Effects of Morphology on the Functionality of Organic Electronic Devices

Organic materials provide a wide variety of advantages of design and properties of molecules and polymers. A lot of research activity is driven toward the realization of solution-processed organic materials in large-area, lightweight, flexible organic optoelectronic devices with low processing costs such as OLEDs, OFETs, solar cells, sensors, e-paper, or radio frequency identification tags. In the past decade, extensive experience has been accumulated both in the preparation of solution-processed organic electronic devices and in the characterization of their functional properties. It has been established that the morphology of the material or blend impacts very strongly on the properties (electrical, optical, chemical) and function of the device. Solution-processed organic materials contain diverse levels of organization at the molecular level, the supramolecular level, and the mesoscopic blend. The benefits of the preparation of large-area organic electronic devices in terms of processability are accompanied by the difficulty to maintain control of the morphology at all levels as required for full optimization of physical properties at the bulk or interfaces, such as light absorption, excitonic characteristics, energy transfer, charge separation, or the charge transport rate. Indeed, simulations show that bulk properties like the mobility or interface characteristics such as the average electrical dipole depend on the atomistic details of the structural organization.[1,2] Very small variations of the synthesis or process conditions can modify dramatically the electronic and optical properties of organic layers.[3] Controlling the growth and the extent of mixing, the connectivity, and the crystallinity of nanosized domains in multicomponent systems (blends) is a very difficult challenge and often requires postprocessing annealing methods to equilibrate the film morphology toward the required microstructure.

The Perspectives presented in this issue bring about several analyses of this pressing question from complementary points of view. Vogelsang and Lupton[4] describe the application of single-molecule spectroscopy techniques to monitor molecular changes and dynamic properties. The paper specifically addresses the method of solvent vapor annealing and the different levels into which it can be split at the single chain level, the solvation regime and the aggregation regime. These methods allow one to obtain a detailed dynamic picture of folding and aggregation of conjugated polymers in the transition from the liquid to solid state, such as the effect of the annealing time on the degree of order and the electronic coherence length of the fibers of polymer polyfluorene. How the solvent vapor annealing affects the intrachain configuration of conjugated polymer molecules can also be monitored.

Ruiz et al.[5] focus on the supramolecular order of the organic material and the relationship to one crucial property, the carrier mobility. Perfectly ordered, closely packed molecules in single crystals show very high mobilities, but these materials are brittle and fragile and difficult to process. On the other hand, disordered materials with a low mobility can be easily processed. The Perspective shows a wide range of materials classified by their degree of supramolecular organization, covering crystalline systems, liquid crystals, and polymeric materials and describing their performance in physical properties. The authors remark that although the effort invested in preparing a given supramolecular organization does not always pay off, the expected emergent functions, improvements in carrier mobilities, have been realized, giving reasons to be optimistic toward the organic semiconductor of the future.

Creddington and Durrant[6] make an ample analysis of organic bulk heterojunction solar cells. The first part of the paper is focused on the explanation of the photovoltage. The central idea is that the energy gap between the blend components is not the full voltage as the occupation of the levels is necessarily reduced by recombination.[7,8] The authors put a large number of materials and cells on a common basis, correcting, on the one hand, the specifics of energetics of different systems by measurement of the electron density (as function of voltage) and then determining the kinetics by the lifetime. They obtained an excellent correlation for the voltage, predicted from the charge density and lifetime and measured at 1 sun, that establishes a very powerful method to gain insight into the photovoltage in the organic solar cells, emphasizing the recombination of quasi-free electrons and holes as the main phenomenon, once the main level energetics are given.[9,10] The second part of the paper is an excursion to determine the effect of morphology on the performance of these blend-based solar cells. A number of case studies indicate that this goal is far from trivial as one has to account not only for the extent of crystallinity, degree of segregation of phases, internal area, and size of the domains but also the influence of the microstructural features on the mobility and specific microscopic recombination mechanism. They remark that the goal of characterization is not only to incorporate the influence of the microstructure on the open-circuit voltage but to provide a direct probe of its functional impact on device performance.

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