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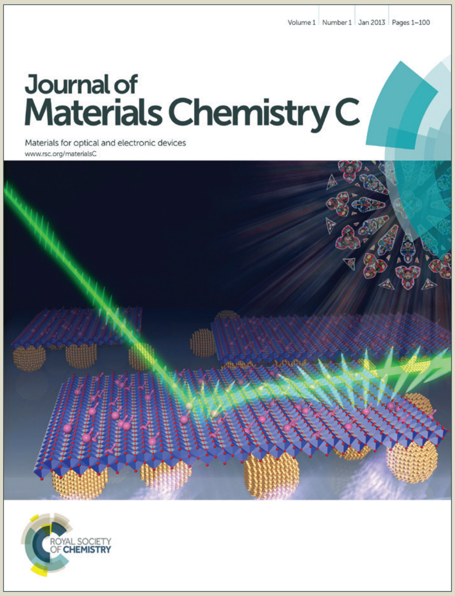

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ARTICLE TYPE

Studying the influence of triplet deactivation on the singlet-triplet inter-conversion in intra-molecular charge-transfer fluorescence based OLEDs by magneto-electroluminescence

Qiming Peng,[a] Aiwu Li,[b] Yunxia Fan,[a] Ping Chen,[a] and Feng Li *[a]

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The forward conversion from singlets to triplets and backward conversion from triplets to singlets are both possible in charge-transfer (CT) fluorescence based organic light-emitting devices (OLEDs), due to the small energy difference between singlet and triplet CT states. Thus clarifying factors affecting the direction of the conversion is important to obtain highly efficient OLEDs based on thermally activated delayed fluorescence (TADF). Here we investigated the inter-conversion between singlets and triplets in a CT fluorescence based OLED via the magneto-electroluminescence (MEL) measurements. The values of MELs turned from negative to positive with the increase of driving voltage and electrically stressing time, indicating the direction of the conversion was changed. Both the increase of driving voltage and stressing time can cause the quenching of triplets through triplet-triplet annihilation and triplet-trap interaction, respectively. So the decreased population ratio of triplet to singlet induces the change of the direction of inter-conversion. Our results demonstrate that the singlet-triplet inter-conversion is a dynamic process, and the deactivation rates of singlet and triplet determine the inter-conversion direction.

1. Introduction

Organic light emitting devices (OLEDs) have the advantages of low-cost, easy processing, lightweight, and flexibility in the applications in flat panel displays and lighting sources.[1-3] After extensive studies over two decades, commercial production of OLEDs has appeared in the market, so reducing the cost should be the next priority in the field of OLEDs. Recent research focus is changed to the charge-transfer (CT) fluorescence based OLEDs, because they are relatively cheap and can harvest the triplets energy and thus improve the efficiency through the thermally activated reverse intersystem crossing (RISC) from triplet to singlet.[4-8] It is said that to gain efficient RISC, a small energy gap between singlet and triplet (ΔE_{ST}) is needed, and the ΔE_{ST} is small in CT materials due to the spatial separation of HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital).[5] However, according to the theory of the non-radiative transitions, the small ΔE_{ST} can also result in the efficient intersystem crossing (ISC) from singlet to triplet.[9,10] In other words, neither the ISC nor RISC can be ignored in the CT fluorescence based OLEDs. And whether the overall direction of the conversion is backward (in this case the triplet energy is harvested) or forward depends on whether the RISC or ISC dominates the inter-conversion. In our previous work,[11] we demonstrated the backward conversion in a twisted intra-molecular CT fluorescent material based OLED, by measuring the magnetic field effects (MFEs) on the electroluminescence (EL), i.e., the magneto-electroluminescence (MEL). However, we noted in some other CT fluorescence based OLEDs, forward conversion was demonstrated.[12,13] These different results lead to a question: what factors affect the direction of the conversion between singlet and triplet in OLEDs? We believe it is important both in science and applications to answer this question, because it will give clues for designing highly efficient OLEDs based on the RISC.

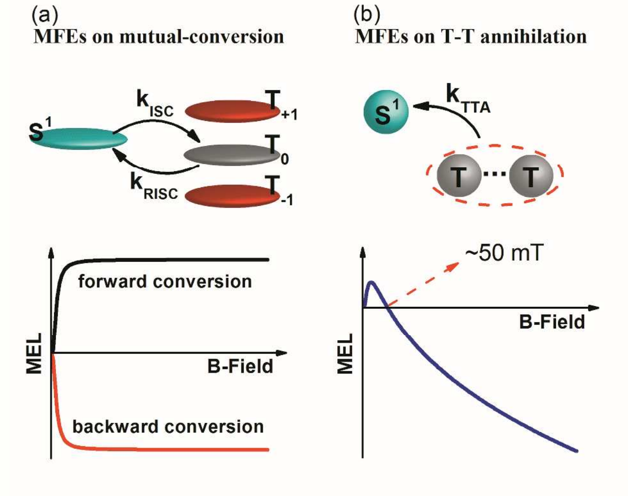

Fig. 1. (a) The top panel: schematically diagram of the MFEs on the inter-conversion between singlets and triplets. The bottom panel: schematic MELs based on the forward and backward conversions. (b) The top panel: schematically diagram of the singlet channel of TTA, the k_{TTA} is magnetic field dependent. The bottom panel: a schematic MEL based on the TTA.

Here, by investigating the MELs, we will show that the direction of conversion between singlet (S^{CT}) and triplet (T^{CT}) CT states can be turned from backward to forward with the decrease of the population ratio of T^{CT} to S^{CT}. The MFEs in organic materials which have been intensively studied are approved to be a good tool to study the physical processes of the organic materials and devices.[14-25] The MEL is defined as: MEL=ΔEL/EL=(EL(B)-EL(0))/EL(0), where the EL(B) and EL(0) are the EL intensity with and without the applied magnetic field, respectively. It is worthy to briefly explain the conversion-mediated MEL (MEL_{con}).[15-29] In OLEDs, when the ΔE_{ST} is small, the singlet and three sub-states of the triplet (T_{+1}, T_0, T_{-1}) are spin-mixed by the hyperfine field, i.e., the inter-conversion occurs between the singlet and T_{+1}, T_0, T_{-1}. When an external magnetic field is applied, the spin-mixing is disturbed. In this case, inter-conversion only occurs between the singlet and T_0, as shown in the top panel of figure 1(a). As a result, the conversion rate will decrease. Therefore, when the ISC is the dominant process, i.e., the direction of the conversion is forward, the MEL_{con} is positive. When the RISC is dominant, i.e., the direction of the conversion is backward, the MEL_{con} is negative. In other words, the MEL_{con} can be a fingerprint for detecting the direction of the conversion. The bottom panel of the figure 1(a) schematically shows the typical MEL_{con} based on the forward (black line) and backward (red line) conversions. The shapes of the MEL_{con} curves can be described as MEL $\propto B^2/(B^2+B_0^2)$, here B is the applied magnetic field and B_0 is the fitting parameter which is intimately related to the hyperfine field (in the range of several mT).[30] It is proposed that the formula can be obtained by calculating the hyperfine Hamiltonian.[31]

In addition to the MEL_{con}, the MFE on the T-T annihilation (TTA) could also result in the change of the EL, i.e. the TTA-mediated MEL (MEL_{TTA}).[27,28] The TTA has been studied over four decades and nowadays expected to be an alternative way for harvesting the energy of triplet excitons in fluorescence OLED.[32-35] In the TTA process, first, two triplets collide, forming a temporary pair. Next, the triplet pair evolves to a ground state plus a singlet or triplet or quintet, depending on the character of the pair.[33] If the triplet pair has the singlet character, a singlet would be generated, as shown in the top panel of figure 1(b). An external magnetic field can change the singlet character of the pair. The singlet character of the triplet pair initially increases to a maxima then gradually decreases (and returns to its initial value at about 50 mT) with the increasing magnetic field, and further decreases then tends to saturate at a high field of several T.[33,34] The typical MEL_{TTA} curve, which can act as the fingerprint to verify the TTA process is schematically shown in the bottom panel of figure 1(b).

2. Experimental

In this work, an twisted intra-molecular charge transfer fluorescent molecule, N,N-diphenyl-4-(9-phenylnaphtho-[2,3-c][1,2,5]thiadiazol-4-yl)aniline (TPA-NZP), was used as the emitter. The synthetic details along with the characterization and purity of the material are referred to our previous work.[7] The molecular structure of the TPA-NZP is depicted as an inset of figure 2. The fluorescence and phosphorescence spectra of the emitter in glassy toluene (or in glassy o-xylene, see the supplementary information) matrix at temperature of 77 K were detected by a Laser flash photolysis spectrometer (Edinburgh LP920), as shown in figure 2. From the spectra, one can obtain that the ΔE_{ST} is about -0.038 eV. It is mysterious that the S^{CT} lies energetically below the T^{CT}. The phosphorescence is probably from a higher triplet excited state from our indepth studies of this material.[7,40] OLEDs with an area of 2×2 mm were fabricated by the multiple-source organic molecular beam deposition method at 5×10^{-4} Pa. The structure of the devices is indium tin oxide (ITO) / N,N'-di-1-naphthyl-N,N'-diphenylbenzidine (NPB) (50 nm) / TPA-NZP (20 nm) / 1,3,5-tri(phenyl-2-benzimidazolyl)-benzene (TPBi) (40 nm) / Lithium fluoride (LiF) (0.8 nm)/Aluminum (100 nm), which is partially depicted as an inset of figure 4. The NPB and TPBi were used as the hole transporting material and electron transporting material, respectively. The energy levels of the HOMOs and LUMOs of the materials were obtained from the cyclic voltammetry measurements. The MEL and transient EL experiments are referred to our previous work.[11,14]

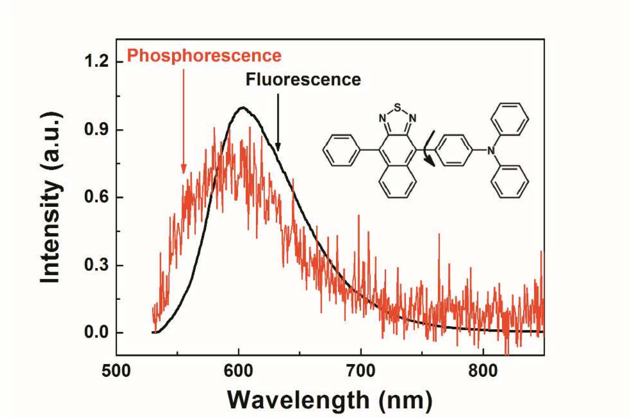

Fig. 2. The Fluorescence (black) and phosphorescence (red) spectra of the emitter (TPA-NZP) in glassy toluene, tested at temperature of 77 K. The inset is the molecular structure of the TPA-NZP.

3. Results and discussion

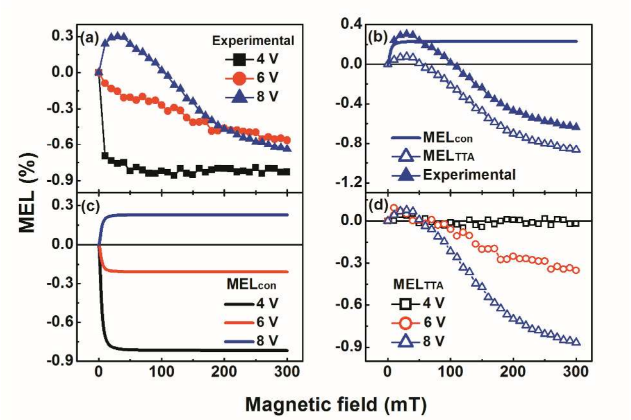

Fig. 3. (a) The experimental MELs of the devices as a function of the magnetic field at several voltages. (b) Decomposing the experimental MEL at 8V by: $MEL_{total}=MEL_{con}+MEL_{TTA}$. (c) and (d) The MEL_{con} and MEL_{TTA} as a function of the magnetic field at several voltages.

Figure 3 (a) shows the MELs of our OLEDs as a function of the magnetic field under voltages of 4 V, 6 V, and 8 V. The curves show significant differences. As mentioned in Introduction, the total MEL (MEL_{total}) of the OLEDs consists of the MEL_{con} and MEL_{TTA}. The MEL_{total} curves can therefore be decomposed as: $MEL_{total}=MEL_{con}+MEL_{TTA}$. This decomposing method was commonly used in organic magnetic field effect studies, for investigating the underlying mechanisms of organic device physics.[27] Figure 3(b) shows the decomposed MELs at 8 V. By the same method, we obtained the MEL_{con} and the MEL_{TTA} at different voltages, which are respectively shown in figure 3 (c) and (d). As can be seen, with the increase of the driving voltage the MEL_{con} changes from negative to positive value, which means the direction of the conversion changes from backward to forward, and at the same time, the MEL_{TTA} becomes more remarkable. The rate of TTA is quadratic proportional to the density of triplet.[29,33] Thus, with the increase of the voltage, the density of triplet increases, leading to the enhanced TTA. Simultaneously, the enhanced TTA consumes more triplets, resulting in the decreased population ratio of T^{CT} to S^{CT}, which should be the reason causing the change of the conversion direction.

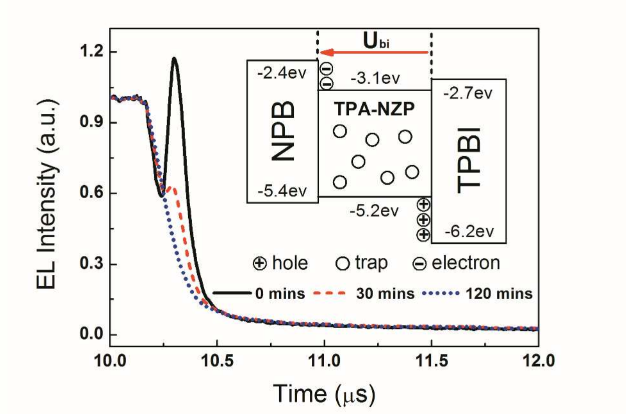

Fig. 4. The transient EL tails when the pulsed voltage is turned off after the OLEDs has been stressed by a voltage of 8 V for 0 minutes (black solid line), 30 minutes (red dashed line), and 120 minutes (blue dotted line). The inset schematically shows the device structure and the U_{bi} resulted from the accumulated carriers in the organic/organic interface.

Further, we adjusted the population ratio of T^{CT} to S^{CT} through the triplet-trap interaction to study the behavior of the inter-conversion. It is proposed that when an OLED is stressed by a high voltage for tens of minutes, defects would be generated in the bulk emitter material.[26,36] In addition, water and oxygen could penetrate into the device because our tests were carried out in the ambient condition. The energy of these defects is within the bandgap of the emitter material, and thus acts as traps.[36] For one thing, these traps would result in a decreased current of the device due to their hindering effect; for another thing, the traps would quench the excitons as the Non-radiative recombination centers. The triplets are more likely to be quenched, owing to their much longer lifetime compared to that of singlets. It has to be mentioned that after the electrically stressing of the OLEDs, some radical cations and anions are also likely to be generated, and their role in this study is the same as that of the trapped carriers. Therefore we can reduce the population ratio of T^{CT} to S^{CT} by stressing the OLEDs with a relatively high voltage. In this work, the stressing voltage is 8 V.

Before measuring the MELs, we first verify that traps are indeed created after we stressed the OLEDs. To do this, we carried out the transient EL experiments. Figure 4 shows the EL tails when the pulsed voltage (5 V) is turned off at three conditions: (a) OLED immediately after fabrication (black solid line); (b) OLED after electric stressed by a voltage of 8 V for 30 minutes (red dashed line); (c) OLED after electric stressed by a voltage of 8 V for 120 minutes (blue dotted line). As can be seen, the overshoot declined and disappeared after we stressed the OLED. This can be explained as below.[37-39] When the energy barrier in the organic/organic interfaces is large, the carriers would accumulate in the interface. The accumulated carriers could create a build-in voltage (U_{bi}), as schematically depicted in the inset of figure 4. After the pulsed voltage is turned off, the singlets formed in the voltage-on period would rapidly decay, but the U_{bi} retains. The accumulated carriers would meet each other under the action of the U_{bi}. When they recombine, an overshoot could be observed.[37] However, when there are traps in the emitter, the carriers accumulated in the interface would recombine with the trapped carriers first, and thus the overshoot diminishes and even disappears if there are enough traps in the emitter.[38,39] So the results shown in Figure 4 demonstrate that traps are indeed created after the devices are electrically stressed, and their population increases as we lengthen the stressing time. Thus with the increase of the stressing time, the population ratio of T^{CT} to S^{CT} would be decreased due to the triplet-trap interaction.

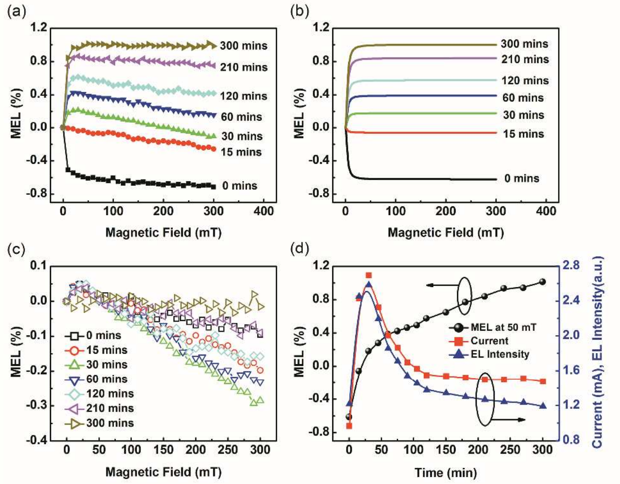

Fig. 5. (a) - (c) The MEL_{total}, MEL_{con}, and MEL_{TTA} (at 5 V) as a function of the magnetic field after stressing the OLEDs for different time range from 0 to 300 minutes. (d) The MELs at 50 mT (black balls), the current flow (red squares), and EL intensity (blue triangles) of the OLEDs as a function of the stressing time.

Figure 5(a) shows the MELs at 5 V after stressing the OLED for different time ranging from 0 to 300 minutes. By decomposing the MELs, we obtained the MEL_{con} and MEL_{TTA} as shown in Figure 5(b) and (c), respectively. The MEL_{con} (at 50 mT) as a function of the stressing time is shown in figure 5(d) (black balls). We can see that the values of MEL_{con} increase and turn from negative to positive, which means the conversion direction changes with the increase of the stressing time. As verified above, more traps are created in the devices with the electrically stressing time increases, leading to the decrease of the population ratio of triplet to singlet, thus inducing the change of the conversion direction from backward to forward.

From figure 5(c), it is interesting to find that the amplitude of the MEL_{TTA} increases when the stressing time increases to 30 minutes, and then diminishes as the stressing time further increases, until it disappears when the electrically stressing time is 300 minutes. We found that with the increase of the stressing time, the current and the EL intensity of the devices initially increase rapidly, and then decrease (see figure 5(d)). Thus the TTA increased with the growing of triplet population resulted from the increased current. Then, due to both the decreased current and the increased triplet-trap interaction, the triplet population decreased, accompanied by the decreased TTA.

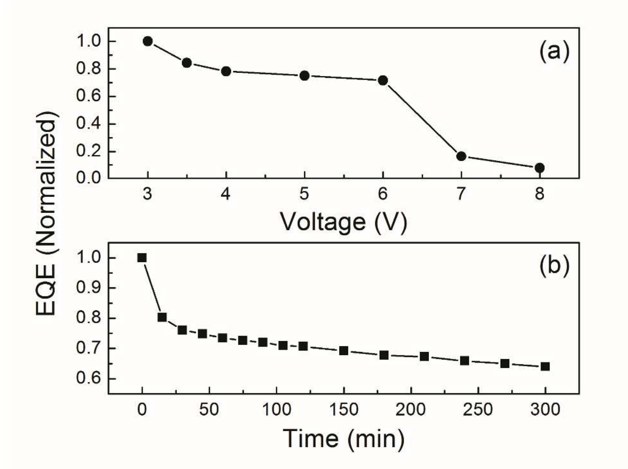

Fig. 6. The normalized external quantum efficiency (EQE) as a function of the driving voltage (panel (a)) and stressing time (panel (b)).

The normalized external quantum efficiency (EQE) as a function of the driving voltage and stressing time are shown in figure 6 (a) and (b), respectively. As can be seen, the EQE gradually decreases with the increase of driving voltage and stressing time. Less triplet were converted into singlet and the direction of inter-conversion was changed may be the partial reason causing the decreased EQE as the driving voltage and stressing time increase, which is consistent with the MEL results.

We changed the emitting material from TPA-NZP to DCJTB (4-(dicyanomethylene)-2-tertbutyl- 6-(1,1,7,7-tetramethyljulolidin-4-yl-vinyl)-4H-pyran), another intra-molecular charge-transfer molecule,[41] to do the same experiments. Similar results were obtained as shown in the supplementary information.

From the above results, we can see that the inter-conversion between singlet and triplet is a dynamic process. When the ΔE_{ST} is small, the spin mixing of the triplet and singlet is efficient, i.e., the inter-conversion is efficient. Whether the overall direction of the conversion is forward or backward is determined by the population ratio of triplet to singlet, which depends on the deactivation rates of the triplet and singlet. If the deactivation rate of the singlet is much larger than that of the triplet, the direction of the conversion is backward and the triplet energy will be harvested efficiently. However, increasing the deactivation rate of the triplet would lead to the decrease of the population ratio of triplet to singlet and consequently result in a forward conversion.

4. Conclusion

In summary, we investigated the inter-conversion between singlet and triplet in a CT fluorescence based OLED via the MEL experiments. As the driving voltage increased, more triplets were consumed by the TTA. Meanwhile the values of the MEL_{con} increased and turned from negative to positive, indicating the direction of the conversion is turned from backward to forward. Further, we purposely reduced the population ratio of triplet to singlet by increasing the triplet-trap interaction. The traps were generated by stressing the devices with a relatively high voltage. With the increase of the stressing time, the values of MEL_{con} increased and turned from negative to positive, demonstrating the change of the direction of the conversion. The transient EL experiments were taken to verify that the traps were generated after we stressed the OLED. Our results revealed that for efficient triplet energy harvest in the fluorescent OLED, enhancing the radiative decay rate of the singlet and decreasing the deactivation rates of triplet, i.e., decreasing the quenching channels of triplet are expected to be important.

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Notes and references

[a] *State Key Lab of Supramolecular Structure and Materials, Jilin University, 2699 Qianjin Avenue, Changchun 130012, People's Republic of China. E-mail: lifeng01@jlu.edu.cn*
[b] *State Key Lab of Integrated Optoelectronics, Jilin University, 2699 Qianjin Avenue, Changchun 130012, People's Republic of China*

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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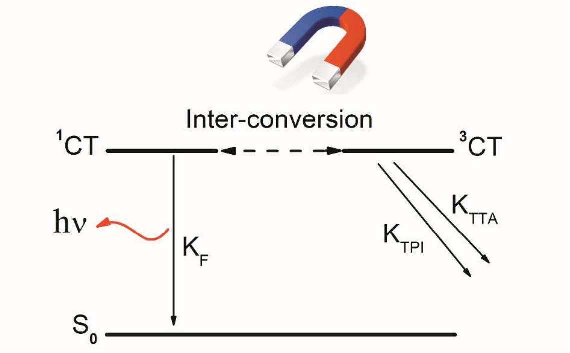
Table of contents entry



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