Investigating the electronic structure and charge transfer dynamics in Donor-Acceptor copolymers: a X-ray absorption and Resonant Photoemission Spectroscopy study

Cleber Marchiori
Department of Engineering and Physics, Karlstad University - Sweden

Organic semiconductors are notable for their ease of processing into thin films from solution. However, achieving the desired film morphology is far from straightforward, as it depends on several factors, including the choice of solvent, the use of additives, and post-processing annealing. Gaining a deeper understanding of how these variables affect the morphology of thin films of conjugated polymers is crucial for enhancing their performance in optoelectronic applications. Here I collect some examples about how the processing conditions can induce molecular orientation of the conjugated backbone within the film.[1,2] By using angle-resolved near edge X-ray absorption fine structure spectroscopy (AR-NEXAFS) and resonant photoemission spectroscopy (ResPES)[3] we first investigated the electronic structure and morphology of thin films of the copolymer poly(9,9-dioctyl-fluorenyl-*co*-bithiophene) (F8T2) in its pristine form, as well as samples processed with the solvent additive 1,8-diiodooctane (DIO) or post-processed by thermal annealing treatment.[4] Measurements were carried out using AR-NEXAFS at S K-edge in total electron yield (TEY) and fluorescence yield (FY) detection modes. The observed dichroism pointed to a preferential face-on orientation of the conjugated backbone, which is increased for F8T2 films processed with DIO. Resonant Auger decay spectra were obtained and analyzed using the Core-Hole Clock (CHC) method. The CHC analysis revealed that the charge-transfer time decreases as the dichroism increases. In a second study, we found that in spin-coated films of the novel acceptor materials Y5 and Y6, used for organic solar cells, a notable face-on molecular organization can be achieved when chloroform is used as solvent, while films processed with chlorobenzene or o-xylene do not display any preferential molecular orientation.[5] Polymeric acceptors based on Y5, on the other hand, revealed to not be so sensitive to the solvent choice. The results of those studies shed light on how the processing conditions impact on the molecular organization within the film and consequently affect the charge dynamics, giving guidelines for optimizing the performance of materials in optoelectronic devices.

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