Mixing and phase-separation in thin films of co-deposited organic semiconductors

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We report on the formation of organic-organic thin-film heterostructures of rod-like conjugated molecules (COMs) by co-sublimation, which exhibit either mixing on the molecular scale or phase separation into ordered domains on the micrometer scale. The mixed structures might be suitable for the use as active layers in organic field-effect transistors, while the phase-separated structures might be applicable in organic bulk hetero-junction solar cells. Pairs of the following five COMs were vacuum co-deposited onto silicon oxide substrates: pentacene (PEN), α,ω-sexithiophene (6T), α,ω-sexiphenyl (6P), and alkyl-chain substituted α,ω-dihexylsexithiophene (DH6T) (see Fig. 1a), i.e., molecule pairs differing in the length of the molecular conjugated core (CC) and/or the overall molecular length were investigated. As main result we found that material pairs with similarly sized CC, such as 4T/PEN (Fig. 1b) and 6T/6P (Fig. 1c), showed the formation of ordered layered structures with intimate mixing on a molecular level. On the other hand, pronounced phase separation was observed for material pairs of dissimilar CC lengths, e.g., 4T/6T and PEN/DH6T (Fig. 1d). We propose that this can be generalized as design rule for the formation of either mixed or phase-separated co-deposited molecular films [1, 2].

Figure 1: Chemical structures of the rod-like molecules used in this study (a). Specular x-ray diffraction data obtained at Hasylab beamline W1 for co-deposited films of 4T/PEN (b), 6T/6P (c) and PEN/DH6T (d).

Our results suggest the general rule that co-deposition of COMs with CC of similar van der Waals length (vdWL) leads to films that exhibit intimate mixing of both materials on a molecular scale. While a change of the total molecular vdWL by the attachment of alkyl end-chains does not lead to phase separation (e.g., DH6T/6P [1], DH6T/6T [2]), phase separated films are obtained by co-deposition of materials with differently sized CC [1] therefore demonstrating the possibility to choose between phase separation and mixing by combining functional rod-like molecules with appropriate CC sizes.

References