

Tuning magnetoresistance and magnetic-field-dependent electroluminescence through mixing a strong-spin-orbital-coupling molecule and a weak-spin-orbital-coupling polymer

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We report a tunable magnetoresistance by uniformly mixing strong-spin-orbital-coupling molecule fac-tris (2-phenylpyridinato) iridium [$\text{Ir}(\text{ppy})_3$] and weak-spin-orbital-coupling polymer poly(*N*-vinyl carbazole) (PVK). Three possible mechanisms, namely charge transport distribution, energy transfer, and intermolecular spin-orbital interaction, are discussed to interpret the $\text{Ir}(\text{ppy})_3$ concentration-dependent magnetoresistance in the PVK+ $\text{Ir}(\text{ppy})_3$ composite. The comparison between the magnetic field effects measured from energy-transfer and nonenergy-transfer $\text{Ir}(\text{ppy})_3$ doped polymer composites indicates that energy transfer and intermolecular spin-orbital interaction lead to rough and fine tuning for the magnetoresistance, respectively. Furthermore, the photocurrent dependence of magnetic field implies that the excited states contribute to the magnetoresistance through dissociation. As a result, the modification of singlet or triplet ratio of excited states through energy transfer and intermolecular spin-orbital interaction form a mechanism to tune the magnetoresistance in organic semiconducting materials.

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I. INTRODUCTION

Organic semiconducting materials can intrinsically exhibit magnetic field-sensitive physical¹⁻⁶ and chemical^{7,8} properties. For example, magnetoresistance can be readily obtained from these nonmagnetic organic semiconducting materials under nonspin-polarized charge injection.⁹⁻¹¹ This magnetoresistance opens a new area for organic materials to be used in spintronic or magnetically tunable optoelectronic devices, although the mechanism of the organic magnetoresistance is still not clear. We found that mixing two soluble organic materials, namely a strong-spin-orbital-coupling phosphorescent fac-tris (2-phenylpyridinato) iridium [$\text{Ir}(\text{ppy})_3$] dye and a weak-spin-orbital-coupling PVK, leads to a concentration-tunable magnetoresistance. There are three possible mechanisms that can account for the tunable magnetoresistance in the PVK+ $\text{Ir}(\text{ppy})_3$ composite. First, the PVK and $\text{Ir}(\text{ppy})_3$ may form high and low magnetoresistance channels in their composite. Adjusting the composite composition may affect the relative transport distribution between the high and low magnetoresistance channels and therefore changes the overall magnetoresistance. Second, energy transfer can occur through Förster and Dexter processes in the PVK+ $\text{Ir}(\text{ppy})_3$ composite. The energy transfer may redistribute the excited states between the PVK and $\text{Ir}(\text{ppy})_3$ components, consequently affecting the overall magnetoresistance when the excited states contribute to the magnetic field-dependent injection current. Third, an intermolecular spin-orbital interaction may be formed between the PVK and $\text{Ir}(\text{ppy})_3$ components in their composite. This intermolecular magnetic interaction can modify the effective spin-orbital coupling and thus may change the overall magnetoresistance. This paper discusses these three possible mechanisms based on magnetic field-dependent electroluminescence (MFE) observed from the designed systems with parallel and series

magnetoresistance-channel connections, nonenergy transfer, and energy transfer characteristics.

II. EXPERIMENTAL

The $\text{Ir}(\text{ppy})_3$ molecules were mixed with the PVK and PMPV by different weight ratios up to 5 wt. % in chloroform, respectively, forming $\text{Ir}(\text{ppy})_3$ doped polymer composite solutions. The 100 nm thick films of the polymer $\text{Ir}(\text{ppy})_3$ composite or pristine polymers were spin cast on precleaned indium tin oxide (ITO) glass substrates from the respective chloroform solutions. The spin-cast films were then dried under vacuum at 70 °C for 12 h. The uniform dispersion of $\text{Ir}(\text{ppy})_3$ molecules in the PVK matrix was monitored by the morphological and electron-dispersion-spectral analyses based on the TEM (transmission electron microscopy) measurements.¹² The single- and double-layer organic light-emitting diodes (LEDs) were fabricated with the architectures of ITO/ $\text{Ir}(\text{ppy})_3$ +PVK/Al and ITO/PVK/ $\text{Ir}(\text{ppy})_3$ /Al, respectively, by thermally evaporating aluminum (Al) electrode under vacuum of 2×10^{-6} Torr. The magnetoresistance was measured at a constant voltage targeted to the injection current of 20 mA/cm² for the organic LEDs. The MFE was characterized at both constant voltage and current. The magnetocurrent refers to the current change $(I_B - I_0)/I_0$ caused by a magnetic field, where I_B and I_0 are the injection current at constant voltage with and without an applied magnetic field. The magneto-photocurrent is defined as the photocurrent change $(I_{\text{PH}(B)} - I_{\text{PH}(0)})/I_{\text{PH}(0)}$ under the influence of a magnetic field. The $I_{\text{PH}(B)}$ and $I_{\text{PH}(0)}$ are the photocurrents at short-circuit condition with and without an applied magnetic field, respectively.

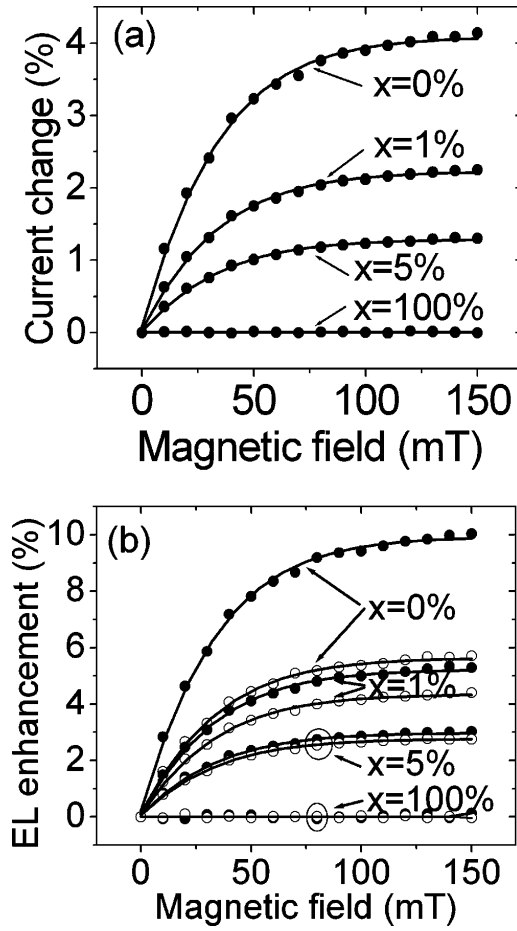


FIG. 1. (a) Enhancement of injection current as a function of magnetic field. (b) MFE from composite at constant voltage (dots) and current (circles). x is the weight concentration of $\text{Ir}(\text{ppy})_3$ dopant in the composite LED of $\text{ITO}/\text{Ir}(\text{ppy})_3(x \text{ wt. } \%) + \text{PVK}/\text{Al}$.

III. RESULTS AND DISCUSSIONS

A. Tunable magnetoresistance from $\text{Ir}(\text{ppy})_3$ doped polymer composite

It can be seen in Fig. 1(a) that the $\text{Ir}(\text{ppy})_3 + \text{PVK}$ composite shows an $\text{Ir}(\text{ppy})_3$ concentration-dependent positive magnetocurrent at constant voltage, namely negative magnetoresistance, based on the single-layer light-emitting diodes (LEDs) with ITO and Al electrodes. Here, the PVK and $\text{Ir}(\text{ppy})_3$ are defined as high and low magnetoresistant materials, respectively. The magnetocurrent includes a rapid increase with the magnetic field from 0 to about 50 mT and then becomes saturated. The maximal current enhancements are 4.0% for the neat PVK, 2.0% for the PVK doped with 1 wt. % $\text{Ir}(\text{ppy})_3$, and 1.2% for the PVK doped with 5 wt. % $\text{Ir}(\text{ppy})_3$, and negligible value for the neat $\text{Ir}(\text{ppy})_3$. This $\text{Ir}(\text{ppy})_3$ concentration-dependent magnetoresistance can be also reflected by the difference between the MFEs measured at constant voltage and current,¹¹ as shown in Fig. 1(b). The three possible mechanisms: charge transport, energy transfer, and intermolecular spin-orbital interaction are discussed below.

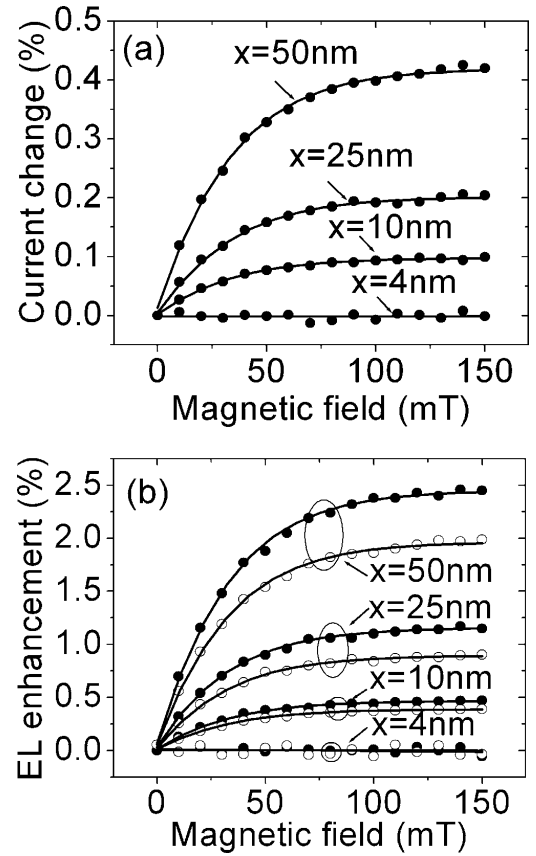


FIG. 2. (a) Magnetic field-dependent current and (b) MFE at constant voltage (dots) and current (circles), respectively, in double-layer LEDs of $\text{ITO}/\text{PVK}(x \text{ nm})/\text{Ir}(\text{ppy})_3(80 \text{ nm})/\text{Al}$. x is the thickness of PVK layer.

B. Charge transport channel effects on magnetoresistance

The charge transport may be approximately divided into two components through PVK matrix and $\text{Ir}(\text{ppy})_3$ dopant in the $\text{PVK} + \text{Ir}(\text{ppy})_3$ composite LED. These two transport components lead to high and low magnetoresistance channels in a parallel connection. As a consequence, varying the $\text{Ir}(\text{ppy})_3/\text{PVK}$ ratio could change the relative transport distribution between the high and low magnetoresistance channels and thus yield an $\text{Ir}(\text{ppy})_3$ concentration-dependent magnetoresistance in the composite. When the condition of two parallel PVK and $\text{Ir}(\text{ppy})_3$ transport channels is removed by using the double-layer LED with the architecture of $\text{ITO}/\text{PVK}/\text{Ir}(\text{ppy})_3/\text{Al}$, we observe in Fig. 2(a) that the use of the PVK hole-transport layer results in a positive magnetocurrent. The 0.4% magnetocurrent is obtained when the 50 nm thick PVK hole-transport layer is used. This magnetocurrent decreases with decreasing the PVK thickness and becomes negligible when the PVK thickness is reduced to 4 nm. Again, the PVK thickness-dependent magnetoresistance can be further suggested by the difference between the MFEs measured at constant voltage and current [Fig. 2(b)]. It is evident that the charge transport through two parallel magnetoresistance channels is not accountable for the $\text{Ir}(\text{ppy})_3$ concentration-tunable magnetoresistance. In addition, the result from the magnetocurrent of the double-layer LED im-

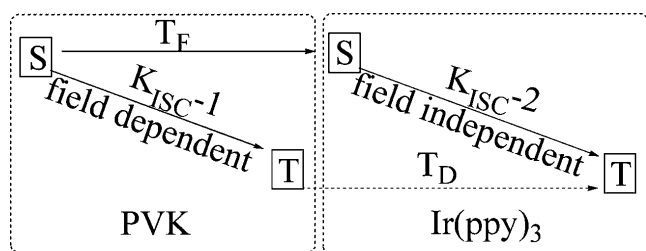


FIG. 3. Intersystem crossing and (Förster T_F and Dexter T_D) energy transfer in the PVK+Ir(*ppy*)₃ composite. K_{ISC-1} and K_{ISC-2} are magnetic field dependent and independent intersystem crossings in PVK matrix and Ir(*ppy*)₃ dopant, respectively.

plies that the intermolecular interaction is formed at the PVK/Ir(*ppy*)₃ layer interface and consequently affects the magnetoresistance. The intermolecular interaction can occur through two possible pathways: energy transfer from the PVK to Ir(*ppy*)₃ and spin-orbital coupling between the PVK and Ir(*ppy*)₃.

C. Energy transfer effects on magnetoresistance

It is known that energy transfer can occur from the PVK to Ir(*ppy*)₃ through the Förster and Dexter processes¹³⁻¹⁵ [Fig. 3(a)] when PVK chains and Ir(*ppy*)₃ molecules are placed within a close proximity in either composite or double-layer structure. This energy transfer can shift magnetic field effects between different components in a polymer composite. It can be seen in Fig. 1(b) that the electrophosphorescence from Ir(*ppy*)₃ dopant shows a significant magnetic field dependence in the PVK+Ir(*ppy*)₃ composite while the neat Ir(*ppy*)₃ does not exhibit an appreciable MFE. In general, the MFE in organic materials can be caused by magnetic field-enhanced electron-hole pair formation,^{7,16} or magnetic field-dependent singlet-triplet intersystem conversion,¹⁷⁻¹⁹ or triplet-triplet annihilation^{4,20,21} under electrical excitation. However, the lack of MFE in the neat Ir(*ppy*)₃ LED does not suggest that a low magnetic field can change the electron-hole pair formation and triplet-triplet annihilation. It has been found that the increase component in the MFE can be attributed to the magnetic field-reduced singlet-triplet intersystem crossing through Zeeman effect.^{17,18,22} The spin-orbital coupling has two effects: spin flip, defined as intersystem crossing; and splitting of degenerate triplet levels, named as intrinsic Zeeman effect. This intrinsic Zeeman effect is given by the Zeeman parameter D . It is also known that an external magnetic field can split the triplet levels and yield an external Zeeman effect. The competition between the intrinsic Zeeman effect and the external Zeeman effect determines the singlet-triplet intersystem crossing in a magnetic field. Furthermore, the intersystem crossing can occur in both electron-hole pair and excitonic states in organic materials. We note that the photoluminescence (PL) from the Ir(*ppy*)₃+PVK composite or the individual components does not show an appreciable magnetic field dependence under photoexcitation. Therefore, the observed MFE under electrical excitation should be due to the intersystem crossing in electron-hole pair states. For most

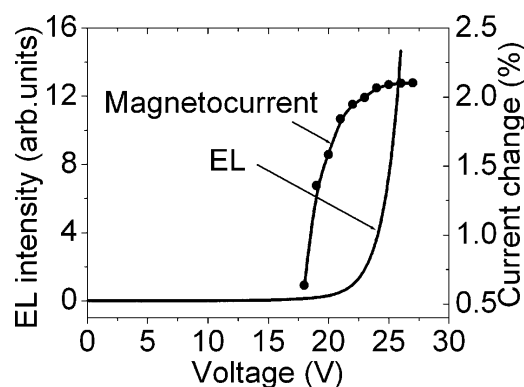


FIG. 4. Voltage-dependent magnetocurrent and EL intensity in PVK+(1 wt. %)Ir(*ppy*)₃ composite LED. The magnetoresistance was measured at the field of 150 mT.

organic materials with aromatic molecular structures, the Zeeman parameter D (intrinsic Zeeman effect) is about 1–10 μ eV,²³ showing a weak to moderate spin-orbital coupling strength. This small Zeeman parameter suggests that an external magnetic field ranging from 10 mT to 100 mT can cause a significant MFE. For phosphorescent materials such as Ir(*ppy*)₃, the D is usually greater than 100 μ eV.^{24,25} This large Zeeman parameter implies that a low magnetic field (<1 Tesla) cannot induce an appreciable MFE. The value of Zeeman parameter explains why the neat PVK and Ir(*ppy*)₃ LEDs show significant and negligible MFEs, respectively. When the weak-spin-orbital-coupling PVK and strong-spin-orbital-coupling Ir(*ppy*)₃ are mixed, the magnetic field-increased singlets in the PVK matrix can be reflected as a magnetic field-increased triplets in the Ir(*ppy*)₃ dopant due to Förster and Dexter transfer, especially in the case where the Förster transfer becomes dominant at a distance of greater than 1 nanometer between an excited PVK and an unexcited Ir(*ppy*)₃ (Fig. 3). This energy transfer-dependent MFE can occur in composite or double-layer structure when the PVK chains and Ir(*ppy*)₃ molecules are in close contact [Figs. 1(b) and 2(b)]. As a result, the long-distance Förster and short-distance Dexter energy transfer essentially form a mechanism to induce magnetic field-dependent singlet-to-triplet ratio in a strong-spin-orbital-coupling phosphorescent dopant through a weak-spin-orbital-coupling polymer matrix based on polymer phosphorescent dye composite. We should further note that the redistribution of singlet-to-triplet ratio in excited states between the weak-spin-orbital-coupling polymer matrix and the strong-spin-orbital-coupling Ir(*ppy*)₃ dopant can lead to a substantial tuning of magnetoresistance when the excited states contribute to the magnetic field effects. Figure 4 shows that the magnetoresistance dramatically decreases when the applied bias is lower than the threshold voltage for generating electroluminescence (EL) in PVK+Ir(*ppy*)₃ composite. This voltage-dependent magnetoresistance can be observed in various organic semiconducting materials.²⁶ Nevertheless, it can be argued from the experimental results in Fig. 4 that the excited states significantly contribute to the magnetoresistance.

D. Intermolecular spin-orbital interaction

We now consider the intermolecular spin-orbital interaction in Ir(*ppy*)₃ doped polymer composite based on the mag-

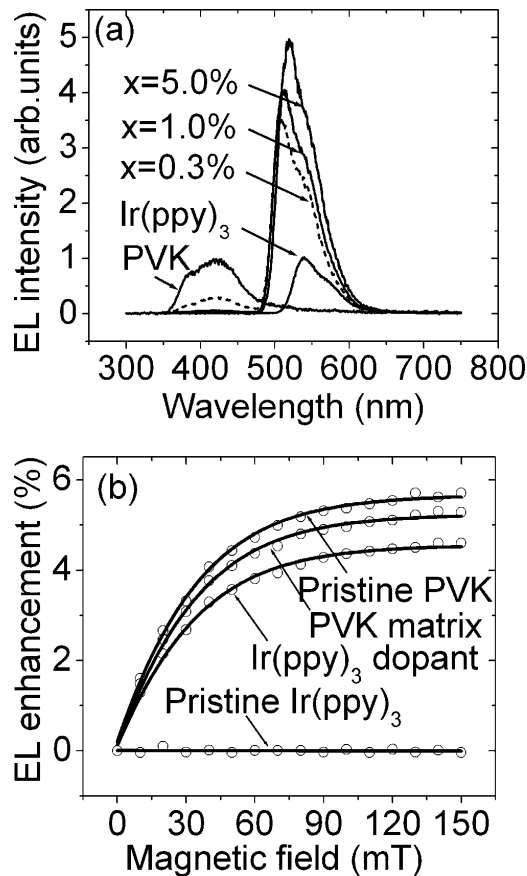


FIG. 5. (a) EL spectra of pristine PVK, pristine $\text{Ir}(\text{ppy})_3$, and $\text{PVK}+(x\%)\text{Ir}(\text{ppy})_3$ composite LEDs. (b) Fluorescence- and phosphorescence-based MFEs from PVK matrix and $\text{Ir}(\text{ppy})_3$ dopant in the dilute $\text{PVK}+(0.3 \text{ wt. } \%)\text{Ir}(\text{ppy})_3$ composite. The MFEs from pristine PVK and $\text{Ir}(\text{ppy})_3$ are also shown as reference.

netoresistance and MFE observed from a nonenergy-transfer polymer $\text{Ir}(\text{ppy})_3$ composite. In general, the delocalized π electrons in polymer matrix can penetrate into the large field of molecular orbit of heavy-metal complex when the polymer chains and $\text{Ir}(\text{ppy})_3$ molecules are brought into contact.^{27,28} This penetration leads to an intermolecular spin-orbital interaction between the electron spins of polymer matrix and the electron orbits of $\text{Ir}(\text{ppy})_3$ dopant, modifying the effective spin-orbital coupling of polymer matrix in the composite. Therefore, mixing a strong-spin-orbital-coupling molecule and a weak-spin-orbital-coupling polymer forms a mechanism to adjust polymer spin-orbital coupling strength. When both fluorescence from the PVK matrix and the phosphorescence from the $\text{Ir}(\text{ppy})_3$ dopant are observed in the dilute $\text{PVK}+(0.3 \text{ wt. } \%)\text{Ir}(\text{ppy})_3$ composite [Fig. 5(a)], it can be seen in Fig. 5(b) that the $\text{Ir}(\text{ppy})_3$ dispersion slightly decreases the fluorescence-based MFE amplitude of the PVK matrix as compared to the value of neat PVK. The MFE amplitudes are 5.6% and 5.1% for the neat and 0.3 wt. % $\text{Ir}(\text{ppy})_3$ doped PVK LEDs, respectively [Fig. 5(b)]. This experimental result suggests that the $\text{Ir}(\text{ppy})_3$ dopant enhances the spin-orbital coupling of PVK matrix. The enhanced spin-orbital coupling further competes with the magnetic field in intersystem crossing and thus results in a reduction of

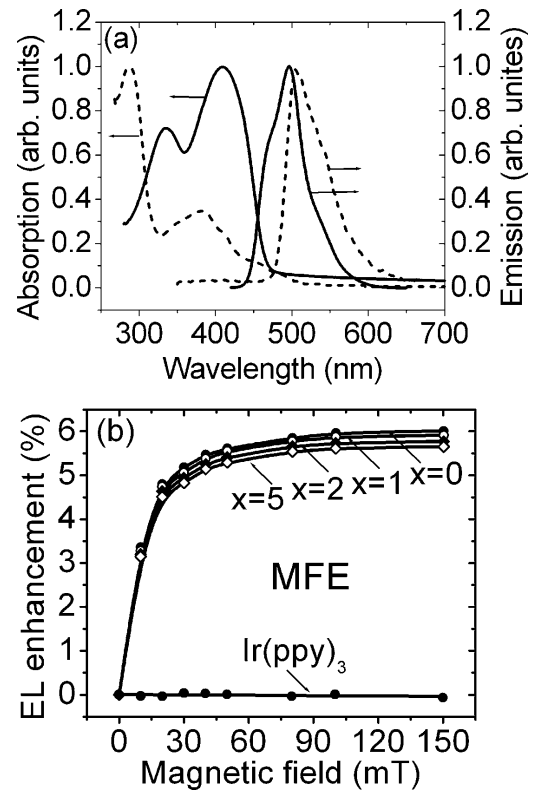


FIG. 6. (a) Absorption and emission spectra of PMPV (solid lines) and $\text{Ir}(\text{ppy})_3$ (dash lines). (b) MFE from PMPV $+(x \text{ wt. } \%)\text{Ir}(\text{ppy})_3$ composite LEDs at constant current of 20 mA/cm^2 . x is the weight concentration of $\text{Ir}(\text{ppy})_3$ dopant in the composite.

fluorescence-based MFE from the PVK matrix. The reduction of fluorescence-based MFE in the PVK matrix can then be reflected as a decrease of phosphorescence-based MFE in the $\text{Ir}(\text{ppy})_3$ dopant through dominant Förster energy transfer from the PVK matrix to the $\text{Ir}(\text{ppy})_3$ dopant in their composite. Furthermore, when the PVK is replaced by poly (*m*-phenylenevinylene-co-2, 5-dioctyloxy-*p*-phenylenevinylene) (PMPV), the negligible spectral overlap between the emission of PMPV and the absorption of $\text{Ir}(\text{ppy})_3$ [Fig. 6(a)] indicates that the dominant Förster transfer is significantly reduced in the PMPV+ $\text{Ir}(\text{ppy})_3$ composite. Figure 6(b) shows that the MFE slightly decreases with the $\text{Ir}(\text{ppy})_3$ concentration. The MFE amplitude changes from 6.0% for neat PMPV to 5.6% for 5 wt. % $\text{Ir}(\text{ppy})_3$ doped PMPV. The EL spectra in Fig. 6(a) indicates that the PMPV and $\text{Ir}(\text{ppy})_3$ emit in a similar spectral range. Hence, the MFE observed from the composite should be associated with both fluorescence from PMPV matrix and phosphorescence from $\text{Ir}(\text{ppy})_3$ dopant. We know that the relative ratio between the fluorescence- and phosphorescence-based MFE amplitudes is determined by the energy transfer in the $\text{Ir}(\text{ppy})_3$ doped polymer composite. Since the energy transfer is minimized in the PMPV+ $\text{Ir}(\text{ppy})_3$ composite, the observed MFE should be mainly due to the dependence of magnetic field on intersystem crossing in the PMPV matrix. Therefore, the experimental data of $\text{Ir}(\text{ppy})_3$ concentration-dependent MFE in Fig. 6(b) provides an additional experimental evidence that the

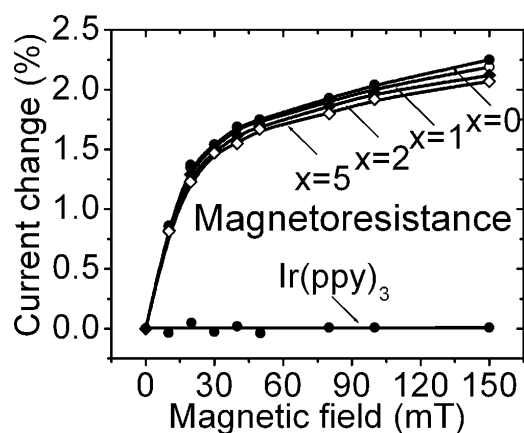


FIG. 7. Magnetocurrents from PMPV+($x\%$)Ir(ppy)₃ composite LEDs.

spin-orbital coupling of polymer matrix can be enhanced due to the intermolecular magnetic interaction upon the Ir(ppy)₃ dispersion. It is interesting to note that the dispersed Ir(ppy)₃ only slightly decreases the magnetoresistance in this nonenergy-transfer composite (Fig. 7). The magnetoresistance decreases from 2.3% for neat PMPV to 2.0% for 5 wt. % Ir(ppy)₃ doped PMPV. This result further indicates that the so-called high and low magnetoresistance channels do not play an important role in tuning magnetoresistance when strong-spin-orbital-coupling molecules are uniformly dispersed in a weak-spin-orbital-coupling polymer matrix. Clearly, the relative distribution of excited states through energy transfer can lead to a substantial tuning of magnetic field effects in Ir(ppy)₃ doped polymer composite. As a result, the comparison between the magnetic field effects measured from the nonenergy transfer PMPV+Ir(ppy)₃ and energy-transfer PVK+Ir(ppy)₃ composites (Figs. 1 and 4) shows that the energy transfer and intermolecular spin-orbital interaction^{29,26} play rough and fine tuning for the magnetoresistance and MFE when a strong-spin-orbital-coupling Ir(ppy)₃ and a weak-spin-orbital-coupling polymer are mixed.

E. Contribution of excited states to magnetoresistance

We now discuss how excited states and spin-orbital coupling can affect the magnetoresistance in organic semiconducting materials. It can be seen in Fig. 8(a) that an external magnetic field increases the photocurrent, generating a magnetophotocurrent in the Ir(ppy)₃+PVK composite. The photocurrent quickly increases with the magnetic field from 0 to about 50 mT and is then saturated. This photocurrent enhancement can be attributed to the magnetic field-increased singlet electron-hole pairs in the PVK matrix due to the external Zeeman effect,^{30,31} based on the fact which the dissociation of singlet electron-hole pairs is largely greater than that of the triplet electron-hole pairs in bulk materials.^{30,32} In particular, we should note that the magnetic field-induced photocurrent enhancement decreases with increasing the Ir(ppy)₃ concentration, showing a concentration-tunable magnetophotocurrent in the Ir(ppy)₃+PVK composite. The

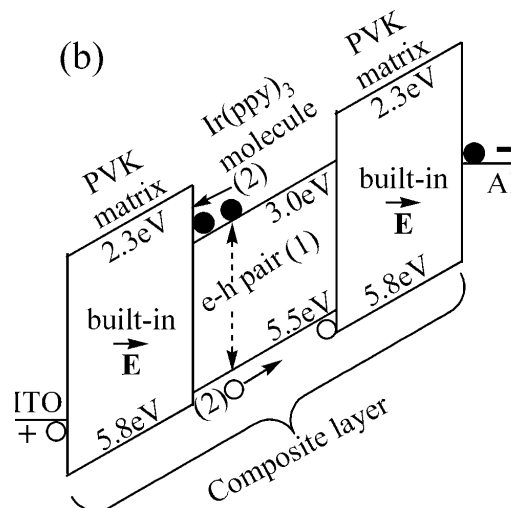
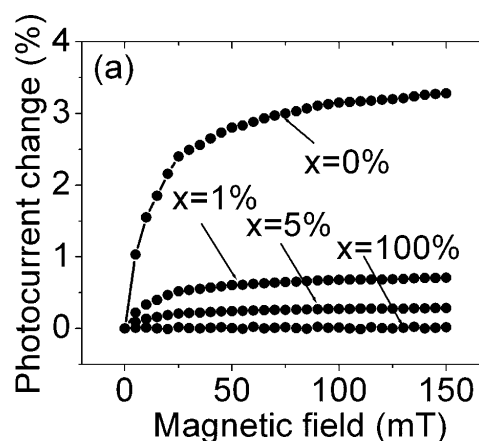


FIG. 8. (a) Photocurrent as a function of magnetic field in the composite LEDs of ITO/Ir(ppy)₃(x wt. %)+PVK/Al under the light illumination of 0.1 mW/cm² at 330 nm. (b) Formation of built-in electric field due to the dissociation of electron-hole pairs in Ir(ppy)₃+PVK composite LED. The HOMO and LUMO are 5.8 eV and 2.3 eV for the PVK (Ref. 33), and 5.5 eV and 3.0 eV for the Ir(ppy)₃ (Ref. 34), respectively. (1): electron-hole pair formation; (2): electron-hole pair dissociation.

magnetic field-induced photocurrent enhancements are 3.6% for the neat PVK, 0.8% for 1 wt. % Ir(ppy)₃ doped PVK, 0.3% for 5 wt. % Ir(ppy)₃ doped PVK, and 0% for the neat Ir(ppy)₃. When the magneto-photocurrent is taken into account, the dissociated charge carriers can be drifted to the interfaces between the Ir(ppy)₃ and PVK components in the Ir(ppy)₃+PVK composite LED under the influence of applied bias, forming a built-in electric field applied on the PVK, as shown in Fig. 8(b). This built-in electric field can further tilt the energy bands of the PVK and consequently enhances the electron and hole injection into the PVK matrix, leading to a positive magnetocurrent or a negative magnetoresistance in the Ir(ppy)₃+PVK composite. Therefore, the excited states can contribute to the magnetoresistance through dissociation in organic semiconducting materials. On the other hand, the Ir(ppy)₃ reduced enhancement of magneto-photocurrent suggests that an external magnetic field has less effects on the density of singlet states upon

dispersing Ir(*ppy*)₃ in the composite. This can be attributed to the increase of spin-orbital coupling of PVK matrix caused by Ir(*ppy*)₃ dopant. The increase of spin-orbital coupling can reduce the effects of magnetic field on the singlet-to-triplet ratio. As a consequence, the modification of spin-orbital coupling can affect the density of dissociated charge carriers and the resultant magnetoresistance in organic materials.

CONCLUSION

In summary, mixing a strong-spin-orbital-coupling molecule and a weak-spin-orbital-coupling polymer can lead to a substantial tuning of magnetoresistance and MFE. The underlying mechanism of tuning magnetoresistance and MFE relies on the energy transfer of excited states between the two components and the modification of spin-orbital coupling in Ir(*ppy*)₃ doped polymer composite. The magneto-photocurrent implies that the dissociation of excited states

contribute to the magnetoresistance in organic semiconducting materials. The energy transfer and modification of spin-orbital coupling can change the overall singlet or triplet ratio and consequently affect the yield of dissociated charge carriers. Furthermore, the dissociated charge carriers form built-in electric field and contribute to the magnetoresistance in organic semiconducting materials. As a result, mixing a strong-spin-orbital-coupling molecule and a weak-spin-orbital-coupling polymer presents a new pathway to tune magnetic field effects (magnetoresistance and MFE) through energy transfer and intermolecular spin-orbital interaction.

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