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Comment

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Comment on 'Enhancement of carrier mobility in MEH-PPV film prepared under presence of electric field' by Quanmin Shi [Chem. Phys. Lett. 425 (2006) 353]

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Abstract

Increased mobility in drop-cast films of MEH-PPV is obtained, when drop cast in the presence of an static electric field. We suggest that this increase is a result of a reduction of nano-domains. © 2006 Elsevier B.V. All rights reserved.

In this Letter, [1] the authors demonstrate that the application of a vertical electric field during drop-casting leads to significantly higher room temperature mobility in thin films of MEH-PPV. Interpreted in terms of Bassler's Gaussian disorder model for organic semiconductors, they suggest that energy disorder is not affected by the application of the static electric field, inferring that the improved mobility is a result of a reduction in positional disorder accompanied by an increase in the mobility prefactor. They suggest that this may be due to increased molecular orientation.

The main point of this comment is to point out to readers that a similar experiment was carried out by Inigo et al. [2] and published in the Journal of Advanced Materials in 2005. Unfortunately, the authors of the present work failed to interact or even reference the results and interpretation of that Letter. That said, this Letter does provide a valuable confirmation of the measurements of measurement of mobility in films of MEH-PPV drop-cast in the presence and absence of a static external electric field. One difference between the current setup and that of the earlier work [2] is the way that the electric field is applied. Fig. 1 shows that in the work of Inigo et al. [2] the application of the electric field perpendicular to the substrate is accompanied by a gradient parallel to the substrate. Shi et al.'s [1] work confirms that the enhanced mobility is due to the electric field not the gradient in the electric field. A second difference is the choice of solvent, the Shi et al. [1], uses toluene, while the previous work [2] made use of chlorobenzene as the solvent. The more recent Letter, [1] thus confirms that this effect is solvent independent.

Both Letters interpret their results within the framework of the Gaussian disorder model of Bassler [3]. They agree that energy disorder is little affected by the addition of the static electric field. While the results of the present Letter, suggest that there is reduction in positional disorder, Inigo et al. [2] by recording the temperature dependence of mobility show that this reduction is a quite substantial reduction from \sim 3.6 to <1.5. Shi et al. then argue that

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Fig. 1. Schematic of the static electric field distribution during dropcasting of the E-cast films. The inset on the top right shows the intensity (gray scale) and direction of the electric field within the drop-cast film.

the enhancement of mobility is a result of a reduction of the positional disorder and an enhancement of the premobility constant. Unfortunately, this is wrong. Borsenburg et al. [Ref. 4, Fig. 7] have shown for an energy disorder of 78 meV (comparable to that for the films investigated) that a reduction in positional disorder of this magnitude results in an almost three order of magnitude decrease (not increase) in mobility. Our own simulations confirm this result.

Within the single domain Bassler model, this leaves the change in the mobility prefactor to account for the differences in mobility. This factor is related to the packing of the MEH-PPV units suggesting that packing in the two films is significantly different. Shi et al. [1] suggest that this change might be due to changes of orientation on the individual polymer level. They suggest that the applied electric field tends to cause the polymers to align with the electric field during solvent evaporation. Unfortunately there is no experimental evidence of this occurring. In fact, if this were true, then one would expect the photoluminescence spectra data for these more highly ordered polymer chains to be slightly red-shifted due to a lengthening of the effective conjugation length. Our work with similar films indicates that this is not the case [2]. Rather than an increase in the secondary peak, there is in fact a decrease in the secondary peak [2, Fig. 4c]. This is consistent with less, not more, interchain interaction and a shorter effective conjugation length [5-8].

Our wide angle X-ray diffraction measurements point to the existence of nano-domains (size \sim 40–100 nm) in dropcast films [9] and the absence of such domains in films drop-cast in the presence of an external electric field [2]. Charge transport would be expected to be more efficient in a homogeneous medium than in one with many grain boundaries. Thus we conclude that the elimination of these domains rather than polymer alignment is responsible for the improved values of mobility.

In summary, the experimental results presented by Shi et al. [1] supports earlier results [2] that application of a static electric field during drop-casting improves charge carrier mobility. However, a better physical explanation for this improved mobility is the elimination of nano-domains in the film. For a fuller explanation of the phenomena, we suggest that the reader view our Letter [2].

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