

PROBE FOR THE FORMATION RATIO BETWEEN EXCITED TRIPLETS AND SINGLET AS GENERATED IN POLYMER LIGHT-EMITTING DIODES*

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Abstract The electroluminescence (EL) produced by a highly luminescent phosphorescent dye $\text{Cu}_4(\text{C}\equiv\text{CPh})_4\text{L}_2$ ($\text{L} = 1.8$ -bis(di-phenylphosphino)-3,6-dioxaoctane, Cu_4) doped polymer as emitting layer is reported. The effects of the charge injection balance on the polymers, in particular, poly(*N*-vinylcarbazole) (PVK) have been studied by using photoluminescence and electroluminescence spectroscopy. Changes in the emission spectra demonstrate the influence of the charge injection balance on the formation ratio of triplet and singlet excitons. This provides a new technical approach to realize the color patterning in polymer LEDs.

Keywords Electroluminescence, Organic, Polymer, Triplet exciton

INTRODUCTION

Recently, organic phosphors have received considerable attention because their efficiency is quadruple that of fluorescent materials^[1-4]. The internal EL quantum efficiency and power efficiency of as high as 80% and 40 lm/W respectively have been achieved in sublimed film device by using tris(2-phenylpyridine)iridium doped with electron-transporting materials 3-phenyl-4-(1'-naphthyl)-5-phenyl-1,2,4-triazole (TAZ)^[5]. The harvesting of triplet excitons in the polymer host for the improvement of the performance of polymer-based EL devices has also been demonstrated^[6, 7]. Inspired by the recent reports of unexpectedly high efficiencies in some polymer EL devices^[8, 9], the statistical ratio of 3:1 for the ratio of triplets to singlets formed under EL conditions was widely discussed in the literature. We noted the more recent results reported by Vardeny *et al.*^[10] that the formation cross-sections of singlet and triplet excitons in conjugated polymers are strongly material-dependent. For the measurement of these ratios, Vardeny *et al.*^[10] used the excited state absorption we report here a novel method using a phosphor as probe. Such measurement provides a route to achieve this ratio between singlets and triplets as generated in the EL devices. We found that this ratio is not only material-dependent, but also device performance-dependent, *e.g.* dependent on the balance between carrier injection and device structures.

EXPERIMENTAL

Materials

The phosphorescent dye, tetranuclear copper (I) complex $\text{Cu}_4(\text{C}\equiv\text{CPh})_4\text{L}_2$ ($\text{L} = 1.8$ -bis(diphenylphosphino)-3,6-dioxaoctane) (Cu_4)^[11, 12] was synthesised by a reported method. The phosphorescence efficiency of Cu_4 in dichloromethane solution is 0.42 with an observed lifetime of 9.8 μs , and has been proved to be suitable for EL

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device fabrication. The semiconductive polymer poly(*N*-vinylcarbazole) (PVK, $M_n = 1.0 \times 10^5$ g/mol) was used as the host matrix.

Fabrication of Devices

The EL cell consists of an indium-tin oxide (ITO)-coated glass substrate; a thin emitting layer (typically, it has a thickness of 100 nm) of Cu₄-doped PVK (Cu₄:PVK) formed by spin-coating its chloroform solution on the ITO-coated glass substrate (sheet resistance 20 $\Omega/\square$). An electron transporting/hole blocking layer of triazole derivative TAZ (thickness 4.5 nm) was deposited on a doped PVK layer at about 2×10^{-6} Torr at a deposition rate of around 0.1 nm/s. A metal cathode (700 nm) with an Ag cap (30 nm) was vacuum deposited on top of these multilayer films at an evaporation rate of 0.3–0.5 nm/s. The active area of the PLED was 2×2 mm². PLED with a structure of ITO/Cu₄:PVK (100 nm)/TAZ (4.5 nm)/metal cathode are used for EL characteristics.

Spectroscopy Measurement

UV/Vis spectra were recorded with a Shimadzu UV-3100 spectrophotometer. Fluorescence of the solutions and films and EL spectra of the device were measured with a Shimadzu RF-5301 PC. All measurements were conducted at room temperature.

RESULTS AND DISCUSSION

The EL Efficiency of PVK - Based Devices

PVK was one of the frequently used polymer emitter and host materials, because aside from the general properties of polymer materials such as better mechanical strength, good film formation, it has hole transport properties and a large band gap (it's film fluorescences in purplish blue peaking at around 420 nm). We measured the EL efficiency of a single layer device of PVK as the emitter with ITO as the anode with Mg:Ag (10:1) or LiF/Al as the cathodes. The results shown in Fig. 1 indicate that the EL efficiency of Mg:Ag electrode device was about 3 times higher than that of LiF/Al device.

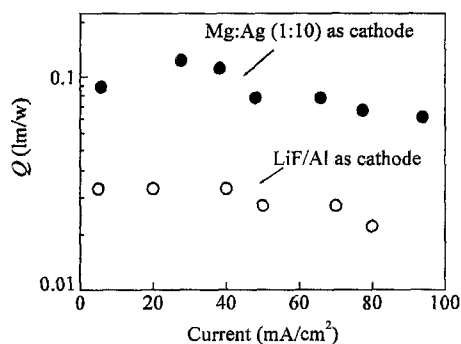


Fig. 1 The efficiency-current characteristics of PVK devices with different electrodes

For an organic EL device, the EL efficiency can be defined as:

$$\phi_{el} = \chi \phi_{pl} \eta_r \eta_e \quad (1)$$

where ϕ_{pl} is the PL efficiency, η_r is the fraction of injected charge carriers that form excitons, η_e is the fraction of emitted photons that are coupled out of the device, χ is the fraction of charge carrier recombinations in the host resulting in singlet excitons, which is 1:4 according to the spin statistics. For the device with the same emitter and the same structure, the ϕ_{pl} and η_r should remain unchanged, thus a general explanation for improved efficiency is the change of the charge injection balance term η_e . The metal with low work function, e.g. Mg, may cause the electron injection from cathode to emitting layer more easily than that from a cathode metal with high work function, e.g. Al.

However, ultimateness of χ being a constant is challenged especially for conjugated polymer system, the possibility of the singlet to triplet ratio being changed in EL devices must be considered. To probe χ in the EL device is the key to clarifying the mechanism of efficiency increase in the Mg:Ag device. A simple route to probe the formation of triplet in polymer host is to dope the phosphor in polymer host. Here, we used a highly luminescent phosphor Cu_4 as the dopant.

Energy Transfer in the Phosphor-Doped PVK Devices

In the phosphor-doped polymer device, the triplet emission can arise from up to three excitation mechanisms: (1) singlet exciton transfer from polymer host by Förster energy transfer, (2) triplet exciton transfer from host by Dexter energy transfer and (3) carrier recombination at the phosphor. If the portion of phosphor is low enough, the possibility of directly catching the carriers by phosphor is also low. The observed emission should result from the excited energy in host transfer to phosphor, and the key to measuring χ is to distinguish the contribution for the phosphor emission, which originates from either the singlet or the triplet excitons formed in PVK.

To test independently the Förster energy transfer, we first used optical excitation, which forms singlet exciton only and the Förster energy transfer mechanism of singlet exciton of PVK to singlet of Cu_4 followed by an intersystem cross should correspond to the observed triplet emission from phosphor. The films consisting of a series of doping concentrations of 1%, 0.5%, 0.25% and 0.2% by mole of Cu_4 in PVK were prepared and excited using 350 nm light which is the excited wavelength of PVK. For the samples with higher Cu_4 -doped level *i.e.* > 0.5 mol%, strong emission was observed from the triplet excited state of Cu_4 at 517 nm with weaker emission from the singlet excited state of PVK at around 420 nm. As shown in Fig. 2, only 420 nm emission was observed for the sample with Cu_4 concentration as low as 0.2 mol%, indicating that the singlet transfer has shown less effect on the PVK films with very low Cu_4 -doped level. We chose this doping concentration for subsequent EL studies.

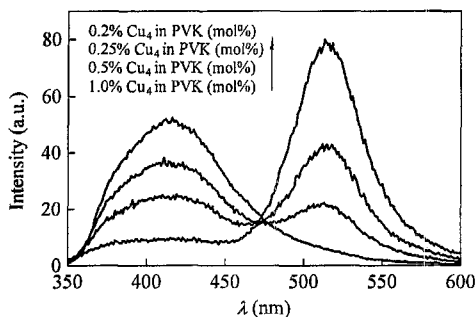


Fig. 2 Photoluminescence spectra of the Cu_4 -doped PVK film with varied Cu_4 -doped level, excited at 350 nm

EL Characteristics of ITO/ Cu_4 :PVK (0.2%)/Cathode Devices

As shown in Fig. 3(a), the EL spectra from the device with a structure of ITO/ Cu_4 :PVK (0.2 mol%)/TAZ/LiF/Al exhibit a strong green emission from the triplet excited state of Cu_4 at 517 nm and another weak emission from PVK at 420 nm. EL efficiency of this Cu_4 -doped device is about 0.1%, which was three times higher than that of PVK only devices. Considering the very low Cu_4 portion in PVK film, the probability of direct charge trapping by Cu_4 is low, thus the triplet exciton, which is formed first on PVK, is likely to transfer to Cu_4 , corresponding to an enhancement in the probability for radiative recombination in Cu_4 . While the singlet excitons formed in PVK that cannot transfer to phosphor acceptor suggested by PL experiments result in the emission from PVK itself at 420 nm. We believe that different PL and EL spectra are the common characteristics of phosphorescence dye-doped fluorescence systems, and no matter what type of energy transfer, exciton in donor molecule with more long lifetime and large diffusion length must have a greater probability of transferring its energy to acceptor molecules. It has been found that in Alq_3 the triplet diffusion length is 140 nm as compared to singlet diffusion length of 10 nm^[13]. Accordingly, the long lifetime triplet exciton will play a dominating role in EL devices.

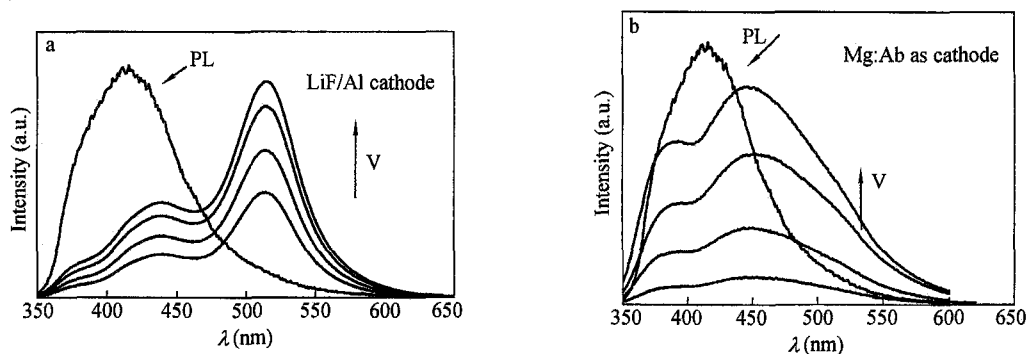


Fig. 3 Electroluminescence spectra of the Cu₄-doped PVK devices at various driving voltages
a) LiF/Al as electrode; b) Mg:Ag as electrode

The EL spectra of the Cu₄-doped PVK with Mg:Ag cathode are shown in Fig. 3(b). Unlike green emission from the LiF/Al device, a blue emission was found from the Mg:Ag device and the emission at around 440 nm becomes stronger while the emission at 517 nm becomes weaker and appears as a shoulder.

The χ value can be calculated from a quantitative analysis of EL spectra. The emission intensity from PVK and Cu₄ can be defined as Eq. (2) and (3) respectively:

$$I_{\text{PVK}} = A\chi(1-\eta_s)\Phi_{\text{PVK}} \quad (2)$$

$$I_{\text{Cu}_4} = A\chi\eta_s\Phi_{\text{Cu}_4} + A(1-\chi)\Phi_{\text{Cu}_4}\eta_T \quad (3)$$

where Φ_{PVK} and Φ_{Cu_4} are the PL efficiency of PVK and Cu₄, respectively. η_s is the Forster energy transfer efficiency of PVK to Cu₄. η_T is the Dexter energy transfer efficiency of PVK to Cu₄. At very low Cu₄-doped levels, the Forster energy transfer is very inefficient, *i.e.*, $\eta_s = 0$, while the Dexter energy transfer is efficient. We assume $\eta_T = 1$. The ratio of triplet to singlet can be calculated according to Eq. (4):

$$\chi/(1-\chi) = (I_{\text{PVK}}/\Phi_{\text{PVK}}) + (I_{\text{Cu}_4}/\Phi_{\text{Cu}_4}) \quad (4)$$

The value of Φ_{PVK} is 0.2 taken from the reported data and the value of Φ_{Cu_4} is 0.42 taken from the PL quantum efficiency measurement of Cu₄ in dilute solution. The measured χ is ≈ 0.5 for the LiF/Al device and ≈ 0.7 for the Mg:Ag device. Their singlet exciton fraction is considerably larger than 0.25 of the spin statistics, which is comparable with the recent data for polymer-based LEDs^[8–10].

Mechanism of the χ Change with Carrier Injection Balance

Before the excitonic singlet to triplet ratio was determined experimentally^[14], it had already been verified by Baldo *et al.*^[13] for a small molecule device. Though these results are consistent with the 3:1 branching ratio expected within the simple statistics of spin multiplicity, changing of this ratio has been observed in the case of varied charge injection balance of the device. That the singlet-triplet ratio can be changed with charge injection has been reported by Cao *et al.*^[8], Friend *et al.*^[9] and Mo^[14] via experimental observation and by Brades *et al.*^[15] from quantum chemistry calculations. They conjectured that either the exciton binding energy is small or that the cross section for an electron-hole pair to form a singlet bound state is significantly higher than that to form a triplet. The exciton binding energy of PVK is unknown, however, as pointed by Kimura *et al.*^[16], in PVK, a helical structure is formed with three monomeric units per rotation. In the helix, the carbazole groups are arranged perpendicular to the axis of the helix and parallel to one other, where the intramolecular electronic exchange interaction between the groups becomes stronger, suggesting a possibility of more delocalization of excitons with weakly bonding energy. The assumption is also supported by comparing the efficiency of PVK only devices with those having Mg:Ag and LiF/Al as electrode, respectively. The PVK only device with Mg:Ag

electrode shows higher efficiency than that of the LiF/Al device. Because only singlet exciton contributes excited energy to the light emission in the PVK only device, this result suggests that a larger number of singlet exciton was formed in Mg:Ag devices.

Color Patterning of PVK-Based Device

The tuning of the emission color by different electrodes provides a new patterning method for PLED. Figure 4 schematically illustrates the patterning technique proposed here. At first, a Cu₄-doped polymer film is spin-coated on the ITO-glass plate. Then by using a shadow mask to cover part of the polymer film, one type of electrode such as LiF/Al is deposited on the polymer layer. By repeating this process, the other electrode Mg:Ag is deposited on the other part of the polymer layer. The shape of the electrodes directly defines the shape of emission patterning. By depositing these two types of electrode on the same ITO strip, two PLEDs with blue and green emission colors are successfully integrated on a glass plate. The chromaticity coordinates of the devices indicate that the color is pure, but it should be noted that in order to get the same brightness of the two devices, the driving voltage should be different due to the difference in the onset voltage of the devices.

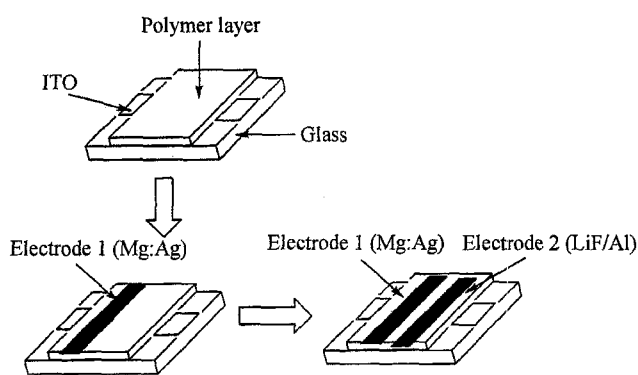


Fig. 4 Scheme of the green/blue PLED integrated on a glass plate through masked electrode with different metals

CONCLUSIONS

Firstly, the different PL and EL spectra are the common characteristics of the phosphorescence dye-doped fluorescence system. Secondly, the formation probability of the triplet and singlet excitons may be changed by varying the charge injection balance. These finding may be helpful for designing the structure of PLED based on phosphorescence materials and/or fluorescence materials. Lastly, in a low level phosphorescence-doped polymer system, the emission color of the PLEDs can be changed by utilizing different metals as the electrode. Based on the observation, a novel simple method for color patterning of PLED has been proposed. By controlling the doping concentration of different color phosphorescence dyes in the same polymer matrix, three different (Red, Green, Blue) color devices have been integrated on one plate just by using three types of electrode.

REFERENCES

- 1 Kraft, A., Grimsdale, A.C. and Holmes, A.B., *Angew. Chem., Int. Ed.*, 1998, 37: 402
- 2 Friend, R.H., Gymer, R.W., Holmes, A.B., Burroughes, J.H., Marks, R.N., Taliani, C., Bradley, D.D.C., Dos Santos, D.A., Brédas, J.L., Lögdlund, M. and Salaneck, W.R., *Nature*, 1999, 397: 121
- 3 Heeger, A.J., *Solid State Commun.*, 1998, 107: 673
- 4 Kido, J., *Physics World*, 1999, 12: 27
- 5 Adachi, C., Baldo, M.A. Forrest, S.R. and Thompson, M.E., *Appl. Phys. Lett.*, 2000, 77: 904

- 6 Ma, Y.G., Che, C.M., Chen, W.H., Zhou, X.M. and Shen, J.C., *Adv. Mater.*, 1999, 11: 852
- 7 Cleave, V., Yahiloglu, G., Barny, P.Le, Friend, R.H. and Tessler, N., *Adv. Mater.*, 1999, 11: 285
- 8 Cao, Y., Parker, I.D., Yu, G., Zhang, C. and Heeger, A.J., *Nature*, 1999, 397: 414
- 9 Ho, P.K.H., Kim, J.S., Burroughes, J.H., Becker, H., Li, S.F.Y., Brown, T.M., Cacialli, F. and Friend, R.H., *Nature*, 2000, 404: 481
- 10 Wohlgenannt, M., Tandon, K., Mazumdar, S., Ramasesha, S. and Vardeny, Z.V., *Nature*, 2001, 409: 494
- 11 Chan, W.H., Zhang, Z.Z., Mak, T.C.W. and Che, C.M., *J. Organomet. Chem.*, 1998, 556: 169
- 12 Ma, Y.G., Chan, W.H., Zhou, X.M. and Che, C.M., *New J. Chem.*, 1999, 263
- 13 Baldo, M.A., O'Brien, D.F., Thompson, M.E. and Forrest, S.R., *Phys. Rev. B*, 1999, 60: 14422
- 14 Ma, Y.G., Lai, T.S. and Wu, Y., *Adv. Mater.*, 2000, 17: 454
- 15 Beljonne, Shuai D., Silbey, R.J. and Brédas, J.L., *Phys. Rev. Lett.*, 2000, 84: 131
- 16 Yoshimoto, K.S., Akana, Y., Hirata, H., Kusabayashi, S., Mikawa, H. and Kassai, N., *J. Polymer Sci.*, A2, 1970, 643