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Changing inter-molecular spin-orbital coupling for generating magnetic field effects in phosphorescent organic semiconductors

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Phosphorescent organic semiconductors normally show negligible magnetic field effects in electronic and optic responses. These phenomena have been generally attributed to strong spin-orbital coupling which can dominate internal spin-dephasing process as compared with applied magnetic field. This paper reports both positive and negative magnetocurrents from phosphorescent organic semiconductors through dissociation and charge-reaction channels when the intermolecular spin-orbital coupling is changed based on materials mixing. Our experimental results indicate that inter-molecular spin-orbital coupling is essentially responsible for the generation of magnetic field effects in phosphorescent organic semiconductors. © 2012 American Institute of Physics. [doi:10.1063/1.3673561]

Organic semiconductors can be divided into fluorescent and phosphorescent types based on singlet and triplet emission. It has been experimentally found that fluorescent organic semiconductors can show magnetic responses in electrical current^{1–3} to externally applied magnetic field (<100 mT), leading to magnetocurrent (MC) with nonmagnetic electrodes. However, phosphorescent organic semiconductors always exhibit negligible MC due to strong spin-orbital coupling (SOC).^{4–6} Based on electrical drifting theory, the MC can be generated by magnetically changing charge mobility or density, forming mobility-based MC (Refs. 7–12) or density-based MC.^{1,13–15} In mobility-based MC, organic semiconductors need to have spin-spin interaction between charge carriers during transport. Applying magnetic field can disturb this spin-spin interaction through magnetic scattering and, consequently, modifies charge mobilities, generating mobility-based MC. However, experimental studies have found that organic semiconductors exhibit negligible mobility-based MC.^{16–19} These experimental findings imply that bulk organic semiconductors lack appreciable inter-charge spin interaction during transport at normal operation conditions. As a result, magnetically changing charge density becomes a practical method to generate MC, leading to density-based MC in fluorescent organic semiconductors.^{1,13–15} More specifically, there are two channels, namely, dissociation and charge-reaction, to generate density-based MC. In dissociation channel, an applied magnetic field can increase the singlet ratio in polaron-pair states through intersystem crossing.^{20,21} This can cause a positive MC through dissociation^{1,13–15} based on the experimental argument that singlets have larger dissociation rates due to stronger ionic properties in wavefunctions as compared to triplets.^{20,22} In charge-reaction channel, the excitons formed from injected

charge carriers can react with excessive charges, generating exciton-charge reaction, when they are within close proximity.^{23–25} The exciton-charge reaction can break excitons into free charges.^{26–28} Although both singlet and triplet excitons can be involved in charge reaction, triplet excitons can dominate charge reaction due to the long lifetimes.¹³ An applied magnetic field can perturb the spin interaction between a triplet exciton and a charge in triplet-charge reaction and, consequently, decreases the triplet-charge reaction-rate constant.²⁹ Therefore, charge reaction channel can lead to a negative MC. This paper reports the experimental studies on the effects of inter-molecular SOC, which comes from inter-molecular magnetic interaction between an electron spin of molecule A and a magnetic field from orbital current of molecule B when molecules A and B are placed within close proximity, on MC based on phosphorescent molecules.

The iridium heavy-metal complex molecule: tris(2-phenylpyridine) iridium (Ir(ppy)₃), and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT) were purchased from America Dye Source, Inc., and H. C. Starck, respectively, for experimental studies. The poly (methyl methacrylate) (PMMA) and polystyrene (PS), purchased from Sigma-Aldrich Co., were used as inert polymer matrices with different dielectric constants to host heavy-metal complex Ir(ppy)₃ molecules for the modification of inter-molecular SOC. The organic light-emitting diodes were fabricated with indium tin oxide (ITO) with 30 nm PEDOT on top and aluminum (Al) electrodes. The MC was measured by recording the change in the device current as a function of magnetic field at constant voltage. The MC amplitude was given by the relative change in electrical current caused by applied magnetic field based on $\frac{I_B - I_0}{I_0}$, where I_B and I_0 are the electrical injection currents with and without an applied magnetic field, respectively. The electron paramagnetic resonance (EPR) was measured by JES-FA200 Electron Spin Resonance

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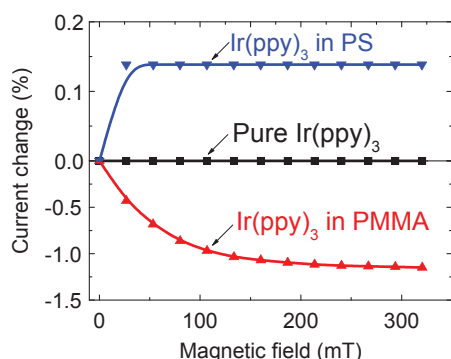


FIG. 1. (Color online) Magnetocurrents are shown for Ir(ppy)₃:PMMA and Ir(ppy)₃:PS composites with the weight ratio of 1:2 as compared to pure Ir(ppy)₃ molecules. The experimental error for magnetocurrent is about 0.01%.

Spectrometer from JEOL, Inc., working at X-band (9 GHz) to characterize inter-molecular SOC.

It can be seen in Fig. 1 that the heavy-metal complex Ir(ppy)₃ exhibits a negligible MC. This negligible MC can be commonly attributed to the strong SOC with the energy of $\sim 100 \mu\text{eV}$ (Ref. 30), which can largely dominate internal spin-dephasing processes as compared to applied magnetic field. However, positive and negative MC can be observed when the Ir(ppy)₃ molecules are dispersed into inert PS and PMMA matrices, respectively. The observed MC clearly suggests that dispersing Ir(ppy)₃ molecules into an inert polymer matrix can lead to a reduction on the SOC of heavy-metal complex molecules. It should be noted that the Ir(ppy)₃ molecules have a strong orbital magnetic field³¹ generated by orbital current due to large atomic number of Ir. This strong orbital magnetic field can interact with π electron spins not only within a single molecule but also between adjacent molecules, generating both intra-molecular and inter-molecular SOC, as schematically shown in Fig. 2. As a result, the overall SOC for heavy-metal complex molecules consists of intra- and inter-molecular components (Eq. (1)),

$$\hat{H}_{so} = \hat{H}_{intra} + \hat{H}_{inter} = (\xi_{intra}\hat{L}_{intra} + \xi_{inter}\hat{L}_{inter}) \cdot \hat{S}, \quad (1)$$

where \hat{L} and \hat{S} are the orbital field and electron spin, respectively. ξ is the SOC constant. We know that the intra-molecular \hat{H}_{intra} is solely dependent of intra-molecular magnetic interaction between orbital field and π electrons in a given molecule. Therefore, once molecular structure is determined, the \hat{H}_{intra} becomes a fixed quantity. However, the inter-molecular \hat{H}_{inter} depends on not only orbital field but also inter-molecular distance. As a consequence, changing inter-molecular distance can largely tune inter-molecular SOC, leading to a modification on overall SOC for phosphorescent organic semiconductors. On contrast, the inter-molecular SOC becomes negligible in fluorescent molecules where orbital field is weak.³²

The decrease in current with magnetic field in Fig. 1 indicates that the triplet-charge reaction is a dominant channel in the generation of density-based MC in the Ir(ppy)₃:PMMA system. On contrast, the increase in current with magnetic field implies that the dissociation is a main channel in the generation of density-based MC in the Ir(ppy)₃:PS system. Clearly, the PMMA and PS matrices lead to negative and positive MCs, respectively, for the phosphorescent Ir(ppy)₃ molecules. It is known that the PMMA and PS have different

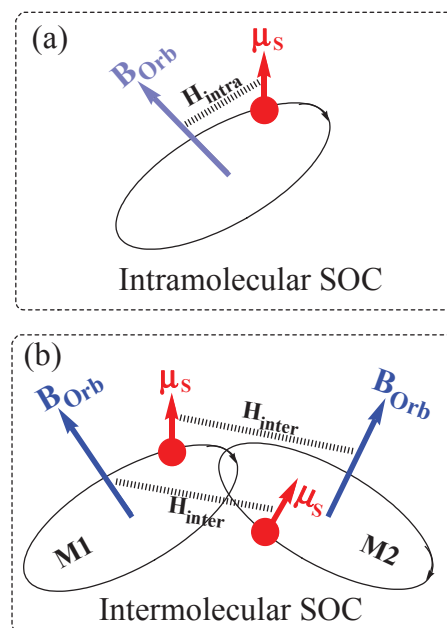


FIG. 2. (Color online) (a) Intra-molecular SOC generated by interaction between a π electron spin μ_s and an orbital magnetic field B_{Orb} located within a single molecule. (b) Inter-molecular SOC generated by interaction between a π electron spin μ_s and an orbital magnetic field B_{Orb} located on adjacent molecules. M_1 and M_2 represent two adjacent Ir(ppy)₃ molecules.

dielectric constants³³ ($\epsilon_{PMMA} = 3.6$, $\epsilon_{PS} = 2.5$). Dielectric matrix can function as a local electric polarization to affect both the dissociation in polaron-pair states and the charge reaction in excitonic states in the generation of density-based MC. Therefore, both dissociation and charge reaction channels can be affected by matrix dielectric constant. On one hand, increasing matrix dielectric constant can increase the dissociation rates for both singlet and triplet polaron pairs through Onsager process^{34,35} by changing the Onsager radius ($R_c = \frac{e^2}{4\pi\epsilon_0\epsilon kT}$). This minimizes the difference between singlet and triplet dissociation yields in polaron pairs. Therefore, increasing the matrix dielectric constant can then decrease the effects of intersystem crossing on the dissociation in polaron-pair states. As a consequence, the dissociation channel of generating positive MC becomes less important upon increasing matrix dielectric constant. On the other hand, the excitonic states are essentially metal-to-ligand charge-transfer states in the Ir(ppy)₃ molecules.^{36,37} The charge-transfer states are more sensitive to local electrical polarization due to their stronger ionic wavefunctions as compared to Frenkel excitons. Therefore, increasing the matrix dielectric constant can enhance the ionic properties of wavefunctions of charge-transfer states through electrical polarization. This can increase the Coulomb interaction between an excitonic state and a charge in the generation of triplet-charge reaction. As a result, the triplet-charge reaction channel of generating negative MC becomes more important upon increasing the matrix dielectric constant. It can be clearly seen in Fig. 1 that the PMMA and PS matrices with higher and lower dielectric constants correspond to negative and positive MCs, respectively, by enhancing triplet-charge reaction and dissociation in the PMMA:Ir(ppy)₃ and PS:Ir(ppy)₃ composites when the inter-molecular SOC is weakened through molecular dispersion.

Now we further examine the inter-molecular SOC when the phosphorescent Ir(ppy)₃ molecules are dispersed in an

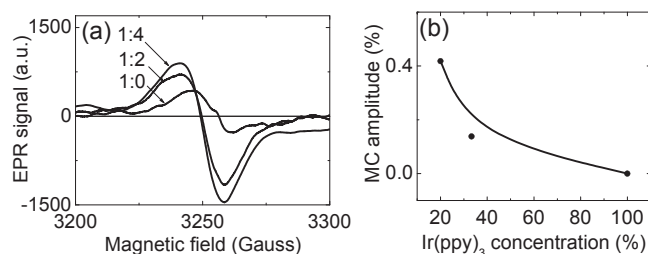


FIG. 3. (a) EPR spectra for Ir(ppy)₃:PS composites with weight ratios of 1:2 and 1:4 as compared to pure Ir(ppy)₃. (b) Magnetocurrent amplitude as a function of Ir(ppy)₃ concentration in Ir(ppy)₃:PS composite. The current density for MC measurements was adjusted to be 100 mA/cm².

inert polymer matrix. We know that dispersing the Ir(ppy)₃ molecules into an inert polymer matrix can, in general, form three phases: separated Ir(ppy)₃ molecules, aggregated Ir(ppy)₃ molecules, and continuous polymer morphologies in polymer:Ir(ppy)₃ composites. For separated Ir(ppy)₃ molecules, changing molecular concentration can directly modify the inter-molecular SOC by varying the inter-molecular distances. For the aggregated Ir(ppy)₃ molecules, changing molecular concentration can change their domain sizes and, consequently, affects the sum of inter-molecular SOC components within a given domain. Based on theoretical estimation,³⁸ we can suggest that the summation of individual inter-molecular SOC components can gradually increase the entire inter-molecular SOC for a single domain before reaching saturation with the domain size of ~ 5 nm. Overall, it can be argued that changing molecular concentration can conveniently tune the inter-molecular SOC through separated and aggregated molecules in the Ir(ppy)₃:polymer composite. Here, we use EPR to characterize the inter-molecular SOC upon Ir(ppy)₃ dispersion in an inert polymer matrix. Fig. 3(a) shows that the EPR peak clearly shifts to a lower magnetic field after the Ir(ppy)₃ molecules are dispersed in an inert polymer matrix. This EPR peak shift indicates that the g factor decreases with increasing Ir(ppy)₃ concentration after the Ir(ppy)₃ molecules are dispersed into the PS matrix. The decrease of g factor of the EPR spectrum suggests that inter-molecular SOC is reduced with decreasing the Ir(ppy)₃ concentration in the Ir(ppy)₃:PS composite. Therefore, the EPR result confirms that dispersing Ir(ppy)₃ molecules in an inert polymer matrix can lead to a reduction in inter-molecular SOC for phosphorescent organic molecules. Furthermore, decreasing the inter-molecular SOC can increase the MC amplitude in the PS:Ir(ppy)₃ composite (Fig. 3(b)). As a result, changing the inter-molecular SOC can essentially tune a density-based MC in phosphorescent organic semiconductors.

In summary, the strong SOC from heavy-metal complex structures leads to negligible magnetic field effects in phosphorescent organic semiconductors. We find that dispersing phosphorescent Ir(ppy)₃ molecules into an inert polymer matrix can generate charge density-based MC. This experimental observation suggests that inter-molecular SOC is a key parameter to generate magnetic field effects in phosphorescent organic semiconductors. The EPR results confirm that dispersing Ir(ppy)₃ molecules into an inert polymer matrix can reduce the inter-molecular SOC. Clearly, our experimental studies indicate that changing inter-molecular SOC forms an effective mechanism to tune magnetic field effects in

heavy-metal complex molecules. Furthermore, changing matrix dielectric constant can switch the density-based MC between dissociation and charge reaction channels, tuning the MC between positive and negative values in phosphorescent organic semiconductors.

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