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Light emitting properties of diheteryl-substituted styryl dyes

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Abstract

Styryl dyes **7a–e** having diheteryl moiety were synthesized and used as an emitter material in organic electroluminescent (EL) devices. The device structure of indium-tin oxide(ITO)/poly(3,4-ethylenedioxythiophene)(PEDOT)/*N*,*N*′-diphenyl-*N*,*N*′-di(m-tolyl)benzidine(TPD)/styryl dye/Al was employed. The EL device with dye **7a** exhibited red light with a maximum luminance 3745 nW/cm^2 at 11 V.

Keywords: Styryl dye; Diheteryl; Electroluminescent (EL); Emitting materials

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1. Introduction

Organic electroluminescent (EL) devices have received attention because of potential application to full colour flat panel displays. The distinctive characteristics of organic ELs are that they utilize organic fluorescent or phosphorescent dyes as an emitter. Therefore, they can produce various emission colours in accordance with a wide selection of organic fluorescent dyes [1–3]. Since Tang and VanSlyke reported that 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 driving voltage of 10 V, those have been extensive studies on layered organic EL devices with the aim of achiving high brightness and full colour 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 have been studied due to their practical application as a full colour flat panel displayers. After Tang's research work, other 8-hyrroxyquinoline derivatives metal complex were also used as emitter [7]. Styryl dyes were once a fairly important group of yellow dyes for a variety of substrates. Some fluorescent derivatives of styryl dye have found a number of practical uses. In this paper, we rerport on the synthesis and EL properties of diheteryl-substituted styryl dyes as an emitting material.

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2. 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.

*2.1. Preparation of styryl dyes (dye **7a–e**) (general method)*

*2.1.1. 2,2′-(1,4-phenylenedivinylene)-bis-3,3-dimethylindolenine: dye **7a***

Dye **7a** was obtained from 2,3,3-trimethylindolenine using previously described procedure [8]. Terephthalaldehyde 1 (0.01 mol, 1.34 g), 2,3,3-trimethylindolenine 2 (0.02 mol, 3.2 g) and benzyltriethylammonium chloride(BTEA) (0.003 mol, 0.70 g) were mixed and stirred. A small quantity of water (about 2 ml) was added if necessary. Highly concentrated sodium hydroxide aqueous solution (3–5 ml) was added dropwise during 40–60 min and at the end of addition the concentration of sodium hydroxide solution adjusted to 50% taking into account the quantity of previously added water. The mixture was stirred at 30–50 °C for several hours. The reaction mixture was diluted with water and neutralized with hydrochloric acid (pH = 8–8.5). The product was filtered, washed with water, aired at 50 °C and cystallised from acetone/hexane.

Yield, 77%, m.p. 184–186 °C. ^{1}H-NMR(($CD_3)_2$-CO, 400 MHz): δ (ppm): 1.49 (s, 12H), 7.26 (t, 2H), 7.35 (t, 2H), 7.37 (d, 2H, $J = 16.3$ Hz), 7.46 (d, 2H, $J = 7.4$ Hz), 7.67 (d, 2H, $J = 7.6$ Hz), 7.85 (d, 2H, $J = 16.4$ Hz), 7.86 (s, 4H). Mass (*m*/*z*): 416 (M^+) anal. calcd. For $C_{30}H_{28}N_2$: C 86.50, H 6.78, N 6.73%; found: C 86.57, H 6.86, N 6.75%.

The dyes **7b–e** were obtained by a similar procedure using 2-methylbenzoxazole 3, 2-methylbenzothiazole 4, lepidine 5 and quinaldine 6, respectively.

*2.1.2. 2,2′-(1,4-phenylenedivinylene)-bis-benzoxazole; dye **7b***

Yield, 70%, m.p. > 300 °C. ^{1}H-NMR(($CD_3)_2$SO, 400 MHz): δ (ppm): 7.45 (t, 2H), 7.54 (t, 2H), 7.72 (s, 4H), 7.87 (s, 4H), 8.00 (d, 2H, $J = 7.9$ Hz), 8.12 (d, 2H, $J = 8.1$ Hz) mass (*m*/*z*) : 364 (M^+). Anal. calcd. For $C_{24}H_{16}N_2O_2$: C 79.11, H 4.43, N 7.69%; found: C 79.13, H 4.40, N 7.67%.

*2.1.3. 2,2′-(1,4-phenylenedivinylene)-bis-benzothiazole; dye **7c***

Yield, 68%, m.p. 287–290 °C. ^{1}H-NMR(($CD_3)_2$-SO, 400 MHz): δ (ppm): 7.47 (m, 2H), 7.53 (m, 2H), 7.72 (s, 4H), 7.88 (s, 4H), 8.00 (d, 2H, $J = 8.0$ Hz), 8.12 (d, 2H, $J = 8.1$ Hz) mass (*m*/*z*): 396(M^+). Anal. calcd. For $C_{24}H_{16}N_2O_2$: C 72.69, H 4.07, N 7.06%; found: C 72.70, H 4.05, N 7.09%.

*2.1.4. 4,4′-(1,4-phenylenedivinylene)-bis-quinoline; dye **7d***

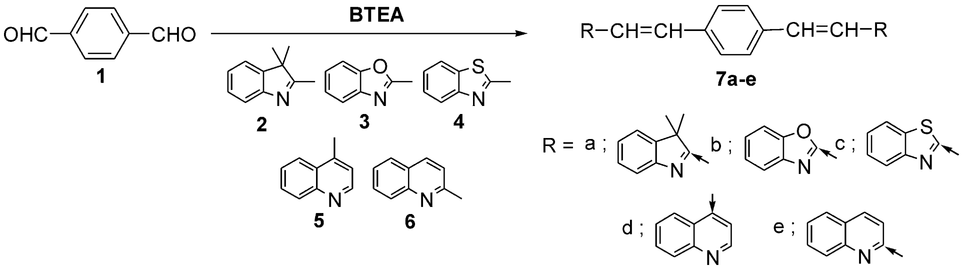
Yield, 64%, m.p. 258–260 °C. ^{1}H-NMR(($CD_3)_2$-SO, 400 MHz): δ (ppm): 7.10 (m, 2H), 7.66 (m, 4H), 7.80 (m, 4H), 7.95 (s, 4H), 8.06 (d, 2H), 8.21 (d, 2H, $J = 16.2$ Hz), 8.60 (d, 2H, $J = 8.4$ Hz) mass (*m*/*z*): 384 (M^+). Anal. calcd. For $C_{28}H_{20}N_2$: C 87.47, H 5.24, N 7.29%; found: C 87.54, H 5.31, N 7.42%.

*2.1.5. 2,2′-(1,4-phenylenedivinylene)-bis-quinoline; dye **7e***

Yield, 40%, m.p. 245–248 °C. ^{1}H-NMR(($CD_3)_2$-SO, 400 MHz): δ (ppm): 7.57 (m, 2H), 7.58 (d, 2H, $J = 16.3$ Hz), 7.77 (m, 2H), 7.83 (s, 4H), 7.89 (d, 2H, $J = 16.4$ Hz), 7.91 (d, 2H, $J = 8.5$ Hz), 7.96 (d, 2H, $J = 7.7$ Hz), 8.01 (d, 2H, $J = 8.4$Hz), 8.38 (d, 2H, $J = 8.6$ Hz) mass (*m*/*z*): 384 (M^+). Anal. calcd. For $C_{28}H_{20}N_2$: C 87.47, H 5.24, N 7.29%; found: C 87.72, H 5.24, N 7.29%.

2.2. Fabrication of EL devices

Styryl dyes **7a–e** and TPD (*N*,*N*′-diphenyl-*N*,*N*′-di(m-tolyl)benzidine) were used as an emitting layer and a hole transporting layer in EL devices. The structure of organic EL devices was ITO/PEDOT/TPD/styryl dye/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 sub-



Scheme 1.

strates. In device with styryl dye, all organic TPD and styryl dye layers and Al cathode were deposited by vacuum thermal evaporation on PEDOT layer under a vacuum of about 2×10^{-6} Torr. The thickness of styryl dye film and Al cathode were about 50 and 100 nm, respectively, which measured by a quartz crystal thickness monitor placed near the substrate. The active area of devices is 3.0×3.0 mm^2. The electrical and luminescent characteristics of EL devices were analyzed by using a sourcemeter 2400 (Keithley) and an optical power meter 1830S (Newport). Photoluminescence (PL) spectra were measured using a Spectra Pro-300I (Princeton Instruments).

3. Results and discussion

It is well known that the active methylene groups react with carbonyl groups, especially an aldehyde, to afford styryl dyes. Bisstyryl dyes **7a–e** were obtained by condensation between 2,3,3-trimethylindolenine 2, 2-methylbenzoxazole 3, 2-methylbenzothiazole 4, lepidine 5, quinaldine 6 and terephthaldehyde 1 using a catalytic amount of benzyltriethylammonium chloride(BTEA) as a phase-transfer catalyst. The general procedures to prepare the dyes are shown in Scheme 1.

The dyes were synthesized in 40–70% yield. The results are summarized in the experimental section. Comparison of the absorption spectra in solution together with the fluorescence spectra in solution and vapor deposited thin film were shown in Table 1.

Dye **7a–e** absorb at 380–392 nm in DMF and emit at 430–500 nm in chloroform. A very broad fluorescence spectrum from 450 to 537 nm was observed for the thin film which indicated significant aggregation and formation of molecular stacking state. On the same way, the thin layer of dye medium absorbs at longer wavelength by 30–50 nm than that in solution of the same dye, and it shows broader absorption spectra in the solid state.

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. 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,

Table 1
UV–vis and fluorescence spectral data of dyes

Dye No.	λ_{max} (nm) DMF	F_{max} (nm)	
		CHCl$_3$	film
7a	392	475, 500	516
7b	382	431, 458	537
7c	390	431, 458	537
7d	390	430, 458	446, 474
7e	380	439	496, 530

Table 2
EL properties of styryl dyes **7a–e**

Dye No.	Turn on voltage	Optical power (nW/cm^2)	EL$_{max}$ (nm)	Color
7a	6V	3745.50	615	Red
7b	5V	5.53	543	Yellow
7c	3V	27.03	540	Yellow
7d	4V	3.38	–	–
7e	8V	277.78	–	–

PEDOT was inserted between the hole injection electrode and TPD as the hole transport layer. Another advantage of the inserting of PEDOT are smoothened the anode surface and facilitated hole injection and reduced the probability for electrical shorts. During the course of our investigation on the synthesis and light emitting property of bis-styryl dyes containing heterocycles, we have found that the dye **7a** is good candidate for emitting materials in organic EL devices. However, the

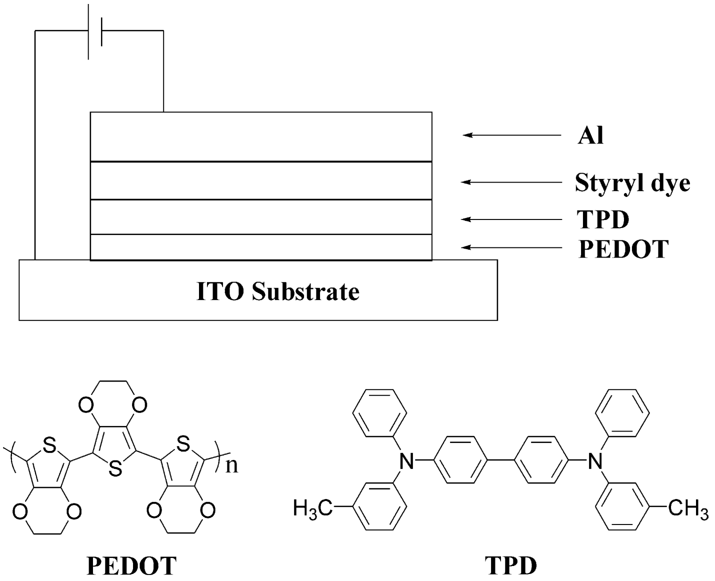


Fig. 1. Device configuration of LED and molecular structures of PEDOT and TPD.

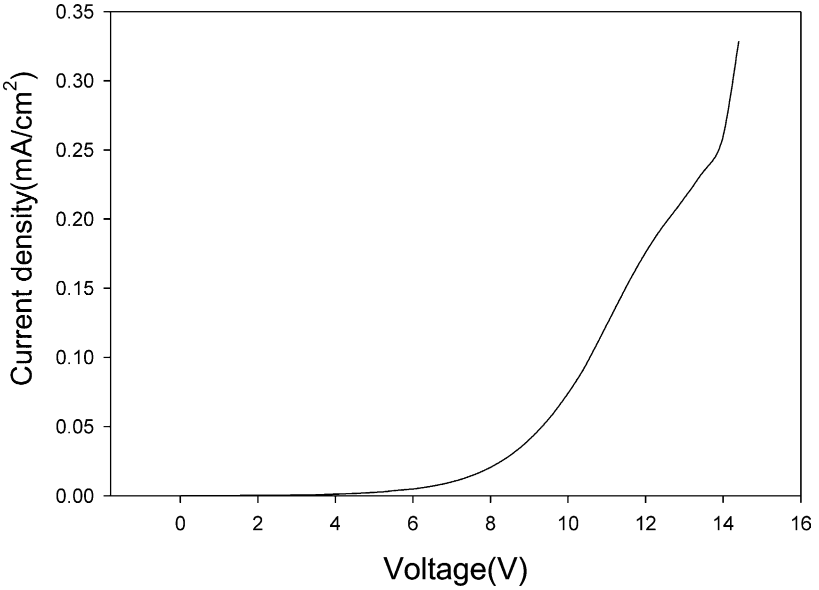


Fig. 2. Applied voltage-current density characteristics of the EL devices with dye **7a**.

maximum luminance of the devices with dye **7b–e** are still low (Table 2).

Fig. 2 shows the characteristics of applied voltage-current density of the EL device with dye **7a**. Turn-on voltage of the OELD with dye **7a** is about 6 V.

The luminance-voltage curve for the EL device is displayed in Fig. 3. Luminance increases with increasing injection current as well as bias voltage. The maximum luminance of the device is 3745 nW/cm^2 at 11 V.

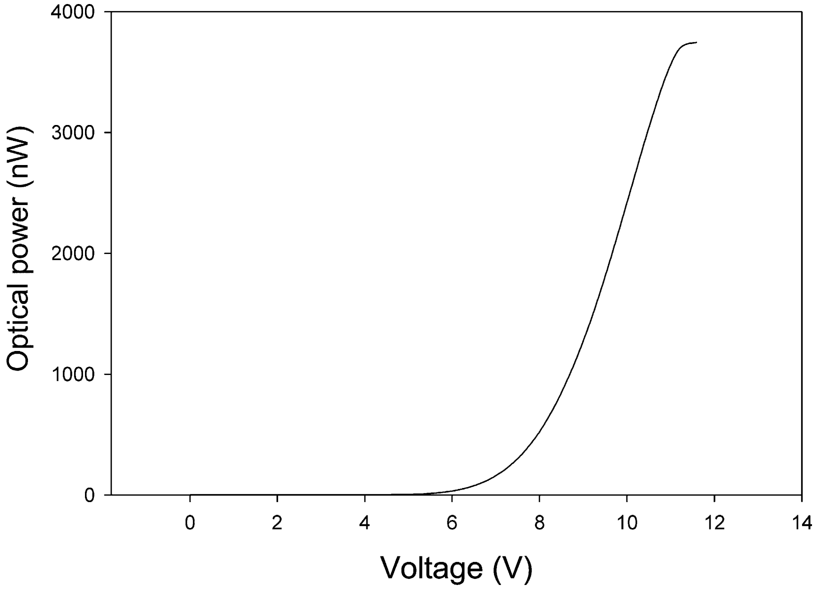


Fig. 3. Luminance-current density characteristics of the EL devices with dye **7a**.

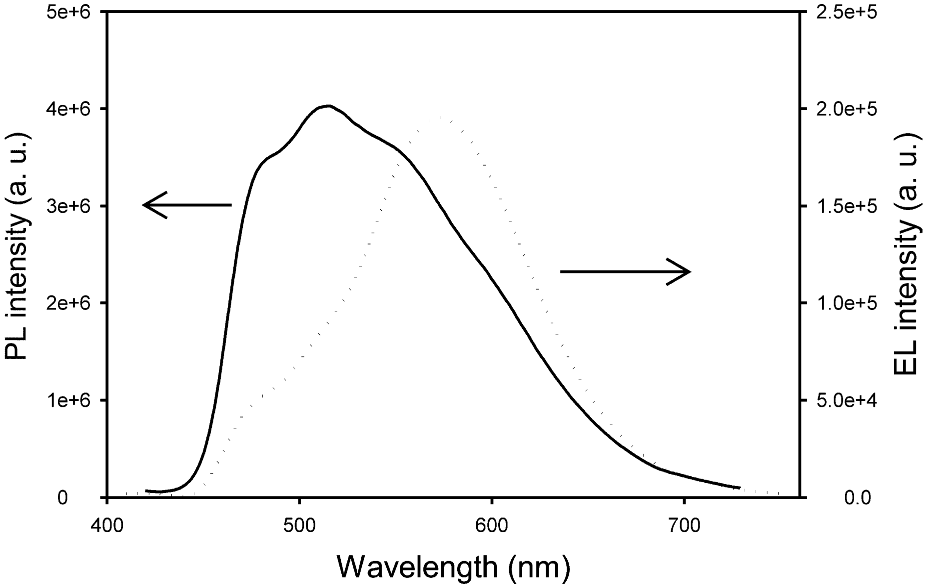


Fig. 4. PL and EL spectra of dye **7a** thin films.

Fig. 4 shows the PL and the normalized EL spectra of the OELDs with a dye **7a**. Strong orange emission with an emission peak at around 615 nm was observed as shown in Fig. 4.

The CIE coordinates of dye **7a** is $x = 0.5636$, $y = 0.4277$, which correspond to the red emission. Further optimization of EL device via multi-layer structure and doping and blending system for better EL performance are in progress.

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