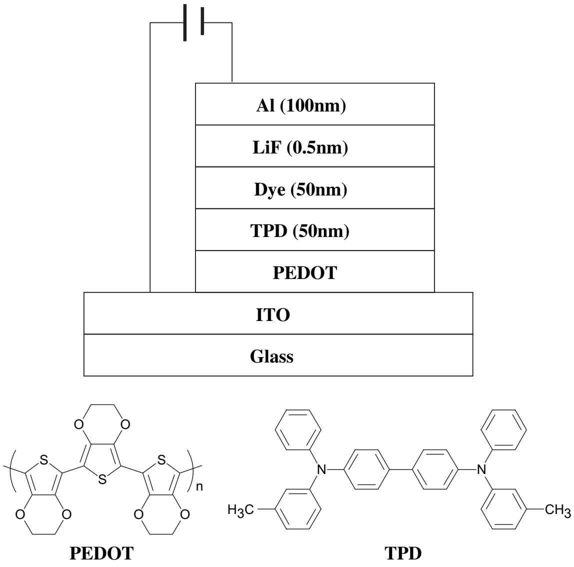


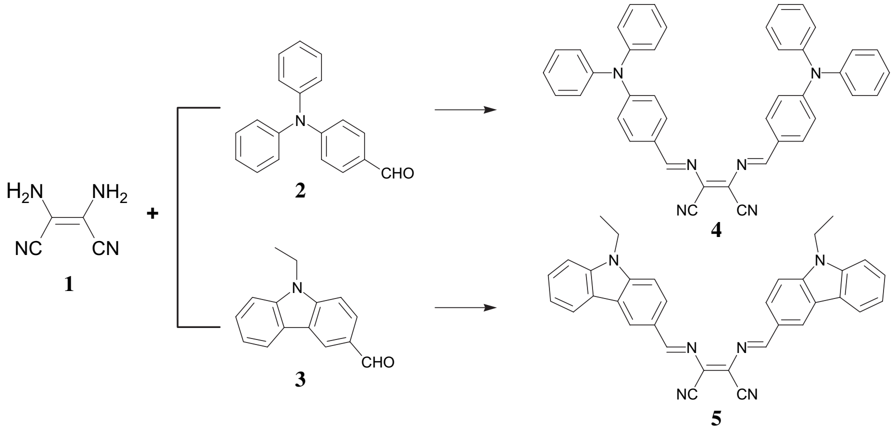
Fig. 1. The structure of materials and device configuration used in this study.

2.3. *Measurement of electrical and luminescent characteristics*

Azomethine dyes **4**, **5** and TPD (*N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-diphenyl-4,4′-diamine) were used as an emitting layer and a hole transporting layer in EL devices. The structure of organic EL devices was ITO/PEDOT/TPD/azomethine dye/LiF/Al. Poly(3,4-ethylenedioxythiophene) (PEDOT) as a hole conducting buffer layer was spin coated on the patterned precleaned indium–tin oxide (ITO)-coated glass substrates. In a device with Al cathode and azomethine dye, all organic TPD and azomethine dye layers were deposited by vacuum thermal evaporation on a PEDOT layer under a vacuum of about 2×10^{-6} Torr. LiF was used for enhancing electron injection efficiency of OLEDs. The thickness of azomethine dye film, LiF layer and Al cathode were about 50, 0.5 and 100 nm, respectively, which were measured by a quartz crystal thickness monitor placed near the substrate. The active area of devices is 3.0×3.0 mm^2. Photoluminescence (PL) spectra were measured using a Spectra Pro-300I (Princetone Instruments). The electrical and luminescent characteristics of EL devices were analyzed by using a source meter 2400 (Keithley) and optical power meter 1830S (Newport). The EL spectrum and Commission Internationale De L'Eclairage (CIE) coordinates were measured with a Spectroradiometer (Minolta CS-1000) (see Fig. 1).

3. Results and discussion

It is well known that the amino groups of diaminomaleonitrile **1** react with carbonyl groups to afford azomethine linkages. Shirai has recently reported that dye **5** showed quite strong red fluorescence, which is



Scheme 1.

anticipated for the red-light-emitting materials for EL devices [9]. The condensation of **1** with arylaldehydes proceeded in the presence of piperidine in benzene, removing the generated water with a Dean–Stark trap. Comparison of the absorption spectra in solution and vapor deposited thin film of dyes are illustrated in Fig. 2. The λ_{max} of dyes was caused due to intramolecular charge transfer chromophoric system in which the arylamine moiety is a donor and the central ethylene moiety is an acceptor, and then λ_{max} produced a bathochromic shift depending on the electron donating ability of the donor moiety. The solid-state PL spectra of azomethine dyes are shown in Fig. 2.

Dye **5** absorbed at 505 nm in chloroform and dye **4** produced bathochromic shift of 35 nm when compared to that of dye **5**. The solid-state PL spectra were recorded with an excitation wavelength corresponding to the absorption maximum wavelength of the dye. In comparison to the absorption spectrum, the emission spectrum was shifted by approximately 100–160 nm towards the red side. The PL spectra of dyes showed that the emission maxima were 695 nm (dye **4**), and 600 nm (dye **5**). They showed a broad band approximately 600–700 nm in the red region.

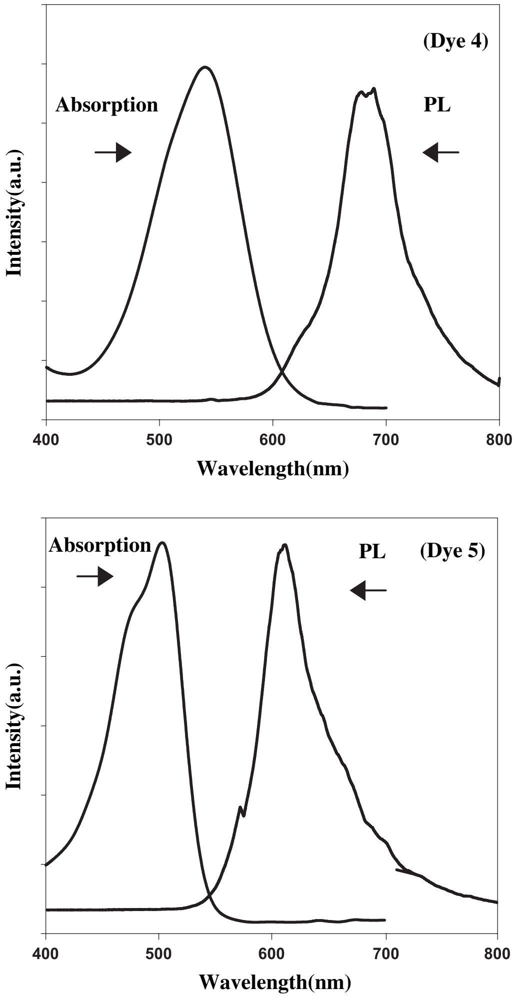


Fig. 2. UV–vis in chloroform and photoluminescence spectra in powder of dyes.

Generation of light in an organic multilayered EL system is the result of recombination of holes and electrons injected from the electrodes. Such recombination in the emitting layer then excites the emitter materials. The properties of the emitting material are important in the performance of EL devices.

At present, although it is very easy to fabricate the full color emitting organic EL devices, bright red-light-emitting EL devices are still scarce. In this study, our objective is to design and synthesize a bisazomethine dye that can be used as an emitter layer in organic EL devices. Today, the advantage of the use of multilayer structure is well accepted on the basis of the understanding of the working mechanism of multilayer thin-film EL devices. Fig. 1 shows the configuration of EL device fabricated in the present study and the structure of PEDOT and TPD. To facilitate hole injection from anode, the hole injection layer PEDOT was inserted between the hole injection electrode and TPD as the hole transport layer. Other advantages of inserting PEDOT are: smoothened anode surface, facilitated hole injection and reduced probability for electrical shorts. The second layer on PEDOT is TPD which is one of the hole transporting compounds. The third layer is made with azomethine dyes as the emitting material. Low power consumption and long life are essential in such applications, and in recent years a great deal of effort has gone into fabricating more efficient and stable devices.

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

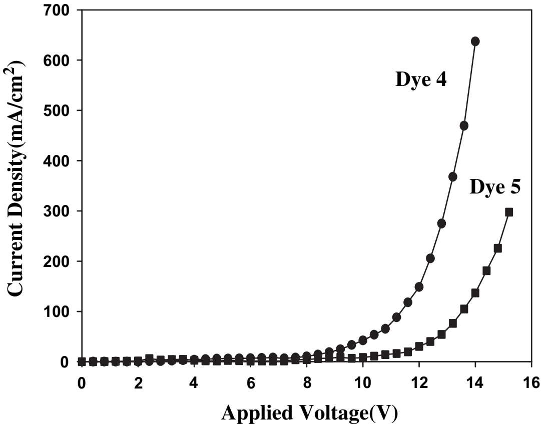


Fig. 3. Voltage–current (*V*–*I*) density characteristics of the EL devices with dyes.

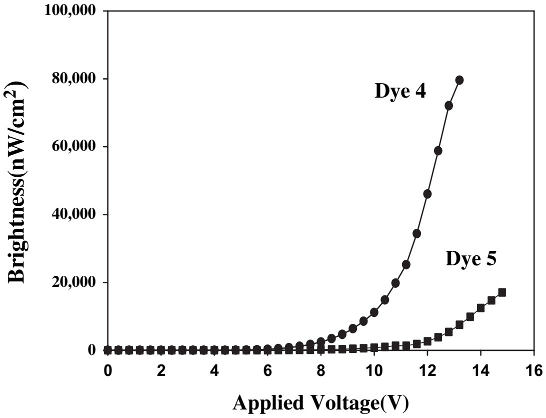


Fig. 4. Voltage–luminescence (*V*–*L*) characteristics of EL devices with dyes.

injection from the cathode to the organic layer is lowered. The evaporation of LiF and Al were fabricated at the rate of 0.1–0.2 Å/s and 4–5 Å/s, respectively.

Fig. 3 shows the characteristics of the current vs. voltage of the EL devices of ITO/PEDOT/TPD/azomethine dye/LiF/Al. The forward current was obtained when the ITO electrode was biased positively and the Al electrode negatively. The forward current increases with increasing forward bias voltage for EL devices. Red light emission was observed for the EL devices under forward bias. With increasing forward bias, both the currents increase rapidly after the turn-on voltage. Fig. 4 shows the voltage–luminescence characteristics of the EL devices. Dye **4** exhibited higher EL efficiency than dye **5** as shown in Fig. 4. The threshold voltage for luminescence is about 8 V in the device with dye **4**. On the other hand, the EL device incorporating the dye **5** layer has a higher threshold voltage of 11 V. The device with dye **4** showed a maximum luminance of 80,000 nW/cm^2 at a current density of approximately 600 mA/cm^2.

Fig. 5 shows the EL spectra of the devices. EL spectra for the devices show a main peak at approximately 655 nm (dye **4**) and 630 nm (dye **5**). The CIE coordinates are $x = 0.68$, $y = 0.29$ in dye **4** and $x = 0.62$, $y = 0.37$ in dye **5**, which correspond to the red emission. In summary, a new class of azomethine dyes has been synthesized and characterized. Bright and saturated red light was observed from EL devices based on the dyes, indicating their potential use as red emitters in EL applications.

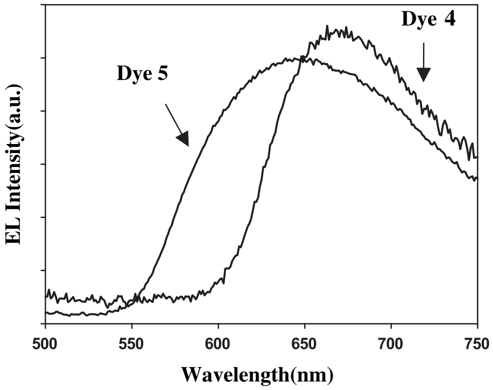


Fig. 5. Electroluminescence (EL) spectra of the multilayer EL devices.

Acknowledgments

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