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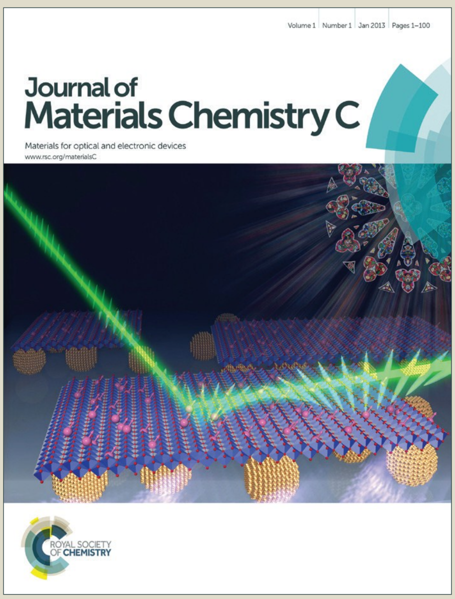

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Paper

Negative magnetoconductance effects in amorphous copper phthalocyanine thin film: trap-assisted bipolaron formation

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Negative magnetoconductance (MC) effects have been observed over a large temperature range from room temperature to 20 K in amorphous copper phthalocyanine (CuPc) thin film. It is found that the negative MC increases when the temperature decreases. The corresponding current density-voltage characteristics of the device at different temperatures reveal that this negative MC is related to the presence of traps in CuPc thin film. Moreover, the magnitude of negative MC scales with current density for nearly three orders. Based on these results, trap-assisted bipolaron formation, a developed mechanism based on bipolaron, has been proposed. We suggest that traps existed in CuPc thin film can assist the formation of bipolaron through lowering the formation energy. This model is further confirmed by the negative MC responses with light illumination.

1. Introduction

Organic semiconductor devices, such as organic light-emitting diodes, solar cells, and field-effect transistors, have been the subject of extensive research in the last two decades and started to benefit our daily lives. Recently, magnetic field effects (MFEs) commonly observed in such organic semiconductor devices have been a hot topic in the organic electronics community.[1] It is found that the current in organic semiconductor devices can be largely changed by applying a small magnetic field.[2-4] This effect is referred to as organic magnetoconductance (MC) or magnetoresistance. Furthermore, the sign of organic MC can be positive (current enhanced) or negative (current decreased), depending on the specific conditions of the devices.[5-9] However, compared to the positive organic MC, the negative MC is less often observed and the precise underlying physics of these effects is still debated.

Several models relied on magnetic field mediated hyperfine mixing[10] between the singlet and triplet states of electron-hole pairs,[2, 11] bipolarons[12] and excitons[13] have been proposed to explain the negative MC effects. Among these models, magnetic field dependent bipolaron formation is considered to be a competing mechanism since the bipolaron formation can take place in both unipolar and bipolar transport.[12, 14] Moreover, the bipolaron model has been recently deemed to be the main origin of the exceptionally large (up to 2000%) MC effect in one-dimensional molecular wires.[15] However, such a bipolaron with two like-charges on one occupied site is suggested to be energetically instable.[16] Its formation might be largely suppressed by the strong Coulomb repulsion between the pair of like-charges.[17]

Recently, there has been growing concern over the impact of traps on the organic MFEs.[17-21] It was observed that electrical conditioning[19] and damaging[17] organic semiconductor devices lead to dramatic enhancements in the magnetoresistance, possibly due to increasing the concentration of traps in devices. In particular, Cox et al. have systematically investigated the role of traps on organic magnetoresistance.[20,21] They proposed that the magnetic field dependent triplet exciton-polaron reactions at trap sites are the origin of magnetoresistance in organic semiconductors.[20] This is because trapping of triplet excitons on the polaron trap sites leads to the formation of metastable triplet exciton-polaron pairs (trions [22]) due to the low energy of trap states. In fact, the negative energy of the trap can also compensate the positive on-site repulsion of doubly occupying states,[17] which is expected to enlarge the probability of bipolaron formation in the trap sites. In this work, we investigated the MC effects in amorphous copper phthalocyanine (CuPc) thin films with the simplest structure in which a single layer of CuPc was sandwiched between the two electrodes (as shown in Fig. 1). Such a simplified structure is expected to reveal more generalized picture. The CuPc was investigated in this work since high density hole traps have been demonstrated in its vacuum-evaporated amorphous thin films.[23, 24] Our results clearly show that the traps can assist bipolaron formation in such amorphous organic semiconductor thin films, which causes large increases in negative MC at low temperatures.

2. Experimental

The experimental setup and device structure are shown in Fig. 1(a). An active layer of 150 nm-thick CuPc (see in Fig. 1(b)) is sandwiched between the indium tin oxide (ITO) anode and 120 nm-thick aluminium (Al) cathode. CuPc (>99.95%) was purchased from Sigma-Aldrich and used as received. The energy levels of the device are diagrammed in Fig. 1(c). Prior to the device fabrication, the ITO/glass substrates were cleaned in ultrasonic baths of detergent, deionized water, acetone, and isopropyl alcohol in sequence and dried in an oven. Then, the cleaned ITO substrates were transferred into vacuum chamber after 5 min UV-Ozone treatment. The organic semiconductor layer of CuPc and Al cathode were fabricated by thermal deposition under a high vacuum of 10^{-5} Pa with rate of 0.3 Å/s and 1 Å/s, respectively. The active area of the devices was 1×2 mm^2. After fabrication, the devices were directly mounted in a close-cycle cryostat which was placed between the poles of an electromagnet (Lakeshore EM647), as shown in Fig 1(a). All the MC measurements were carried out under vacuum. The details of the MC

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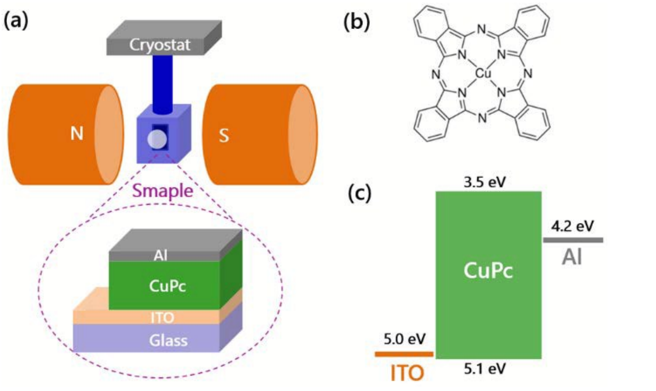

Fig. 1 (a) Schematic illustration of the experimental setup and device structure; (b) Molecular structure of CuPc; (c) Energy levels of the device.

measurements have been described elsewhere.[9] It is noteworthy that the MC results are confirmed to be independent on the direction of the applied magnetic field. The optical absorption spectra of CuPc thin films were measured by UV-visible spectrophotometer.

3. Results and discussion

Figure 2 shows the MC responses of the CuPc single layer device at different temperatures. The MC is defined as the relative change in current as a function of magnetic field, i.e. MC=[*I*(B)-*I*(0)]/*I*(0). At room temperature (290 K, as shown in Fig 2. (a)), very small negative MC effects (< -0.1%) are recorded. The line shapes of the ultra-small negative MC are irregular (see the inset in Fig. 2(a)). At low temperature of 200 K (Fig. 2 (b)), the negative MC responses are largely enhanced. The maximum value of the negative MC at 200 K is obtained to be -2.2% at 4V. Moreover, it is seen that negative MC increases monotonically with increasing the strength of magnetic field, following non-Lorentzian shapes. With further decreasing the temperature, the negative MC becomes much larger and the line shapes of the MC keep unchanged. The maximum values of negative MC are obtained to be -3.3% at 100 K (Fig. 2(c)) and -4.0% at 20 K (Fig. 2(d)), respectively. It is strange that the maximum magnitude of the

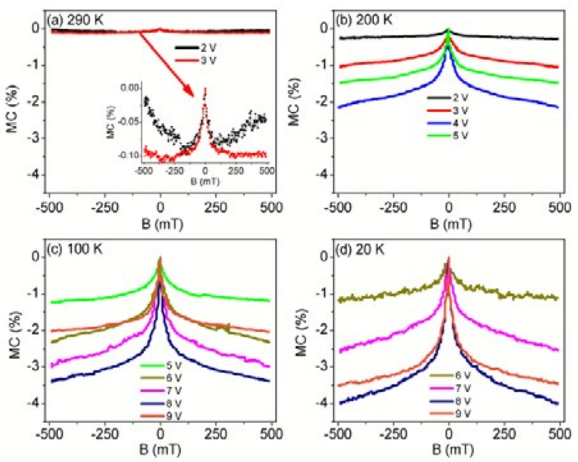

Fig. 2 MC responses of the ITO/CuPc/Al single layer device in dark and at different temperatures: (a) 290 K; (b) 200 K; (c) 100 K; and (d) 20K.

negative MC increases monotonically with lowering the working temperature. Moreover, it is noteworthy that the variation in the magnitude of negative MC with applied bias is not monotonic. Decreasing in negative MC at high voltages is a common feature at low temperatures (for example, the MC under 5 V at 200 K, Fig. 2(b)).

In order to reveal the underlying mechanism for the observed negative MC, current density-voltage (*J*-*V*) characteristics of the thin film devices were measured firstly since charge transport properties in the devices can be qualitatively reflected in *J*-*V* characteristics. Figure 3(a) shows the *J*-*V* characteristics of ITO/CuPc/Al thin film device on double logarithmic scale measured at temperatures ranging from room temperature to 20 K. It is clearly shown that the *J*-*V* characteristics at all temperatures follow a power law behaviour in the MC measured range. This behaviour is given by $J \propto V^m$,[24] where *m* is the power law index that denotes the transport mechanism. In the case where *m*=2, the charge transport in the regime is governed by trap-free space-charge-limited-current (SCLC). When *m*>2, the charge transport is governed by SCLC with traps. After the best fit slope to the *J*-*V* curves (Fig. 3(a)), the values of *m* are obtained to be 3, 6, 8 and 10 for 290, 200, 100 and 20 K respectively, indicating a trap-limited current in the device.[25] However, it is noteworthy that the value of *m* at room temperature is very close to that for the trap-free SCLC. This means that there are some shallow traps in the device and the trap population is much less than the population of transport levels.[23] While at low temperatures the occupancy of the trap level increases. Upon comparing the MC results (Fig. 2) and the *J*-*V* characteristics (Fig. 3(a)) at different temperatures, one can find that the traps play a crucial role in generating negative MC. At room temperature with a small quantity of shallow traps being occupied, no considerable negative MC is observed in the ITO/CuPc/Al device (see in Fig. 2(a)). On the contrary, notable negative MC is obtained in the CuPc device at low temperatures where more traps are occupied (Fig. 2(b-d)).

Based on the SCLC theory, the current with trap filling is governed by an exponential distribution of traps.[23] Thus, the relationship between *m* and the characteristic trap energy E_t can be defined by: m-1= E_t /k_BT,[23,26] where E_t is directly related to the steepness and depth of the exponential trap distribution. Figure 3(b) plots the maximum MC values and E_t as a function of temperature. It is shown that the maximum MC value increases while the E_t decreases with lowering the temperature. This temperature dependence of E_t is well consistent with the results reported by Campbell et al.[26] The smaller value at lower temperature indicates a much steeper trap distribution closer to the highest occupied molecular orbital. Thus, we suggest that the larger negative MC is related to the steep trap distribution in the device at low temperatures.

There are several possible MC models that relate to traps in the present device. The first one is trapped trion model in which the MC is generated based on the spin selective formation of metastable charged triplet excitons in the trap sites.[20] As shown in Fig. 1(c), the good contact and energetic alignment between the ITO and CuPc allow the very efficient hole injection from ITO anode to CuPc under forward bias. Thus, the current transport in the ITO/CuPc/Al device would be dominated by the majority carriers of hole. However, some electron injection would also happen via thermionic emission even at low applied bias. In this case, a handful of excitons are formed in the ITO/CuPc/Al device after electron injection. Therefore, the charged triplet excitons might be also formed on the trap sites in CuPc thin

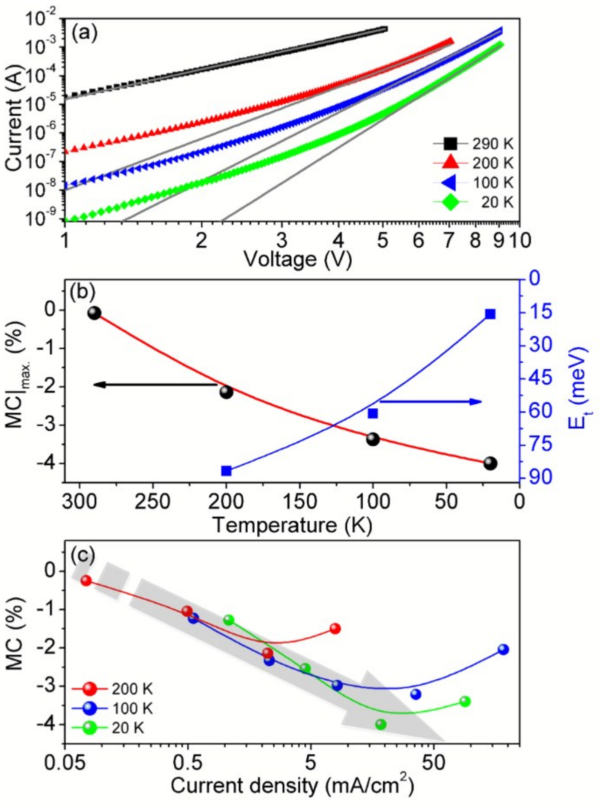

Fig. 3 (a) J-V characteristics of ITO/CuPc/Al device on double logarithmic scale measured at different temperatures. The gray solid lines in (a) are fitting results using the power law equation of $J \propto V^m$; (b) The maximum MC values and characteristic trap energy E_t as a function of temperature; (c) The magnitude of negative MC as a function of current density at low temperatures. The colour solid lines are splines and the gray arrow is guide to the eyes.

film. However, it should be noted that this trapped trion model is expected to produce positive MC.[20, 21] The absence of positive MC (or positive MC components) in our results suggests that the trapped trion model is not suitable. Very recently, Yang et al.[27] have stressed the intra-molecule triplet exciton can increase the on-site binding and make the electron states more localized, which results in a negative MC from quantitative calculation. Unfortunately, the magnitude of MC extracted from this model is very small (0.3%) even at a large trap strength (0.5 eV).[27] This magnitude is one order smaller than that obtained in the present devices (as shown in Fig. 2). Therefore, the above discussions indicate strongly that the exciton mechanisms would be not dominant in our devices, leaving the model based on bipolaron.

Bipolarons (doubly occupying states with two like-charges) are expected to be formed in disorder organic semiconductors [28] if the spins of two like-charges is of singlet character.[12] However, the formation of such doubly occupying states will be strongly suppressed by the Coulomb force between the two like-charges on the same molecular site.[16, 17] In the presence of traps, however, the bipolaron formation is made possible since the negative energy of the traps can compensate the positive on-site repulsion of doubly occupying states. Therefore, we suggest that the traps in CuPc thin films can assist the bipolaron formation through lowering the formation energy of doubly occupying states. In this case, the trap-assisted bipolaron formation opens a charge transport path that was previously blocked, allowing more carriers to pass by hopping (as shown in Fig. 4(a)). However, on applying an external magnetic field (see in Fig. 4(b)), the formation of bipolaron is spin-blocked since the spins of the positive polarons experience approximately the same field.[12] Thus, the hole hopping through the bipolaron path is blocked, resulting in a reduced current and so a negative MC.

Figure 3(c) plots the negative MC against current density at low temperatures. It can be seen that for all measured temperatures the magnitude of negative MC scales with current density for nearly three orders. This result further strengthens the notion that the negative MC observed in this work is caused by the trap-assisted bipolaron formation since the bipolaron model predicts an effect that scales with current density.[29] As current increases in the device, traps are being filled and the number of the bipolarons increases. Therefore, under the bipolaron model the negative MC is proportional to the current density in the device. However, it should be noted that there are some deviations from the linear behavior at high current density. It is shown that the negative MC turns to decrease at high current density. We suggest that the deviations might be caused by the electron injection from the cathode at high applied bias voltages. As mentioned above, there might be some electron injection from cathode into CuPc at high bias voltages although the energy barrier for electron injection is much larger than that for hole injection in the ITO/CuPc/Al device. The injected electrons would strongly couple with the oppositely charged bipolarons. As a result, the bipolarons would be quenched, causing a decreasing in negative MC.

The above results have demonstrated that the negative MC in the ITO/CuPc/Al device is closely correlated to the bipolarons: negative MC becomes larger or weaker as the number of bipolaron increases or decreases, respectively. In order to further confirm the effects of traps on the bipolaron formation and also negative MC, the MC measurements were performed under illumination. When the device is illuminated the situation changes largely due to the presence of

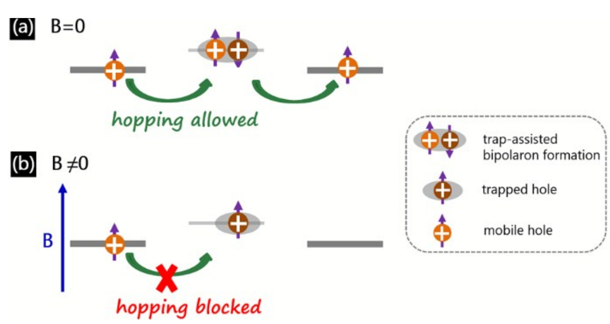

Fig. 4 Schematic description of possible routes for hole hopping in CuPc thin film with traps. It is assumed that charge transport in CuPc thin film can be described by an effective transport level (gray bold lines) and a distribution of trap states (gray thin lines) below this transport. (a) In the absence of magnetic field, trap-assisted bipolaron formation favors hole hopping through the trap site; (b) In the presence of magnetic field, hole hopping through the trap site is blocked since trap-assisted bipolaron formation is suppressed by the magnetic field.

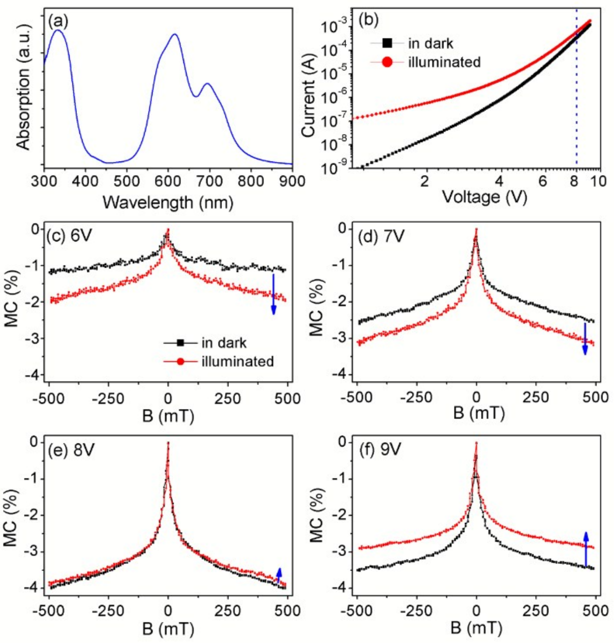

Fig. 5 (a) Optical absorption spectrum of CuPc thin film. (b) Current-voltage characteristics of the ITO/CuPc/Al single layer device at 20 K in dark and under illumination. (c)-(f) Comparison of negative MC responses in the device with and without illumination at 20 K under different voltages: (c) 6 V; (d) 7 V; (e) 8 V; and (f) 9 V.

photogenerated excited states (excitons and/or electron-hole pairs) in the device.[30] Then, the bipolaron formation on the trap sites would be promoted or suppressed, depending on the relaxation paths of the photogenerated excited states. Firstly, the photogenerated excited states are likely to dissociate into charge carriers. These photogenerated charge carriers would enhance the current flowing through the device, which is expected to promote the formation of bipolarons. On the other hand, the photogenerated excited states (especially the triplet excitons with long lifetime) remained in the device might also react with the hole occupied trap sites, forming the charged excitons-like metastable pairs. In this case, the trap-assisted bipolaron formation is largely suppressed since the trap sites are consumed by the photogenerated excited states.

Figure 5(a) shows the typical optical absorption spectrum of CuPc thin film. A He-Gd UV laser of 325 nm near the B-band of the CuPc absorption was used as light source (2 mW) to illuminate the device. Fig. 5(b) displays the current-voltage characteristics of the ITO/CuPc/Al single layer device at 20 K in dark and under illumination. It can be seen that illumination by the UV light leads to a dramatic enhancement on the current at low bias voltages, suggesting that the photogenerated charge carriers play important roles on charge transport in this regime. At high bias voltages larger than 8 V, the changes in current with illumination become negligible. Fig. 5 (c)-(f) compare the negative MC of the device with and without illumination at 20 K under different voltages. Interestingly, the negative MC is enlarged with light illumination at low bias voltages (Fig. 5 (c) and (d)). This result might be caused by the light-promoted bipolaron formation on the trap sites as discussed above. At low bias voltages, the traps are being filled. Thus, the large amount of photogenerated charge carriers (as illustrated in Fig. 5(b)) help to fill the traps and promote biploaron formation on the trap sites. Contrary to the observation at low voltages, the negative MC further decreases under illumination at high voltage of 9 V (Fig. 5(f)). We suggest that the decreases in negative MC at high voltages are resulted from the interaction between the photogenerated excited states and traps. At high voltages, all the traps are filled and the photogenerated charge carriers are not dominant in the current any more (Fig. 5(b)). As discussed early, the photogenerated excited states can react with trap sites occupied by holes to form charged excitons-like metastable pairs, suppress the bipolaron formation on the trap sites. Therefore, the negative MC decreases. Moreover, at a mediate voltage of 8 V, the promotion and suppression effects of illumination on the bipolaron formation cancel each other out, resulting in no obvious changes (a slight decrease) in negative MC with light (Fig. 5(e)). It is noteworthy that the promotion effects at low voltages and suppression effects at high voltages on negative MC by light illumination are also observed at 200 K and 100 K (not shown here), confirming that the trap-assisted bipolaron formation is the origin of negative MC observed in CuPc thin film at low temperatures.

4. Conclusions

In summary, we have investigated the negative MC in an ITO/CuPc/Al thin film device at low temperatures. The maximum values of negative MC increase as the temperature decreases. It is also found that the magnitude of negative MC scales with current density for nearly three orders. Upon comparing the MC results and the *J-V* characteristics at different temperatures, we suggested that traps existing in CuPc thin films play a crucial role in generating negative MC. The trap-assisted bipolaron formation accounting for the observed negative MC in CuPc thin film has been demonstrated. At last, the negative MC responses in ITO/CuPc/Al device have been investigated under light illumination. The promotion effects at low voltages and suppression effects at high voltages on negative MC by light illumination further confirm the notion that trap-assisted bipolaron formation is the origin of negative MC observed in CuPc thin film.

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We developed the bipolaron model to explain the negative MC in ITO/CuPc/Al single layer device, suggesting that traps existed in CuPc thin film can assist the formation of bipolaron through lowering the formation energy.