Contribution ID: **24** Type: **Oral**

In-situ GIWAXS of thermally-induced co-crystallization in Doped Organic Semiconductor Films

Tuesday, 6 September 2022 16:15 (20 minutes)

Among the vast number of organic semiconductors (OSCs) developed in the last decades, [1]benzothieno [3,2-b]benzothiophene (BTBT) derivatives have emerged as one of the best performing materials for p-type organic field-effect transistors (OFETS). However, the understanding and control of molecular doping, as a versatile platform for tuning the optoelectric properties of OSCs, remains a challenge for further advancements in organic electronics.
In this work, we address the structural properties of BTBT films during the sequential deposition of a p-type dopant, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_6TCNNQ), with special attention to the comparison of two BTBT derivatives, namely 2,7-dioctyl-BTBT (C_8-BTBT-C_8) and 2,7-diphenyl-BTBT (DPh-BTBT). Grazing incidence wide-angle X-ray scattering (GIWAXS) was performed at the NCD-SWEET Beamline of ALBA in the course of thermal annealing of the films. Although both BTBT-based films are isostructural, with the (001) plane parallel to the substrate surface and a herringbone packing of the BTBT cores, we find important structural differences upon the deposition of F_6TCNNQ intended to dope the OSC. The deposition of F_6TCNNQ on C_8-BTBT-C_8 results on the formation of a co-crystalline mixed phase at the interface with charge-transfer complex (CTC) properties, which is further promoted by thermal annealing, whereas F_6TCNNQ on DPh-BTBT results in a planar heterostructure, without intermixing of both molecules. These structural differences are expected to be crucial for doping efficiency.

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Session Classification: AUSE A - 06/09/22 II