Magneto-Dielectric Effects Induced by Optically-Generated Intermolecular Charge-Transfer States in Organic Semiconducting Materials

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Traditionally, magneto-dielectric effects have been developed by combining ferroelectric and magnetic materials. Here, we show a magneto-dielectric effect from optically-generated intermolecular charge-transfer states in an organic semiconducting donor:acceptor (PVK:TCNB) system. We observe in magnetic field effects of photoluminescence that a magnetic field can change singlet/triplet population ratio in intermolecular charge-transfer states. Furthermore, our theoretical analysis and experimental evidence indicate that the singlets and triplets in charge-transfer states have stronger and weaker electrical polarizations, respectively. Therefore, the observed magneto-dielectric effect can be attributed to magnetically-dependent singlet/triplet ratio in intermolecular charge-transfer states. In principle, a magneto-dielectric effect can be generated through two different channels based on magneto-polarization and magneto-current effects when the singlet/triplet ratio in intermolecular charge-transfer states is changed by a magnetic field. We find, from the simulation of dielectric effects, that magneto-polarization and magneto-current effects play primary and secondary roles in the generation of magneto-dielectric effect.

M agneto-dielectric effects refer to the phenomena where a magnetic field can modify dielectric constant through internally coupled electric and magnetic parameters[1–3]. In general, magneto-dielectric phenomena can be obtained by combining magnetic and ferroelectric structures[4–7] based on thin films[8,9] hetero-junctions[10,11], and nanostructures or radicals[12–15]. The magneto-electric responses are an important property in the development of multifunctional materials in information storage and sensing applications[9,16,17]. We know that organic semiconducting materials can exhibit magnetic field effects on photoluminescence, electroluminescence, electrical current, and photocurrent through excited states[18–23]. In general, the magnetic field effects rely on two facts: (i) a magnetic field can modify the singlet/triplet ratio in excited states and (ii) singlets and triplets have different contributions to light emission and charge transport. Here, we should note that the singlets and triplets can also have different ionic properties due to spin configuration-modulated orbital motions in their wavefunctions. With different ionic properties, singlets and triplets can exhibit different electrical polarizations in response to external electric field. Therefore, magnetically changing the singlet/triplet ratio may form a new mechanism to generate a magneto-dielectric phenomenon in organic semiconducting materials. We should note that the magneto-dielectric phenomenon from magnetically modified singlet/triplet ratio is essentially a new phenomenon in the family of magnetic field effects in organic semiconducting materials. In this work, a typical donor: acceptor system containing poly(9-vinylcarbazole) (PVK) and 1,2,4,5-tetrachloro-3-nitrobenzene (TCNB) was utilized to investigate the magneto-dielectric response through photoexcitation-assisted impedance measurement in an electrically-controlled magnetic field. Our studies find that magnetic field-dependent singlet/triplet ratio in intermolecular charge-transfer states can lead to an optically tunable magneto-dielectric function in organic materials.
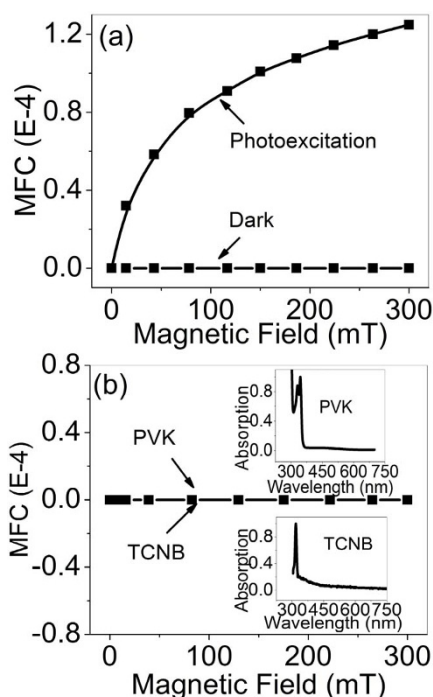
Figure 1 | (a) Magnetic field effects on capacitance (MFC) are shown for ITO/PVK:TCNB/Al device under dark and photoexcitation conditions. (b) Zero MFC was observed from both ITO/PVK/Al and ITO/TCNB/Al devices under photoexcitation condition. The inset figures show the normalized absorption spectra from the PVK stand-alone film and TCNB dispersed in PMMA film, respectively.
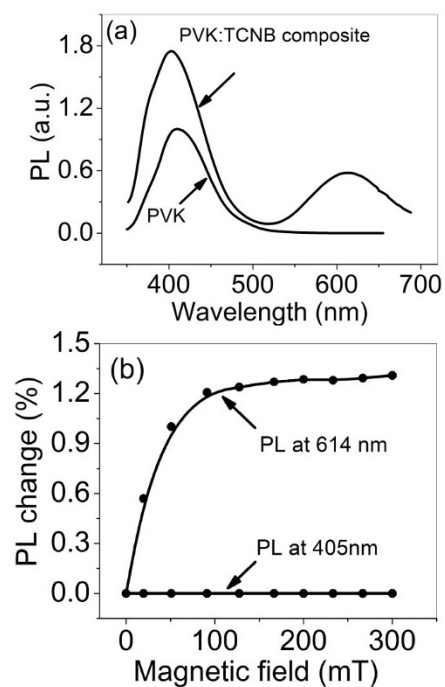

Figure 2 | (a) PL spectra are shown for PVK:TCNB composite and pristine PVK film, the pristine TCNB does not have an appreciable PL emission (not shown). (b) Magnetic field effect on PL (MFE$_{PL}$) is shown for intermolecular charge-transfer states of PVK:TCNB composite. The PL from intramolecular excited states (excitons) in PVK component exhibits zero MFE$_{PL}$.

Results

Fig. 1 (a) shows an interesting phenomenon: the capacitance changes with magnetic field, namely magnetic field-dependent capacitance (MFC), in the ITO/PVK:TCNB/Al device under photoexcitation at 325 nm using a IK series He-Cd laser. The MFC is defined as $\Delta C/C_0 = (C_B - C_0)/C_0$, where C_B and C_0 are capacitance with and without magnetic field, respectively. The laser beam is illuminated perpendicular to the device through the ITO side and the magnetic field applied parallel to the device plane, however, it should be noted that no appreciable change on the MFC amplitude was found with different angles between the device plane and the direction of the magnetic field. This magnetic field-dependent capacitance suggests that a photoexcitation can generate a magneto-dielectric response in the organic PVK:TCNB composite. On contrast, no magneto-dielectric signal can be observed from the same PVK:TCNB device under dark condition. Even under photoexcitation, the device fabricated with pristine PVK or TCNB does not exhibit a magneto-dielectric signal (Fig. 1 (b)). Clearly, the observed magneto-dielectric response can be attributed to the photoinduced excited states in the PVK:TCNB composite.

It is known that photoexcitation can generate both intermolecular and intramolecular excited states, namely charge-transfer states and Frenkel excitons in the PVK:TCNB composite. We can see from Fig. 2 (a) that the photoluminescence from the PVK:TCNB composite consists of short-wavelength (410 nm) and long-wavelength (614 nm) peaks. The short-wavelength peak from the PVK:TCNB composite coincides with the emission from pure PVK. Therefore, the short-wavelength and long-wavelength peaks can be assigned to excitons generated in PVK and charge-transfer states at the PVK/TCNB interface in the PVK:TCNB composite. Nevertheless, our photoluminescence results confirm that a photoexcitation can generate charge-transfer states in the donor:acceptor (PVK:TCNB) composite. Early experimental studies in EPR (electron parametric

resonance), transient absorption, and electroluminescence have also shown that charge-transfer states can be significantly formed in donor:acceptor systems under photoexcitation[24–26]. In particular, we should note in Fig. 2 (b) that the photoluminescence from charge-transfer states at the PVK:TCNB interface shows a considerable dependence of magnetic field. Clearly, the magnetic field dependence of photoluminescence provides a direct evidence to indicate that a magnetic field can increase the singlet/triplet population ratio in the charge-transfer states in the PVK:TCNB composite. This satisfies the first necessary condition: magnetic field-dependent singlet/triplet ratio in charge-transfer states, required for the development of magneto-dielectric response. Early experimental studies have also suggested that a magnetic field (<100 mT) can appreciably change the population ratio between singlets and triplets in intermolecular electron-hole pairs (polaron pairs) through singlet-triplet intersystem crossing, leading to magnetic field-dependent singlet/triplet ratio[27–31]. We should also note that the photoluminescence from excitons exhibits negligible dependence of magnetic field, which is consist with other experimental results[19,32,33]. The difference in magnetic field effects between intermolecular charge-transfer states and intramolecular excitons can be attributed to the following hypothesis: whether the singlet/triplet ratio can be changed essentially depends on whether a magnetic field can perturb the equilibrium of singlet-triplet intersystem crossing established by the competition between spin-conserving process, supported by internal spin-exchange interaction, and spin-random process caused by hyperfine coupling[34,35]. In charge-transfer states, a magnetic field can cause an appreciable perturbation on the equilibrium of singlet-triplet intersystem crossing due to weak spin-exchange interaction and spin-orbital coupling or hyperfine coupling.

Now we look at the second necessary condition: the singlets and triplets in charge-transfer states have different electrical polarizations. The stronger and weaker electrical polarizations from singlet and triplet electron-hole pairs have been suggested by theoretical and
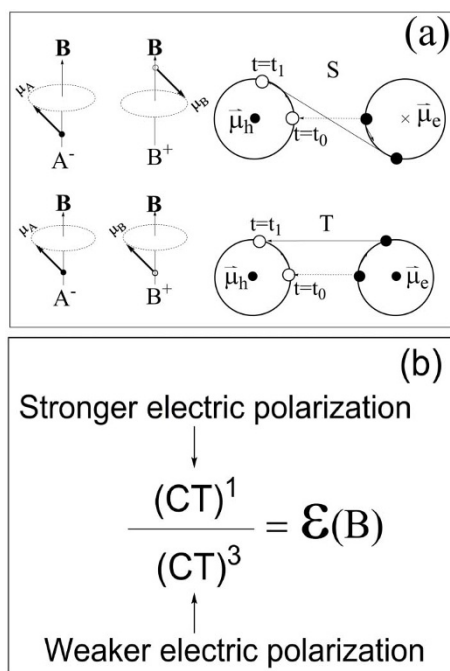
Figure 3 | (a) Magnetic and electric dipoles are shown for singlet and triplet inter-molecular excited states with spin precessions and orbital motions. (b) Magnetic field-dependent singlet/triplet ratio in inter-molecular excited states corresponds to a magneto-dielectric response in organic materials.

spectroscopic studies[36,37]. Furthermore, magnetocurrent studies have also suggested that singlets and triplets in intermolecular electron-hole pair states have stronger and weaker electrical polarizations to explain magnetic field-dependent charge density through spin-dependent charge dissociation in electrical conduction[38–40]. In molecular orbital theory, we can schematically see that anti-parallel and parallel spin-correlated electron and hole pairs correspond to larger and smaller electrical dipoles in a two-dimensional configuration (Fig. 3 (a)). Specifically, the orbital motions in singlet and triplet states are regulated by anti-parallel and parallel spin precessions, respectively. A singlet state corresponds to a clock-wise orbital motion for the electron and an anti-clock-wise orbital motion for the hole in an intermolecular charge-transfer state due to anti-parallel spin precessions. However, a triplet corresponds to a clock-wise orbital motion for both electron and hole due to parallel spin precessions. As a result, the singlet and triplet can exhibit larger and smaller electric dipoles, respectively. The stronger and weaker electrical polarizations from singlets and triplets can also be experimentally argued by following experimental observations. First, we have observed that charge-transfer states can generate positive magnetic field effects of photocurrent at high field regime (>150 mT)[41–43]. This experimental observation implies that magnetically increasing the singlet/triplet ratio in charge-transfer states can lead to an increase in photocurrent through dissociation in bulk-hetero-junction solar cells. Second, the dissociation of charge-transfer states at donor:acceptor interfaces can largely undergo field-dependent Onsager process[44] in the generation of photocurrent. Therefore, from magnetic field effects of photocurrent we can experimentally argue that singlets and triplets in charge-transfer states have stronger and weaker electrical polarizations. Thus, intermolecular charge-transfer states satisfy both conditions: (i) magnetic field-dependent singlet/triplet ratio and (ii) singlet/triplet ratio-dependent electrical polarization, for the development of magneto-dielectric response in organic semiconducting materials (Fig. 3 (b)).

In principle, magnetically changing singlet/triplet ratio in inter-molecular charge-transfer states can lead to a magneto-dielectric

effect in the ITO/PVK:TCNB/Al device through two different channels based on magneto-polarization and magneto-current effects, namely polarization and transport-based magneto-dielectric effects[45–48]. Obviously, the polarization and transport-based magneto-dielectric effects come from magnetic field-dependent polarization and magnetic field-dependent current, respectively, when an alternating field of 50 mV is applied in the photoexcitation-assisted dielectric measurement. Here, we examine the polarization and transport-based magneto-dielectric responses through theoretical and experimental analyses when a magnetic field changes the singlet/triplet ratio in charge-transfer states. The polarization-based magneto-dielectric response (MFC$_P$) can be given by

$$MFC_P = \frac{\delta\varepsilon}{\varepsilon} \tag{1}$$

where ε is the dielectric constant of PVK:TCNB composite film without applied magnetic field and $\delta\varepsilon$ is the change in dielectric constant of PVK:TCNB composite film caused by an applied magnetic field through charge-transfer states. On the other hand, magnetically changing the singlet/triplet ratio in charge-transfer states can lead to a magnetocurrent[23,39,49–51] based on the fact that singlets and triplets have different dissociation rates due to their different ionic properties[52,53]. A magneto-current may be reflected as a magneto-dielectric response (namely transport-based magneto-dielectric response) in the capacitance measurement when an alternating electric field drifts the charge carriers in the ITO/PVK:TCNB/Al device. Here, the transport-based magneto-dielectric response can be described by magnetic field-dependent charge density given by

$$MFC_T = \frac{\delta n}{n} \tag{2}$$

where δn is the change in charge density caused by magnetic field through spin-dependent dissociation of charge-transfer states and n is the charge density without magnetic field. To distinguish polarization and transport-based magneto-dielectric responses, we inserted a tunneling barrier, insulating PVA (polyvinylachol) layers, into the PVK:TCNB device with the device architecture of ITO/PVA/PVK:TCNB/PVA/Al to explore polarization and transport effects on magneto-dielectric response when the singlet/triplet ratio in charge-transfer states is changed by a magnetic field. With the PVA dielectric layers, the polarization-based magneto-dielectric response MFC$_P$ (see supplemental material) can then be given

$$MFC_P = \frac{\varepsilon_B - \varepsilon}{\varepsilon} = \frac{d_{PVK}\varepsilon_{PVA}}{(2d_{PVA}\varepsilon_{PVK} + d_{PVK}\varepsilon_{PVA})}\frac{\delta\varepsilon_{PVK,B}}{\varepsilon_{PVK}} \tag{3}$$

where ε_B and ε are the effective dielectric constants for the PVK:TCNB composite film with and without magnetic field; ε_{PVA} is the dielectric constant for PVA layer; $\delta\varepsilon_{PVK}$ represents the dielectric change ($\varepsilon_B - \varepsilon$) for the entire PVK:TCNB composite film caused by a magnetic field under photoexcitation (here we ignore the contribution from TCNB due to its negligible optical absorption at photoexcitation wavelength); d_{PVA} and d_{PVK} are the thicknesses for PVA and PVK:TCNB layers.

In a transport-based magneto-dielectric response, insulting PVA layers provide a tunneling barrier between the PVK:TCNB film and respective electrode, and consequently causes charge accumulation at the interface of PVA/(PVK:TCNB) when applied alternating electric field drifts the charge carriers towards respective electrodes within the active PVK:TCNB film. With the tunneling through the insulating PVA layers (supplemental material), the transport-based magneto-dielectric response can be given by

$$MFC_T = \frac{Q_B - Q}{Q} = \frac{n_0(1 + \delta n)(1 - T) - n_0(1 - T)}{n_0(1 - T)} = \frac{\delta n}{n_0} \tag{4}$$
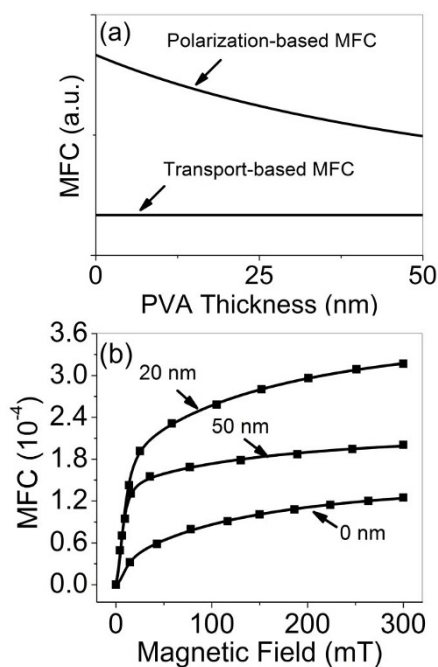
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Figure 4 | (a) Theoretical simulation for polarization-based and transport-based MFC as a function of PVA thickness in ITO/PVA/PVK:TCNB/PVA/Al device. (b) Experimental (solid dots) and theoretical data (solid lines) from equation (6) to show MFC at different PVA layer thicknesses under illumination.

where Q_B and Q are the charge carriers accumulated at the PVA/(PVK:TCNB) interface for the situations with and without magnetic field, n_0 is the number of charge carriers under photoexcitation, δn is the change in the number of charge carriers caused by the magnetic field under photoexcitation, T is the tunneling probability through the PVA layer to respective electrode. Our theoretical analysis from Eq. (4) indicates that inserting insulating PVA layers does not change the transport-based magneto-dielectric response. This is because the same tunneling rate, determined by the barrier height and thickness, applies on to the charge transports in both situations before and after applying magnetic field in the given device of ITO/PVA/PVK:TCNB/PVA/Al. As a consequence, the insulating PVA layers decrease the charge transports equally for the situations with and without magnetic field, leading to an un-changed transport-based magneto-dielectric response (MFC$_T$).

Fig. 4 (a) shows MFC$_P$ and MFC$_T$, separately, as a function of the layer thickness of insulating PVA used in the ITO/PVA/PVK:TCNB/PVA/Al device based on theoretical calculation from equation (3) and (4) [using $\varepsilon_{PVK} = 3.0$[54] for PVK:TCNB film and $\varepsilon_{PVA} = 2.2$[55] for PVA film]. We can see that the value of MFC$_P$ decreases with increasing dielectric PVA thickness while the value of MFC$_T$ keeps unchanged. This distinctive dependence of magneto-capacitance with the dielectric film thickness forms a mechanism to separate the polarization and transport contributions to the observed magneto-dielectric effect. Fig. 4 (b) shows the experimental data of magneto-dielectric response measured at different PVA thicknesses in the ITO/PVA/PVK:TCNB/PVA/Al device. It can be seen that inserting PVA layers with film thickness of 20 nm can increase the magnitude of magneto-dielectric response. Further increasing the PVA thickness to 50 nm can then lead to a decrease on the magnitude of magneto-dielectric response. We know from our theoretical analysis (shown in Fig. 4 (a)) that polarization and transport-based magneto-dielectric effects are dependent and in-dependent of tunneling barrier thickness, respectively. Based on our theoretical analysis, the non-monotonic dependence of magneto-dielectric response on insulating PVA thickness can qualitatively suggest that polarization and

transport-based magneto-dielectric responses are primary and secondary effects, respectively, in the ITO/PVK:TCNB/Al device when the intermolecular charge-transfer states are exposed to an alternating electric field of 50 mV in the capacitance measurements. In particular, inserting tunneling layers can vary the relative weight ratio between polarization-based and transport-based magneto-dielectric responses.

Discussion

Here, we use simulation to quantitatively estimate the polarization and transport-based magneto-dielectric responses from intermolecular charge-transfer states in the ITO/PVK:TCNB/Al device. In general, magnetic field effects can be described by Lorentzian $\left(\dfrac{B^2}{|B|^2 + B_0'^2} \right)$ and non-Lorentzian $\left(\dfrac{B^2}{(|B| + B_0)^2} \right)$ functions in organic materials[35,56–58]. The two constants: B'_0 and B_0, represent internal magnetic interactions in Lorentzian and non-Lorentzian functions. We propose that non-Lorentzian and Lorentzian functions are for polarization and transport-based magneto-dielectric responses, respectively, based on the following two considerations. First, in polarization-based magneto-dielectric response, an applied alternating electric field polarizes charge-transfer states in the PVK:TCNB composite. This induced electrical polarization can generate a larger orbital current in covalently linked molecules and consequently yields a stronger internal magnetic interaction through the coupling between electron spin and orbital current[59]. With stronger internal magnetic interaction the non-Lorentzian function can be used to describe magnetic field effects[60]. Thus, we use the non-Lorentzian function for polarization-based magneto-dielectric response (MFC$_P$). On the other hand, the transport-based magneto-dielectric response comes from the change in charge density caused by a magnetic field in the PVK:TCNB layer through dissociation of photo-generated intermolecular charge-transfer states. In this channel, electrical polarization is not considered, leading to the hyperfine as an only internal magnetic interaction. This can thus correspond to a weaker internal magnetic interaction[61]. Therefore, we use the Lorentizan function to describe the transport-based magneto-dielectric response (MFC$_T$). Here, we consider a general situation that the observed magneto-capacitance contains both polarization and transport components (MFC$_P$ and MFC$_T$), as given by equation (5).

$$
\begin{aligned}
MFC &= A_1 \cdot MFC_P + A_2 \cdot MFC_T \\
&= A_1 \cdot \left[\frac{d_{PVK:TCNB}\varepsilon_{PVK:TCNB}}{2 d_{PVA}\varepsilon_{PVK:TCNB} + d_{PVK:TCNB}\varepsilon_{PVA:TCNB}} \right] \cdot \frac{B^2}{(|B| + B_0)^2} \\
&+ A_2 \cdot \frac{B^2}{(|B|^2 + B_0')^2}
\end{aligned} \quad (5)
$$

where A_1 and A_2 are two coefficients for polarization and transport contributions to magneto-dielectric response. By fitting the experimental data of magneto-capacitance at different PVA thicknesses by using Eq. (5), we can then obtain the values for coefficients A_1 and A_2 as well as for internal magnetic interactions (B_0, and B'_0). Table 1 shows the values for A_1, A_2, B_0, and B'_0 at different dielectric PVA film thicknesses based on the simulation. The simulation results quantitatively confirm the following three interesting phenomena.

Table 1 | Simulation results based on the equation (5)

PVA layer thickness	A₁	B₀ (mT)	A₂	B₀′ (mT)
0 nm	1.204×10^{-4}	68.645	0.444×10^{-4}	11.01
20 nm	2.379×10^{-4}	81.947	2.021×10^{-4}	8.837
50 nm	1.291×10^{-4}	82.319	1.504×10^{-4}	6.629

First, the polarization-based magneto-dielectric response is a primary effect in the ITO/PVK:TCNB/Al device with $A_1 = 1.204 \times 10^{-4}$ and $A_2 = 0.444 \times 10^{-4}$ when the intermolecular charge-transfer states are exposed to an applied alternating electric field. The transport-based magneto-dielectric response is a secondary effect caused by the drift of dissociated charge carriers from charge-transfer states under applied alternating electric field. Second, when the tunneling PVA layers are used with a thickness of 20 nm, polarization and transport-based magneto-dielectric responses have similar contributions with $A_1 = 2.379 \times 10^{-4}$ and $A_2 = 2.021 \times 10^{-4}$. This is because inserting tunneling PVA layers can decrease the polarization-based magneto-dielectric response and leaves the transport-based magneto-dielectric response un-changed, as suggested by the theoretical analysis (Fig. 4 (a)). Third, when the thickness of tunneling PVA layer increases to 50 nm, transport-based magneto-dielectric response has slightly larger contribution to polarization-based magneto-dielectric response ($A_1 = 1.291 \times 10^{-4}$ and $A_2 = 1.504 \times 10^{-4}$). This indicates that further increasing the tunneling PVA thickness can further decrease polarization-based magneto-dielectric component while the transport-based magneto-dielectric response is in-dependent of tunneling PVA thickness. In addition, we should also note that the magnitude of magneto-dielectric response is increased after the insertion of PVA layers as compared to the situation before the insertion of PVA layers (Fig. 3(b)). This means that using the insulating PVA layers can reduce the leaking current, which is nothing related to magnetic field effects, in the ITO/PVA/PVK:TCNB/PVA/Al device during magneto-dielectric measurement. Nevertheless, our studies indicate that intermolecular charge-transfer states can generate magneto-dielectric response primarily from electrical polarization effects when a magnetic field changes the singlet/triplet ratio in organic semiconducting donor:acceptor (PVK:TCNB) system.

In conclusion, a magneto-dielectric response is demonstrated as a new phenomenon in the family of magnetic field effects based on organic donor:acceptor (PVK:TCNB) system with the device structure of ITO/PVK:TCNB/Al under photoexcitation. The development of magneto-dielectric response relies on two experimental requirements: (i) magnetic field-dependent singlet/triplet ratio and singlet/triplet ratio-dependent electrical polarization from intermolecular charge-transfer states. The experimental evidence from magnetic field effects of photoluminescence and photocurrent indicate that intermolecular charge-transfer states can fulfill these two requirements. Furthermore, magneto-dielectric response developed by intermolecular charge-transfer states can, in principle, come from magneto-polarization and magneto-current effects when a magnetic field changes the singlet/triplet ratio in intermolecular charge-transfer states in organic semiconducting materials. We find, from experimental and theoretical analyses, that magneto-polarization and magneto-current effects play primary and secondary roles in the generation of magneto-dielectric response based on intermolecular charge-transfer states in the donor:acceptor (PVK:TCNB) system. Therefore, using intermolecular excited states presents a new mechanism to develop optically-tunable magneto-dielectric response in organic semiconducting materials.

Methods

The semiconducting materials: poly(9-vinylcarbazole) (PVK) and 1,2,4,5-tetra-chloro-3-nitrobenzene (TCNB) used in this work were purchased from Sigma Aldrich Inc. The donor:acceptor (PVK:TCNB) composite films were spin cast on pre-cleaned ITO substrates with a thickness of 200 nm from the chloroform solution containing the PVK and TCNB in a weight ratio of 200 : 3. The devices used for magneto-capacitance studies were fabricated with the sandwich architecture of ITO/PVK:TCNB/Al. Aluminum (Al) electrodes were thermally deposited under the vacuum of 7×10^{-7} torr with the thickness of 80 nm. The PVA (polyvinyl alcohol) was used as low-dielectric insulating films with a thickness of 20 nm or 50 nm to sandwich the donor:acceptor (PVK:TCNB) composite film with the device architecture of ITO/PVA/PVK:TCNB/PVA/Al to explore polarization and transport contributions during the generation of magneto-capacitance. The magneto-capacitance measurements were performed on the fabricated devices located in a magnetic field by using an Agilent E4980A LCR meter with zero DC bias and 50 mV AC field at 1K Hz. The 325 nm photoexcitation energy (12 mW/cm²) produced from IK series He-Cd laser was used to generate intermolecular excited states of PVK:TCNB complex. The magneto-capacitance was defined as $\frac{\Delta C}{C} = \frac{C_B - C}{C}$, the C_B and C are the capacitances with and without magnetic field, respectively. All the measurements are done under nitrogen atmosphere at room temperature.

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Acknowledgments

Author contributions

B.H. designed the experimental scheme and analyzed experimental data with H.D.Z. H.D.Z. and L.Y. carried out the experiments. M.X.L. and L.H. helped on the experimental measurements. H.D.Z. wrote the initial draft of manuscript. B.H. revised the manuscript. All the co-authors reviewed the manuscript.

Additional information