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A Red Doped OLEDS with a Good Device Performance at High Doping Concentration

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*A new red fluorescent material, (2*E*,2′*E*)-3,3′-[4,4″-bis(dimethylamino)-1,1′:4′,1″-terphenyl-2′,5′-diyl]bis[2-(2-thienyl)acrylonitrile] (ABCV-Th), for organic light emitting diodes (OLEDs) was synthesized and characterized. Photoluminescence spectrum of ABCV-Th in chloroform solution was peaked at 618 nm. The red doped OLEDs with the structure of ITO/NPB/MADN:ABCV-Th (x%)/BCP/Alq_3/Liq/Al were fabricated to investigate the influence of doping concentration on the device performance. The ABCV-Th doped device with doping concentration of 15% showed the Commission Internationale d'Eclairage (CIE_{xy}) coordinate of (0.58, 0.42) at the maximum luminance of 7320 cd/m^2 and this is comparable to that of the traditional 4-(dicyanomethylene)-2-methyl-6-(julolidin-4-yl-vinyl)-4*H*-pyran (DCM2) doped OLED (CIE_{xy} = 0.58, 0.41, 1032 cd/m^2 at 18 V).*

Keywords: ABCV-Th; a new red fluorescent material; a red-emissive; organic light-emitting diodes; red doped OLEDs

INTRODUCTION

Organic light-emitting diodes (OLEDs) have attracted increasing attention in recent years and are considered to hold the promise of

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the next generation flat-panel displays due to their low-voltage operation, wide-viewing angle, high contrast and mechanical flexibility [1–5]. It has been reported some green and blue emissive materials used in OLEDs revealed high device performance. However, the red light-emitting materials have remained to be the weakest part in realizing the full color display with low efficiency and poor color purity [6,7]. Concentration quenching due to the interaction among molecules at high concentration is common and serious problem for small molecule-based OLEDs. In case of red fluorescent materials, they are highly susceptible to concentration quenching [6,8]. A few papers about nondoped red OLEDs with amorphous red emissive material were only reported [9]. Although there is a serious concentration quenching problem for OLED application, it is well known that DCM2 is a crucial material for red OLEDs.

In this study, a new red fluorescent material, ABCV-Th, preventing concentration quenching for OLED application has been designed, synthesized and studied. To examine the effect of molecular structure of red emissive material on photoluminescence and electroluminescence, dependence of surface morphology on molecular structure was investigated by comparison of atomic force microscopy (AFM) image of ABCV-Th thin film with that of DCM2 thin film. The device performance was measured with varying the concentration of ABCV-Th dopant in order to verify the effect of doping concentration.

EXPERIMENTAL

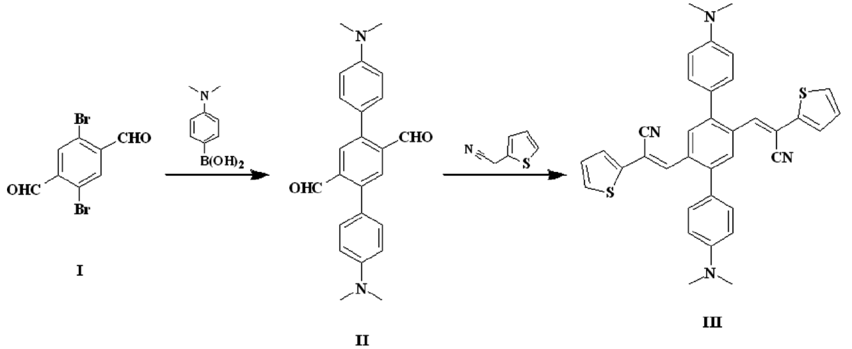
Synthesis

A new red-emissive material, ABCV-Th was synthesized as shown in Scheme 1.

2,5-Dibromoterephthalaldehyde (I) was prepared from the oxidation of 1,4-dibromo-2,5-dimethylbenzene.

4,4″-Bis(dimethylamino)-1,1′:4′,1″-terphenyl-2′,5′-dicarbaldehyde (II) was obtained from the reaction of 2,5-Dibromoterephthalaldehyde (I) with 4-(dimethylamino)phenylboronic acid by cross Suzuki coupling. Yield: 94%; ^{1}H-NMR (500 MHz, $CDC1_3$) δ(ppm) 10.105 (s, 2H), 8.060 (s, 2H), 7.315 (d, 4H), 6.830 (d, 4H), 3.048 (s, 12H); ^{13}C-NMR (125 MHz, $CDC1_3$) δ(ppm) 192.85, 192.80, 150.45, 143.64, 136.36, 131.07, 129.88, 123.00, 112.15, 40.33.

(2E,2′E)-3,3′-[4,4″-bis(dimethylamino)-1,1′:4′,1″-terphenyl-2′,5′-diyl]-bis[2-(2-thienyl)acrylonitrile] (ABCV-Th) (III) was prepared from the Knoevenagel reaction of 4,4″-bis(dimethylamino)-l,1′:4′,l″-terplienyl-2′,5′-dicarbaldehyde (II) with 2-thiophenacetonitrile. Yield: 61%;



SCHEME 1 The synthesis of a new red material, ABCV-Th.

^{1}H NMR (500 MHz, $CDC1_3$) δ(ppm) 8.172 (s, 2H), 7.476 (s, 2H), 7,402 ~ 7.381 (m, 6H), 7.286 (d, 2H), 7.088 ~ 7.070 (dd, 2H), 6.833 (d, 4H), 3.033 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ(ppm) 40.598, 76.943, 77.200, 77.452, 107.368, 112.408, 117.342, 126.606, 126.660, 127.165, 128.257, 130.165, 131.292, 132.783, 139.532, 140,110, 140.819, 150.365; MS (FAB) calcd for $C_{36}H_{30}N_4S_2$ (M^+) *mlz* 582.19, found 582.

Fabrication of OLED

OLEDs were fabricated on a glass substrate precoated with a 100 nm thick layer of the indium-tin-oxide (ITO) having a sheet resistance of 30 Ω/square. The ITO substrates were chemically cleaned by using sonication with acetone, methyl alcohol, and distilled water at 60°C for 15 min, respectively. Thereafter, pre-cleaned ITO was treated with O_2 plasma under the conditions of 2×10^{-2} Torr and 125 W for 2 min. The cleaned substrate was immediately loaded into the deposition chamber in order to avoid from the air contamination. All organic materials and metal were grown in succession without breaking vacuum ($\sim 8 \times 10^{-7}$ Torr). The devices with the structure of ITO (100 nm)/N,N′-diphenyl-N,N′-(2-napthy1)-(1,1′-phenyl)-4,4′-diamine (NPB) (50 nm)/2-methyl-9,10-di(2-naphthyl)anthracene (MADN): ABCV-Th (x%) (30 nm)/2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) (10 nm)/tris-(8-hydroxyquinoline) aluminum (Alq_3) (20 nm)/lithium quinolate (Liq) (2 nm)/Al (100 nm) were fabricated, in which NPB, MADN: ABCV-Th, BCP, Alq_3, and Liq were used as a hole transporting layer (HTL), an emitting layer (EML), a hole blocking layer (HBL), an electron transporting layer (ETL) and an electron injection layer (EIL), respectively. The deposition rates were 1.0 ~ 1.1 Å/sec for organic materials and 0.1 Å/sec for Liq, respectively. After the deposition of the organic layers, the Al cathode was deposited at a rate of 10 Å/sec without a vacuum break.

MEASUREMENTS

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian Unity INOVA 500 spectrometer operating at 499.761 MHz and 125.701 MHz, respectively. Mass spectrum (FAB-MS) was measured on an JEOL JMS-AX505WA using standard conditions. The AFM measurements were performed using NS4A in the tapping mode, on a $1 \times 1\,\mu$m scale.

The current density-luminescence-luminous efficiency, Commission Internationale De L'Eclairage (CIE$_{xy}$) coordinates and power efficiency-voltage characteristics were measured and recorded at once with chroma meter CS-100A (Minolta), in which current and voltage were controlled with measurement unit (model 236, Keithely). The HOMO and LUMO energy levels of ABCV-Th and MADN were obtained from cyclic voltametric method using a Kosentech KST-P1 at a scan rate of 50 mV s^{-1} with ABCV-Th and MADN thin films deposited on indium tin oxide (ITO) substrate as the samples, dimethylformaide (DMF) as the solvent and tetrabutylammonium tetrafluoroborate (n-Bu$_4$NBF$_4$) as the electrolyte (0.05 M). The UV-visible absorption photoluminescence (PL), and electroluminescence (EL) spectra were measured by HP model 8453 and Perkin Elmer LS-55, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the molecular structures of DCM2 and ABCV-Th. ABCV-Th has a noncoplanar molecular structure whereas DCM2 has a planar. Although both of the DCM2 and ABCV-Th molecules have intramolecular charge transfer (ICT) characters, the DCM2 molecule is very polar whereas the ABCV-Th molecule is almost nonpolar due to the existence of both antiparallel electron withdrawing moieties and those electron donating groups. As shown in Figure 2, AFM based analysis well illustrates that the surface morphology of organic thin film depends on the properties of organic molecule. In Figure 2, top view of AFM image of DCM2 thin film showed an ordered packing of particles like a crystalline packing whereas that of ABCV-Th thin film showed an amorphous like view. Accordingly, fluorescence quenching due to dipole-dipole attraction among molecules or stacking of molecules in solid state was not observed in ABCV-Th. The UV-visible

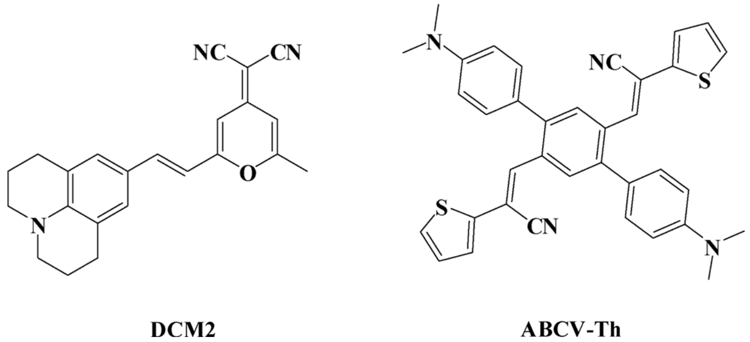


FIGURE 1 The molecular structure of DCM2 and ABCV-Th.

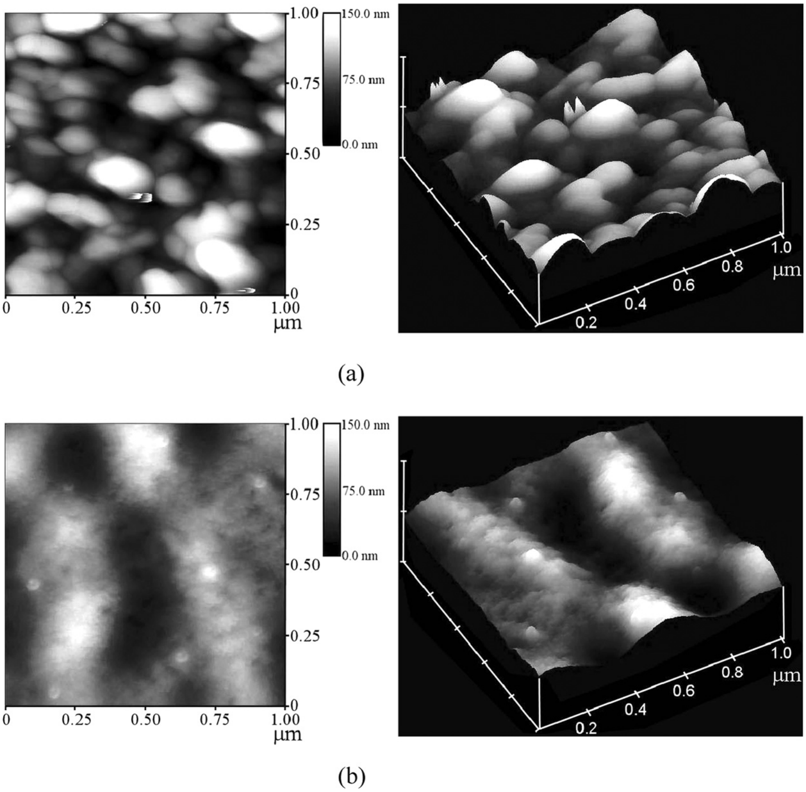


FIGURE 2 Tapping-mode AFM topographic images (1 μm × 1 μm) of DCM2 and ABCV-Th thin films in (a) ITO/NPB (40 nm)/DCM2 (80 nm) and (b) ITO/NPB (40 nm)/ABCV-Th (80 nm).

absorption and photoluminescence (PL) spectra of ABCV-Th in chloroform and thin solid film were all together shown in Figure 3. The PL emission of ABCV-Th in solution and solid, excited at 336 nm and 340 nm, respectively, were peaked at 618 nm and 635.5 nm, respectively. In both of them, there are large Stokes shifts. Owing to the large Stokes shifts, there is hardly an overlap between absorption and emission of light by the ABCV-Th molecule. This leads to little self-absorption of the emitted light so that the ABCV-Th is advantageous for OLEDs application.

Figure 4 shows the UV-visible spectrum of ABCV-Th and PL spectra of some compounds considered to be candidates for host materials in chloroform, in which the candidates for host materials were 4,4′-*N,N*′-dicarbazole-biphyenyl (CBP), 4,4′-bis(2,2′-diphenylvinyl)-1,1′-biphenyl (DPVBi), and 2-methyl-9,10-di(2-naphthyl)anthracene (MADN). To select a suitable host material, device performance was measured for the ABCV-Th doped OLEDs using these compounds as the host materials with doping concentration of 5%, in which the device with MADN host material was measured to the highest luminance of 10300 cd/m^2 at 14 V (the luminance of devices with CBP and DPVBi host materials were measured to be 3090 cd/m^2

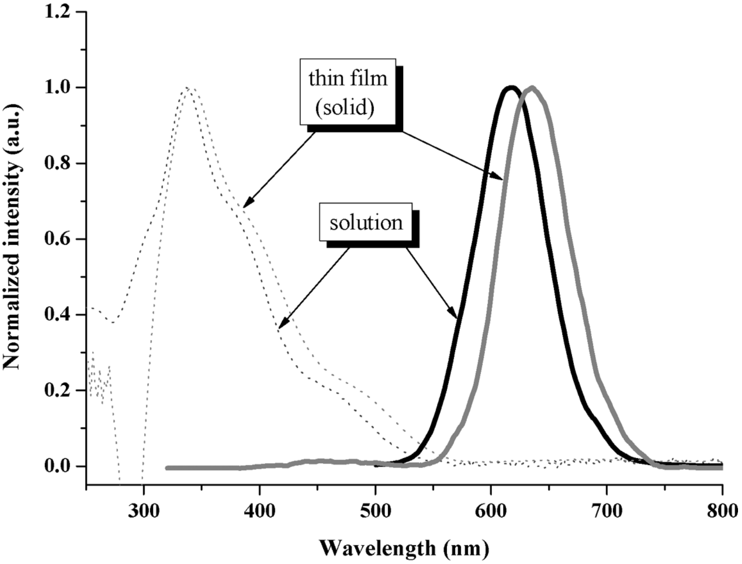


FIGURE 3 Normalized UV-visible absorption and photoluminescence spectra of ABCV-Th in chloroform and thin solid film deposited on quartz plate with a thickness of 100 nm.

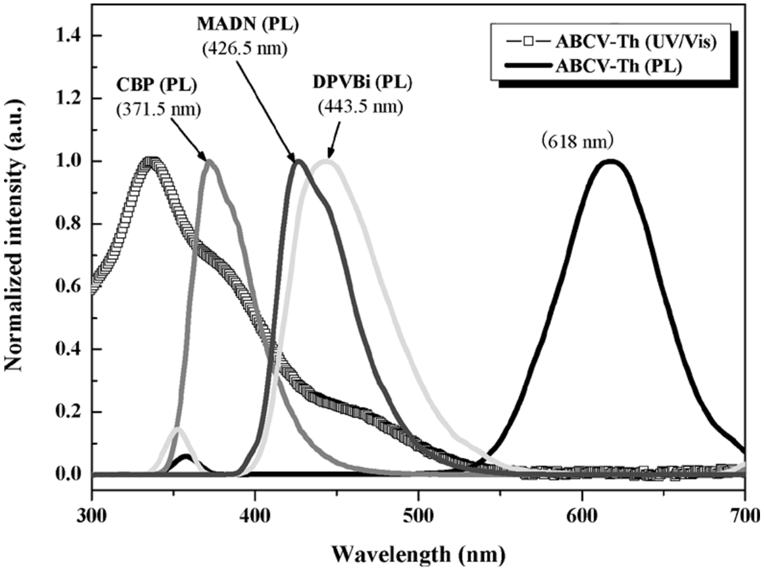


FIGURE 4 Normalized UV-visible absorption spectrum of ABCV-Th and photoluminescence spectra of ABCV-Th and host materials (CBP, MADN and DPVBi) in chloroform.

and 5600 cd/m^2 at 14 V, respectively). Accordingly, MADN was selected as a host material for the ABCV-Th doped OLEDs. Figure 5 shows the schematic energy band diagram of the device with the structure of ITO/NPB (50 nm)/MADN: ABCV-Th (30 nm)/BCP (10 nm)/Alq$_3$ (20 nm)/Liq (2 nm)/Al where the energy levels of MADN and ABCV-Th were obtained by the cyclic voltametric method. Figure 6 shows the normalized EL spectra of the ABCV-Th doped OLEDs at 12 V with doping concentration of 5%, 10%, 15%, and 20%, respectively. Although, for device with doping concentration of 5%, there is still a trace of MADN emission peaked at ~450 nm due to incomplete energy transfer from host to guest molecules, the MADN emission can be suppressed by increasing the dopant concentration to 15%. Although color purity was improved to red ($\mathrm{CIE}_{xy} = 0.59$, 0.40) by increasing the dopant concentration to 15%, there was not a further improvement of color purity by increasing that. The effect of the dopant concentration on color purity is shown in Figure 7. Figure 8 shows the characteristics of current density versus luminance and luminous efficiency (inset) of the ABCV-Th doped OLEDs with doping concentration of 5%, 10%, 15%, and 20% where the maxima luminance are 11400 cd/m^2, 8940 cd/m^2, 7320 cd/m^2, and 6820 cd/m^2 at

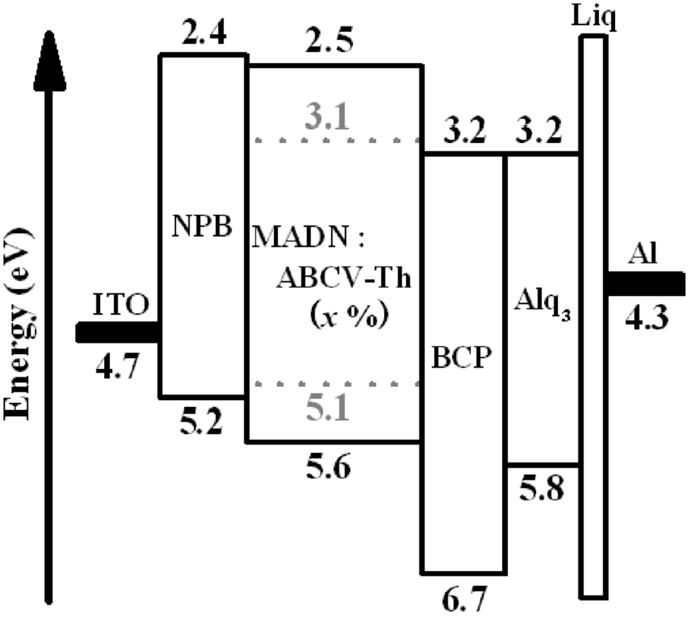


FIGURE 5 The schematic energy band diagram of the device, ITO/NPB (50 nm)/MADN: ABCV-Th (30 nm)/BCP(10 nm)/Alq_3 (20 nm)/Liq (2 nm)/Al.

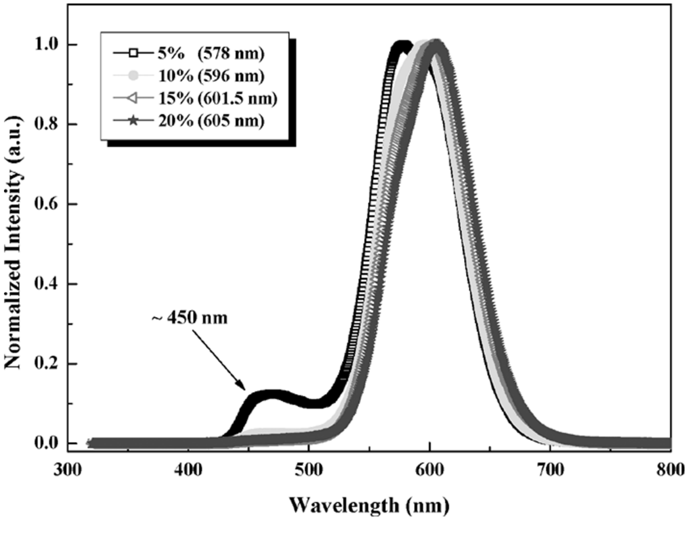


FIGURE 6 Normalized EL spectra of ABCV-Th doped OLEDs using MADN as the host material at various dopant concentration.

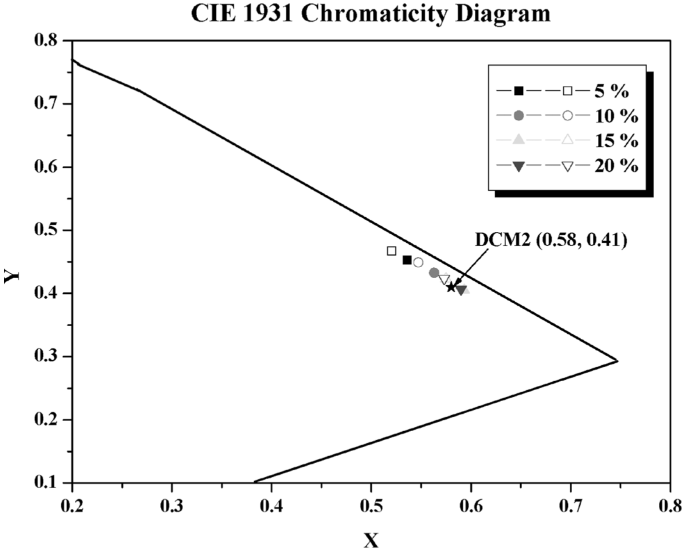


FIGURE 7 The effect of doping concentration on the CIE$_{xy}$, coordinates of the ABCV-Th doped OLEDs with MADN host material at the voltages of 6 V (solid) and 14 V (open).

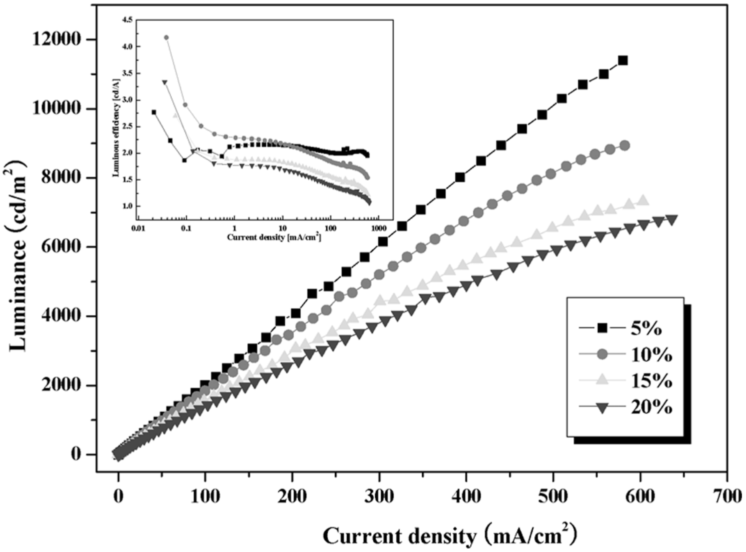


FIGURE 8 The luminance-current density characteristics of OLEDs (Inset: The luminous efficiency-current density characteristics of OLEDs).

TABLE 1 The Performance Characteristics of OLEDs

	Max. current density (mA/cm^2)	Max. luminance (cd/m^2)	Max. luminous efficiency (cd/A)	Max. power efficiency (lm/A)
5%	737@17 V	11400@580 mA/cm^2	2.77@0.021 mA/cm^2	2.29@0.021 mA/cm^2
10%	697@18 V	8940@582 mA/cm^2	4.17@0.038 mA/cm^2	3.64@0.038 mA/cm^2
15%	674@17.4 V	7320@603 mA/cm^2	2.70@0.059 mA/cm^2	2.49@0.059 mA/cm^2
20%	672@16 V	6820@636 mA/cm^2	3.34@0.035 mA/cm^2	3.28@0.035 mA/cm^2

580 mA/cm^2, 582 mA/cm^2, 674 mA/cm^2, and 672 mA/cm^2, respectively. Selected EL performance of the ABCV-Th doped OLEDs with the MADN host material was summarized in Table 1.

CONCLUSIONS

A red emissive material, ABCV-Th, was designed to prevent concentration quenching in solid state and synthesized. MADN was selected as a suitable host material for the ABCV-Th doped OLEDs. Although the device configuration was not fully optimized, it was demonstrated that the EL performance of the ABCV-Th doped OLEDs using MADN as the host material was improved by increasing the dopant concentration to 15 ~ 20%. At dopant concentration of 15%, the device exhibited good EL performance such as a maximum luminance of 7320 cd/m^2 and red emission with CIE_{xy} coordinate of (0.58, 0.42) at 12 V.

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