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Low-voltage Scanning Electron Microscopy Imaging of Doped Organic Semiconductors Films

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Electron microscopy is becoming one of the most important experimental tools to characterize thin films of organic semiconductors. One of the most widespread techniques is transmission electron microscopy which continues to be the method of choice in unraveling the nanomorphology formed by the interpenetrating networks of conjugated polymers and fullerene in films for organic photovoltaics [1]. From a general perspective optoelectronic devices based on organic semiconductors are seeing large improvements in their performances with the use of dopants mixed at low weight-percentages (<10%) with the semiconductor [2, 3]. Clustering of dopant molecules, changes to the semiconductor morphology and in general dopant distribution inside the film are all crucial aspects for the development and design of this technology. However, such aspects have been poorly addressed, likely because of the lacking of suitable experimental techniques. In this communication we present experiments demonstrating the possibility to map dopant distributions with nm resolution in organic semiconductor thin films. The technique which is based on low-voltage scanning electron microscopy (SEM) provides information of the semiconductor morphology as well and promises to be a method of choice for these functional soft materials. We have investigated two sets of samples obtained by spin coating the technologically relevant polymers poly(3-hexylthiophene) (P3HT) and poly[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl]] (PCPDTBT) on silicon. The polymers had 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F4-TCNQ) added as dopant inducing an excess of holes in the semiconductors. We have observed that a low acceleration voltage, below 1 KV, is critical in obtaining images of the polymer morphology and identifying areas in which dopant molecules are clustering. The two samples show different characteristics; PCPDTBT exhibit a lamellar morphology as pristine, which is slightly disrupted by the presence of F4-TCNQ at 5% ratio, without seeing clustering of F4TCNQ molecules on a tens of nm scale. On the other hand, P3HT exhibits clustering of F4-TCNQ with a patchy pattern on a hundreds of nm scale for concentrations above 5%. By performing imaging at different scan rates and simulating the electron back-scattering yields for the materials constituting the films we show that imbalanced charging between the doped and undoped regions is the origin of the observed contrast. The results show that low-voltage SEM is a powerful tool in investigating the morphology of doped organic semiconductors. [1] M. Hallermann, I. Kriegel, E. Da Como et al. Adv. Funct. Mater. 2009, 19, 3662. [2] F. Deschler, E. Da Como, T. Limmer et al. Phys. Rev. Lett. 2011, 107, 127402. [3] A. Tunc, A. De Sio, D. Riedel, F. Deschler, E. Da Como et al. Org. Electr. 2012, 13, 290.