Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information (S2) – Fast EL Decay

In this work, we studied the transient electroluminescence of a polyfluorenes-blend based light emitting diodes under an open-circuit condition. We observed a bi-exponential decay of the transient electroluminescence, a fast decay with a lifetime of tens of nano-seconds, followed by a slow decay with a lifetime of hundreds of nano-seconds. The slow decay is governed by the discharging of the pre-existing charges in the space charge regions, and is determined by the transit/crossing time between the space charge regions, as profoundly discussed in the main manuscript.

On the other hand, we found that the fast decay is almost unaffected upon changes in the space charge regions and changes in the electric field. Previous studies of transient EL showed a similar behavior of the fast EL decay, and two main explanations were suggested regarding the physical mechanism beyond the process. One approach suggests that this decay arises from newly formed excitons during the falling edge of the voltage pulse [1]. This is based on the observance that commercial pulse generators are usually designed to cope with an impedance of 50Ω, while OLEDs typically have a higher impedance. Therefore, a non-ideal switching occurs and a genuine open-circuit condition is achieved only after tens of nano-seconds followed by the turning-off of the device. During the falling time of the voltage, there is a decaying external electric field that keeps driving the pre-existing electrons and holes toward the recombination zone, and new excitons are formed and radiatively recombined. Our self-developed setup for transient EL measurements was designed to avoid such a scenario with a relatively slow decay of the external field. Thus, this proposed mechanism is unlikely to be the one that governs the fast EL decay. In a different work, Sinha et al. attributed the fast decay to back transfer from non-emissive (or very weakly emissive) localized excited states with a partial charge transfer characteristic to emissive interchain excited singlets [2]. In contradiction

to the generation of new excitons during the falling time of the voltage, the later approach relates to the dynamics of the pre-existing excitons that undergo new pathways for radiative emission. Such localized excited states that have both excitonic characteristics, as well as charge-transfer characteristics, are often supported in polymeric heterojunction systems [3-5]. Moreover, the latter states exhibit a lifetime in the time domain of tens of nano-seconds.

In a PFO:F8BT blend-based device, we found an existing fast EL decay with a lifetime of ~80 nano-seconds. In order to examine the correlation between the measured lifetime to the emission from charge-transfer states, we changed the film's morphology. The active layer morphology strongly affects the interface density, and thus have an important role in the formation of bulk-states. We fabricated devices with different film morphologies by changing the polymer's composition of the active layer. The examined compositions were 95:5, 75:25, 50:50, and 25:75 wt/wt PFO:F8BT, and the resulted morphologies were measured using atomic force microscopy, and are shown in Figure S1.

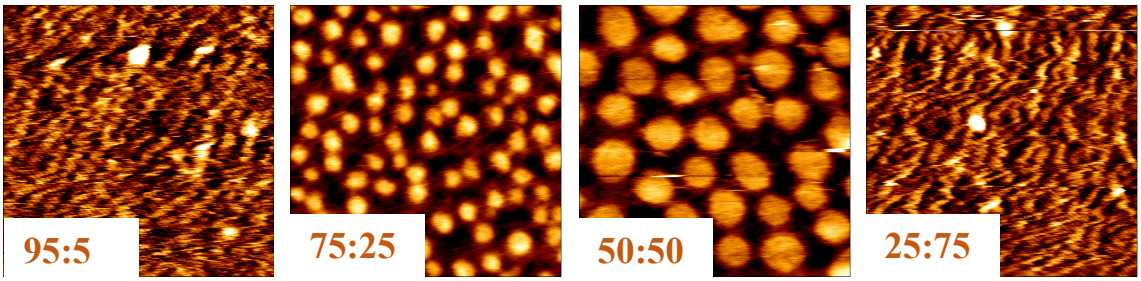

FIG. S1. 3µm x 3µm AFM scans of a PFO:F8BT blend films with different polymer blend composition

As can be seen in Figure S1, sub-micron coexisting phases with different compositions were formed; a higher-lying, protruding F8BT-rich phase, and a lower-lying, matrix-like PFO-rich phase[6]. Increasing F8BT concentration leads to a stronger phase separation with larger domains, reaching a maximum at 50:50 ratio. Beyond this ratio, the phase separation weakened

and smaller domains are obtained. The corresponding fast EL decay of each of the devices are summarized in table SI.

TABLE SI. Fast transient electroluminescence lifetime and relative population as a function of the polymer blend composition

Blend ratio PFO:F8BT	Fast Lifetime	Population
95:5	78 ns	0.64
75:25	80 ns	0.58
50:50	79 ns	0.38
25:75	82 ns	0.46

While the lifetime is barely changed and stays constant with a value of ~80 nano-seconds, the relative amplitude/population is strongly affected by the film's morphology. The increase in the population accompanied by an increase in the heterojunction sites. One can see that the lowest population (i.e., relative emission amplitude) occurred in the device composing 50:50 PFO:F8BT, a device with the strongest phase separation and therefore, with lower interface density where charge-transfer states can be formed.

References

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