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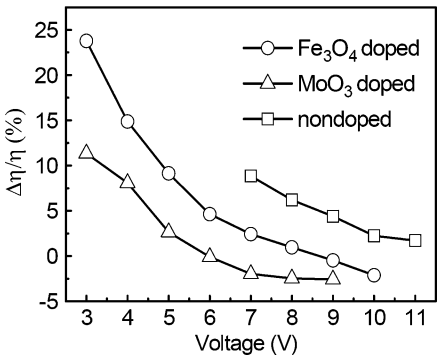

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Efficiency Enhancement in Organic Light-Emitting Devices With a Magnetic Doped Hole-Transport Layer

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Abstract: Magnetic field effects on tris-(8-hydroxyquinoline) aluminum-based organic light-emitting devices (OLEDs) by employing Fe_3O_4 as a magnetic dopant in the hole-transport layer (HTL) have been studied. The magnetic doped OLEDs exhibit efficient injection and transport of holes, and its performances are further enhanced after a magnetic field is applied. The enhancement of luminance and current efficiency of 20% and 24% has been obtained from the magnetic doped devices, while they are only 8% and 9%, respectively, for the nondoped devices under an applied magnetic field of 500 mT. Organic magnetoresistance induced by the magnetic doped HTL is the main origin of increased electroluminescence for the magnetic doped OLEDs.

Index Terms: Organic light-emitting devices (OLEDs), magnetic field effects, Fe_3O_4, magnetic dopant.

1. Introduction

Improvement of efficiency has been a research focus of organic light-emitting devices (OLEDs) for its applications in flat panel display and solid-state lighting [1]–[3]. Although 100% internal quantum efficiency can theoretically be achieved by introducing triplet emitter, a 25% singlet exciton formation ratio has been a bottleneck in improving the efficiency of the conventional fluorescent OLEDs [4], [5]. Recently, using a magnetic electrode has been accepted as a possible way to increase the singlet ratio by externally introducing the spin polarized carriers [6]–[10]. However, inefficient carrier injection from the magnetic electrode and short diffusion length of the spin polarized carriers in organic film are substantial obstacles to realizing highly efficient recombination of the spin polarized carriers [10], [11]. Organic magnetoresistance (OMAR) in the organic semiconductor is another possible way to enhance the singlet ratio through a hyperfine scale magnetic field-dependent mixing of the singlet and triplet states or triplet-triplet annihilation. Unfortunately, the OMAR-induced enhancement of efficiency is usually limited to less than 10% [12]–[14].

Fe_3O_4 is a widely used ferromagnetic material in spintronic devices due to its unique electrical and magnetic properties. In our previous works, Fe_3O_4 has been extended its application to OLEDs as an efficient anodic buffer [15] and p-dopant [16] to effectively enhance the hole injection and transport.

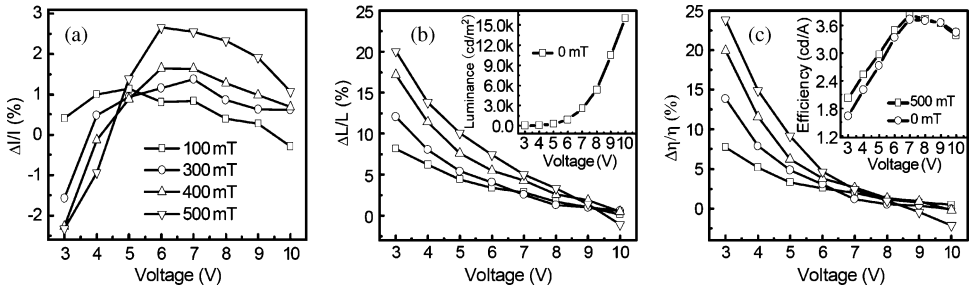

Fig. 1. Applied magnetic field and voltage dependence of the enhancement of the current (a) luminance (b) and current efficiency (c) for the magnetic doped OLEDs. Inset in (b): Luminance–voltage curves of the magnetic doped devices in the absence of magnetic field. Inset in (c): Current efficiency–voltage curves of the magnetic doped devices in the presence and absence of the 500-mT field, respectively.

Efficient injection of spin polarized holes have been approved very recently by depositing an Fe_3O_4 nanofilm on an indium tin oxide (ITO) anode as a spin aligner and anodic buffer, and 10.5% enhancement of current efficiency has been observed with an applied magnetic field [17]. However, short diffusion length of the spin polarized holes in the organic film is still a limitation to fully enable their arrival to the recombination region for the magnetic buffered OLEDs. In this paper, OLEDs with a magnetic dopant of Fe_3O_4 in a hole-transport layer (HTL) are fabricated and characterized. Magnetic field-dependent electroluminescence (EL) was observed, and a large enhancement of 24% for the current efficiency was obtained. The OMAR induced by both the magnetic dopant and the organic functional layers are found to play important role in enhancing the EL of the magnetic doped OLEDs.

2. Experiments

The basic device structure consists of a 25-nm Fe_3O_4 doped *N*, *N*′-diphenyl-*N*, *N*′-bis(1-naphthyl)-(1,1′-biphenyl)-4,4′-diamine (NPB) and 15-nm NPB as the HTL, 50-nm tris-(8-hydroxyquinoline) aluminum (Alq_3) as an emitting and electron-transport layer, and LiF (1 nm)/Al (100 nm) as the cathode. All the layers were sequentially evaporated by thermal evaporation in a high vacuum system with the pressure of less than 5×10^{-4} Pa onto an ITO-coated glass substrate. The evaporation rate is $\sim$1 Å/s for the Fe_3O_4 and $\sim$2 Å/s for the NPB when evaporating the doped layer. The evaporation rate is $\sim$1 Å/s for the neat organic layers, $\sim$0.02 Å/s for the LiF layers, and $\sim$5 Å/s for the Al cathode. The atomic compositions of the evaporated Fe_3O_4 have been confirmed to stoichiometrically consist of Fe_3O_4 by x-ray photoelectron spectroscopy measurement [17]. Superparamagnetism behavior of the evaporated Fe_3O_4 thin film has been observed by characterization of a superconducting quantum interference device in our previous work [17]. The Fe_3O_4 doped NPB layer is prepared by evaporating the Fe_3O_4 and NPB synchronously with the volume ratio of 1 : 2. The current density–voltage–luminance (J–V–L) characteristics of the devices were measured by a Keithley 2400 programmable voltage-current source and a Photo Research PR-655 spectrophotometer. The active area of the devices was 2×2 mm^2. The magnetic field was parallel to the direction of the current flow in the devices, and it varied from 0 to 500 mT by precise control of the distance between the permanent magnet and the device. In order to remove any effects due to drifting in the device characteristics before and after each field measurement, a measurement at null field was taken [18], [19]. These two null-field measurements were averaged and used to calculate the change in current, luminance, and current efficiency with applied magnetic field. The enhancement of the current, luminance (L), and current efficiency (η) are defined by their relative difference in the presence and in the absence of a magnetic field (B), e. g., $[\eta(\mathrm{B}) - \eta(0)]/\eta(0) = \Delta\eta/\eta$. All of the measurements were conducted under ambient condition.

3. Result and Discussions

The effects of the magnetic field on the EL performance of the magnetic doped OLEDs are summarized in Fig. 1, which obviously show dependence of magnetic field and applied voltage. The

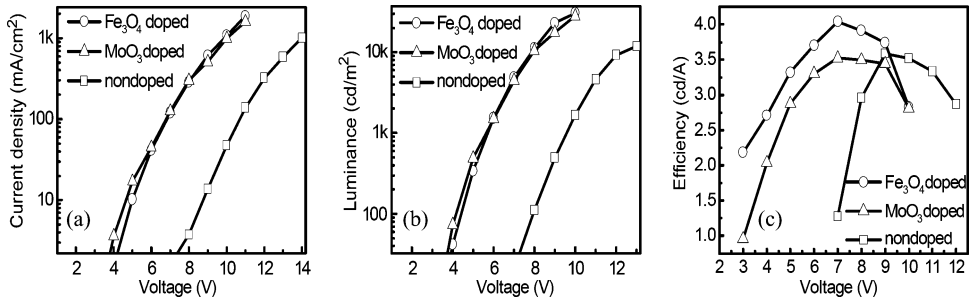

Fig. 2. (a) Current density–voltage, (b) luminance–voltage, and (c) current efficiency–voltage characteristics of the Fe_3O_4 doped, MoO_3 doped, and non-doped devices.

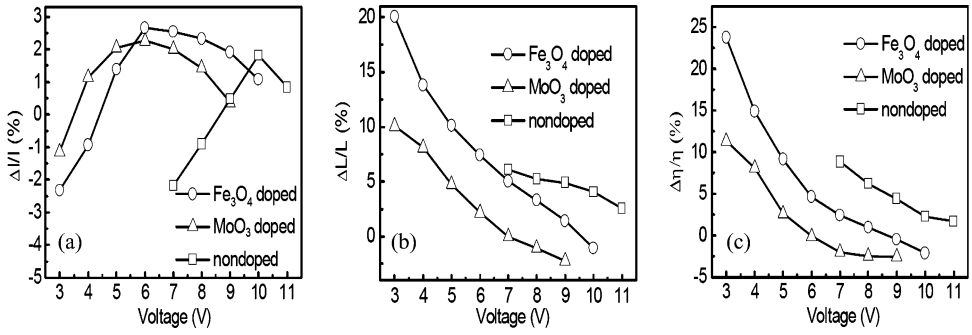

Fig. 3. Applied voltage dependence of the enhancement of the current (a) luminance (b) and current efficiency (c) for the Fe_3O_4 doped, MoO_3 doped, and non-doped OLEDs.

$\Delta I/I$ shows similar behavior under a different applied magnetic filed. It increases with the increasing applied voltage and reaches the maximum at around 6 V. With a further increase of the applied voltage, the $\Delta I/I$ is gradually decreased. The maximum $\Delta I/I$ of about 2.65% at 6 V is obtained when the applied magnetic field is 500 mT. The $\Delta L/L$ increases and tends to be saturated with the increasing magnetic field, while it decreases with the increasing applied voltage and reaches zero at around 10 V. The maximum luminance enhancement of 20% was obtained at 500 mT and 3 V. The $\Delta\eta/\eta$ shows a similar behavior with that of $\Delta L/L$, and 24% of maximum enhancement was obtained at 500 mT and 3 V. The enhancement factor of both luminance and efficiency decrease with the increasing applied voltage, especially at a high magnetic field. The inset in Fig. 1(c) shows the measured current efficiency of the magnetic doped devices in the presence and in the absence of the magnetic field, respectively. The OLEDs clearly exhibit a higher efficiency when a magnetic field is applied.

The magnetic field would have effects on the EL of the OLEDs via mixing the singlet and triplet electron-hole pairs [13] or inducing the triplet-triplet annihilation [14], etc. in organic functional materials, which is very sensitive to the device parameters. To verify the contribution of the magnetic dopant on the EL performance, we fabricated the control devices with MoO_3 as the nonmagnetic dopant, which is a widely used p-dopant in OLEDs. Moreover, the nondoped devices with the structure of ITO/NPB (40 nm)/Alq_3 (50 nm)/LiF (1 nm)/Al (100 nm) was also fabricated as a control. The EL characteristics of these devices without the magnetic field is shown in Fig. 2, which indicates that the OLEDs with either Fe_3O_4 or MoO_3 as p-dopant show largely enhanced current density and luminance compared with the nondoped devices. Therefore, both Fe_3O_4 and MoO_3 show similar effects on the enhacement of the hole injection and transport in OLEDs. Both Fe_3O_4 and MoO_3 have been demonstrated as efficient p-dopant in OLEDs, and charge transfer complex can be formed with the HTL, which results in the generation of free holes and, therefore, enhanced hole transport. In addition, enhanced hole injection can be obtained due to the reduced injection barrier by surface dipole formation [16], [20].

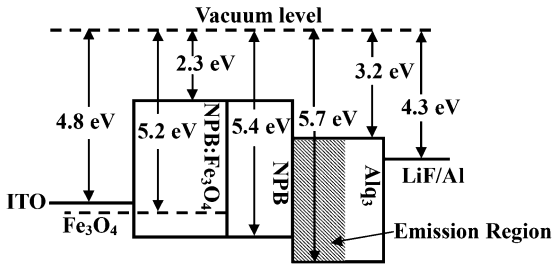

Fig. 4. Energy band diagram for charge injection and transport in the magnetic doped OLEDs.

Fig. 3 shows the enhancement of current, luminance, and efficiency versus applied voltage at 500 mT for each device. For all the devices, the current enhancement increases with increasing driving voltage up to a maximum and then decays, and the maximum $\Delta I/I$ is around 2%, except for a higher driving voltage for the nondoped devices. The maximum $\Delta L/L$ and $\Delta\eta/\eta$ for the MoO_3 doped devices is 10% and 11% at 3 V, respectively, while it is 6% and 8.8% at 7 V for the nondoped devices. The magnetic field effect on the nondoped devices could be attributed to the OMAR of the organic functional layers through the filed-dependent intersystem crossing, which have been studied rather extensively in OLEDs [12]–[14], [21], [22]. The onset voltage of the field effect for the MoO_3 doped devices is much lower than that of the undoped devices due to the enhanced hole injection, which probably results in its' slightly higher enhancement, since it is believed that excitons are essential for the magnetic field effect [19]. While in the case of the Fe_3O_4 doped devices, much higher enhancement has been observed. The maximum $\Delta L/L$ and $\Delta\eta/\eta$ are 20% and 24%, respectively, at the same magnetic field of 500 mT. As can be seen from Figs. 1 and 3, the enhancement factor of luminance and efficiency decreases with the increasing driving voltage, and even a minus increment appears at high voltage for both magnetic and nonmagnetic doped OLEDs. The phenomena has been observed previously [17], [19], [22], and it was estimated that the magnetic filed may disturb the recombination of the second charge carriers (dissociated electrons and holes) or the triplet-triplet annihilation process and, therefore, cause the reduced singlet population [22]. These processes would also affect the carrier transport, and therefore, the OMAR also shows the voltage dependence. However, further theoretical and experimental research is still needed to verify the origins of these phenomena.

The above data indicates that the magnetic dopant should play a crucial role in obtaining the OMAR-induced high EL enhancement for the magnetic doped OLEDs. The energy band diagram is illustrated in Fig. 4 for OLEDs with the magnetic doped HTL. The Fermi level of Fe_3O_4 is 5.2 eV [23], which is between the Fermi level of ITO (4.8 eV) and the highest occupied molecular orbital level of NPB (5.4 eV). Therefore, the doped Fe_3O_4 can result in a two-step hole injection at the anode interface, i.e., from ITO to Fe_3O_4 and then from Fe_3O_4 to NPB. In addition, the injected holes could hop between the Fe_3O_4 in the HTL, because a high doping concentration ($\sim$33% by volume) results in a short distance between the dopant sites. Therefore, the magnetization of the Fe_3O_4 in the HTL would have effect on the hole injection and transport, and the internal field induced by the magnetic dopant plays an important role in the excitons and bipolar formation process, which would contribute to the OMAR and result in a higher EL enhancement. We should note that the OMAR induced by the organic functional layers would also contribute to the EL enhancement of the Fe_3O_4-doped OLEDs, which has been observed in the above MoO_3 doped and nondoped devices.

4. Conclusion

In summary, we have demonstrated enhanced EL performance of the OLEDs with a magnetic doped HTL. Both the organic function layers and the magnetic dopant contribute to the OMAR-induced EL improvements under an applied magnetic field. However, the EL of the magnetic doped OLEDs exhibits much higher EL enhancement factor than that of the MoO_3 doped and nondoped devices, because the magnetization of the Fe_3O_4 dopant has an effect on the carrier transport.

Therefore, use of a magnetic dopant in OLEDs presents an efficient pathway to enhance the EL efficiency of the fluorescent OLEDs.

References

[1] H. Kanno, Y. Hamada, and H. Takahashi, "Development of OLED with high stability and luminance efficiency by co-doping methods for full color displays," *IEEE J. Sel. Topics Quantum Electron.*, vol. 10, no. 1, pp. 30–36, Jan. 2004.

[2] J. Park, N. Suganuma, and Y. Kawakami, "Dual partial dye doping for chromaticity tuning and performance enhancement of white OLEDs," *J. Display Technol.*, vol. 4, no. 1, pp. 61–69, Mar. 2008.

[3] B. W. D'Andrade and S. R. Forrest, "White organic light-emitting devices for solid-state lighting," *Adv. Mater.*, vol. 16, no. 18, pp. 1585–1595, Sep. 2004.

[4] T. Earmme, E. Ahmed, and S. A. Jenekhe, "Highly efficient phosphorescent light-emitting diodes by using an electron-transport material with high electron affinity," *J. Phys. Chem. C*, vol. 113, no. 43, pp. 18 448–18 450, Oct. 2009.

[5] A. Köhler, J. S. Wilson, and R. H. Friend, "Fluorescence and phosphorescence in organic materials," *Adv. Mater.*, vol. 14, no. 10, pp. 701–707, May 2002.

[6] P. O. Ruden and D. L. Smith, "Theory of spin injection into conjugated organic semiconductors," *J. Appl. Phys.*, vol. 95, no. 9, pp. 4898–4904, Feb. 2004.

[7] J. Wilkinson, A. H. Davis, K. Bussmann, and J. P. Long, "Evidence for charge-carrier mediated magnetic-field modulation of electroluminescence in organic light-emitting diodes," *Appl. Phys. Lett.*, vol. 86, no. 11, pp. 111109-1–111109-3, Mar. 2005.

[8] E. Shikoh, T. Kawai, A. Fujiwara, Y. Ando, and T. J. Miyazaji, "Spin injection into organic light-emitting diodes with a ferromagnetic cathode and observation of the luminescence properties," *J. Magn. Magn. Mater.*, vol. 310, no. 2, pp. 2052–2054, Nov. 2006.

[9] D. Wu, Z. H. Xiong, X. G. Li, Z. V. Vardeny, and J. Shi, "Magnetic-field-dependent carrier injection at $La_{2/3}Sr_{1/3}MnO_3$/ and organic semiconductors interfaces," *Phys. Rev. Lett.*, vol. 95, no. 1, pp. 016802-1–016802-5, Jul. 2005.

[10] B. F. Ding, Y. Q. Zhan, Z. Y. Sun, X. M. Ding, X. Y. Hou, Y. Z. Wu, I. Bergenti, and V. Dediu, "Electroluminescence and magnetoresistance of the organic light-emitting diode with a $La_{0.7}Sr_{0.3}MnO_3$ anode," *Appl. Phys. Lett.*, vol. 93, no. 18, pp. 183307-1–183307-3, Nov. 2008.

[11] E. Shikoh, A. Fujiwara, Y. Ando, and T. Miyazaki, "Spin injection into organic light-emitting devices with ferromagnetic cathode and effects on their luminescence properties," *Jpn. J. Appl. Phys.*, vol. 45, no. 9A, pp. 6897–6901, Sep. 2006.

[12] J. Kalinowski, M. Cocchi, D. Virgili, P. D. Marco, and V. Fattori, "Magnetic field effects on emission and current in Alq_3-based electroluminescent diodes," *Chem. Phys. Lett.*, vol. 380, no. 5/6, pp. 710–715, Oct. 2003.

[13] H. Odaka, Y. Okimoto, T. Yamada, H. Okamoto, M. Kawasaki, and Y. Tokura, "Control of magnetic-field effect on electroluminescence in Alq_3-based organic light emitting diodes," *Appl. Phys. Lett.*, vol. 88, no. 12, pp. 123501-1–123501-3, Mar. 2006.

[14] C. Gärditz, A. G. Mückl, and M. J. Cölle, "Influence of an external magnetic field on the singlet and triplet emissions of tris-(8-hydroxyquinoline) aluminum (III) (Alq)," *J. Appl. Phys.*, vol. 98, no. 10, pp. 104507-1–104507-4, Nov. 2005.

[15] D. D. Zhang, J. Feng, Y. F. Liu, Y. Q. Zhong, Y. Bai, Y. Jin, G. H. Xie, Q. Xue, Y. Zhao, S. Y. Liu, and H. B. Sun, "Enhanced hole injection in organic light-emitting devices by using Fe_3O_4 as an anodic buffer layer," *Appl. Phys. Lett.*, vol. 94, no. 22, pp. 223306-1–223306-3, Jun. 2009.

[16] D. D. Zhang, J. Feng, H. Wang, Y. Bai, Q. D. Chen, S. Y. Liu, and H. B. Sun, "Improved hole injection and transport of organic light-emitting devices with an efficient p-doped hole-injection layer," *Appl. Phys. Lett.*, vol. 95, no. 26, pp. 263303-1–263303-3, Dec. 2009.

[17] J. Feng, D. D. Zhang, Y. F. Liu, Y. Bai, Q. D. Chen, S. Y. Liu, and H. B. Sun, "Magnetic nanofilm of Fe_3O_4 for highly efficient organic light-emitting devices," *J. Phys. Chem. C*, vol. 114, no. 14, pp. 6718–6721, Mar. 2010.

[18] P. Desai, P. Shakya, T. Kreouzis, and W. P. Gillin, "The role of magnetic fields on the transport and efficiency of aluminum tris(8-hydroxyquinoline) based organic light emitting diodes," *J. Appl. Phys.*, vol. 102, no. 7, pp. 073710-1–073710-5, Oct. 2007.

[19] P. Desai, P. Shakya, T. Kreouzis, and W. P. Gillin, "Magnetoresistance and efficiency measurements of Alq_3-based OLEDs," *Phys. Rev. B, Condens. Matter*, vol. 75, no. 9, pp. 094423-1–094423-6, Mar. 2007.

[20] F. X. Wang, X. F. Qiao, T. Xiong, and D. G. Ma, "The role of molybdenum oxide as anode interfacial modification in the improvement of efficiency and stability in organic light-emitting diodes," *Org. Electron.*, vol. 9, no. 6, pp. 985–993, Dec. 2008.

[21] B. Hu and Y. Wu, "Tuning magnetoresistance between positive and negative values in organic semiconductors," *Nat. Mater.*, vol. 6, no. 12, pp. 985–991, Dec. 2007.

[22] L. Xin, C. Li, F. Li, S. Liu, and B. Hu, "Inversion of magnetic field effects on electrical current and electroluminescence in tri-(8-hydroxyquinoline)-aluminum based light-emitting diodes," *Appl. Phys. Lett.*, vol. 95, no. 12, pp. 123306-1–123306-3, Sep. 2009.

[23] M. Fonin, R. Pentcheva, Y. S. Dedkov, M. Sperlich, D. V. Vyalikh, M. Scheffler, U. Rüdiger, and G. Güntherodt, "Surface electronic structure of the Fe_3O_4(100): Evidence of a half-metal to metal transition," *Phys. Rev. B, Condens. Matter*, vol. 72, no. 10, pp. 104436-1–104436-3, Sep. 2005.