

Light-Emitting Diodes Based on a Carbazole-Derivatized Dopant: Origin of Dopant Excitation as a Function of the Device Structure

Chung-Wen Ko, Yu-Tai Tao,^{*,†} Jiann T. Lin,^{*} and K. R. Justin Thomas

Institute of Chemistry, Academia Sinica, Taipei, Taiwan 115, Republic of China

Received July 27, 2001. Revised Manuscript Received October 17, 2001

Efficient green-emitting OLEDs were fabricated by using the carbazole derivative 9-ethyl-*N,N*-diphenyl-*N,N*-dipyren-1-yl-9H-carbazole-3,6-diamine (C-Et) as a dopant in different layers in a multilayered structure. Depending on the energy levels of the various layers involved, dopant emission can be realized through either energy transfer or the carrier trapping mechanism. By doping into the CBP layer of the device ITO/NPB (40 nm)/CBP:5% C-Et (20 nm)/TPBI (40 nm)/Mg:Ag (50 nm)/Ag(100 nm), a maximum luminance of 48 300 cd/m², a maximum quantum efficiency of 3.90%, and a maximum power efficiency of 5.28 lm/W can be achieved.

Introduction

Since Tang et al. reported¹ that use of a laser dye dopant in tris(8-hydroxyquinolinonato)aluminum (Alq) could enhance the efficiency and stability of OLEDs, doping luminescent dyes into the charge carriers became a popular and effective way to achieve better performance and tune the color.^{2–6} The improvement may be due to a higher luminescent efficiency in the isolated state of the luminophore and the stability of the amorphous state of a mixed layer versus a pure layer. In general, the emission mechanism of the dye-doped OLEDs was suggested to be energy transfer or carrier trapping.⁷ The mechanism of energy transfer involves either a dipole-induced Coulombic interaction between the host excitons and the dye dopants (Förster energy transfer) or an electron-exchange interaction between them (Dexter energy transfer).⁸ In the case of carrier trapping, the dye acts as an electron trap and/or a hole trap. To have efficient carrier trapping, the HOMO level of the dopant needs to be higher than the HOMO level of the host and/or the LUMO level needs to be lower than the LUMO of the host. Therefore, the charge carrier will remain in the HOMO (or LUMO) level of the dopant and eventually recombine with a counter charge that enters the LUMO (or HOMO) level. The electroluminescence (EL) spectrum of a dye-doped OLED

can possibly result from either or both mechanisms and is sometimes hard to distinguish. On the other hand, the photoluminescence (PL) of the same doped film can involve only the energy transfer process, since free carriers are not generated by photoexcitation in the absence of an electric field. The difference between the EL and PL spectra can sometimes reveal the pathway by which dopants get excited.⁹

Criteria of choosing a dopant include the degree of spectral overlap with the host material, the emission wavelength of the dopant, and the photoluminescence quantum yield, among others. A dopant with a higher quantum yield is more likely to raise the luminescence efficiency of the otherwise less efficient host material. Recently we demonstrated¹⁰ a series of carbazole derivatives as efficient emitters as well as hole transporters in the fabrication of two-layered OLED devices, among which the 9-ethyl-*N,N*-diphenyl-*N,N*-dipyren-1-yl-9H-carbazole-3,6-diamine (C-Et) gave a very bright green emission, despite the rather low quantum yield found for this dye in solution. In an attempt to further raise the quantum efficiency, a device configuration with this material as dopant was attempted. In this article, we report the doping of this molecule into different charge transporting layers of the devices of ITO/NPB/TPBI/Mg:Ag and ITO/NPB/CBP/TPBI/Mg:Ag, where NPB, CBP, and TPBI stand for 4,4'-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl, 4,4'-dicarbazolyl-1,1'-biphenyl, and 2,2',2''-(1,3,5-benzenetriyl)tris[1-phenyl-1H-benzimidazole], respectively. It was demonstrated¹¹ recently that the recombination areas of the two devices are different. In the former case, the charge recombination occurs mainly in the NPB layer whereas, in the latter case, the introduction of a CBP layer promotes

[†] Electronic mail: ytt@chem.sinica.edu.tw.

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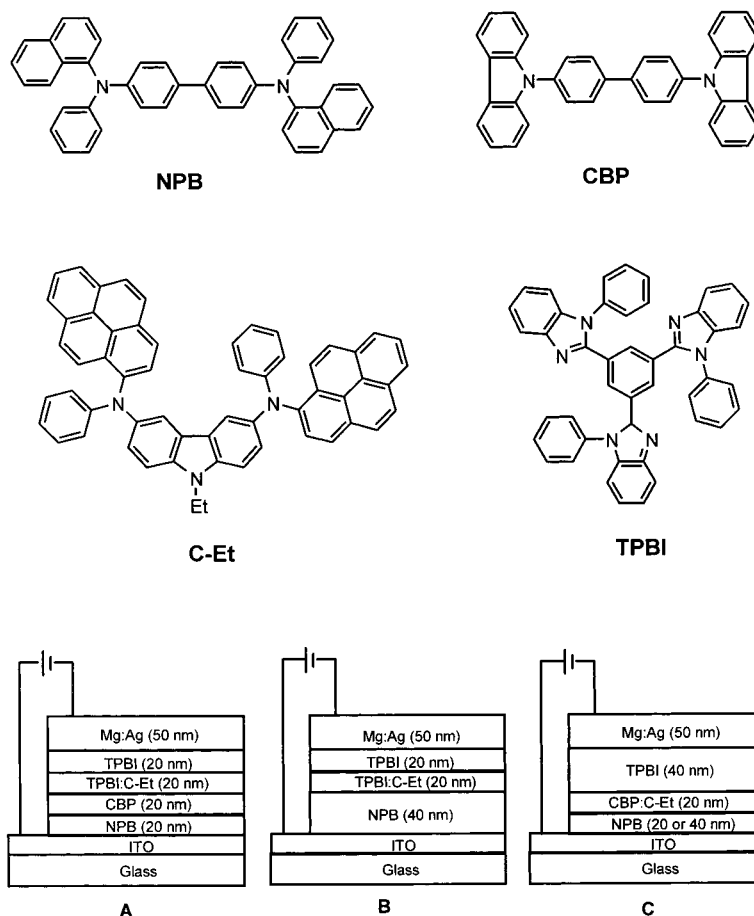


Figure 1. Structures of materials and device configurations used in the study.

the hole-crossing to the TPBI layer so that the recombination occurs mainly in the TPBI layer. It is demonstrated that, depending on the location of the dopant in the device, the efficiency and performance characteristics vary. The difference is interpreted by suitable placement of the HOMO/LUMO of the dopant relative to that of the host material. Also, depending on the device structure, the same dopant emission may result from different excitation pathways. Suggestion of the EL mechanism of these devices was made.

Experimental Section

The syntheses of TPBI, CBP, NPB, and C-Et were reported previously.^{10–13} Absorption and emission spectra were taken with a Hewlett-Packard 8453 absorption spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. The samples for the PL measurement were prepared by a parallel deposition of the doped film on a glass slide during the EL device fabrication. Cyclic voltammetric experiments were done using a BAS 100B electrochemical analyzer. A three-electrode cell system with glassy carbon, a platinum wire, and a silver wire as working, counter, and reference electrode, respectively, was used, while 0.1 M tetrabutylammonium hexafluorophosphate was a supporting electrolyte and freshly distilled, degassed dichloromethane was used as the solvent. The HOMO level was calculated from the oxidation potential according to a literature report.¹⁴ The LUMO level

was calculated using the UV absorption edge method. The detailed device fabrication was described previously.¹²

Results and Discussion

The structures of materials and the device configuration are shown in Figure 1. The C-Et dye has a UV absorption that spans from 250 to 450 nm, with absorption maxima at 408, 328, and 274 nm, respectively. A single emission peak at 548 nm in dichloromethane was found by excitation at any of the absorption maxima. The quantum yield (0.03) is nevertheless lower compared to those of dyes commonly used in OLEDs. The high device efficiency found in the EL device¹⁰ using this material as a pure hole-transporting as well as light-emitting layer is interesting. Either favorable factor such as recombination efficiency, improved injection efficiency, or high quantum yield for the pure film is responsible for the observation. The HOMO/LUMO levels measured indirectly by cyclic voltammetry are 4.91 and 2.33 eV, respectively. An analysis of the spectral data and energy levels characteristics led to the suggestion that TPBI be chosen as the host for the device fabrication. TPBI is an electron-transporting material with a wide band gap.¹¹ To take advantage of the energy transfer process, formation of an exciton in the host material is desired. Because of the hole-blocking effect of TPBI in a two-layered ITO/NPB/TPBI/Mg:Ag device,^{11,15} a second hole-transporting layer

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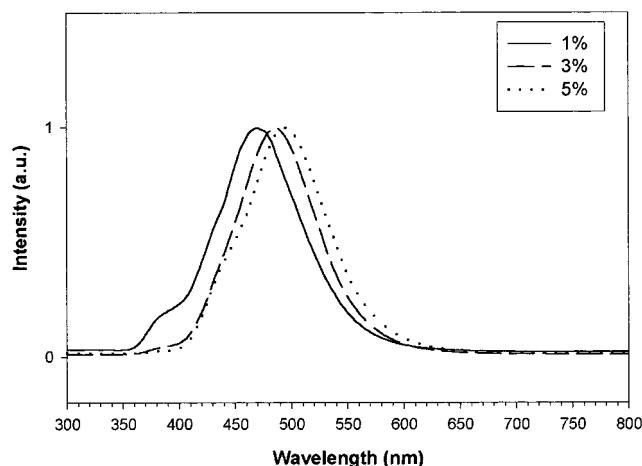


Figure 2. EL spectra of the device ITO/NPB (20 nm)/CBP (20 nm)/TPBI:x% C-Et (20 nm)/TPBI (20 nm)/Mg:Ag.

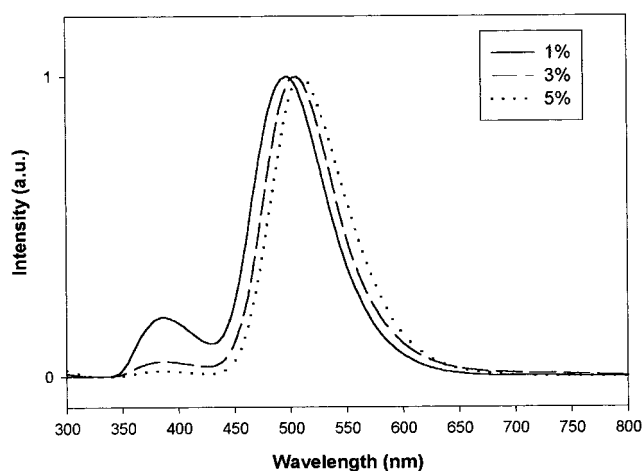


Figure 3. PL spectra of TPBI films doped with various amounts of C-Et.

CBP¹³ serves to promote hole-transport into the TPBI layer so that charge recombination can occur there. Thus, the devices of ITO/NPB (20 nm)/CBP (20 nm)/TPBI:C-Et (20 nm)/TPBI (20 nm)/Mg:Ag (50 nm)/Ag (100 nm) with various concentrations of C-Et were fabricated. The EL spectra are shown in Figure 2. At 1% (w/w) doping level, an emission maximum at 466 nm, accompanied by a shoulder at ~380 nm was observed. The unsymmetrical shape of the emission peak indicates that there is a small component from NPB (at ~450 nm), which was shown to exist in the EL spectrum of the ITO/NPB/CBP/TPBI device. The shoulder at around 380 nm, assigned to the TPBI emission, decreases with increasing doping concentration from 1 to 5%. The emission shifts toward longer wavelength with increasing dopant concentration. The PL spectra of these C-Et-doped TPBI films (Figure 3), which were prepared in the same batch as the device fabrication, show a similar trend in that a shoulder of the TPBI emission diminishes with increasing dopant concentration. The apparent difference between the EL spectra and the PL spectra is due to the complication caused by an additional contribution from the HTL material (NPB) that distorted the shape and position of the EL

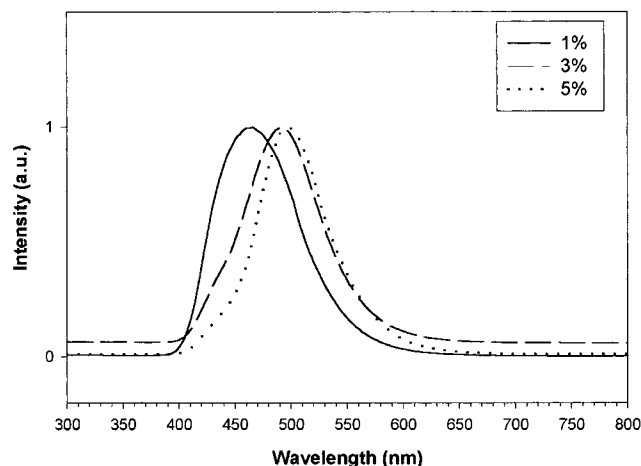


Figure 4. EL spectra of the device ITO/NPB (40 nm)/TPBI:x% C-Et (20 nm)/TPBI (20 nm)/Mg:Ag.

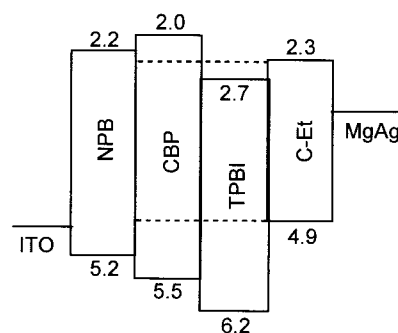


Figure 5. Energy alignment of various layers involved in the device.

spectra. The correlation between EL and PL implies the dopant emission originates mainly from energy transfer from TPBI excitons. In contrast, in the device structure of ITO/NPB (40 nm)/TPBI:C-Et (20 nm)/TPBI (20 nm)/Mg:Ag (50 nm)/Ag (100 nm), where the CBP layer was eliminated, the EL spectra of the devices showed C-Et emission together with a contribution from NPB, but no trace of TPBI emission was found (Figure 4). This excludes the energy transfer mechanism as a major pathway of dopant excitation. Because of the large barrier (~1 eV) between the HOMO level of NPB and that of TPBI, no holes cross over to the TPBI molecules. Instead, it is suggested that the holes cross directly to the HOMO level of the dopant molecules and become trapped at the dopant sites. This is all shown to be possible by examining the relative energy levels of the species involved (Figure 5). There is little barrier for the hole-injection to the dopant sites. A small barrier (0.4 eV) for electron transport to the LUMO of C-Et can be overcome at the applied electric field so that recombination at the dopant sites is possible. This is in agreement with the observation that no TPBI emission was observed. Should energy transfer be a main pathway, significant residual emission from TPBI would be seen at low dopant concentrations such as 1% and 3%. Increasing the doping concentration of C-Et in TPBI will provide more trap sites and thus increase the emission of C-Et and decrease the emission of NPB. This is reflected in the EL maximum: the λ_{em} maximum was blue shifted to 466 nm when the doping concentration was 1%, whereas the λ_{em} maximum was 496 nm when the doping concentration was increased to 5%. By

Table 1. Performances of Devices Fabricated in This Study

device structure	voltage (V) at 100 mA/cm ²	luminance (cd/m ²) at 100 mA/cm ²	max. luminance (cd/m ²) at 15.0 V	max. quantum efficiency (%)	max. power efficiency (lm/W)
NPB/CBP/TPBI:1% C-Et/TPBI	8.2	1960	14 400	1.53@6.5V	1.06@6.0V
NPB/CBP/TPBI:3% C-Et/TPBI	8.4	3020	21 400	1.83@6.5V	1.62@6.5V
NPB/CBP/TPBI:5% C-Et/TPBI	8.4	3530	28 300	1.88@6.5V	1.93@6.5V
NPB/TPBI:1% C-Et/TPBI	5.2	532	18 900	1.25@7.5V	0.97@5.0V
NPB/TPBI:3% C-Et/TPBI	6.1	2710	21 900	1.85@3.5V	3.14@3.5V
NPB/TPBI:5% C-Et/TPBI	5.3	4570	42 200	2.17@4.0V	4.03@4.0V
NPB (20 nm)/CBP:1% C-Et/TPBI	8.6	2610	22 100	1.53@9.0V	0.98@8.0V
NPB (20 nm)/CBP:3% C-Et/TPBI	8.7	4830	33 500	2.42@7.0V	2.57@6.5V
NPB (20 nm)/CBP:5% C-Et/TPBI	9.2	6980	39 000	3.15@6.5V	4.39@5.5V
NPB (40 nm)/CBP:1% C-Et/TPBI	8.6	3750	29 900	2.24@6.5V	2.13@6.0V
NPB (40 nm)/CBP:3% C-Et/TPBI	8.6	5520	44 900	2.92@6.5V	3.27@6.0V
NPB (40 nm)/CBP:5% C-Et/TPBI	9.2	9170	48 300	3.90@7.0V	5.28@6.0V

comparing with the peak position and the shape for the PL spectrum, a slight contribution from NPB is still suggested. The NPB emission is present presumably because of a smaller gap between the LUMO of TPBI and that of NPB. The presence of C-Et molecules may provide an additional step between the two levels. Further evidence of a carrier trapping mechanism is the voltage dependence of the EL spectra. With increasing applied voltage, the relative contribution of the NPB emission increased.⁹ The performances of the above two types of device configuration are listed in Table 1. It is noted that the performance improves with increasing dopant concentration in either configuration. But the device characteristics such as turn-on voltage, maximum luminance, maximum power efficiency, and maximum quantum efficiency are in general better for that without a CBP intermediate layer. For the same overall device thickness, the current density with the three-layered device is significantly smaller than that for the two-layered device (Figure 6). The introduction of an additional layer creates extra interfaces for the charge carriers to move across, even though it may reduce the barrier height. This three-layered structure, nevertheless, was found useful in harvesting light from blue dopants in TPBI.¹¹ The best device among these is the one with 5% C-Et dopant in TPBI in a two-layered device, which reaches a maximum luminance of 42 200 cd/m² at 15 V, a quantum efficiency greater than 2.17%, and a power efficiency of 4.03 lm/W for this blue-green device. These data are notably higher than those based on a simple two-layered device with the C-Et as a pure layer.¹⁰

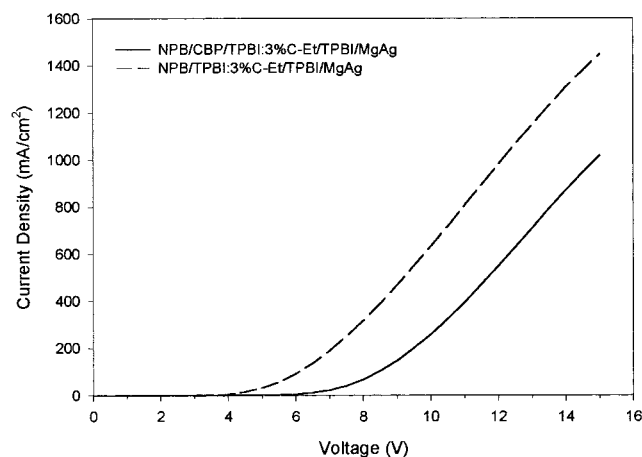


Figure 6. I - V characteristics of the ITO/NPB/CBP/TPBI:C-Et/TPBI/Mg:Ag device and the ITO/NPB/TPBI:C-Et/TPBI/Mg:Ag device.

The persistent presence of NPB emission may be due to a dopant with a LUMO level higher than that of the host. A better host material for C-Et would be one with a LUMO higher and a HOMO lower than those for C-Et. This seems to be the case for CBP, which has a LUMO level at 2.0 eV and a HOMO level at 5.5 eV. Thus, devices with C-Et doped into CBP were also fabricated. For a configuration of ITO/NPB (20 or 40 nm)/CBP:C-Et (20 nm)/TPBI (40 nm)/MgAg (50 nm), the current-voltage-luminance (I - V - L) measured at ambient conditions were shown in Figure 7. Little or no NPB emission (at ~ 450 nm) was observed in the EL spectra when the dopant concentration changed from 1% to 5% (Figure 8). A comparison of the EL of the device with the PL spectra of the same film (Figure 9)

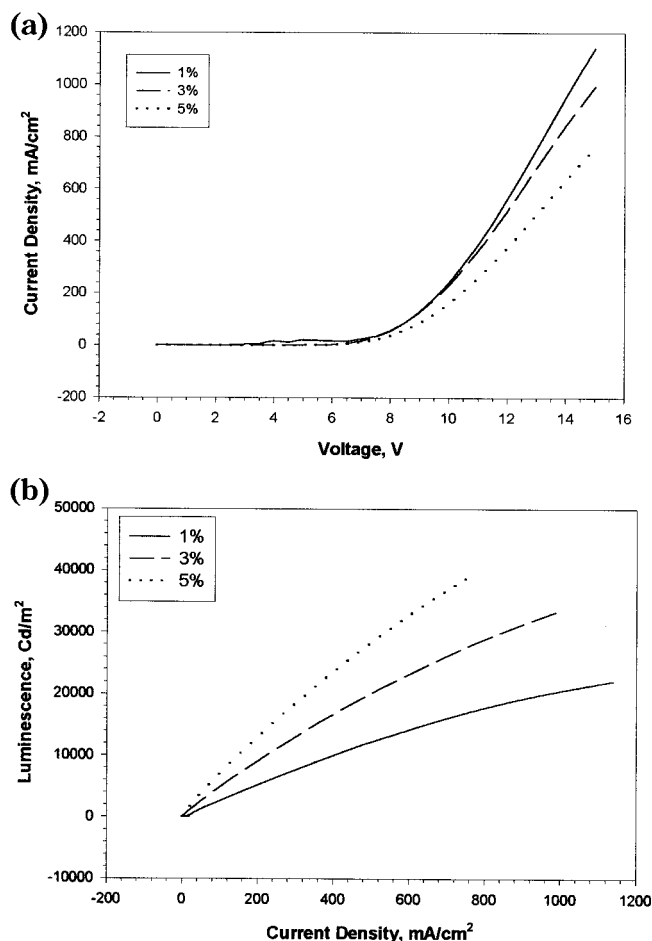


Figure 7. (a, top) I - V and (b, bottom) L - I characteristics of the device ITO/NPB (20 nm)/CBP:3% C-Et (20 nm)/TPBI (40 nm)/Mg:Ag.

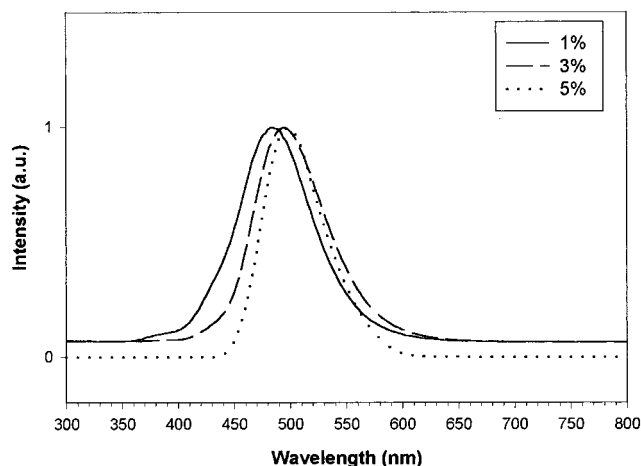


Figure 8. EL spectra of the device ITO/NPB (20 nm)/CBP: x% C-Et (20 nm)/TPBI (40 nm)/Mg:Ag.

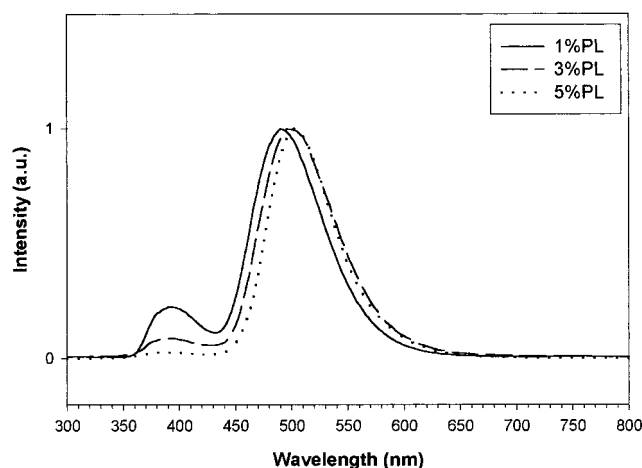


Figure 9. PL spectra of CBP films doped with various amounts of C-Et.

indicates some deviation between the two. The component of CBP emission (at ~ 390 nm) is much more reduced in the EL spectra than in the PL spectra. Thus, carrier trapping by C-Et is suggested to be the major pathway for the dopant excitation. With the energy gap of C-Et lying within the energy gap of CBP, the trapping effect is more effective and fewer electrons were injected into the NPB layer. The device performances are also listed in Table 1. The performance in general improved when the dopant concentration was increased from 1%

to 5%. Further improvement was achieved with a thicker NPB layer (40 nm). Thus, with a device configuration of ITO/NPB (40 nm)/CBP:5% C-Et (20 nm)/TPBI (40 nm)/Mg:Ag (50 nm), a brightness of 48 300 cd/m^2 at 15 V and a power efficiency of 5.28 lm/W at 4 V were obtained. The external quantum efficiency of 3.90% is higher than doping into the TPBI layer¹⁶ and more than double that of the two-layered device, where the C-Et serves as the HTL as well as the emitter.¹⁰

Conclusion

In summary, we have demonstrated very efficient green OLEDs using a carbazole derivative C-Et as the emissive dopant. Depending on the structure of the device and the host material, dopant excitation can be realized either by energy transfer or by carrier trapping. The available channel of carrier trapping implies that a spectral overlap of the host emission and dopant absorption is not a necessary condition for the choice of dopant. With a device structure of ITO/NPB/CBP/TPBI: C-Et/TPBI/Mg:Ag, the dopant excitation is realized mainly because of the energy transfer between the TPBI excitons and the dopant molecules. With a structure of ITO/NPB/TPBI:C-Et/TPBI/Mg:Ag, the carrier trapping appears to be responsible for the dopant emission. When doping into a more suitable host such as in the devices of ITO/NPB/CBP:C-Et/TPBI/Mg:Ag, a better device performance was achieved, presumably because of a more effective carrier trapping effect of the dopant. In particular, with a device structure of ITO/NPB (40 nm)/CBP:5% C-Et (20 nm)/TPBI (40 nm)/Mg:Ag (50 nm)/Ag (100 nm), a maximum luminance of 48 300 cd/m^2 , a maximum quantum efficiency of 3.90%, and a maximum power efficiency of 5.28 lm/W were achieved.

Acknowledgment. We thank Academia Sinica for financial support of this work.

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(16) The external quantum efficiency of 3.9% appears to be unusually high considering the quantum yield of the dye in dichloromethane solution (0.03), the light coupling-out efficiency (~ 0.2), and the maximum recombination efficiency (1.0). However, it should be noted that the quantum yield of the fluorescence could be much higher when the dye is doped in a solid solution, where thermal motion and collision with neighboring molecules are much reduced. See: Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970.