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Identify triplet-charge interaction in rubrene-based diodes using magneto-conductance: Coexistence of dissociation and scattering channels

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ABSTRACT

Although it is known that triplet excitons can be quenched via triplet-charge interaction (TQI), it is still unclear how this process occurs in rubrene-based devices. We found that magneto-conductance (MC) can be used to probe the detailed mechanism of TQI in rubrene-based organic light-emitting diodes and observed the coexistence of negative and positive MC responses in the high-field region when holes and electrons were the dominant charged species at different interfaces adjoining the rubrene layer, respectively. Further analysis suggests that the negative MC response was originated from the dissociation of triplet excitons by holes, while the positive MC response was due to electron scattering by triplet excitons. The MC responses of the devices were examined under different injection currents and temperatures to confirm our hypothesis. This work gives significant insight into mechanisms of TQI in organic semiconductors, which will allow for the design of new and improved devices.

1. Introduction

Rubrene has attracted great interests in the scientific community because of its unique optoelectronic properties that makes it desirable for use in organic semiconductor devices. For example, the energy of a singlet exciton within rubrene is resonant with that of two triplet excitons ($E_{S_1} \approx 2E_{T_1}$)[1–5], which facilitates bimolecular reactions, including singlet fission (STT) and triplet fusion (TTA), ($S_1 + S_0 \leftrightarrow T_1 + T_1$)[4,6–8]. STT can lead to highly efficient organic solar cells (OSCs) [9], while TTA can increase the theoretical quantum efficiency of fluorescent organic light-emitting diodes (OLEDs) up to 62.5% [10,11]. And the utilization of triplet excitons is especially important for these two processes in rubrene-based devices. However, the high densities of triplet excitons that are generated in rubrene-based devices through STT can be quenched via triplet-charge interaction (TQI) [4]. Therefore, it is important to understand TQI in triplet exciton-rich organic semiconducting devices.

TQI generally occurs via two magnetic field (B) sensitive channels: (i) the dissociation channel, in which the triplet excitons are dissociated into free electrons (e) and holes (h) when they react with free (C) or trapped (C_t) carriers ($T + C/C_t \rightarrow e + h + C$) [12–14] and (ii) the scattering channel, in which triplet excitons collide with free carriers ($T + C \rightarrow T + C$), resulting in a decrease of charge mobility [12,15]. The presence of an external B can suppress their rate constants [16], which causes the generation of magneto-conductance (MC) signals with opposite signs. In 2007, Desai et al. proposed that a positive MC response was due to free carrier scattering by triplets while a negative MC response was caused by triplet dissociation [12]. Hu. et al. observed a negative MC response and attributed it to triplet dissociation that was caused by interactions with secondary charge carriers in the unbalanced charge injection conditions that were present [15]. Recently, we have observed that localized triplet excitons and triplet charge-transfer-complexes play crucial roles in the scattering and dissociation channels of TQI [17], respectively. However, the presence of TQI in rubrene-based devices is seldom reported, especially it is unclear whether the TQI process undergoes via dissociation or scattering channels.

In this work, the MC effects of four different rubrene-based devices were measured at a range of operating currents and temperatures. The MC curves were strongly affected by the polarity of

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the charges (electrons and holes) that had accumulated at different interfaces near rubrene layer existed in the devices and could be fitted to the sum of one Lorentzian and two non-Lorentzian empirical formulas. Further analysis indicated that the distinct changes that were observed in the high *B* range of the MC effects were caused by the dissociation and scattering channels of TQI that coexisted. The dissociation of triplet excitons by holes resulted a negative MC response while the scattering of electrons by triplet excitons generated a positive MC response. This work showed that MC can be used to identify the different TQI processes that exist in a device, and will enable the design and optimization of device structures that minimize the quenching of triplet excitons.

2. Experimental section

Rubrene was used as the fluorescent emissive layer, *N*,*N*′-di(naphthalene- 1-yl)-*N*,*N*′-diphenyl-benzidine (NPB) was used as a hole-transporting material, 4,4′,4″-*tris* (*N*-3-methylphenyl-*N*-phenylamino)triphenylamine (*m*-MTDATA) was used as an electron-blocking material, bathocuproine (BCP) was used as an electron-transporting and hole-blocking material, *tris*-(8-hydroxyquinoline)aluminum (Alq_3) was used as an electron-transporting layer, and lithium fluoride (LiF) was used to improve the electron injection efficiency.

Four different device structures were used to investigate TQI by modifying the accumulation of charges at different interfaces near emissive layer within the devices. They had the following configurations: ITO/NPB (60 nm)/rubrene (30 nm)/BCP (50 nm)/LiF (1 nm)/Al (120 nm) (Dev.1), ITO/NPB (60 nm)/rubrene (30 nm)/Alq_3 (50 nm)/LiF (1 nm)/Al (120 nm) (Dev.2), ITO/*m*-MTDATA (60 nm)/rubrene (30 nm)/BCP (50 nm)/LiF (1 nm)/Al (120 nm) (Dev.3), and ITO/NPB (60 nm)/rubrene (30 nm)/BCP (50 nm)/Al (120 nm) (Dev.4). The devices contained indium tin oxide (ITO) and aluminum (Al) electrodes with active areas of 2 mm × 2 mm that were deposited by thermal evaporation under vacuum (~10^{-6} Pa). The devices were mounted to the cold finger of a closed-cycle cryostat (Janis: CCS-350S), which was located between the poles of an electromagnet (Lakeshore EM647). A *B* with a maximum strength of ±500 mT was applied in a direction parallel to the device surface. A Keithley 2400 multimeter was used to provide the voltage bias and record the current signals, while a Keithley 2000 multimeter was used to record the EL intensity that was measured using a Si photodiode.

3. Results and discussion

The normalized electroluminescence (EL) spectra of Dev.1 and 2 are shown in Fig. 1a (insert). The emission maxima (563 nm) and low energy shoulder peaks (600 nm) of the two devices were the same, which was consistent with the EL emission of rubrene [4]. Dev.2 exhibited an additional high energy shoulder (~523 nm) that

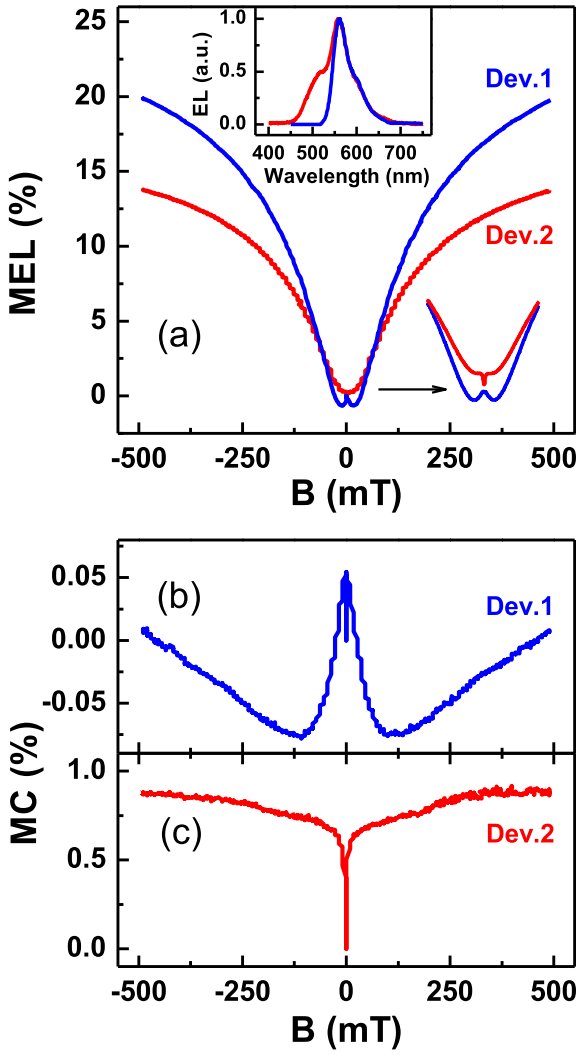

Fig. 1. (a) MEL responses (the expansion shows the MEL up to 100 mT) and normalized EL spectra (top inset) of Dev.1 and 2 under an injection current of 100 μA at R.T. (b) and (c) MC curves of Dev.1 and 2 with an injection current of 100 μA at R.T.

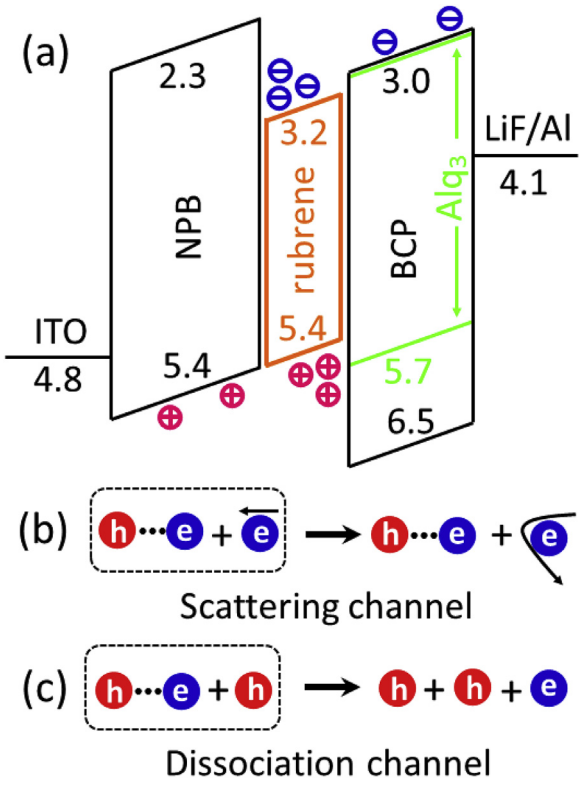

Fig. 2. (a) Energy level diagrams of Dev.1 and 2. The electron-transporting layer of Dev.1 is BCP while that of Dev.2 is Alq_3. (b) Schematic diagram showing the scattering of electrons by triplet excitons that occurs in the rubrene-based devices (black arrows around electrons represent its direction of motion). (c) Schematic diagram showing triplet exciton dissociation by holes in the devices. The e, h and h···e represent electron, hole and triplet exciton respectively.