

Magnetic-Field Effects in Organic Semiconducting Materials and Devices

By Bin Hu,* Liang Yan, and Ming Shao

It has been experimentally discovered that a low magnetic field (less than 500 mT) can substantially change the electroluminescence, photoluminescence, photocurrent, and electrical-injection current in nonmagnetic organic semiconducting materials, leading to magnetic-field effects (MFEs). Recently, there has been significant driving force in understanding the fundamental mechanisms of magnetic responses from nonmagnetic organic materials because of two potential impacts. First, MFEs can be powerful experimental tools in revealing and elucidating useful and non-useful excited processes occurring in organic electronic, optical, and optoelectronic devices. Second, MFEs can lead to the development of new multifunctional organic devices with integrated electronic, optical, and magnetic properties for energy conversion, optical communication, and sensing technologies. This progress report discusses magnetically sensitive excited states and charge-transport processes involved in MFEs. The discussions focus on both fundamental theories and tuning mechanisms of MFEs in nonmagnetic organic semiconducting materials.

1. Introduction

Magnetic-field effects (MFEs) are defined as changes caused by an applied magnetic field in the electroluminescence, photoluminescence, photocurrent, and electrical-injection current in organic semiconducting materials. The amplitude of the MFEs is given by the relative change in percentage

$$\text{MFE} = \frac{S_B - S_0}{S_0} \times 100\%$$

where S_B and S_0 are the signal intensities with and without an applied magnetic field. In the 1960s and 1970s, a low magnetic field (<500 mT) was observed to considerably change a number of properties in organic semiconducting materials.^[1–3] These MFEs most probably occur when the excited states involved in photoluminescence, electroluminescence, and photocurrent change their dynamic processes when a magnetic field is applied. An excited state is defined as an electron–hole (e–h) pair in organic semiconductors. Excited states can be divided into intermolecular

(namely polaron pairs), when electron and hole are located on different molecules, and intramolecular (namely excitons), when the electron and hole are located in a single molecule. When electron-spin multiplicities are considered, the electron and hole can have antiparallel and parallel spin orientations in e–h pairs, leading to singlet and triplet inter- and intramolecular excited states. Two internal interactions can occur between electrons and holes in an excited state, namely long-range Coulombic attraction $((1/4\pi\epsilon)(e^2/r))$ and short-range spin–exchange interaction $(J_0 e^{(-r/2L)})$, where r is the e–h separation distance, e the electron charge, ϵ the dielectric permittivity, and L and J_0 are the charge location radius and coupling matrix, respectively, for a donor–acceptor pair at Van der Waals separation. The Coulombic attraction accounts for the binding energy between the electron and

hole in an excited state, while the spin–exchange interaction generates an energy difference between singlet and triplet states. In general, MFEs are intimately tied to spin configuration, spin correlation, and spin flip during e–h pair formation and post-development in excited states.

Notably, photophysics studies of radical-pair formation have provided a fundamental foundation toward the understanding of spin physics of excited states involved in MFEs.^[4–7] In particular, it was found that the radical-pair formation undergoes spin-coherent and spin-random captures, namely germinate and nongerminate recombination, respectively, under photoexcitation.^[8–12] The germinate recombination tends to form singlet radical pairs due to coherent electron and hole spin precessions. However, the nongerminate recombination yields both singlet and triplet radical pairs with statistic ratios of 1:3 due to random-spin capture. The singlet and triplet radical pairs can be mutually converted in both germinate and nongerminate recombination when the spin-flip mechanism is present due to hyperfine coupling (HFC) or spin–orbital coupling (SOC). Essentially, the radical pairs can be, in a first-order approximation, treated as intermolecular excited states: polaron pairs. As a result, the spin physics of radical pairs can provide a guideline for the development of MFEs based on spin motion and spin-dependent e–h capture. Figure 1 shows that the electron and hole spin polarizations coherently precess around both internal nuclear magnetic field and external magnetic field with different orientations, to form singlet and triplet excited states at e–h

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captures. In essence, the e–h spin–exchange interaction is accountable for the coherent spin orientations and precessions within an e–h pair. There are two pathways to change singlet and triplet ratios. First, changing electron and hole coherent spin orientations can directly affect the e–h spin-pairing configurations, and the resultant singlet and triplet ratios at formation. Second, perturbing the spin correlation between electrons and holes can lead to a mutual conversion between singlet and triplet excited states, and redistribute the singlet and triplet populations. Through these two pathways, an external magnetic field can, in principle, change photoluminescence, electroluminescence, electrical current, and photocurrent by varying the singlet and triplet ratios involved in excited processes and charge transport. Recently, MFEs have drawn strong interest toward the development of organic spintronics^[13,14] in which electronic, optical, and magnetic properties can be integrated for the development of next-generation semiconductor devices for energy conversion, sensing, and optical-communication applications. It is clear that MFEs will not only open an area for nonmagnetic organic semiconducting materials to be used for spintronics, they will also provide powerful experimental tools for the “visualization” of intrinsic useful and non-useful excited processes in organic optoelectronic devices.

1.1. Electron and Hole Capture Toward Formation of Excited States

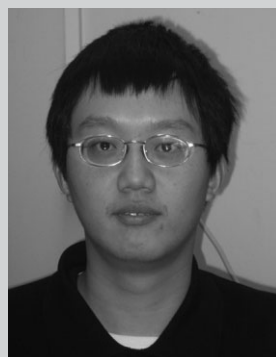
When an electron is captured with a hole within their Coulombic capture radius, both inter- and intramolecular e–h pairs can be formed in organic semiconducting materials. The intermolecular e–h pairs are also named polaron pairs when the electron and hole are bound to different molecules, with the e–h separation distance being normally larger than 1 nm. The intramolecular e–h pairs are defined as Frenkel excitons when the electron and hole are bound to a single molecule, with the e–h separation distance smaller than 1 nm. It is further noted that the e–h separation distances have a broad distribution in polaron pairs, with long, intermediate, and contact distances. However, the e–h separation distances in excitons are well defined within a narrow distribution. There are two major differences between polaron pairs and excitons due to their difference in e–h separation distance. First, polaron pairs have lower binding energies as compared to excitons. Second, the singlet–triplet energy difference ΔE_{ST} caused by spin-exchange interactions is much smaller in polaron-pair states than in excitonic states. The ΔE_{ST} can become negligible with increasing e–h separation distances in polaron-pair states. In excitonic states, ΔE_{ST} can be significantly large when the electron and hole are closely located in a single molecule (see Fig. 2).

It is known that the excited states are a critical issue in the determination of MFEs. In essence, electron and hole capture determine the formation of excited states through intercharge electrical and spin interactions. It is noted that the electron and hole capture depend on the Coulombic capture radius ($R_C = (e^2/\epsilon KT)$) and the physical contact time, where R_C is the Coulombic capture radius, K the Boltzmann constant, and T the temperature. When electrons and holes are moving in an organic semiconducting material, the Coulombic capture radius is



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determined by the electrical screening resulting from the dielectric-field background. On the other hand, the electron and hole contact time is dependent on charge mobility. Therefore, internal dielectric field and charge mobility can affect the

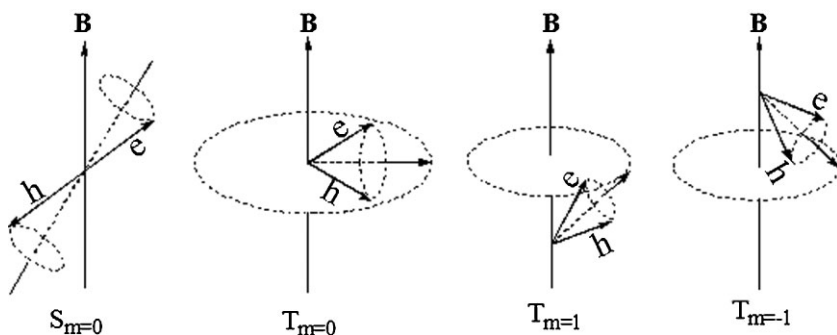


Figure 1. Electron and hole spin precessions in an external magnetic field **B** for singlet and triplet e-h pairs.^[15]

formation of excited states and consequently the amplitude of resultant MFEs.

It is noted that the electron and hole spin polarizations precess around nuclear spin or the magnetic field generated by orbital current. The correlation between electron and hole precessions determines that both singlet and triplet e-h pairs can be formed at e-h capture. The random recombination of electron and hole spin polarizations statistically yields the singlet and triplet ratios of 1:3 in organic materials.^[15–22] An external magnetic field can induce an additional precession for the combined electron and hole spin polarizations (Fig. 1).^[15] In particular, an applied magnetic field can perturb the electron and hole precession rates and partially destroy the coherent relationship between electron and hole spin precessions.^[23–26] This can lead to a mutual conversion between overall singlet and triplet excited states. As a consequence, an external magnetic field may modify the singlet and triplet ratios by perturbing the coherent electron and hole precessions during e-h recombination.

1.2. Intersystem Crossing (ISC) in Inter- and Intramolecular Excited States

After randomly spin-orientated electrons and holes are captured based on coherent spin precessions to generate singlet and triplet excited states, the HFC or SOC forms a mechanism to flip the electron-spin orientation based on magnetic scattering, and

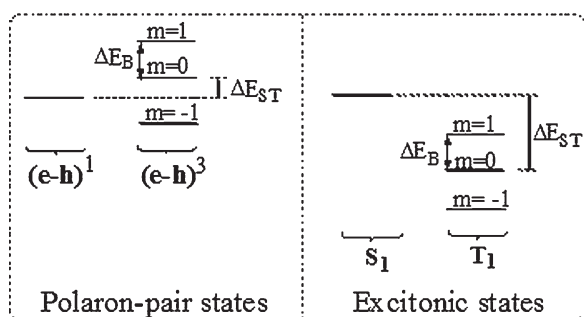


Figure 2. Energy levels for polaron-pair and excitonic states in an external magnetic field. ΔE_{ST} and ΔE_B are the singlet-triplet energy difference and magnetic splitting energy, respectively. $(e-h)^1$ and $(e-h)^3$ are singlet and triplet polaron-pair states. S_1 and T_1 are lowest singlet and triplet excitonic states.

causes an ISC between singlet and triplet excited states. In general, the internal magnetic interaction from HFC or SOC can lead to an ISC in both polaron-pair and excitonic states, with rates K_{ISCP} and K_{ISCE} , respectively. On the other hand, the internal magnetic interaction resulting from HFC or SOC can split three degenerate triplet energy levels with spin angular momentums of $m=0$, $m=+1$, and $m=-1$, leading to internal Zeeman splitting and consequently changing the energy difference between singlet and subtriplet levels. Clearly, the internal magnetic interaction has two opposite effects: increasing and decreasing

ISC through spin flip and internal Zeeman splitting, respectively. The observed ISC is determined essentially by the competition between these two opposite effects. Therefore, there are only two parameters that matter in the determination of ISC rate: i) singlet-triplet energy difference, ΔE_{ST} , and ii) internal magnetic-interaction-induced singlet and triplet mixing.

When an external applied magnetic field is comparable to the internal magnetic interaction in strength, an external magnetic field can further increase the triplet splitting (namely, external Zeeman effect), and consequently modifies the singlet-triplet ISC. In principle, magnetic-field-dependent singlet and triplet ratios can consist of two contributions, from spin-dependent formation of excited states and from the field-sensitive ISC. This leads to formation-based and ISC-based MFEs, respectively, in organic semiconducting materials. There are two necessary conditions, namely magnetic requirements, for the ISC to be magnetic-field dependent (Scheme 1). First, the external Zeeman splitting ΔE_{EZ} must be larger than the internal Zeeman splitting ΔE_{IZ} . Second, the external Zeeman splitting should be comparable to the singlet-triplet energy difference ΔE_{ST} caused by the e-h separation-distance-dependent spin-exchange interaction.

Based on these magnetic requirements, it is obvious that an external magnetic field can change the ISC rate (K_{ISCP}) in polaron-pair states, but has little influence on the ISC rate (K_{ISCE}) in excitonic states. Therefore, K_{ISCP} and K_{ISCE} can be named field-dependent and -independent parameters, respectively. Clearly, the field-dependent K_{ISCP} can lead to magnetic-field-dependent singlet and triplet ratios in polaron-pair states. We should note that the field-dependent K_{ISCP} can also result in magnetic-field-dependent singlet and triplet exciton ratios when the polaron pairs evolve into excitons under electrical excitation (Fig. 3). However, an external magnetic field has little influence on the singlet and triplet exciton ratios through ISC in excitonic states when polaron-pair states are absent under photoexcitation. As a result, adjusting the e-h separation distance in excited states can change the magnetic-field dependence of ISC, and consequently determines whether ISC-based MFEs can be observed in organic semiconducting materials.

It should be further noted that changing the e-h capture distance essentially changes the relative contributions from spin-

$$\begin{aligned} \Delta E_{EZ} &> \Delta E_{IZ} \\ \Delta E_{EZ} &> \Delta E_{ST} \end{aligned}$$

Scheme 1. Magnetic requirements for the realization of MFEs.

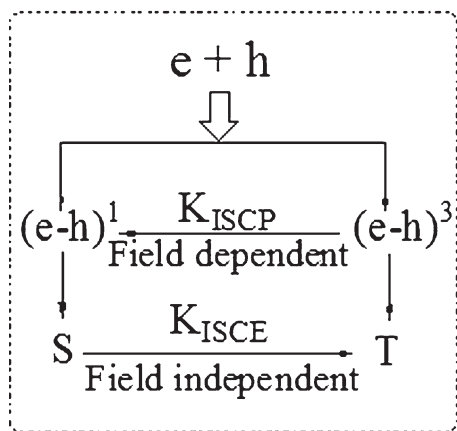


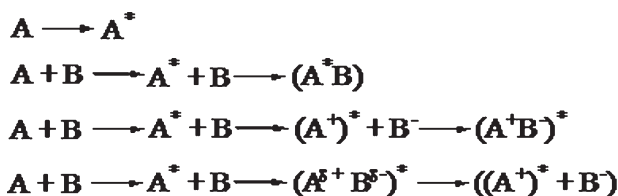
Figure 3. Intermolecular excited states (polaron pairs) and intramolecular excited states (excitons) with magnetic-field-dependent and -independent ISC K_{ISCP} and K_{ISCE} , respectively. $(e-h)^1$ and $(e-h)^3$ represent singlet and triplet polaron pairs. S and T are singlet and triplet excitons.

dependent formation and field-dependent ISC to MFEs in organic semiconducting materials. At short $e-h$ capture distances, the spin-dependent formation can be mainly accountable for MFEs, because ISC becomes field insensitive, according to Scheme 1. However, at large $e-h$ capture distances, field-dependent ISC becomes dominant in MFEs. Therefore, the interplay between formation-based and ISC-based MFEs depends on the $e-h$ capture distance in organic semiconducting materials. This presents the opportunity of tuning MFEs by changing the $e-h$ capture distance.

2. MFEs on Photoluminescence (MFE_{PL})

Photoluminescence results from radiative emission of photon absorption-generated excited states. In principle, both intra- and intermolecular excited states can be generated with singlet and triplet configurations by photon absorption in organic semiconducting materials (Scheme 2).

The intramolecular excited states are essentially Frenkel excitons with electrons and holes located in a single molecule. In contrast, the intermolecular excited states can consist of exciplexes, charge-transfer complexes, and donor-acceptor pairs. The exciplex is generated when an excited molecule A^* is coupled with an unexcited molecule B to form an intermolecular excited



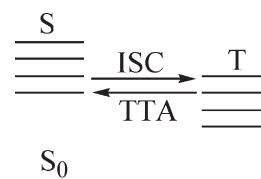
Scheme 2. Schematic formation for intramolecular excitons (A^*), intermolecular exciplexes (A^*B), intermolecular charge-transfer complexes ($(A^+B^-)^*$), and donor-acceptor pairs [$(A^+)^* + B^-$]. A and B are two different molecules. The superscript $*$ indicates an excited state. The A^+ and B^- are positive and negative molecules.

state: an excited “complex molecule (A^*B).” If A and B are similar molecules, this intermolecular excited state is called an excimer. The charge-transfer complex is formed when charge transfer occurs within an exciplex. The formation of a charge-transfer complex includes two steps: i) charge transfer between the excited molecule A^* and the unexcited molecule B , to generate $(A^+)^*$ and B^- , and ii) coupling between $(A^+)^*$ and B^- to form an excited complex $(A^+B^-)^*$. The donor-acceptor pair is usually produced in less-polar media after charge transfer occurs between the photoexcited molecule A and the unexcited molecule B . In particular, intermolecular excited states can be formed when the two sufficient conditions are satisfied: intramolecular excitation and intermolecular dipole-dipole interaction. In general, an external magnetic field can change the singlet and triplet ratios through formation and intersystem conversion, leading to MFEs in photoluminescence based on intra- and intermolecular excited states.

2.1. Intramolecular Excited States in MFE_{PL}

Due to the spin-selection rule, photon absorption can only generate singlet excitons by exciting an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) in a single molecule based on photon absorption.^[27] There are two spin-dependent processes: ISC and triplet-triplet annihilation (TTA), which can redistribute the singlet and triplet populations in excitonic states (Scheme 3). If an applied magnetic field can perturb the ISC or TTA, MFEs of photoluminescence can be expected. We note that the singlet-triplet energy difference ΔE_{ST} in excitonic states is normally between 0.5 and 1.5 eV in organic materials.^[27,28] This spin-exchange interaction-induced ΔE_{ST} is much larger than the external Zeeman splitting ΔE_{EZ} , dissatisfying the two magnetic requirements (Scheme 1) to activate MFEs. As a consequence, an external magnetic field cannot perturb the singlet-triplet ISC in intramolecular excited states (Frenkel excitons). This leaves TTA as a possible channel to generate MFEs based on intramolecular excited states under photoexcitation.

Two triplet excitons can interact through electrical dipole-dipole interaction and consequently annihilate into one singlet excited state.^[29–31] This process is called TTA, and can be described by bimolecular reaction dynamics.^[32] Particularly, the TTA rate is quadratically proportional to the triplet density. The light emission from the singlet excitons generated from TTA is named delayed fluorescence.^[33–35] In addition, the TTA must satisfy both spin momentum and energy conservation requirements. In general, there are two particular processes involved in TTA in organic materials: $T_{m=0} + T_{m=0} \rightarrow S$ and



Scheme 3. ISC and triplet-triplet annihilation. S_0 is ground state. S and T are singlet and triplet excitonic states.

$T_{m=\pm 1} + T_{m=\pm 1} \rightarrow S$. The former can occur through exchange interactions without activation of the spin-flip mechanism. The latter requires an effective spin-flip mechanism induced by HFC or SOC. In principle, a low magnetic field can reduce TTA and generate a negative effect in delayed fluorescence by reducing spin flip or weakening the singlet character of the triplet states involved in TTA (Merrifield theory^[2,36]). It was observed from time-resolved photoluminescence that the lifetime of TTA-generated delayed fluorescence increases with magnetic field.^[1] The intensity measurements have also shown that the delayed fluorescence can decrease considerably with increasing applied magnetic field in Anthracene crystals.^[2,36–38] These experimental results clearly indicate that an external magnetic field can reduce the TTA, leading to a negative MFE_{PL} in organic materials. However, we have measured the steady-state photoluminescence from organic semiconducting molecules and polymers with weak, intermediate, and strong SOC strengths at different temperatures as a function of magnetic field.^[39–42] The steady-state photoluminescence shows unappreciable dependence of magnetic fields up to 1 T.

It is further noted that the photoexcited singlet and triplet excitons can partially dissociate into free electrons and holes due to intermolecular dipole–dipole interaction, and the dissociated electrons and holes can recombine to form excitons with singlet and triplet configurations due to intercharge Coulombic attraction. An external magnetic field may affect the dissociation and recapture, and consequently change the singlet and triplet ratios, in reformed excitons, leading to MFEs of photoluminescence based on recombination processes. In general, there are three major channels for excitons to release their energies: radiative emission, nonradiative multiphonon emission, and dissociation. The radiative excitonic emission gives rise to prompt photoluminescence that can be either fluorescence, if singlets emit, or phosphorescence, if triplets emit. The nonradiative multiphonon emission transfers excitonic energies to chemical-bond vibrations to produce heat. The dissociation of excitons is the process responsible for generating free electrons and holes through intermolecular interactions. The dissociation can occur via either the Poole–Frenkel process,^[43] due to field-assisted thermal ionization, or the Onsager process,^[44] due to internal Coulombic interactions in organic materials. The common feature the Poole–Frenkel and Onsager models is that the electrical field reduces the energy required to Coulombically dissociate e–h pairs. The difference between the models is that the thermal diffusion of hot excitons is considered in the Onsager model for dissociation. The dissociation of photoexcited excitons were further studied both experimentally and theoretically in the Noolandi^[45–48] and Arkhipov^[49–52] models. On the other hand, the dissociated electrons and holes can recombine to form intermolecular e–h pairs followed by the relaxation into intramolecular Frenkel excitons due to Coulombic attraction. The recombination of dissociated electrons and holes can be approximately treated as the recombination of photoexcitation-generated radical pairs. As a result, the recombination of dissociated electrons and holes undergoes germinate and nongerminate processes. It can be assumed that the recombination of dissociated electrons and holes generates singlet excited states (in the germinate process, due to coherent spin polarizations from their parent precursors) or both singlet and

triplet excited states with 1:3 ratio (in a nongerminate process, due to random spin polarizations) according to the spin-physics theory of radical pairs.^[4–7] In addition, the ISC is also applicable to both germinate and nongerminate processes. When the intermolecular excited states are relaxed into intramolecular excited states (Frenkel excitons), charge-recombination photoluminescence can be expected. The light emission from the recombination of dissociated electrons and holes is defined as charge recombination photoluminescence. In particular, an external magnetic field may increase the $I_{\text{Recombination}}$ by changing the singlet and triplet ratios through ISC, leading to a positive magnetic-field effect in charge-recombination photoluminescence.

In general, the photoluminescence intensity (I_{PL}) can consist of prompt excitonic (I_{Exciton}) and charge-recombination ($I_{\text{Recombination}}$) components,^[53] given by

$$I_{\text{PL}} = I_{\text{Exciton}} + I_{\text{Recombination}} \quad (1)$$

Combining the contributions from prompt and charge-recombination photoluminescence, four types of MFEs of photoluminescence can be expected: positive, negative, positive then negative, and negative then positive changes based on intramolecular excited states in organic materials. However, we examined organic semiconducting materials with weak, intermediate, and strong SOC strengths, and found that steady-state photoexcitation generates unappreciable MFEs of photoluminescence. This experimental result suggests that i) an external magnetic field cannot change the ISC in excitonic states, ii) the delayed-fluorescence component generated by TTA is much smaller than the steady-state photoluminescence component, and iii) the recapture of dissociated electrons and holes does not generate a considerable charge-recombination photoluminescence component in common organic semiconducting materials.

2.2. Intermolecular Excited States in MFE_{PL}

Intermolecular excited states, including excimers, exciplexes, charge-transfer complexes, and donor–acceptor pairs, can be, in principle, formed in solid or liquid states in organic materials. In principle, the formation of intermolecular excited states is determined by the internal-electrical-polarization field background and the intermolecular electrical dipole–dipole interaction. In solid state, the formation of intermolecular excited states involves energy transfer and migration of excited states between different molecules. In the liquid state, however, the molecular motion mainly accounts for the formation of intermolecular excited states. The intermolecular excited states can offer significant tuning properties in light-emission color and intensity through material selection and mixing for solid-state lighting, lasing, and sensing applications. In particular, the relatively large e–h separation distances can lead to a situation in which the two magnetic requirements (Scheme 1) can be satisfied to activate MFEs in intermolecular excited states.

Intermolecular excited states can be essentially treated as radical pairs formed through germinate and nongerminate processes in spin physics. Therefore, intermolecular excited

states can be formed with singlet and triplet configurations. There are two important interactions occurring within an intermolecular excited state: long-range Coulombic attraction, from intermolecular electrical dipole–dipole interactions, and short-range internal magnetic interactions, from HFC and SOC. The long-range Coulombic attraction is responsible for the binding energies in intermolecular excited states. The internal electrical polarization field can significantly influence the formation of excimers, exciplexes, charge-transfer exciplexes, and donor–acceptor pairs by perturbing the intermolecular Coulombic attraction. The short-range magnetic interaction forms a mechanism to flip electron spins, and it causes internal Zeeman splitting of triplet intermolecular excited states, consequently generating ISC between singlets and triplets in intermolecular excited states. Because SOC requires large penetration of π electrons into the magnetic field generated by molecular orbital current, HFC is mainly accountable for the internal magnetic interaction and ISC in intermolecular excited states when heavy-metal complex structures are absent. Intermolecular excited states can also experience radiative emission, nonradiative multiphonon emission, and charge dissociation to release their energies. When an external magnetic field changes the singlet and triplet ratios in intermolecular excited states, MFEs can then be observed in excimers,^[54–56] exciplexes,^[9–12,57–59] charge-transfer complexes,^[60–64] and donor–acceptor pairs^[65] based on the fact that singlets and triplets have different contributions to radiative emissions and intermolecular interactions in excited states, due to their different spin configurations, involved in electronic transitions, and ionic natures, involved in intermolecular electrical dipole interactions.

Magnetic field-dependent singlet and triplet ratios in intermolecular excited states can be, in general, realized through three possible channels: spin-dependent formation, field-sensitive ISC, and deviation of Lande's g factors. First, spin-dependent formation can yield negative magnetic-field effects of photoluminescence, if an external magnetic field can influence spin polarizations between the electron in the excited molecule and the hole in unexcited molecule toward triplet formation with a parallel-spin configuration. However, it can be both experimentally and theoretically suggested that a low magnetic field cannot alter the spin polarizations in nonmagnetic semiconducting materials. Second, an external magnetic field can cause an external Zeeman splitting on triplet intermolecular excited states, and thus change the ISC if the external Zeeman splitting is greater than the internal Zeeman splitting. Third, the g factors can be differently deviated from the g factor of free electrons for positive and negative precessing polarons due to different Larmor precession frequencies, forming Δg mechanism for MFEs.^[66] This implies that an external magnetic field can shift the population from triplets to singlets in intermolecular excited states.^[66] Since Δg is usually about 10^{-2} – 10^{-3} for organic radicals,^[67,68] the Δg mechanism may be effective only under strong magnetic fields ($B > 1\text{ T}$). As a result, field-dependent ISC becomes an effective mechanism for MFEs in intermolecular excited states under photoexcitation, based on the satisfaction of two magnetic requirements (Scheme 1). The sufficient external Zeeman splitting can generate two possible outcomes for ISC in intermolecular excited states (Fig. 4). For the states with relatively small e–h separation distances, the large singlet–triplet energy

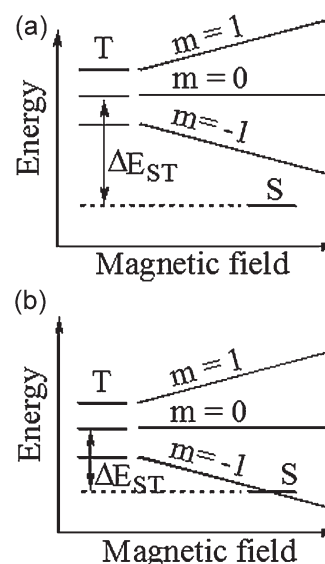


Figure 4. External Zeeman splitting effects on ISC in intermolecular polaron-pair states. a) Polaron-pair states with large singlet–triplet energy difference ΔE_{ST} due to short e–h separation distance. b) Polaron-pair states with small singlet–triplet energy difference ΔE_{ST} due to long e–h separation distance.

difference caused by the spin–exchange interaction can be much larger than the Zeeman splitting. Applying a magnetic field can reduce the energy gap between singlet and triplet ($m = -1$, Fig. 4a). When the ISC is considered as a phonon-assisted transition from $T_{m=-1}$ to S , reducing the energy gap facilitates the ISC, and consequently increases the singlet ratio. As a result, magnetic field-dependent ISC can yield an increase in photoluminescence, leading to positive magnetic-field effects in the intermolecular excited states, with relatively short e–h separation distances. When the e–h separation distance is relatively large, continuously increasing the external Zeeman splitting can cause an intersect point between singlet and triplet ($m = -1$) levels, forming a level-crossing point (Fig. 4b). As a consequence, the ISC would show a nonmonotonic change: first increase and then decrease, with continuously increasing magnetic field before and after the level-crossing point, respectively. This implies that a magnetic-field-dependent ISC gives rise to positive and then negative MFEs in the intermolecular excited states with relatively large e–h separation distances. Nevertheless, the type of MFE_{PL} that can be observed depends on the internal magnetic interaction resulting from HFC and SOC and on the singlet–triplet energy difference ΔE_{ST} resulting from the spin–exchange interaction determined by the e–h separation distance. Furthermore, the MFE_{PL} can be used as an experimental tool to explore the spin-dependent e–h formation, charge dissociation and recombination, and magnetic-field-dependent ISC for intermolecular excited states in organic semiconducting materials.

Adjusting the e–h separation distance through material mixing can readily modify the MFE in intermolecular excited states. This is because changing the e–h separation distance can affect both the singlet–triplet energy difference ΔE_{ST} and the intermolecular magnetic interaction. Specifically, increasing the e–h separation

distance decreases the singlet–triplet energy difference ΔE_{ST} through spin–exchange interaction (Fig. 5a). On the other hand, increasing the e–h separation distance dramatically reduces the SOC, but has little influence on HFC, in intermolecular excited states. As a consequence, an external magnetic field can more largely perturb the ISC upon increasing the e–h separation distance, according to Scheme 1. This provides a mechanism to tune MFEs in intermolecular excited states under photoexcitation. It has been found that 2,5-bis(5-*tert*-butyl-2-benzoxazolyl)-

thiophene (BBOT) and *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) can form strong intermolecular excited states: exciplexes.^[69,70] Figure 5b shows the broad photoluminescence spectrum peaked at 525 nm from an intermolecular exciplex. The photoluminescences from BBOT and TPD are located at 440 and 400 nm, respectively. We can clearly see in Figure 5c that the photoluminescence from the intermolecular exciplex shows an appreciable positive magnetic-field effect, while the intramolecular excited states from TPD and BBOT exhibit independence of magnetic field in photoluminescence. Furthermore, decreasing the density of intermolecular exciplexes by adjusting chromophore (BBOT + TPD with 1:1 molar ratio) concentration in poly(methyl methacrylate) (PMMA) leads to an increase in the MFE_{PL} . Although magnetic-field-dependent ISC was only a possibility,^[71] this concentration-dependent MFE_{PL} confirms that adjusting the e–h separation distance through material mixing forms a convenient methodology to tune the MFE of photoluminescence using intermolecular excited states.

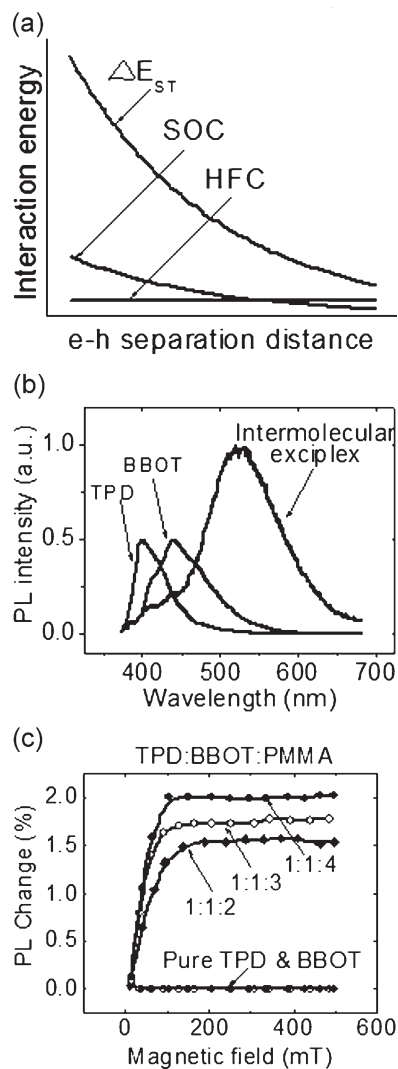


Figure 5. e–h separation-distance effects on the intermolecular exchange interaction, intermolecular magnetic interactions (HFC and SOC), and magnetic-field dependence of photoluminescence. a) Singlet–triplet energy difference ΔE_{ST} , SOC energy, and HFC energy.^[91] b) Photoluminescence spectra for intramolecular exciton emission from pure TPD and BBOT and for the intermolecular exciplex formed between TPD and BBOT in a PMMA matrix at the excitation wavelength of 360 nm. c) Photoluminescence dependence of the magnetic-field intermolecular exciplex formed between TPD and BBOT dispersed in a PMMA matrix (with molar ratios indicated) and photoluminescence independence of magnetic field for intramolecular excited states in TPD and BBOT.

3. MFEs on Photocurrent (MFE_{PC})

A low magnetic field was seen to be able to change the photocurrent of anthracene crystals.^[72–81] This phenomenon, named as MFEs on the photocurrent (MFE_{PC}), can be readily observed in organic semiconducting materials^[82–85] and also in organic-material complex systems^[60,86,87] with an amplitude of about 5%. It can be envisioned that the MFEs on photocurrents can elucidate not only photoexcited processes but also photovoltaic channels in organic semiconducting materials. MFEs on photocurrent can be used as an “inside-out” experimental approach to reveal detailed singlet and triplet photovoltaic processes in organic solar cells.^[39,65,88]

The photocurrent generation consists of four necessary processes: light absorption, formation of excited states, generation of charge carriers from photoexcited states, and transport of charge carriers in organic semiconducting materials. In particular, the generation of charge carriers from photoexcited states is sensitive to the magnetic field, and consequently accounts for MFE_{PC} in organic semiconducting materials.

There are two photovoltaic channels for excited states to generate photocurrent: exciton dissociation and exciton–charge reaction in organic semiconducting materials.^[65] The exciton dissociation is driven by intermolecular electrical dipole–dipole interactions. The exciton–charge reaction is essentially Coulombic scattering between an excited state and a charge carrier. Due to the long lifetime involved in exciton–charge contacts, triplet excitons can dominate the exciton–charge reaction. The studies of phosphorescence and delayed-fluorescence quenching indicate that excitons can interact with trapped charge carriers with the outcome of detrapping them.^[82,89–92] In addition, the triplet excitons can also react with free charge carriers in organic materials, with the outcome of dissociating e–h pairs.^[93,94] The e–h separation was also shown in the MFEs on electroluminescence, where dissociated electrons and holes maintain their spin polarizations from their parent triplet excitons and the reform triplet excitons from their recombination.^[95] This exciton–charge reaction can provide strong local electrical force to break strongly

bound e-h pairs in excitonic states for the generation of charge carriers. It is noted that the major outcome of the light absorption is the generation of singlet intramolecular excited states: singlet Frenkel excitons based on the spin-selection rule. However, singlet excitons can be partially converted into triplet excitons through ISC caused by the internal magnetic interaction from HFC or SOC. Therefore, both singlet and triplet excitons can exist in organic semiconducting materials under photoexcitation. In addition, the singlet excitons can dissociate into intermolecular excited states: singlet polaron pairs, due to their low binding energies toward the generation of photocurrent. The singlet polaron pairs can be partially converted into triplet polaron pairs through ISC. As a result, photon absorption generates both excitons and polaron pairs with singlet and triplet configurations toward the generation of photocurrent. In principle, both excitons and polaron pairs in singlet and triplet states can be involved in dissociation and charge reaction to generate photocurrent. However, the singlets and triplets in excitonic and polaron-pair states have largely different contributions to these two photo-voltaic channels of dissociation and charge reaction, due to their different binding energies, ionic natures, and lifetimes. For the dissociation occurring in excitonic states, the singlets can have a dominant contribution due to the lower binding energies as compared to triplet excitons. However, for the exciton-charge reaction in excitonic states, triplets can be intensely involved, due to the sufficient physical contact with charge carriers based on their long lifetimes. For the dissociation in polaron-pair states, both singlets and triplets can have very significant contributions, because of their lower binding energies. However, the singlets have a larger dissociation rate relative to triplets.^[85,96] This is because the singlet wave function has more ionic characteristics that can effectively interact via intermolecular electrical interaction for dissociation. The remaining singlet and triplet polaron pairs may also experience charge reactions with similar reaction rates due to their similar lifetimes. As a result, the major channels for the generation of photocurrent can be described by the dissociation dominated by singlets and the charge reaction dominated by triplets (Fig. 6a).

An external magnetic field can change the photocurrent through the singlet-dominated dissociation and triplet-dominated exciton-charge reaction, by perturbing the singlet and triplet ratios in polaron-pair states through ISC and exciton-charge reaction rate constant, leading to MFE_{PC} . Specifically, applying a magnetic field can increase the number of singlet polaron pairs through field-dependent ISC K_{ISC} due to the satisfaction of the two magnetic requirements (Scheme 1), leading to a positive component in the MFE_{PC} .^[83,84] Second, the triplet exciton-charge reaction can decrease with magnetic field and yield a negative component in the MFE_{PC} . Since an applied magnetic field has little influence on singlet and triplet exciton ratios due to the field-independent ISC K_{ISCE} in excitonic states, the magnetic field-dependent triplet exciton-charge reaction can be attributed to the reaction rate constant, through removing the spin degeneracies of triplet substates.^[29] Figure 6b shows the MFE_{PC} for three typical organic semiconducting materials, poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEHPPV), poly(3-methylthiophene) (P3HT), and *fac* tris(2-phenylpyridine) iridium $Ir(ppy)_3$. The triplet exciton densities are about 1.0% in MEHPPV,^[97] 70% in P3HT,^[98] and 100% in $Ir(ppy)_3$.^[99] It can

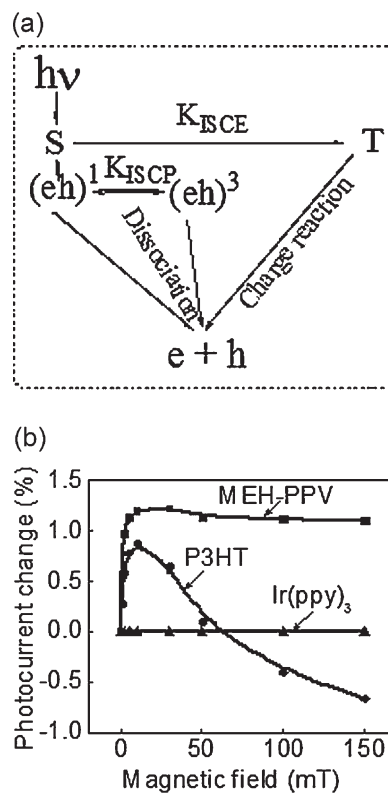


Figure 6. Photovoltaic channels and magnetic-field dependence of photocurrent. a) Two photovoltaic channels: dissociation dominated by polaron pairs and exciton-charge reaction dominated by triplet excitons. b) Magnetic-field dependence of photocurrent for MEHPPV, P3HT, and $Ir(ppy)_3$.

be seen in Figure 6b that MEHPPV shows only the positive component, due to a nearly 100% singlet exciton fraction, while P3HT contains both positive and negative components, due to significant triplet exciton fraction in the MFE_{PC} . The comparison between MEHPPV and P3HT implies that the negative component in the MFE_{PC} can be attributed to the triplet exciton-charge reaction.^[82] Furthermore, the experimental result in which the triplet $Ir(ppy)_3$ does not show any MFE_{PC} suggests that the effects on triplet exciton-charge reaction rate constant depend on SOC. This is because when the SOC is not very strong, a low magnetic field can weaken the ionic characteristic of the triplet excitons, and consequently decrease the triplet-charge reaction governed by electrical dipole-dipole interactions.^[1] Nevertheless, it can be assumed that the triplet exciton-charge reaction rate constant is responsible for the negative MFE_{PC} in organic semiconducting materials.

We note that there are two important issues related to positive and negative components in the MFE_{PC} in organic semiconducting materials. First, it still demands direct experimental proof to support that the positive MFE_{PC} are due to the dissociation of polaron pairs, namely polaron-pair model,^[82-84] based on magnetic-field-dependent singlet and triplet ratios in polaron-pair states. Second, there is still controversy about whether the negative MFE_{PC} comes from triplet exciton-charge reaction, named charge reaction model,^[82-84] or from the intersection

between singlet and triplet ($T_{m=-1}$) levels, named level crossing model.^[60,85,86] To explore the direct experimental evidence for polaron-pair model-based positive MFE_{PC} , we recently examined the positive MFE_{PC} before and after the polaron-pair states were removed upon introducing donor-acceptor interaction through doping. We found that removing polaron-pair states have led to a significant reduction in positive MFE_{PC} . Specifically, we used the photovoltaic system P3HT doped with surface-functionalized fullerene 1-(3-methyloxycarbonyl)propyl(1-phenyl)^[6,6]C₆₁ (PCBM). The donor-acceptor interaction can be effectively formed between the P3HT chain and the PCBM molecule interfaces.^[100,101] Especially, the donor-acceptor interaction density can be adjusted by changing the PCBM concentration in the P3HT. The donor-acceptor interaction density essentially determines the dissociation probability of e-h pairs in polaron-pair and excitonic states. Due to the different lifetimes and binding energies, the probabilities of dissociating polaron pairs should be much larger than that of dissociating excitons at low donor-acceptor interaction densities resulting from low PCBM doping. As the PCBM concentration increases, donor-acceptor interaction-enhanced exciton dissociation eventually occurs. It can be seen in Figure 7a that the positive MFE_{PC} gradually decreases with increasing PCBM doping concentration. The weak donor-acceptor interaction from 1% PCBM doping can completely remove the positive component, but leaves the negative component unchanged in the MFE_{PC} . We know that the low donor-acceptor interaction density can sufficiently dissociate polaron pairs while the exciton dissociation requires high donor-acceptor interaction densities due to the difference in lifetime and binding energy between polaron pairs and excitons.^[65] As a result, this observation provides direct experimental evidence that polaron-pair states are responsible for the positive MFE_{PC} . In addition, we found that the charge-transfer complexes, equivalent to intermolecular e-h pairs, formed from the recombination of dissociated electrons and holes between P3HT chains and PCBM molecule interfaces give rise to positive MFE_{PC} at high fields (Fig. 7b). This is because i) the ISC between singlet and triplet charge-transfer complex states is sensitive to the magnetic field due to the large e-h separation distance, and ii) singlet and triplet charge-transfer complexes can redissociate into free charge carriers with high and low rates, due to their different ionic characteristics involved in dissociation.^[65] It is further noted that this high-field positive MFE_{PC} can be reduced by applying an electrical field due to electrical field-assisted dissociation of charge-transfer complexes (Fig. 7b). This voltage-dependent MFE_{PC} confirms that positive MFE_{PC} comes from the dissociation of polaron-pair states in organic semiconducting materials. For the comparison between triplet exciton-charge reaction and level-crossing models proposed for negative MFE_{PC} , we recently found that increasing triplet-exciton density can lead to negative MFE_{PC} at low magnetic fields. Specifically, we uniformly dispersed fluorescent Alq₃ and phosphorescent Ir(ppy)₃ molecules into a poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) matrix to form singlet and triplet systems, respectively, under photoexcitation. Notably, the selected fluorescent Alq₃ and phosphorescent Ir(ppy)₃ have similar electronic levels and absorbances, with the LUMO and HOMO of 3.2 and 5.7 eV for Alq₃^[102] and 3.0 and 5.4 eV for Ir(ppy)₃,^[103] respectively. More importantly, the dispersed Ir(ppy)₃ molecules can largely increase the triplet

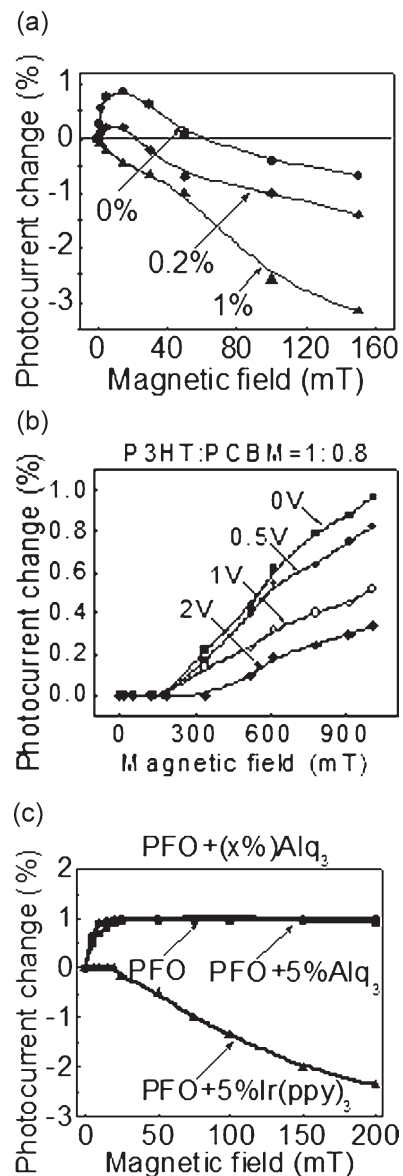


Figure 7. MFEs of photocurrent (MFE_{PC}) versus doping, voltage, and triplet density.^[65] a) MFE_{PC} versus PCBM doping ($x\%$ = PCBM weight concentration). b) High-field MFE_{PC} versus applied reverse bias in solar cell of ITO/PEDOT/P3HT:PCBM (1:0.8)/Al. c) MFE_{PC} for pure PFO, Alq₃ doped PFO, and Ir(ppy)₃ doped PFO.

exciton ratio in the PFO matrix under photoexcitation,^[104,105] while the dispersed Alq₃ molecules have unappreciable influence on the triplet exciton ratio. Figure 7c shows that increasing the triplet exciton density can induce negative MFE_{PC} upon Ir(ppy)₃ dispersion. However, the MFE_{PC} stays unchanged when the triplet exciton density is not appreciably varied upon Alq₃ dispersion. This experimental result suggests that the triplet-charge reaction accounts for the negative MFE_{PC} , and the level-crossing mechanism cannot be activated in low magnetic fields in organic semiconducting materials.

4. MFEs on Electroluminescence (MFE_{EL})

An external magnetic field can change steady-state electroluminescence (EL), leading to MFEs of electroluminescence (MFE_{EL}) at constant injection current in nonmagnetic common organic semiconducting materials.^[41,106–109] This phenomenon indicates that nonmagnetic organic semiconductors have potential applications in spintronic devices where electronic, optical, and magnetic properties can be mutually controlled. On the other hand, the studies of MFE_{EL} can enhance the critical understanding of intrinsic useful and non-useful excited processes in respective optoelectronic devices. It was reported in 1975, based on time-resolved measurements, that an applied magnetic field of 900 mT can reduce the delayed electrofluorescence leading to negative MFE_{EL} in anthracene crystals. This experimental results indicate that a high magnetic field can reduce the TTA under electrical excitation,^[106] which has been observed under photoexcitation.^[1,2,110,111] Positive MFE_{EL} have also been observed in Alq₃-based light-emitting diodes at low magnetic fields.^[112] The EL from the radiative singlet excitons in Alq₃ rapidly increases with magnetic field by about 5%, and then becomes saturated at around 300 mT. The authors proposed that an external magnetic field, when stronger than the internal magnetic interaction HFC, can increase singlets through the ISC in polaron-pair states based on the Zeeman splitting effect, therefore leading to an increase in the density of light-emitting singlet excitons after polaron pairs are evolved into excitons. At high magnetic field (~2 T), non-monotonic MFE_{EL} were also observed in the Alq₃-based light-emitting diodes, where the EL first increases from 0 to about 50 mT (estimated from their published data), and then slowly decreases under fields of up to 1.9 T in steady-state measurements.^[95,113] In general, MFE_{EL} can be caused by spin-dependent e–h pairing and field-dependent ISC in polaron-pair states in organic semiconducting materials, according to the spin-physics theory of radical pairs.^[4–7] It is noted that an external magnetic field can have little influence on the electron and hole spin orientations during e–h recombination, because the related Zeeman effect is much smaller than the thermal energy $K_B T$ in nonmagnetic organic semiconducting materials. However, applied magnetic fields can perturb the electron and hole spin precessions, changing the singlet and triplet ratios in polaron pairs through the transition between overall singlet and triplet states by altering electron and hole precession frequencies based on the Δg mechanism.^[66] The field-dependent ISC can, in principle, include the contributions from both ISC in polaron-pair states and TTA in excitonic states. Published data have clearly shown that i) positive MFE_{EL} can be observed when the e–h pairing is maximized at balanced bipolar electron and hole injection^[41] and ii) negative MFE_{EL} can appear when the exciton–charge reaction occurs at unbalanced bipolar electron and hole injection.^[42,95] Although the mechanisms of MFE_{EL} demand further investigation, it can be experimentally suggested that the ISC in polaron-pair states, the TTA in excitonic states, and exciton–charge reaction are three important issues involved in the positive and negative MFE_{EL} in organic semiconducting materials.

Clearly, the understanding the MFE_{EL} from nonmagnetic organic semiconducting materials requires further discussions. First, it needs to be further determined whether the magnetic field-induced modification of singlet and triplet ratios comes from ISC or from the spin-dependent formation in polaron-pair

states. Second, it demands further understanding about how the TTA and triplet–charge reaction generate negative MFE_{EL} in steady state. Third, it is unclear whether intermolecular SOC should be considered in the MFE_{EL}. We know that random electron and hole capture generates four polaron-pair states with 25% fraction for each state: one singlet ($(e-h)^1$) and three triplet ($(e-h)^3_{m=1}$, $(e-h)^3_{m=0}$, $(e-h)^3_{m=-1}$) states based on spin statistics, if spin correlation is weak. The polaron pairs, regarded as intermolecular excited states, can evolve into intramolecular excited states: Frenkel excitons in both singlet and triplet states as the e–h separation decreases due to Coulombic attraction. The spin-selection rule only allows the emission from singlet Frenkel excitons, leading to electrofluorescence. However, electrophosphorescence resulting from triplet emission can be observed when strong SOC exists to flip electron spins. Clearly, we should carefully examine MFEs on both electrofluorescence and electrophosphorescence in order to further discuss the positive and negative MFE_{EL}.

4.1. Electrofluorescence-Based MFE_{EL}

Electrofluorescence-based MFE_{EL} can be readily observed in common organic semiconducting materials (Fig. 8a). In principle, the light-emitting singlet exciton ratio can be changed by an external magnetic field through either spin-dependent e–h pairing during the formation of excited states or the post electronic processes after the formation of excited states. If e–h pairing is spin-dependent in the formation of polaron pairs, negative MFE_{EL} can be observed because i) the spin–spin

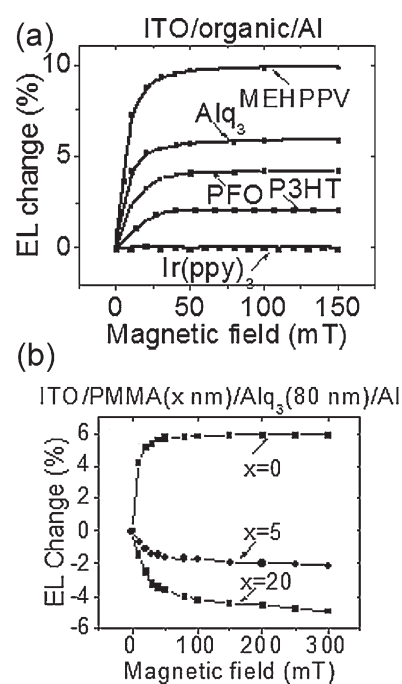


Figure 8. MFEs of electroluminescence (MFE_{EL}) and MFE_{EL} tuning. a) MFE_{EL} for various organic semiconducting materials. b) Tuning MFE_{EL} from positive to negative values by adjusting bipolar charge injection toward an unbalanced state using a thin insulating PMMA layer.

interaction in the spin-dependent charge recombination tends to form singlet excited states, and ii) an applied magnetic field, when stronger than internal magnetic interaction, can perturb the e–h spin interaction during e–h pairing, and shifts the population from singlets to triplets. It should be particularly noted that the formation of polaron pairs can result from injected electrons and holes, namely primary charge carriers, or regenerated electrons and holes from dissociation and exciton–charge reaction in excited states, namely secondary charge carriers. Accordingly, the polaron pairs can be divided into primary and secondary types. Published results have shown that negative MFE_{EL} can be observed when two unbalanced electrodes are used for electron and hole injection.^[95] This experimental result implies that unbalanced bipolar electron and hole injection leads to negative MFE_{EL} at low magnetic fields. We found that the electrofluorescence-based MFE_{EL} clearly changes from positive to negative values when the bipolar electron and hole injection is adjusted toward an unbalanced state by reducing the hole injection through increasing the insulating PMMA layer thickness in Alq₃-based light-emitting diodes (Fig. 8b). It is noted that unbalanced bipolar charge injection reduces the e–h pairing for the formation of polaron pairs and excitons, and therefore increases the triplet exciton–charge reaction in organic light-emitting diodes.^[114] The relevant outcome of triplet exciton–charge reactions is the generation of secondary electrons and holes by destroying the bound e–h pairs in excitonic states. The secondary electrons and holes can be recaptured to form polaron pairs with singlet and triplet configurations due to Coulombic attraction through germinate and nongerminate processes, generating secondary polaron pairs. Furthermore, the germinate recombination of secondary charge carriers with coherent electron and hole spin precessions maintains the original spin polarizations of their parent excitons in the formation of secondary-type polaron pairs. The nongerminate recombination of secondary charge carriers can be included in the category of the formation of primary-type polaron pairs because the singlet and triplet formation yields the statistic 1:3 ratio based on random recombination of spin polarizations at long e–h separation distances. It should be further noted that the germinate capture of secondary electrons and holes occurs at much short distances after the exciton–charge reaction as compared to the nongerminate capture of primary electrons and holes injected from electrodes. In a first-order approximation, it can be assumed that the primary and secondary polaron pairs are formed from long-distance and short-distance charge captures, respectively. As a result, the EL can accordingly consist of two contributions from primary and secondary charge captures. The MFE_{EL} can then be divided into primary and secondary components, as shown in Equation 2.

$$MFE_{EL} = MFE_{EL, \text{primary}} + MFE_{EL, \text{secondary}} \quad (2)$$

It can be assumed that the secondary electrons and holes can experience spin correlation in the short-distance germinate charge capture as compared to the primary electrons and holes in long-distance charge capture. An external magnetic field can interfere with the spin correlation, and consequently changes the singlet and triplet formation ratios in secondary polaron-pair states. This can lead to formation-based negative MFE_{EL} , due to secondary charge capture. On the other hand, the singlet–triplet

ISC in secondary polaron-pair states can be insensitive to applied magnetic fields because of the large energy difference between singlet and triplet levels caused by spin–exchange interactions at short e–h separation distances. ISC-based MFE_{EL} should be then negligible in the EL generated from the short-distance germinate charge capture of secondary electrons and holes. As a result, the overall $MFE_{EL, \text{secondary}}$ should be negative. In contrast, the long-distance charge capture of primary electrons and holes experiences negligible spin interaction during the formation of polaron pairs. The absence of spin interaction implies that an external magnetic field has little influence on the singlet and triplet formation ratios in primary polaron-pair states. This leads to unappreciable formation-based MFE_{EL} due to primary charge capture. However, the long e–h capture distance allows the singlet–triplet ISC in primary polaron-pair states to be magnetic-field sensitive, generating ISC-based positive MFE_{EL} . Therefore, the overall $MFE_{EL, \text{primary}}$ should be positive. The observed MFE_{EL} combining $MFE_{EL, \text{primary}}$ and $MFE_{EL, \text{secondary}}$ can yield positive and negative components. Changing the balancing degree of bipolar electron and hole injection can modify the relative ratio between $MFE_{EL, \text{primary}}$ and $MFE_{EL, \text{secondary}}$ and consequently lead to a tuning in MFE_{EL} between positive and negative values, as shown in Figure 8b.

In addition, a photoluminescence study based on time-resolved measurements of delayed fluorescence has found that TTA can lead to a negative MFE_{PL} . However, in steady state, the PL independence of the magnetic field^[115,116] has suggested that TTA should have unappreciable contribution to MFE_{EL} . Furthermore, if the TTA is the governing mechanism for negative MFE_{EL} , adjusting bipolar injection toward an unbalanced state would generate positive MFE_{EL} because an unbalanced bipolar injection can largely consume triplet excitons by having charge reaction, and therefore reduce the TTA probability. This is inconsistent with experimental results where unbalanced bipolar injection corresponds to negative MFE_{EL} . Therefore, the experimental result of bipolar injection-dependent MFE_{EL} does not suggest that the TTA has a significant contribution to negative MFE_{EL} at low fields in the steady-state.

4.2. Electrophosphorescence-Based MFE_{EL}

Electrophosphorescence results from triplet emission in excitonic states activated by strong SOC. The strong SOC requires heavy-metal complex structures to increase the internal magnetic interaction between electron spins and orbital magnetic field. It is noted that the use of heavy-metal complex increases not only intramolecular SOC but also intermolecular spin–orbital interaction in phosphorescent materials. In contrast, fluorescent materials, such as most organic semiconducting materials, have very weak intermolecular magnetic interactions, mainly resulting from HFC. A low magnetic field can compete with the weak internal magnetic interaction and modify the singlet and triplet ratios in polaron-pair states, leading to negative MFE_{EL} based on electrofluorescence. However, it is difficult to generate electrophosphorescence-based MFE_{EL} because the strong intermolecular SOC does not allow the ISC in polaron-pair states to be field sensitive.^[41]

We note that increasing the intermolecular distance in dilute solid solutions can significantly decrease the intermolecular SOC,

but leaves the intramolecular SOC approximately unchanged in phosphorescent heavy-metal complex molecules. When the intermolecular SOC is sufficiently weakened at large intermolecular distances, the ISC in polaron-pair states can become sensitive to a low magnetic field by satisfying the two magnetic requirements (Scheme 1). As a consequence, an external magnetic field can increase the singlet polaron pairs at the expense of consuming triplet polaron pairs. The change in singlet and triplet polaron-pair ratios can be reflected as an increase and decrease in singlet and triplet exciton densities, respectively, after polaron pairs evolve into excitons (Fig. 9a). However, the near 100% ISC in excitonic states, which is magnetic-field independent, always converts singlet excitons into triplet excitons. This leads to a negligible change in triplet exciton ratio, and even an external magnetic field can change the singlet and triplet polaron-pair ratios after the intermolecular SOC is sufficiently weakened by increasing the intermolecular distance. As a result, it is difficult to generate electrophosphorescence-based MFE_{EL} using molecular dispersion if the excitonic ISC is near 100% in phosphorescent molecules with strong SOC, such as iridium complex molecules. It can be seen in Figure 9b that dispersing iridium (III) tris(2-(4-tolyl)pyridinato-N,C2) (Ir(mppy)₃) molecules into a PMMA matrix does not lead to appreciable MFE_{EL} based on phosphorescence. In addition, adjusting the balancing degree of bipolar injection at different current densities does not yield phosphorescence-based MFE_{EL} in iridium dyes in both pure-PMMA blend forms. This means that the TTA and triplet-charge reaction cannot generate any MFE_{EL} in strong SOC phosphorescent materials. It can be thus suggested that the strong SOC disables phosphorescence-based MFE_{EL} when the excitonic ISC is near 100%. However, magnetic-field-sensitive ISC in polaron-pair states should yield phosphorescence-based

MFE_{EL} in organic semiconducting materials with intermediate SOC if the excitonic ISC is not 100%. This scenario can be supported by the phosphorescence-based MFE_{EL} observed from Alq₃, which has considerable SOC strength.^[113]

It has been experimentally found that electrophosphorescence-based MFE_{EL} can be observed when phosphorescent iridium complex molecules are dispersed in an active-organic-material matrix.^[41,107] Figure 9b clearly shows that the phosphorescence becomes magnetic-field dependent when the phosphorescent heavy-metal complex Ir(mppy)₃ is dispersed in a poly(*N*-vinylcarbazole) (PVK) matrix. The respective EL spectra are shown in Figure 9c. We know that the singlet and triplet exciton ratios are sensitive to the magnetic field through the ISC in polaron-pair states in the PVK matrix under electrical excitation due to the weak SOC. However, an external magnetic field cannot change the singlet and triplet exciton ratios in the Ir(mppy)₃ molecules, due to the strong intra-SOC and near-100% excitonic ISC. Furthermore, we note that energy transfer can occur from the PVK matrix to the dispersed Ir(mppy)₃ molecules through Förster and Dexter channels for singlet and triplet excitons,^[41] respectively. Because Förster and Dexter are long- and short-range processes, the Förster process can dominate the energy transfer from the PVK matrix to the Ir(mppy)₃. Due to efficient Förster and inefficient Dexter transfers, magnetic-field-induced increases of singlet excitons in the PVK matrix can be reflected as increases of triplet excitons in the dispersed Ir(mppy)₃ molecules in the PVK + Ir(mppy)₃ blend when the ISC in excitonic states is near 100% in the Ir(mppy)₃ molecules (Fig. 9d). As a consequence, this internal energy transfer can cause phosphorescence-based MFE_{EL} when phosphorescent heavy-metal complex molecules are dispersed into an active polymer matrix. In essence, energy-transfer-induced MFE_{EL} present a new mechanism of inducing MFEs based on electrophosphorescence.

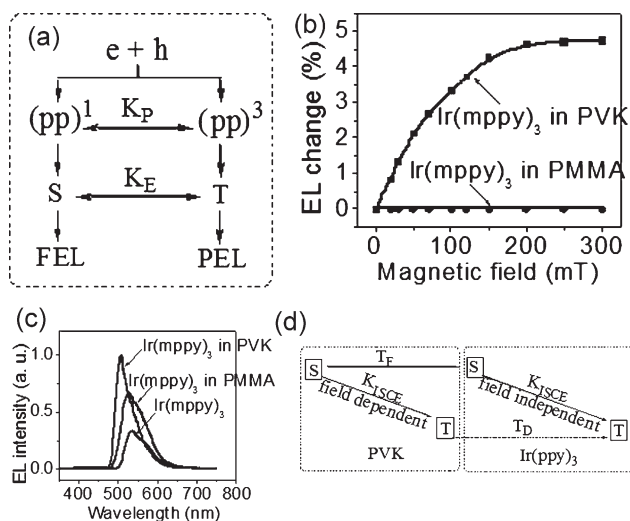


Figure 9. Electroluminescence processes, MFEs of electroluminescence (MFE_{EL}), and energy-transfer effects on singlet and triplet excitonic ratios.^[41] a) Electrofluorescence and electrophosphorescence processes. b) MFE_{EL} for 1 wt% Ir(mppy)₃ dispersed in PVK and PMMA matrices, respectively. c) EL spectra for pure Ir(mppy)₃, 1% Ir(mppy)₃ dispersed in PMMA, 1% Ir(mppy)₃ dispersed in PVK. d) Förster (T_F) and Dexter (T_D) energy transfer in excitonic states from the PVK matrix to Ir(mppy)₃ dopant together with field-dependent and field-independent excitonic ISCs.

5. MFEs on Injection Current: Magnetoresistance

EL studies have shown that a low external magnetic field (<300 mT) can increase the electrical-injection current by about 2% in nonmagnetic organic Alq₃-based light-emitting diodes.^[112] The MFEs of electrical-injection current were also observed using different electrode materials in Alq₃.^[95] This phenomenon was then further studied and named as organic magnetoresistance (OMA).^[117,118] These experimental findings have clearly indicated that nonmagnetic organic semiconducting materials can have considerable magnetic responses in electrical-injection currents. Scientifically, the understanding of OMA can reveal intrinsic magnetic-field-sensitive charge generation and transport processes in nonmagnetic organic semiconducting materials. Technically, the magnetoresistance (MR) presents unique possibilities in the use of common nonmagnetic organic semiconducting materials for magnetically controllable electronic devices.

We know that the electrical-injection current is determined by both potential-barrier height and thickness at respective electrode interfaces in organic light-emitting diodes based on the tunneling theory.^[119] A specific potential barrier is determined by the energy difference between the organic semiconducting material and

respective electrode material. With given cathode and anode materials, the potential thickness is inversely proportional to the applied electrical voltage. When both electrode materials and applied electrical voltage are fixed, the bulk electrical-injection current is determined by the charge-carrier densities and mobilities based on the Drude model, given by

$$J = e \times n \times \mu \quad (3)$$

where J is the bulk injection current and n and μ are the charge density and mobility. Because both electrodes and organic semiconducting materials are nonmagnetic, the MR requires that charge density or charge transport be sensitive to the magnetic field applied. This reasoning suggests that the MR phenomenon can be developed through two different channels based on the charge density or charge transport, respectively, as described by Equation 4:

$$MR = MR(n) + MR(\mu) \quad (4)$$

In general, the bulk charge density can be sensitive to the applied magnetic field when the secondary charge carriers generated from magnetic-field-sensitive singlet and triplet excited states are counted. On the other hand, the charge transport can be magnetic-field sensitive if i) different types of charge carriers exist, ii) different types of charge carriers have low and high mobilities, and iii) interconversions between different types of charge carriers are magnetic-field dependent. In principle, organic semiconducting materials can exhibit excited-states-based MR and charge-transport-based MR.

5.1. Excited-States-Based Magnetoresistance

Experimental results have shown that the MR dramatically increases when the electrical-injection current is approaching the bipolar injection threshold for the realization of excited states.^[120–128] This provides direct evidence that excited states are largely involved in MR in organic semiconducting materials. It was suggested that the excited-states-based MR can be attributed to the MFEs of e–h pair dissociation in the generation of secondary charge carriers^[42] or the magnetic-field dependence of e–h recombination in injected charge carriers.^[121] It is noted that the secondary charge carriers can be generated through two different magnetic-field-sensitive channels: dissociation^[85,113,129–131] and charge reaction^[1,82,94,132–134] in excited states. It has been experimentally shown that the dissociation and charge reaction form two major channels to generate photocurrent in organic materials under photoexcitation.^[65] Because of different binding energies and lifetimes, singlet and triplet excited states can have different contributions to the dissociation and charge reaction in the generation of secondary charge carriers. As a consequence, magnetic-field-dependent singlet and triplet ratios can lead to negative and positive MR based on dissociation and charge reaction in organic semiconducting materials.^[42,121,122,135,136] Specifically, the secondary charge generation consists of dissociation dominated by polaron pairs, due to their low binding energies, and exciton–charge reaction

dominated by triplet excitons, due to long triplet lifetimes for sufficient physical contact with charge carriers. In the dissociation channel, the singlet polaron pairs have relatively larger dissociation rates as compared to triplet polaron pairs, because singlet polaron pairs can more effectively interact with the local electrical polarization field for dissociation due to their ionic characteristics.^[85,96] As a consequence, an external magnetic field can increase the dissociation in polaron-pair states by increasing the singlet polaron-pair ratio through field-dependent ISC K_{ISCP} in the generation of secondary charge carriers, leading to negative MRs ($-MR_S$, Fig. 10a). On the other hand, an external magnetic field can decrease the triplet–charge reaction by reducing the triplet exciton density or charge-reaction rate constant.^[91] Therefore, an external magnetic field can decrease the secondary charge generation through triplet–charge reaction channel, yielding positive MRs ($+MR_T$, Fig. 9a). The observed overall MR should reflect the combination of the dissociation-induced negative MR ($-MR_S$) and the charge-reaction-related positive MR ($+MR_T$).

When the generation of secondary charge carriers is considered, the proposed MR theory involving dissociation and

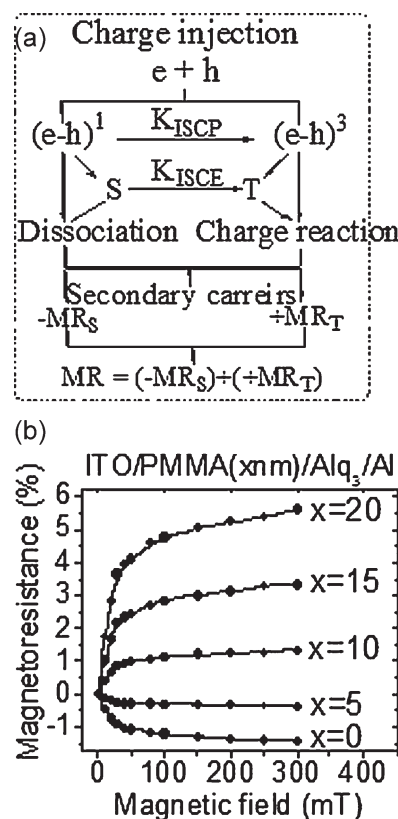


Figure 10. MR generation and tuning.^[42] a) Schematic diagram for positive and negative MR components: $-MR_S$ from the dissociation dominated by singlet excited states; $+MR_T$ from the charge reaction dominated by triplet excited states. $(e-h)^1$ and $(e-h)^3$ are singlet and triplet intermolecular e–h pairs. S and T represent singlet and triplet excitons. K_{ISCP} and K_{ISCE} are ISC in e–h pair and excitonic states, respectively. b) Tuning MR from negative to positive values by adjusting bipolar injection toward an unbalanced state using a hole-blocking PMMA layer in the double-layer Alq₃-based light-emitting diode of ITO/PMMA(x nm)/Alq₃(80 nm)/Al.

charge reaction indicates that adjusting the relative ratio between negative $-MR_S$ and positive $+MR_T$ can lead to a substantial tuning of the overall MR between positive and negative values. Essentially, tuning the MR requires the modification on the contributions of dissociation and charge reaction to the generation of secondary charge carriers. There are two ways to relatively change the dissociation and charge reaction in organic light-emitting diodes: adjusting the balancing degree of bipolar charge injection or changing the applied electrical field. First, changing the balancing degree of bipolar injection can modify the e–h pairing product toward the formation of excited states and the excessive charge carriers to alter the exciton–charge reaction. Specifically, the dissociation in polaron-pair states can become a dominated process at balanced bipolar injection, while the exciton–charge reaction is enhanced at an unbalanced bipolar injection in the generation of secondary charge carriers. As a consequence, changing bipolar charge injection can lead to MR tuning between positive and negative values.^[42] In addition, varying the applied electrical field can change the electrical force for the dissociation in polaron-pair states and the physical contact probabilities between long-lifetime triplet excitons and charge carriers for triplet–charge reactions. Therefore, tuning MR with positive and negative signs can be expected by adjusting the applied electrical field in organic light-emitting diodes.^[122] Figure 10b shows that the MR clearly changes from negative to positive values when the bipolar charge injection is adjusted toward an unbalanced state by increasing the hole-injection-blocking PMMA-layer thickness in the double-layer Alq₃-based organic light-emitting diode of ITO/PMMA(*x* nm)/Alq₃(80 nm)/Al. As a result, using magnetic-field-dependent excited processes in polaron-pair dissociation and exciton–charge reaction presents a unique pathway to obtain tunable excited-states-based MR from nonmagnetic organic semiconductor devices.

5.2. Charge Transport-Based Magnetoresistance

It has been experimentally reported that OMA can be observed in organic light-emitting diodes when single-carrier charge injection is realized using different electrode materials.^[137,138] These experimental findings indicate that magnetic-field-dependent charge transport can be developed in nonmagnetic organic semiconductor devices.^[139] Based on the fact that single-carrier charge injection does not generate excited states in organic semiconducting materials, the single-carrier-generated MR can be named charge-transport-based MR. It is further noted that an external magnetic field cannot change charge mobilities in nonmagnetic materials. As a result, one can reasonably assume that i) singlet charge injection forms different types of charge carriers with magnetic-field-dependent intertype conversions and ii) the different types of charge carriers have low and high mobilities in organic semiconducting materials. We know that injected charge carriers strongly interact with lattice vibrations, forming charged polarons in organic materials.^[140] Particularly, optical absorption has shown that both polarons and bipolarons can exist under electrical excitation.^[141] The relevant interconversions are given in Equation 5, where P^- and P^+ are negative and positive polarons, and bP^{2-} and bP^{2+} represent negative and positive bipolarons. It can be assumed that charged polarons and

bipolarons have high and low mobilities due to their different lattice distortions, respectively.



Based on spin-dependent interconversion between polarons and bipolarons, it was proposed that an external magnetic field can change the bipolaron density and consequently affect the overall charge transport in nonmagnetic semiconducting materials.^[142] Specifically, bipolarons can be formed with both singlet and triplet configurations. An external magnetic field can compete with an internal magnetic interaction from HFC or SOC, and then reduces the electron spin flip. As a consequence, the total bipolaron density becomes a function of applied magnetic field. Because polarons and bipolarons have different mobilities, magnetically changing the polaron and bipolaron densities essentially leads to positive and negative MR in organic semiconducting materials. This proposed bipolaron mechanism can also apply to excited-states-based MR under bipolar charge injection. Nevertheless, it can be suggested that the single carrier-based MR is determined by i) the coexistence of different types of charge carriers, ii) magnetic-field-dependent intertype conversions, and iii) low and high mobilities of different types of charge carriers.

It is clear that the recently discovered magnetic-field-dependent injection current demonstrates a novel phenomenon: MR from nonmagnetic organic semiconductor devices. The understanding of both bipolar and unipolar injection-based MR can reveal the fundamental mechanisms of magnetic field-dependent excited states and charge transport. On the other hand, the MR is presented as a powerful tool to experimentally visualize charge capture, charge generation, and charge transport in inter- and intramolecular excited states in light-emitting and photovoltaic devices.

6. Conclusion

It has been experimentally found that nonmagnetic organic semiconducting materials can have significant responses to a low magnetic field in electroluminescence, photoluminescence, photocurrent, and electrical-injection current. Experimental and theoretical studies have indicated that the intrinsic excited states and related charge transport are sensitive to magnetic fields due to electron-spin multiplicities and spin–spin interactions. Specifically, an external magnetic field can change singlet and triplet ratios in excited states through two possible processes: i) spin-dependent e–h pairing toward the formation of excited states and ii) interconversions between singlet and triplet excited states. Because singlets and triplets have different contributions to the excited state–excited state interactions, the dissociation of excited states, and the excited state–charge reaction, an external magnetic field can influence the relevant electronic, optical, and optoelectronic properties, leading to MFEs in nonmagnetic organic semiconducting materials. Essentially, whether singlet and triplet ratios in excited states can be changed with the application of a magnetic field determines whether MFEs can occur. The

photoluminescence dependence of the magnetic field with intermolecular excited states together from the photoluminescence independence of the magnetic field on intramolecular excited states in steady states clearly suggests that the e–h separation distance and its related spin-exchange interaction in the excited states are the main factors that determine MFEs. At long e–h separations and weak exchange interactions, the ISC becomes magnetic-field sensitive in the intermolecular excited states, and is therefore accountable for primary MFEs. At short e–h separation distances and strong exchange interactions, secondary MFEs may be observed involving intramolecular excitonic processes, that is, TTA and triplet–charge reactions. The magnetic-field dependence of the photocurrent indicates that the intermolecular excited states (polaron pairs) correspond to positive magnetic-field effects through dissociation. The intramolecular excitons give rise to negative magnetic-field effects through exciton–charge reactions. The magnetic-field dependence of the electroluminescence shows that the e–h separation distance at charge capture for the formation of excited states determines whether the spin-dependent e–h pairing or the field-dependent ISC is the governing mechanism for MFEs. Specifically, at long-distance e–h capture, the ISC is the dominant mechanism responsible for positive magnetic-field effects. However, at short-distance e–h capture, the spin-dependent e–h pairing plays an important role in the determination of negative magnetic-field effects. Magnetic-field-dependent injection currents confirm that the intermolecular excited states with long e–h separation distance and the intramolecular excited states with short e–h separation distance have positive and negative contributions to the generation of charge carriers through dissociation and charge reaction, respectively. As a result, the MFEs can be attributed to both e–h separation-distance-dependent spin interaction and ISC in organic semiconducting materials. These interesting MFEs can lead to new potential applications using nonmagnetic organic semiconducting materials for magnetic electronic and optical devices. It is also clear that a better knowledge of MFEs can increase the critical understanding of useful and non-useful excited processes and charge transport occurring in organic electronic and optical devices.

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