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Substituent effects of 2,3-dicyano-5-[4-(diethylamino)styryl]-7-methyl-6*H*-1,4-diazepines on their use as red dopants in single-layer organic electroluminescence devices

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Abstract

6-Substituted 2,3-dicyano-5-[4-(diethylamino)styryl]-7-methyl-6*H*-1,4-diazepines were applied as red dopants in single-layer organic electroluminescence (EL) devices. EL maxima were observed at around 610 nm and the EL intensity of the 6-alkyl derivatives was higher than that of the unsubstituted variant under fixed bias voltage due to increased current density and improved η_{ext} in the devices.

Keywords: Electro luminescence (EL); Red dopant; 2,3-Dicyano-6*H*-1,4-diazepines; Organic electroluminescence device (OLED)

1. Introduction

EL devices have attracted much attention for their use in flat panel displays for which it is important to develop red, green, and blue emitting materials in order to realize full-color display; in particular, it is important to obtain low-mass red emitters. Europium [1], iridium [2], osmium [3], and platinum complexes [4,5], azomethines [6], pyrans [7,8], xanthenes [9], oxiazines [9], cyanines [9], styryls [9], porphyrins [10], and 1,2,5-oxadiazole[3,4-*c*]pyridines [11] are well known as red dopants. 2,3-Dicyano-5-[4-(diethylamino)styryl]-7-methyl-6*H*-1,4-diazepines have been reported to show red fluorescence [12]. In order to secure dopants, it is of significance to investigate substituent effects. In this context, to our knowledge, no information concerning the substituent effects of dopants on EL performance has been reported thus far. This paper concerns the substitution effects of 2,3-dicyano-5-[4-(diethylamino)-styryl]-7-methyl-6*H*-1,4-diazepines on their performance in single-layer EL devices.

2. Experimental

2.1. Materials

6-Substituted 2,3-dicyano-5-[4-(diethylamino)styryl]-7-methyl-6*H*-1,4-diazepines **1** were prepared as described previously [12].

2.2. Fabrication of EL device

ITO glass was sonicated in water, acetone, and isopropyl alcohol and the treated glass was kept under an ozone atmosphere with UV irradiation. The ITO

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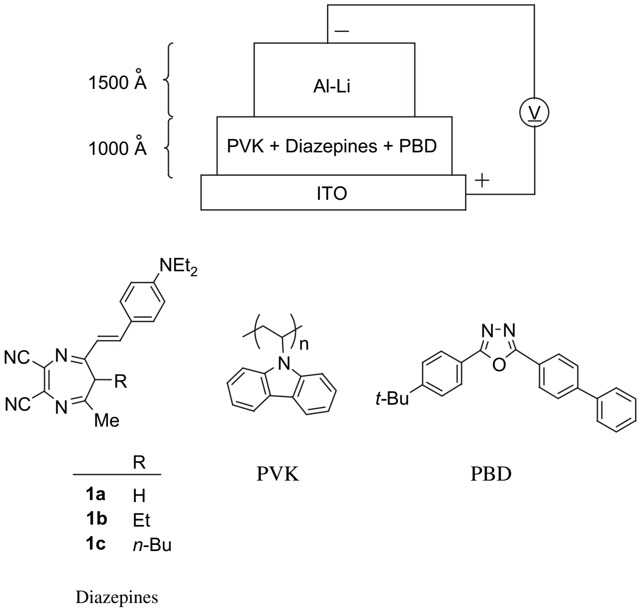

Fig. 1. Structure of EL device and materials.

glass was used as anode. To a toluene solution (3 ml) of poly(vinylcarbazole) (PVK) (40 mg) and 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxaziazole (PBD) (40 mg) was added 2,3-dicyano-5-[4-(diethylamino)styryl]-7-methyl-6*H*-1,4-diazepine **1** (1.1 μmol). The mixture was spin-coated (1000 rpm, 10 s then 2000 rpm, 10 s) on the ITO glass giving a film thickness of 1000 Å. A cathode electrode of aluminum–lithium (99:1) alloy was prepared by vapour deposition (0.5 nm s^{-1}). The corresponding EL device as well as the chemical structures of PVK, PBD, and **1** are shown in Fig. 1.

3. Results and discussion

The EL spectra of **1a** are shown in Fig. 2. The EL intensity around 610 nm was normalized. The weak emission peak based on PVK and/or PBD was also observed at around 450 nm [13]; this peak decreased as the concentration of **1a** increased. When the concentration was 0.45 mass%, this peak disappeared.

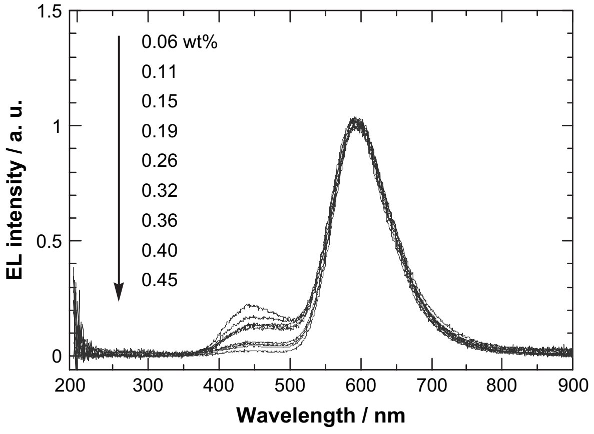

Fig. 2. EL spectra of **1a**.

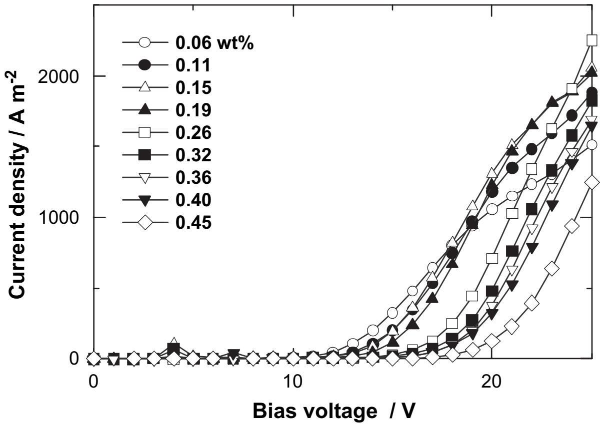

Fig. 3. Relationship among concentration of **1a**, bias voltage, and current density.

Fig. 3 shows the relationship between bias voltage and current density at various concentrations of **1a**. As the concentration of **1a** increased, a large increase in driving voltage was observed which suggests that 2,3-dicyano-5-[4-(diethylamino)styryl]-7-methyl-6*H*-1,4-diazepines trap charge carriers.

Fig. 4 indicates the relationship between the EL efficiency and the concentration of **1a**; maximum efficiency was observed at 0.11 mass%, and then decreased with further increase in concentration. On the basis of this result, the optimized concentration for **1a** was selected as 0.45 mass%, because the fluorescence from PVK and/or PBD was completely disappeared at 0.45 mass% of **1a** as shown in Fig. 2. Therefore, the same molar amount (1.1 μmol) of **1b** and **1c** was used to compare EL performance.

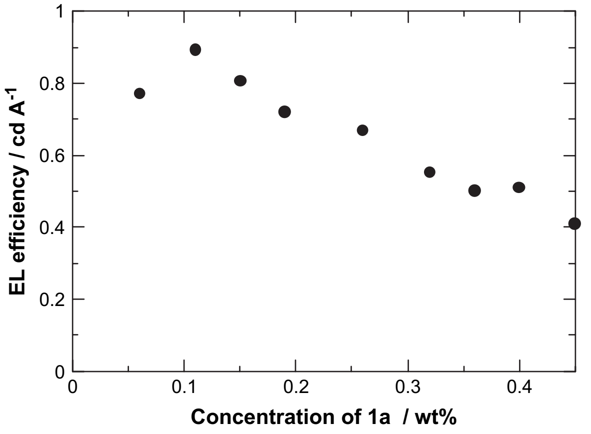

Fig. 4. Relationship between EL efficiency in range of bias voltage 0–25 V and concentration of **1a**.

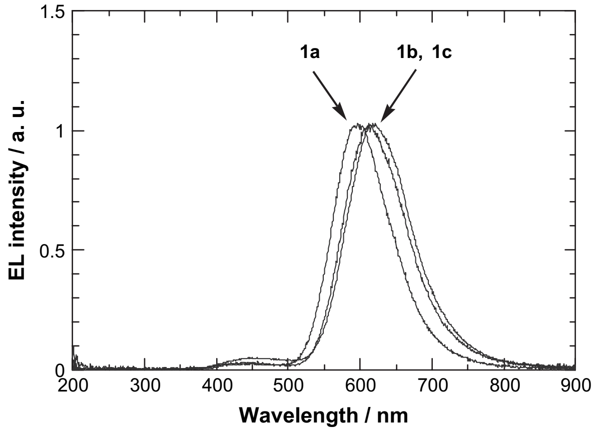

Fig. 5. EL spectra of **1a**, **1b**, and **1c**.

Fig. 5 shows the normalized EL spectra of **1a**, **1b**, and **1c**; EL maxima of **1a** and **1b**, **1c** were observed at 604 and 617 nm, respectively.

The relationship between the bias voltage and EL intensity of **1a**, **1b**, and **1c** is indicated in Fig. 6. The 6-alkyl derivatives **1b** and **1c** displayed higher EL intensity than the unsubstituted compound **1a** at fixed bias voltage.

To understand why the 6-alkyl derivatives **1b** and **1c** possessed larger EL intensity than the unsubstituted variant **1a**, the relationship between the bias voltage and current density was examined (Fig. 7). The current density of **1b** and **1c** was ca. two times higher than that of **1a** at a fixed bias voltage.

The current density (J) in devices is expressed by Eq. (1),

$$J=(9/8)\times\varepsilon\times\varepsilon_0\times\mu_{\mathrm{eff}}\times\left(V^2/L^3\right) \qquad (1)$$

where ε, ε_0, μ_{eff}, V, and L represent the dielectric constant of the film, dielectric constant in vacuum, carrier mobility, bias voltage, and film thickness, respectively. Thus, current density is mainly affected by the dielectric constant of the film and carrier mobility at fixed bias voltage. When the trap sites of charge carrier exist in the film, the carrier mobility decreases, with the result that the current density falls in the devices. Since compound **1a** acts as a trap, the current density of the device using **1a** is lower than that of a non-doped device under fixed bias voltage. Since the same molar amounts of **1a**, **1b**, and **1c** are doped in the film, the number of trap sites is the same. When less charge carrier, compared with **1a**, is trapped by **1b** and **1c**, the current density in the device using **1b** and **1c** is larger than that of **1a**. The HOMO and LUMO energy levels are scarcely affected, because the alkyl group at the 6-position in **1b** and **1c** is not conjugated with the chromophore. Meanwhile, the introduction of alkyl group can change the size of molecule. It is known that the carrier mobility of bulky *tert*-butyl-substituted rubrene decreases due to the corresponding greater distance between the molecules [14]. Thus, in comparison with **1a**, the bulky 6-substituted derivatives **1b** and **1c** may inhibit the carrier trapping from host PVK and/or PBD, resulting in improvement of current density in the EL devices.

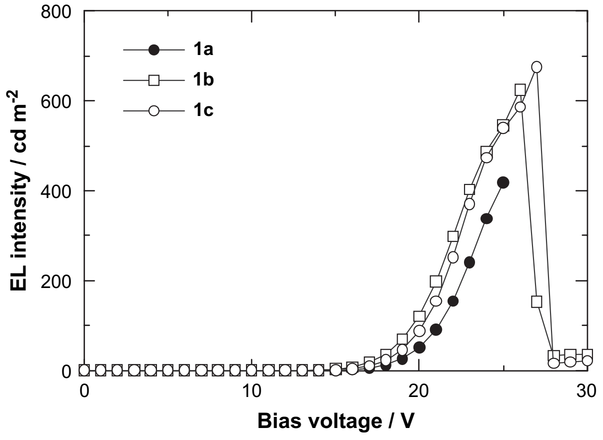

Fig. 6. Relationship between bias voltage and EL intensity of **1a**, **1b**, and **1c**.

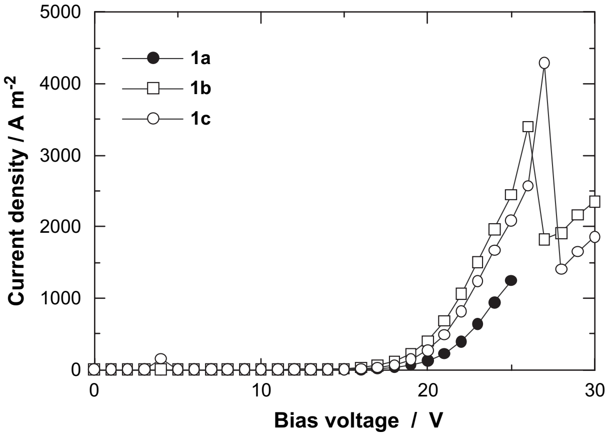

Fig. 7. Relationship between bias voltage and current density of **1a**, **1b**, and **1c**.

The EL efficiency of **1a**, **1b**, and **1c** is shown in Fig. 8; the unsubstituted derivative **1a** showed higher EL efficiency than the alkyl derivatives **1b** and **1c**. As compound **1a** can trap larger amount of carriers than either **1b** or **1c**, the EL efficiency of **1a** may be higher than that of **1b** and **1c**.

As EL intensity is proportional to the product of current density and EL efficiency, it can be proposed that the higher EL intensity of **1b** and **1c** can be attributed to increased current density under fixed bias voltage.

The relationship between the EL intensity and current density is indicated in Fig. 9; the difference in EL intensity between **1a** and **1b**, **1c** was not large as anticipated. For example, the difference of EL intensity between **1a** and **1c** at 1000 A m^{-2} was only 50 cd m^{-2}

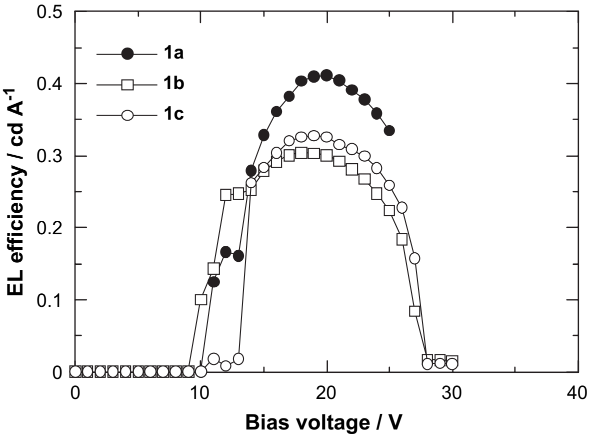

Fig. 8. EL efficiency of **1a**, **1b**, and **1c**.

whereas the current density of **1c** is ca. two times larger than that of **1a** as shown in Fig. 7. Hence, when the current density of **1a** is 1000 A m^{-2}, the EL intensity of **1a** is estimated to be 350 cd m^{-2}. Meanwhile, when the current density of **1c** is 2000 A m^{-2}, the EL intensity is estimated to be 500 cd m^{-2}. Thus, the supposed difference in the EL intensity between **1a** and **1c** is 150 cd m^{-2}, being much larger than the observed one, 50 cd m^{-2}.

To explain this result, the substituent effect on external quantum efficiency (η_{ext}) was examined. The EL intensity depends on η_{ext}, which is expressed by Eq. (2),

$$\eta_{ext} = \gamma \times \eta_r \times \varphi_F \times \eta_p \qquad (2)$$

where γ, η_r, φ_F, and η_p represent charge balance factor, fraction of total excitons, internal fluorescence quantum yield, and light-extraction efficiency, respectively. The η_r value for fluorescent materials is usually estimated to be 25%. η_p depends on the refraction index of the organic layer and is same throughout this work. Thus, η_{ext} is proportional to the product of γ and φ_F.

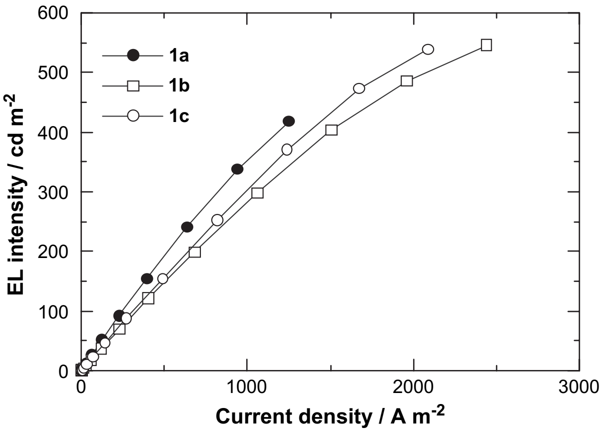

Fig. 9. Relationship between current density and EL intensity of **1a**, **1b**, and **1c**.

The φ_F value is represented by the fluorescence intensity in the PL spectrum. The PL spectra of **1a**, **1b**, and **1c** in the PVK-PBD 1:1 mixed film are shown in Fig. 10. The PL spectra were similar to those of the EL spectra as shown in Fig. 5. The film was doped with the same molar amount (1.1 μmol) of **1a**, **1b**, and **1c**, as employed for the EL devices. The fluorescence intensities of **1b** and **1c** were slightly larger than that of **1a** which indicates that the higher fluorescence intensity of the 6-substituted 2,3-dicyano-5-[4-(diethylamino)styryl]-7-methyl-6*H*-1,4-diazepines in the film could increase the φ_F value in the EL devices. Since the EL intensity of **1a** was slightly higher than that of **1b** and **1c**, as shown in Fig. 9, it is clear that the 6-alkyl group disorders the charge balance (γ) in the devices. Whilst it is not clear how the 6-alkyl group disorders the charge balance, it should be pointed out that the alkyl group at the 6-position could increase φ_F, which could improve η_{ext}.

4. Conclusions

6-Substituted 2,3-dicyano-5-[4-(diethylamino)styryl]-7-methyl-6*H*-1,4-diazepines acted as red dopants in single-layer EL devices; EL maxima were observed around 610 nm. The 6-alkyl group reduced carrier trapping to improve the current density under fixed bias voltage. In contrast, the inhibition of carrier trapping in the 6-alkyl derivatives lowered EL efficiency. However, as the φ_F of the 6-alkyl derivatives was slightly larger than that of its unsubstituted counterpart, the improvement of η_{ext}, the difference in EL intensity between **1a** and **1b**, **1c** was not large as supposed.

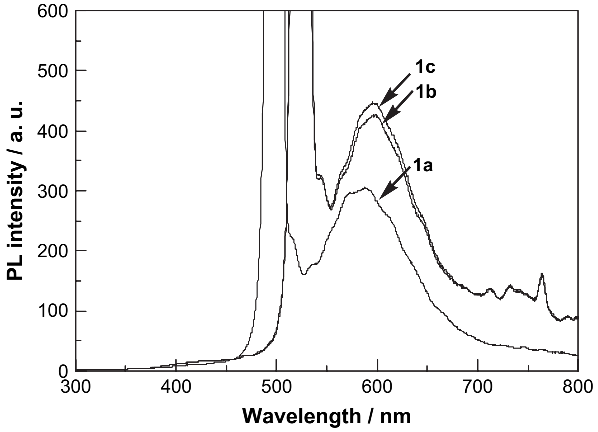

Fig. 10. PL spectra of **1a**, **1b**, and **1c** in PVK-PBD film. To a toluene solution (3 ml) of PVK (40 mg) and PBD (40 mg) was added 2,3-dicyano-5-[4-(diethylamino)styryl]-7-methyl-6*H*-1,4-diazepines **1** (1.1 μmol). The solution was spin-coated (1000 rpm, 10 s then 2000 rpm, 10 s) on ITO glass and dried. Compounds **1a**, **1b**, and **1c** were excited at 491, 523, and 523 nm, respectively.

Therefore, the EL intensity of the 6-alkyl derivatives was higher than the unsubstituted compound under fixed bias voltage due to increased current density and improved η_{ext} in the devices.

References

[1] Fang J, You H, Gao J, Ma D. Improved efficiency by a fluorescent dye in red organic light-emitting devices based on a europium complex. Chem Phys Lett 2004;392(1–3):11–6.

[2] Zhn WG, Ke Y, Wang F, Liu CZ, Yuan M, Cao Y. Red electrophosphorescence of novel Ir-complexes in PLEDs. Synth Met 2003;137(1–3):1079–80.

[3] Carlson B, Phelan GD, Kaminsky W, Dalton L, Jiang X, Liu S, et al. Divalent osmium complexes: synthesis, characterization, strong red phosphorescence, and electrophosphorescence. J Am Chem Soc 2002;124(47):14162–72.

[4] Lu W, Mi BX, Chan MCW, Hui Z, Zhu N, Lee ST, et al. $(\hat{C}\hat{N}N)Pt(C\equiv C)_nR(H\hat{C}\hat{N}N{=}$6-aryl-2, 2′-bipyridine, $n = 1-4$. $R =$ aryl, $SiMe_3$) as a new class of light-emitting materials and their applications in electrophosphorescent devices. Chem Commun 2002;(13):206–7.

[5] O'Brien DF, Giebeler C, Fletcher RB, Cadby AJ, Palilis LC, Lidzey DG, et al. Electrophosphorescence from a doped polymer light emitting diode. Synth Met 2001;116(1–3):379–83.

[6] Wang P, Hong Z, Xie Z, Tong S, Wong O, Lee CS, et al. A bis-salicylaldiminato schiff base and its zinc complex as new highly fluorescent red dopants for high performance organic electroluminescence devices. Chem Commun 2003;(14):1664–5.

[7] Chen CH, Tang CW, Shi J, Klubek KP. Recent developments in the synthesis of red dopants for Alq3 hosted electroluminescence. Thin Solid Films 2000;363(1–2):327.

[8] Ohmori Y, Kajii H, Sawatani T, Ueta H, Yoshino K. Enhancement of elecroluminescence utilizing confined energy transfer for red light emission. Thin Solid Films 2001;393(1–2):407–11.

[9] Suzuki H. Orientational enhancement in the electroluminescence of ionic emissive dyes doped in poly(vinylcarbazole). Thin Solid Films 2001;393(1–2):352–7.

[10] Sakakibara Y, Okutsu S, Enokida T, Tani T. Red organic electroluminescence devices with a reduced porphyrin compound, tetraphenylchlorin. Appl Phys Lett 1999;74(18):2587–9.

[11] Gorohmaru H, Thiemann T, Sawada T, Takahashi K, Nishii K, Ochi N, et al. Preparation of 4,7-dihetaryl-1,2,5-oxadiazolo[3,4-c]-pyridines as red fluorescent materials. Heterocycles 2002;56(1–2):421–31.

[12] Horiguchi E, Matsumoto S, Funabiki K, Matsui M. Fluorescence spectra of 6-substituted 2,3-dicyano-5-[4-(diethylamino)styryl]-7-methyl-6*H*-1, 4-diazepines in solid state. Chem Lett 2004;33(2):170–1.

[13] Blumstengel S, Sokolik I, Dorsinville R, Voloschenko D, He M, Lavrentovich O, et al. Photo-, and electroluminescence studies of 2,5-bis[2′-(4″-(6-hexoxybenzyl))-1′-ethenyl]-3,4-dibutylthiophenes. Synth Met 1999;99(1):85–90.

[14] Fong HH, So SK, Sham WY, Lo CF, Wu YS, Chen CH. Effects of tertiary butyl substitution on the charge transporting properties of rubrene-based films. Chem Phys 2004;298(1–3):119–23.