Tuning magnetoresistance between positive and negative values in organic semiconductors

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Magnetic-field-dependent injection current, namely magnetoresistance, is readily observable in organic semiconductor devices. This provides a non-contact approach to tune organic optoelectronic properties by using a magnetic field. Here, we demonstrate that this magnetoresistance can be changed between positive and negative values by adjusting the dissociation and charge reaction in excited states through changing the bipolar charge injection in organic light-emitting diodes. This finding reveals that the magnetic-field-dependent generation of secondary charge carriers from the dissociation and charge reaction affects the injection current by forming further space charges at the organic–electrode interfaces and therefore accounts for the tunable magnetoresistance. Furthermore, the dissociation and charge reaction have opposite dependences on magnetic field in the generation of secondary charge carriers, consequently leading to negative and positive magnetoresistance, respectively. As a result, adjusting the dissociation and charge reaction in excited states provides a convenient pathway to tune the magnetoresistance in organic semiconductors.

Magnetoresistance refers to the phenomenon in which electrical resistance changes as a function of an external magnetic field. Magnetic-field-dependent resistance can usually be observed under spin-polarized charge injection when the spin-up and spin-down polarizations experience different transport processes in a semiconductor medium[1,2]. However, electroluminescence studies have shown that an external magnetic field can change the electrical injection current in single-layer organic light-emitting diodes (OLEDs) under non-spin-polarized charge injection[3,4]. This magnetic phenomenon was confirmed by a double-layer design with different electrode materials[5] and named organic magnetoresistance[6,7]. This type of magnetic-field effect indicates that intrinsic magnetic-field-dependent properties are involved in electrical injection current in organic semiconducting materials. It has been found that (1) the excited states can contribute significantly to the organic magnetoresistance[8,9] and (2) the modification of spin–orbital coupling can lead to a tuning of organic magnetoresistance in OLEDs[8,10]. Clearly, understanding the organic magnetoresistance dependence can impact on both magnetic control of fundamental electronic and optical properties in optoelectronic devices and application of organic semiconductors in magnetic devices. Fundamental theory indicates that when electrons and holes approach each other during transport in organic semiconducting molecules under the influence of applied electric field, both singlet and triplet electron–hole (e–h) pairs can be formed by considering the relative spin orientations with antiparallel and parallel configurations[11,12]. These e–h pairs have a relatively large intercharge separation distance as the electrons and holes are located in different molecules, giving intermolecular e–h pairs. When the e–h separation distance decreases, the electrons and holes can be captured in single molecules and form molecular e–h pairs, namely excitons with singlet and triplet spin configurations. Therefore, the excited states can evolve from e–h pairs to excitons by reducing the intercharge distance in organic semiconducting materials. In general, the excited states consist of both e–h pairs and excitons in organic materials under electrical excitation[13]. It is noted that singlet and triplet excited states inevitably experience dissociation[14–18] and charge reaction[19–23], generating secondary electrons and holes[24]. These secondary electrons and holes can drift to respective electrodes under the influence of electrical field and form further space-charge carriers at anode–organic and organic–cathode interfaces in OLEDs. In particular, the generated secondary electrons and holes can change the electrical injection current when the coulombic interaction at the respective electrode interfaces is considered. Because the singlet and triplet excited states have different contributions to the dissociation and charge reaction owing to their different binding energies and lifetimes, an external magnetic field can change the generation of secondary charge carriers and consequently affects the electrical injection current by varying the singlet and triplet ratios through field-dependent intersystem crossing (ISC). As a result, changing the singlet and triplet ratios may lead to a substantial tuning of electrical injection current through dissociation and charge reaction in the generation of secondary charge carriers in organic semiconducting materials.

The singlet and triplet ratios can be changed by an external magnetic field if the ISC is field dependent[25]. There are two conditions that must be satisfied for the ISC to be field dependent. First, the magnetic splitting caused by the applied field must be larger than the internal splitting intrinsically induced by the spin–orbital coupling. The former and latter are known as external and internal Zeeman effects, respectively. For most organic materials with aromatic molecular structures, the internal splitting can be assumed to be about 1–10 μeV (ref. 26). This small internal splitting

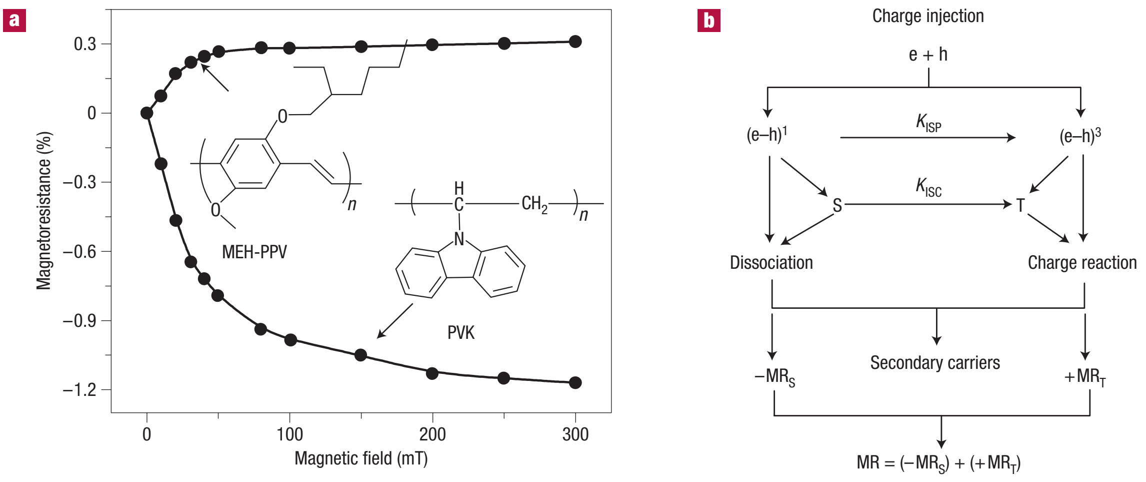

Figure 1 **Magnetoresistance characteristics and processes. a**, Positive and negative magnetoresistance for reverse-biased ITO/MEHPPV(60 nm)/Al and forward-biased ITO/PVK(60 nm)/Al OLEDs. The insets show the chemical structures of MEHPPV and PVK. **b**, Schematic diagram for positive and negative magnetoresistance components $-\mathrm{MR}_\mathrm{S}$ from the dissociation dominated by singlet excited states and $+\mathrm{MR}_\mathrm{T}$ from the charge reaction dominated by triplet excited states. $(\mathrm{eh})^1$ and $(\mathrm{eh})^3$ are singlet and triplet intermolecular e–h pairs. S and T represent singlet and triplet excitons. K_ISP and K_ISC are ISCs in e–h pair and excitonic states, respectively.

suggests that a magnetic field ranging from 10 mT to 100 mT can change the ISC and consequently affects the singlet and triplet ratios. Second, the magnetic splitting energy, ΔE_B, of three triplet sublevels should be larger than the singlet–triplet energy difference, ΔE_ST, caused by spin-exchange interaction. If ΔE_B is greater than ΔE_ST, an external magnetic field can reduce the ISC and leads to an increase and a decrease in the singlet and triplet ratios, respectively. Therefore, the comparison between the ΔE_ST and ΔE_B essentially determines whether the ISC is field dependent when the external Zeeman effect is greater than the internal Zeeman effect[14]. Furthermore, the field dependence of ISC can be significantly changed by the distance-dependent spin-exchange interaction when the excited states evolve from the intermolecular e–h pairs to molecular excitons with decreasing e–h separation distance. In the first-order approximation, the magnetic-field-induced change in singlet and triplet ratios can be reflected in the generation of secondary charge carriers through dissociation and charge reaction. This scenario naturally implies that the singlet- and triplet-related generation of secondary charge carriers can yield negative and positive magnetoresistance in a magnetic field.

Figure 1a shows the positive and negative magnetoresistance with maximal values of 0.3% and −1.8% from poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (MEHPPV) and poly(N-vinyl carbazole) (PVK) OLEDs, respectively, under bipolar electrical injection. Recent studies of magnetic-field-dependent current have indicated that the excited states contribute to the observed magnetoresistance[8,9]. In principle, the excited states can dissociate or react with charge carriers to generate secondary electrons and holes in organic semiconducting materials. The dissociation can go through either the Poole–Frenkel process[27] owing to thermal activation or the Onsager process[28] owing to diffusion and coulombic interaction. On the other hand, the excited states can react with trapped or free carriers in a bulk organic material or even with an electrode to generate the secondary electrons and holes. An external magnetic field can affect the generation of secondary charge carriers from the dissociation and charge reaction and consequently changes the electrical injection current by varying the singlet and triplet ratios through field-dependent ISC.

There are two ISCs associated with e–h pairs and excitonic states (Fig. 1b). The field dependence of ISC in e–h pairs or excitonic states is essentially determined by the relative values between the spin-exchange-induced singlet–triplet energy difference, ΔE_ST, and the magnetic splitting energy, ΔE_B. The ΔE_ST increases with decreasing intercharge distance from e–h pairs to excitons[29] (see the Methods section for details). In particular, in excitonic states the ΔE_ST can be further changed when the electron and hole are closely located in a single molecule where the Pauli exclusion minimizes the kinetic energy to avoid 'electron collision'. Figure 2 shows a general schematic diagram of the singlet and triplet energy levels for e–h pairs and excitons in a magnetic field. Obviously, an external magnetic field can considerably reduce the ISC rate, K_ISP, in e–h pair states but has little influence on the ISC rate, K_ISC, in excitonic states. Therefore, the K_ISP and K_ISC can be named as field-dependent and field-independent parameters, respectively. The field-dependent K_ISP can lead to magnetic field-dependent singlet and triplet e–h pair ratios. We should note that the field-dependent K_ISP can also result in magnetic field-dependent singlet and triplet exciton ratios when the e–h pairs relax into excitonic states under electrical excitation[13]. However, under photoexcitation, an external magnetic field cannot appreciably change the singlet and triplet exciton ratios because of the field-independent K_ISC when the e–h pair states are absent. This reasoning is supported by the fact that the electroluminescence involving both e–h pairs and excitons can show significant dependence on magnetic field in MEHPPV, PVK and Alq_3 under electrical excitation, whereas the respective photoluminescence involving only excitonic states does not depend on magnetic field[30,31]. It should be further noted that the photoluminescence from charge-transfer states with an intermediate e–h separation distance can show magnetic-field dependence[32]. Nevertheless, whether the excited states can exhibit magnetic-field-dependent ISC depends on the e–h separation distance in the comparison between ΔE_ST and ΔE_B in organic semiconducting materials.

We now discuss how singlet and triplet ratios affect the magnetoresistance through dissociation and charge reaction in OLEDs. In principle, both singlet and triplet excited states can be involved in the dissociation and charge reaction[33]. However, the

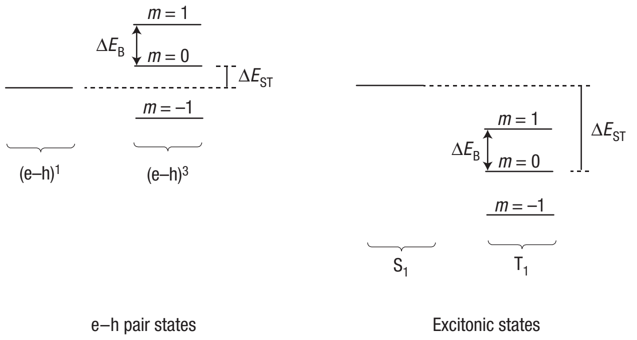

Figure 2 The energy levels for e–h pair and excitonic states in an external magnetic field. ΔE_{ST} and ΔE_B are the singlet–triplet energy difference and magnetic splitting energy, respectively.

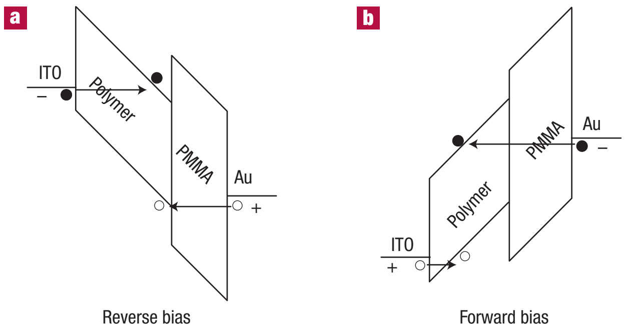

Figure 3 Modification of bipolar charge injection by a PMMA charge-blocking layer in a double-layer ITO/polymer/PMMA/Au device. a, Reverse bias towards balanced bipolar injection. **b**, Forward bias towards an unbalanced state. The filled and open circles are electrons and holes, respectively.

dissociation and charge reaction may have positive and negative dependences on the magnetic field, leading to negative and positive magnetoresistance through the generation of secondary charge carriers. The magnetic-field-dependent photocurrent indicates that the excitons first become e–h pairs and then dissociate into free electrons and holes as the e–h separation distance increases during dissociation of excited states[34,35]. On the other hand, the excitons can directly dissociate into free charge carriers without experiencing e–h pair states when the donor–acceptor interaction or applied electrical field is sufficient[19,36–38]. Therefore, it can be argued that both e–h pairs and excitons can contribute to the generation of secondary charge carriers through dissociation. However, the e–h pairs have a dominant contribution to the dissociation as compared with the excitons due to the different binding energies resulting from the electrostatic attraction between the electron and the hole. Furthermore, the singlet e–h pairs can more efficiently dissociate into secondary charge carriers relative to the triplet e–h pairs owing to different dissociation rates[14,39]. An external magnetic field can increase the generation of secondary charge carriers based on dissociation by boosting the singlet e–h pairs through the field-dependent ISC rate, K_{ISP} (refs 40,41). As a result, the dissociation of excited states essentially leads to a negative magnetoresistance in OLEDs. On the other hand, both e–h pairs and excitons can be involved in the reaction with charge carriers[33]. For the charge reaction in the e–h pair states, an external magnetic field can only cause little reduction in the generation of secondary charge carriers, namely limited positive magnetoresistance, by decreasing the triplet ratio through the field-dependent K_{ISP}. This is because the singlet and triplet e–h pairs have similar lifetimes and binding energies. However, for the charge reaction in excitonic states, the triplets have a greater involvement as compared with the singlets owing to the former's overwhelming long lifetime. Therefore, an external magnetic field can significantly reduce the charge reaction by decreasing the triplet exciton ratio, giving positive magnetoresistance. Indeed, the triplet exciton + charge reaction was directly confirmed in anthracene by the reduced delayed fluorescence on hole injection[29]. In general, there are three ways for triplet excitons to react with charge carriers[42] and yield positive magnetoresistance in a magnetic field (equation (1)). First, the triplet excitons (T) can collide with trapped carriers, Q^*, to generate secondary charge carriers through a detrapping process[23,43]. Second, the triplet excitons can also react with free charge carriers, Q, in organic materials[44]. The relevant outcome of this type of reaction is the e and h separation of triplet excitons[21]. Third, the triplet excitons can diffuse to the electrode interface owing to their long diffusion length for charge reaction to generate secondary carriers[36]. The charge transfer studies indicate that such an exciton + electrode reaction occurs within the narrow zone of about 2 nm at the organic–metal interface[45].

$$\begin{aligned} &\mathrm{T}+\mathrm{Q}^* \rightarrow \mathrm{S}_0+\mathrm{Q} \\ &\mathrm{T}+\mathrm{Q} \rightarrow \mathrm{e}+\mathrm{h}+\mathrm{Q} \qquad (1) \\ &\mathrm{T}+\text{electrode} \rightarrow \mathrm{e}+\mathrm{h} \end{aligned}$$

In general, an external magnetic field can weaken the triplet exciton + charge reaction in OLEDs under electrical excitation by either decreasing the triplet exciton ratio through field-dependent K_{ISP} or reducing the charge reaction rate constant through removing the spin degeneracies of triplet substates[46]. The unappreciable magnetoresistance together with the negligible magnetic field effect of the photocurrent from the phosphorescent $\mathrm{Ir(ppy)_3}$ OLED[10,36] suggests that a low magnetic field does not considerably change the charge reaction rate constant. This implies that an external magnetic field has to change the triplet exciton ratio to significantly modify the triplet exciton + charge reaction. Nevertheless, the triplet-dominated exciton + charge reaction can lead to a positive magnetoresistance in OLEDs when an external magnetic field decreases the triplet exciton ratio. At a given magnetic field, the comparison of triplet destruction between anthracene crystals with and without defects indicates that the charge velocity is a rate-determining factor in the triplet + charge reaction[44]. This result suggests that free charge carriers are more efficient than trapped charge carriers in destroying triplet excitons. In contrast, the photocurrent studies show that the triplet excitons can react significantly with trapped carriers[23,43]. By considering these two opposite results, we can understand that the real interaction time between the charge carriers and triplet excitons determines the triplet + charge reaction probability at given triplet and charge densities. For the triplet + electrode reaction, we note that the positive MEHPPV magnetoresistance does not show considerable dependence on the film thickness at a given current density. In addition, reverse bias results in a larger positive magnetoresistance when the e–h capture zone is away from the metal electrode as compared with the forward bias with the recombination zone close to the metal electrode[8]. These results do not suggest that the T + electrode reaction is a significant channel in the magnetic-field effect of the triplet exciton + charge reaction. Nevertheless, it can be concluded that the dissociation

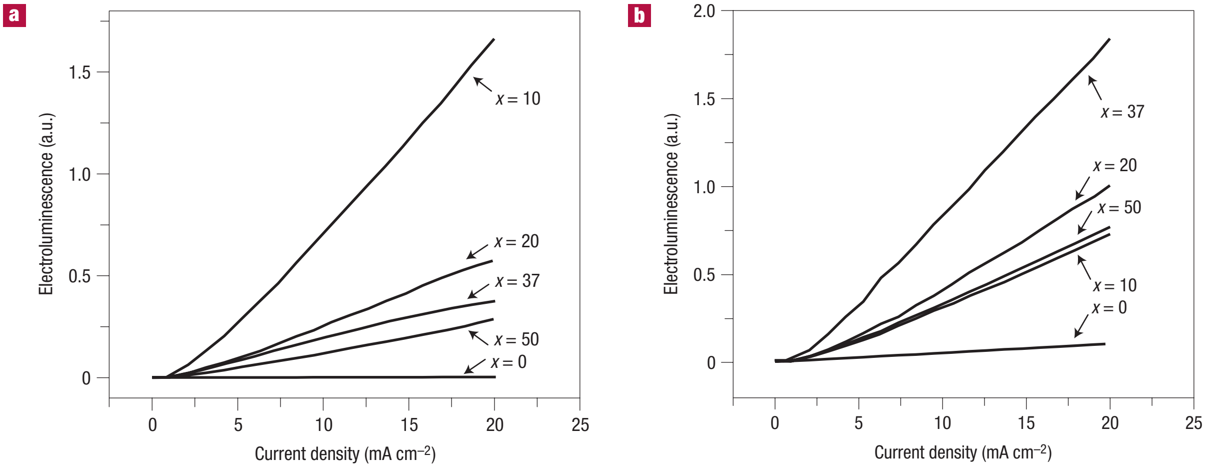

Figure 4 **Electroluminescence–current characteristics for double-layer ITO/MEHPPV(60 nm)/PMMA(*x* nm)/Au devices with different PMMA thicknesses. a**, Forward bias. **b**, Reverse bias.

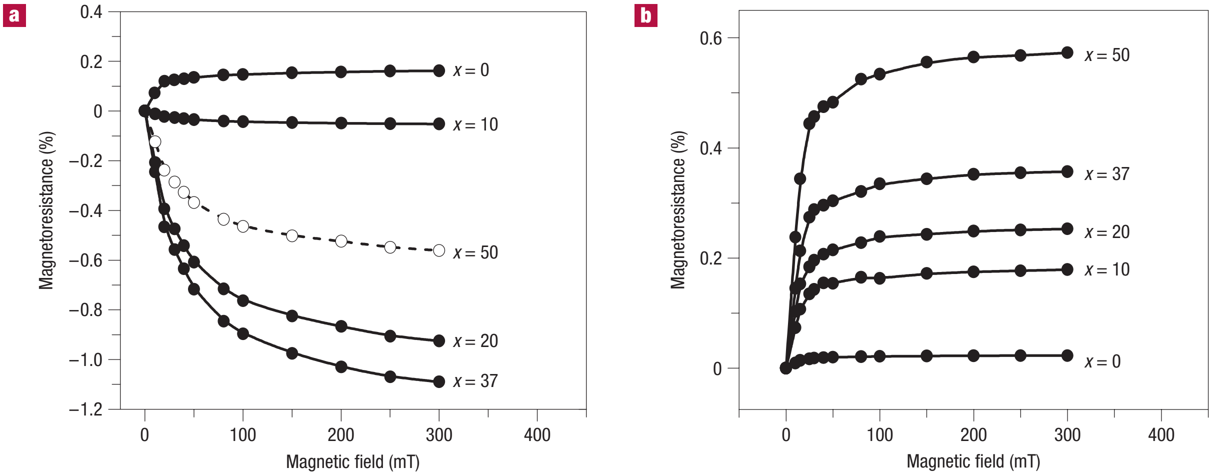

Figure 5 **Tuning of positive magnetoresistance by adjusting electron and hole injection in double-layer ITO/MEHPPV(60 nm)/PMMA(*x* nm)/Au OLEDs with different PMMA film thicknesses. a**, Magnetoresistance at the reverse bias towards balanced bipolar injection by adjusting hole injection. **b**, Magnetoresistance at forward bias towards unbalanced bipolar injection by adjusting electron injection.

and charge reaction in excited states yield negative and positive magnetoresistance components when the singlet-to-triplet ratio is reduced on applying magnetic field. We should note that the observed magnetoresistance essentially reflects the sum of negative and positive components: $-\mathrm{MR_S}$ from the dissociation dominated by singlet e–h pairs and $+\mathrm{MR_T}$ from the exciton + charge reaction dominated by triplets in OLEDs (Fig. 1b). It can then be suggested from the experimental data shown in Fig. 1a that dissociation and charge reaction are two respective dominant processes accountable for the negative and positive magnetoresistance observed in the PVK and MEHPPV devices, respectively.

We now examine the magnetoresistance tuning by adjusting the relative contributions from the dissociation and triplet + charge reaction in organic semiconducting materials. Equation (1) shows that the charge carriers are a deciding factor to invoke the triplet + charge reaction. These charge carriers should be the excessive electrons or holes in the pairing process for the formation of excited states in OLEDs. We note that a balanced bipolar charge injection can increase the electron–hole pairing rate and the formation yield of excited states. Therefore, balancing the bipolar injection can boost the relative ratio of formed excitons to excessive charge carriers within the devices, and consequently suppresses the exciton + charge reaction and relatively strengthens the dissociation effect in the generation of secondary charge carriers[47]. On the other hand, an unbalanced bipolar injection can reduce the ratio of formed excited states to excessive charge carriers, enhancing the charge reaction but weakening the dissociation effect. As a result, changing the balancing degree of bipolar charge injection can be used as a ‘lever bar’ to adjust the relative effect between dissociation and charge reaction for tuning the organic magnetoresistance. Here, we use an insulating thin film of poly(methyl methacrylate) (PMMA) to adjust either electron or hole injection density to change the balancing degree of bipolar injection in the related OLEDs. In addition, the use of

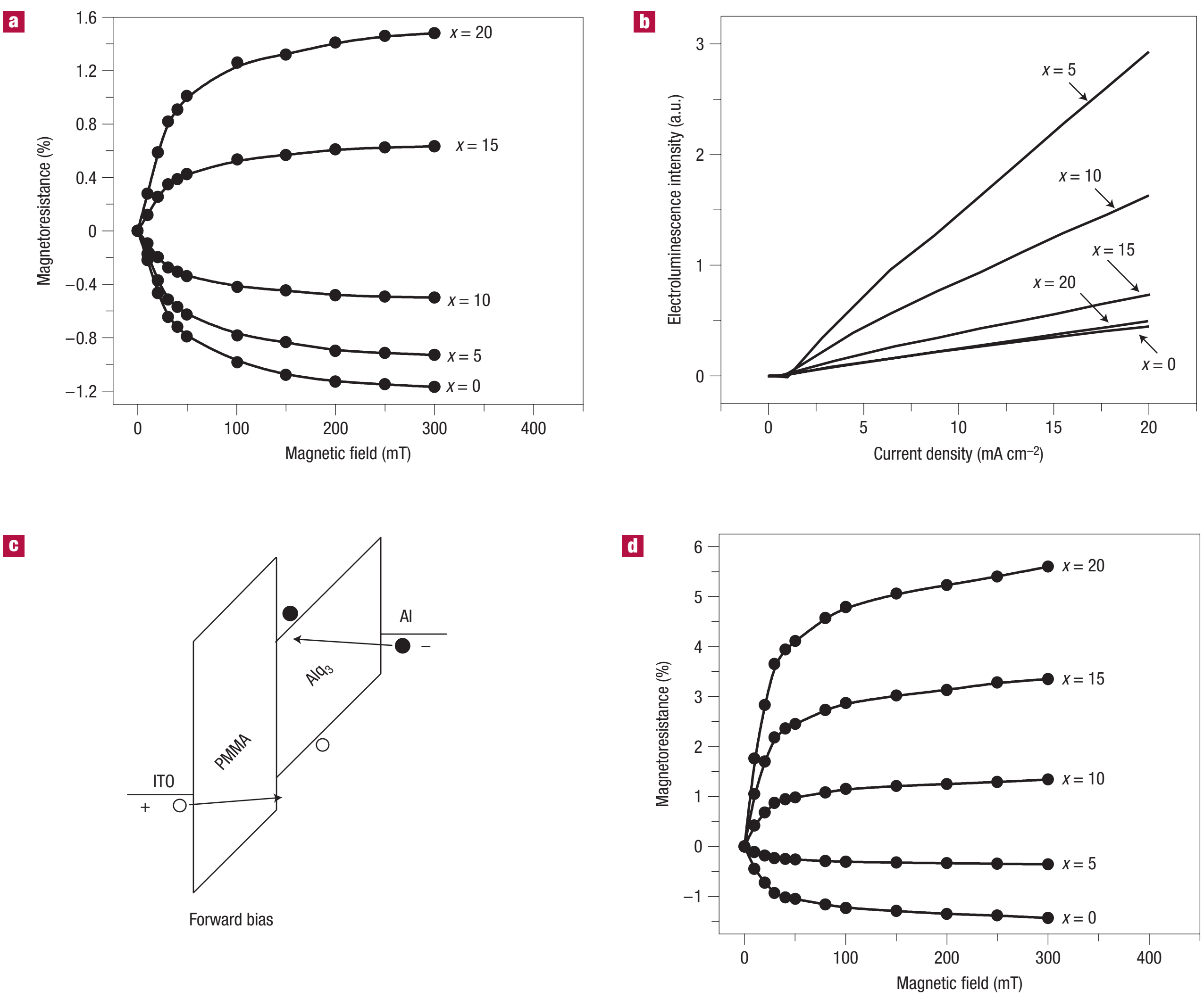

Figure 6 **Tuning of negative magnetoresistance by adjusting electron and hole injection in double-layer PVK and Alq$_3$ OLEDs with different PMMA film thicknesses.** **a**, Magnetoresistance of ITO/PVK(60 nm)/PMMA(x nm)/Al at forward bias towards unbalanced bipolar injection. **b**, Electroluminescence–current characteristics towards unbalanced bipolar injection at forward bias for the double-layer ITO/PVK(60 nm)/PMMA(x nm)/Al devices. **c**, Band diagram to show unbalanced injection by adjusting hole injection in the double-layer Alq$_3$ device with a hole-blocking PMMA layer at forward bias. **d**, Magnetoresistance of the double-layer ITO/PMMA(x nm)/Alq$_3$(60 nm)/Al device at forward bias towards unbalanced bipolar injection.

the thin PMMA layer can remove the metal electrode effects on both spin–orbital coupling and organic magnetoresistance in OLEDs[8,48]. The band diagram in Fig. 3 shows that at reverse bias the PMMA charge-blocking layer increases the potential barrier for the majority hole injection from the Au electrode towards a balanced bipolar injection for enhancing the dissociation contribution of excited states. However, at forward bias the PMMA layer further reduces the minority electron injection from the Au electrode towards a more unbalanced bipolar injection for facilitating the exciton + charge reaction. The reduction in the electroluminescence efficiency confirms that the bipolar injection becomes more unbalanced at forward bias with increasing PMMA thickness from 10 nm to 50 nm in the double-layer indium tin oxide (ITO)/MEHPPV/PMMA/Au OLED (Fig. 4a). On the other hand, at reverse bias the electroluminescence efficiency increases first with PMMA thickness from 10 nm to 37 nm and then decreases with further increasing PMMA thickness from 37 nm to 50 nm (Fig. 4b). The non-monotonic increase and decrease of the electroluminescence efficiency suggest that at reverse bias the bipolar injection goes towards a balanced state first and then an unbalanced state by continuously reducing the majority hole injection from the Au electrode with increasing PMMA thickness. We should note in Fig. 5a that at reverse bias the positive MEHPPV magnetoresistance gradually changes to a negative value (−1.09%) when the PMMA layer thickness increases up to 37 nm towards a balanced bipolar injection. This result indicates that adjusting bipolar injection from an unbalanced towards a balanced state can convert a positive magnetoresistance to a negative value in OLEDs. Further increasing the PMMA film thickness (>37 nm) from a balanced to an unbalanced state decreases the amplitude of the already negative magnetoresistance. The negative magnetoresistance becomes −0.56% for a 50-nm-thick PMMA layer. The decrease of the already negative magnetoresistance can be explained as follows. At reverse bias, further reducing the hole injection by increasing the PMMA thickness (>37 nm) passes the balanced state of bipolar injection for maximally pairing electrons and holes (Fig. 4b), and thus increases the exciton + charge reaction and the resultant positive magnetoresistance component. Therefore, the observed magnetoresistance, namely the sum of negative and positive magnetoresistance components, becomes lower for a thicker PMMA film (>37 nm) owing to the change of bipolar injection from a balanced towards an unbalanced state. Figure 5b shows that, at forward bias, the positive MEHPPV magnetoresistance increases from 0.02% to 0.55% when the PMMA enlarges the unbalancing degree of forward bipolar charge injection and further strengthens the exciton + charge reaction.

We now apply the modification of the balancing degree of bipolar injection to negative magnetoresistant material PVK. It can be seen in Fig. 6a that the negative magnetoresistance gradually changes from a negative (−1.17%) to a positive value (1.50%) on increasing the PMMA film thickness up to 20 nm in the double-layer ITO/PVK/PMMA/Al device. Therefore, adjusting the bipolar charge injection towards an unbalanced state through controlling the electron injection current (Fig. 6b) can change negative magnetoresistance to a positive value. This phenomenon was further confirmed by changing the hole injection current towards an unbalanced bipolar charge injection in the negative magnetoresistant material Alq_3 (Fig. 6c,d). In conclusion, adjusting the dissociation and charge reaction in excited states forms a mechanism to tune the organic magnetoresistance between positive and negative values through the generation of secondary charge carriers in organic semiconducting materials.

METHODS

The organic semiconducting materials used here include MEHPPV, PVK and tris-(8-hydroxylquinoline) aluminium (Alq_3). The polymer thin films were spin-cast from solution in a nitrogen atmosphere. The Alq_3 thin film was thermally evaporated under vacuum. The film thicknesses were measured using a DekTek-II surface profiler. The metal electrodes were also prepared by vacuum thermal deposition. The vacuum used for the thermal deposition was 2×10^{-6} torr. The single-layer OLEDs were fabricated with ITO and Al as electrodes. In the double-layer OLEDs, the inert polymer PMMA was applied as a charge-blocking layer to change electron or hole injection to modify the balancing degree of bipolar charge injection in the respective OLEDs. The double-layer polymer/PMMA structures were fabricated using the organic solvents chloroform and nitromethane to spin-cast semiconducting polymer and charge-blocking PMMA, respectively. Using nitromethane to spin-coat the insulating PMMA layer avoids the problem of dissolving the semiconducting polymer underlayers in the fabrication of double-layer polymer/PMMA OLEDs. The double-layer PMMA/Alq_3 structure was prepared by spin-casting the PMMA underlayer followed by vacuum deposition of Alq_3 film. ITO and gold (Au) with mutually similar workfunctions of 4.8 eV (ref. 49) and 4.9 eV (ref. 50) were used as electrodes in the double-layer MEHPPV OLED to obtain symmetric bipolar charge injection at forward and reverse biases. Furthermore, the ITO and Au were also used in the double-layer PVK and Alq_3 devices to change the bipolar injection from a balanced towards an unbalanced state at forward operation. In addition, the use of a PMMA layer can remove the emission quenching caused by the metal electrode, as indicated by the relatively low electroluminescence efficiency of the single-layer MEHPPV OLED (see the slope at $x = 0$ in Fig. 4a,b).

The magnetic-field effects were measured by placing the respective OLEDs in a magnetic field generated by an electric magnet. The electroluminescence and current were characterized using a Jobin Yvon Florolog-3 spectrometer with an optical fibre connection and a Keithley 2400 electrometer with non-magnetic wiring, respectively. The magnetoresistance was studied by measuring the injection current as a function of magnetic field at constant voltage adjusted to an injection current density of 20 mA cm^{-2} for the respective OLEDs in liquid nitrogen. The observed magnetic-field effects were found to be independent of the orientation of the OLEDs.

The spin-exchange energy, J, in excited states was determined on the basis of equivalent ion pairs and given by $J = J_0\exp[-\alpha(r_e - r_h)]$, where J_0 is the constant defined as the energy when the e and h are in contact and α is the decay parameter. The $(r_e - r_h)$ represents the e–h separation distance. The magnetic splitting energy, ΔE_B, of three triplet substates caused by an external magnetic field was described by the Zeeman effect: $\Delta E_B = g\mu_B B$, where g is the electron spin g factor, μ_B is the Bohr magneton and B is the external magnetic field. Note that the spin-exchange interaction energy and magnetic splitting energy were used in the text to discuss the magnetic-field dependence of ISC as a function of the intercharge separation distance when the excited states evolve from e–h pairs to excitons in organic semiconducting materials.

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