Resonant Soft X-ray Scattering

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Since their inception approximately 15 years ago, resonant soft X-ray scattering (R-SoXS) methods [1-3] have become powerful techniques to investigate low Z materials, in particular thin films of organic molecules and polymers [4, 5]. This is in large part due to their ability to achieve high compositional contrast without labelling (e.g., staining, deuteration) and the ability to exploit rich materials specific spectral signatures at the Carbon K-edge [6, 7]. This intrinsic high scattering contrast allows the in-plane structure in 30-500 nm thin films to be investigated directly in a transmission geometry without resorting to a grazing incidence geometry. Additionally, the long wavelengths (~2-5 nm) used in R-SoXS yields much larger scattering angles than in traditional small angle x-ray scattering (SAXS, ~ 0.1 nm). Yet, the long wavelength-limit and the small angle limit yield the same mathematical approximation. The long and short wave-length methods thus result in equivalent data and measure the same structure in the samples, except that R-SoXS has a better signal/background ratio due to the lack of strong scattering from interfaces with the vacuum or the substrate and it is also easier to probe small q-regime (i.e. larger length scales) due to the larger wavelength utilized. Unique to R-SoXS, is its ability to be sensitive to bond orientation [8, 9]. The challenge of this sensitivity is the increased need for sophisticated analysis methods [10]. Despite these advantages, dedicated facilities for R-SoXS operation have been slow in being constructed. This might be due in part to the flipside of soft x-rays having high contrast and high cross-sections: (1) Significantly complexity is added of having to operate the sample and detector in a vacuum environment, (2) control of the sample environment (solvent, T, etc.) is very challenging, and (3) the optics of the beamline has to be kept clean from Carbon contamination [11]. A new facility in addition to the one at the ALS has recently come online at the NSLS-II. Additionally, both dedicated facilities aim to control the sample environment between two thin Si_3N_4 windows.

This presentation will delineate some of the historic developments and similarities and differences between the short and long-wavelength X-ray scatting methods and exemplify the capabilities of R-SoXS through a number of examples, including recent method advances and use of R-SoXS in grazing incidence geometry. One example is presented below, focusing on the use of scattering anisotropy that results from molecular orientation contrast to understand the complex impact of molecular orientation relative to the donor/acceptor interface in an organic solar cell. 2D anisotropic R-SoXS patterns such as that exemplified in Figure 1 were utilized. The scattering anisotropy was quantified by using integration over sectors and calculating differences over sum ratios. At the same time, the total scattering intensity allowed to assess the relative composition fluctuations (related to the purity of the domains, and the intensity distribution to assess the relative lengths scales of the morphology created. No other parameter, including those describing molecular packing extracted from wide-angle x-ray scattering, but the molecular anisotropy parameter correlated to the short circuit current density and the fill factor, both of which are directly proportional to the device efficiency.

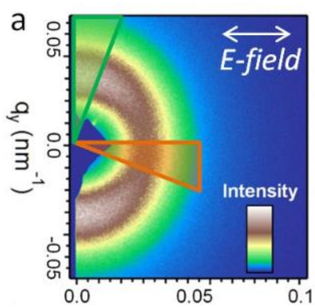

Figure 1: Anistropic scattering patterns arising from orientation-composition correlations in an PNDT-DTBT:PCBM organic photovoltaic blend.

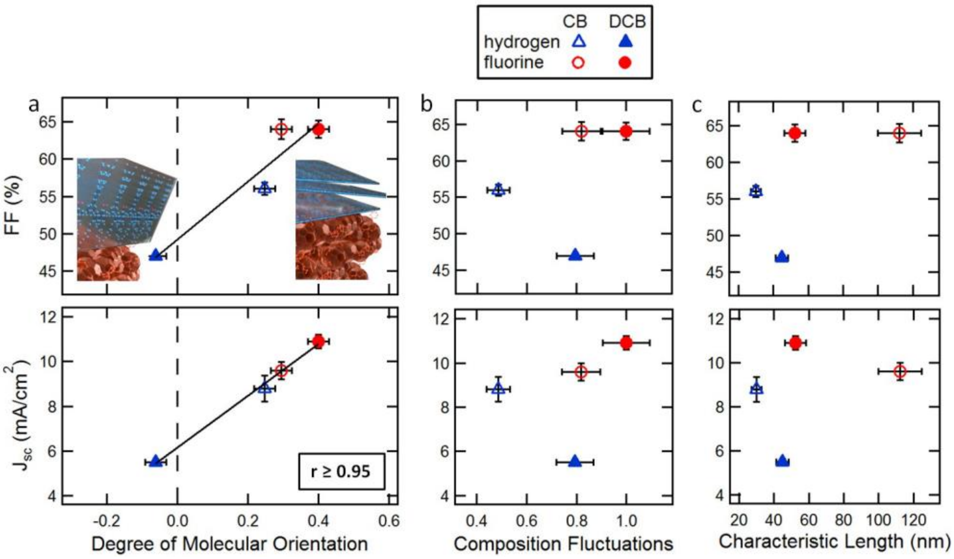

Figure 2: Device performance strongly correlates with the degree of molecular orientation for fluorinated and un-fluorinated PNDT-DTBT:PCBM blends cast from chlorobenzene and dichlorobenzene. – Inset in Fig. 2a visualizes an edge-on versus face-on location orientation of the polymer backbone with respect to a donor-acceptor interface.

R-SoXS has been particularly popular for assessing the morphology of organic photovoltaic devices, but other examples of its utilization include applications to block copolymers, nanofibers, micelles in milk, aerogels.

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