

## Optimized Damage-Reduction 60 keV Monochromated Electron Energy-Loss Spectroscopy Measurements of Optical Properties at the Donor/Acceptor Interface in Organic Photovoltaic Devices

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The key to improving the performance of OPVs is to understand the donor/acceptor interface within the device. The two primary areas of understanding that correlate to this interface that can affect the performance of the device are the morphology of the interface and the local electronic structure at the interface [1]. Multiple groups using different characterization techniques have extensively studied the morphology of the interface [2, 3, 4]. However, the local electronic structure at the interface has largely been ignored as these measurements require the use of electron energy-loss spectroscopy (EELS) to measure these optoelectronic properties as the transmission electron microscope is the only instrument that results in the high spatial resolution necessary to probe the interface [5].

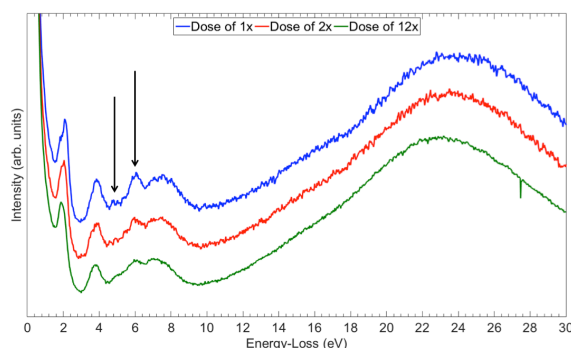
Unfortunately, the materials used in OPVs, including copper phthalocyanine (CuPc), fullerene-C<sub>60</sub>, poly(3-hexylthiophene) (P3HT), and [6,6] phenyl C<sub>61</sub> butyric acid methyl ester (PCBM), are highly sensitive to the electron beam and are easily damaged when attempting to acquire low-loss EELS spectra. This damage results in broken bonds, which then leads to EELS spectra that are not representative of the pure material. This is shown in Figure 1, in which the intensity of peaks in the CuPc EELS spectrum diminishes as the electron dose exposed to the sample increases. Therefore, if the EELS spectra collected are actually of the organic material after it has undergone beam damage, the analysis resulting in the optoelectronic properties and, ultimately the local electronic structure, will be incorrect, leading to false conclusions correlating the donor/acceptor interface to the power conversion efficiency.

Thus, in order to collect EELS data, an optimized single spectrum acquisition method has been devised to ensure that the samples undergo no beam damage prior to EELS spectra acquisition such that the collected spectra are representative of the materials studied. This method will be discussed during the session and was used to collect EELS spectra for the four aforementioned materials using an FEI Titan<sup>3</sup> 60-300 Image-Corrected S/TEM utilizing a 60 keV monochromated electron beam. To ensure that these spectra were undamaged, the optoelectronic properties collected using EELS were compared to those collected using variable angle spectroscopic ellipsometry (VASE), which is a technique that utilizes a light beam, rather than an electron beam, so that the samples are not damaged during the measurement (albeit with much lower spatial resolution) [6]. For example, the complex dielectric function calculated from the data collected from both methods are shown in Figure 2 for C<sub>60</sub>, and, as is clear from the plots, both methods agree favorably meaning that the optimization method works. These spectra now serve as standards for all four of these materials for when the donor/acceptor interface (i.e. CuPc/C<sub>60</sub> and P3HT/PCBM) are studied.

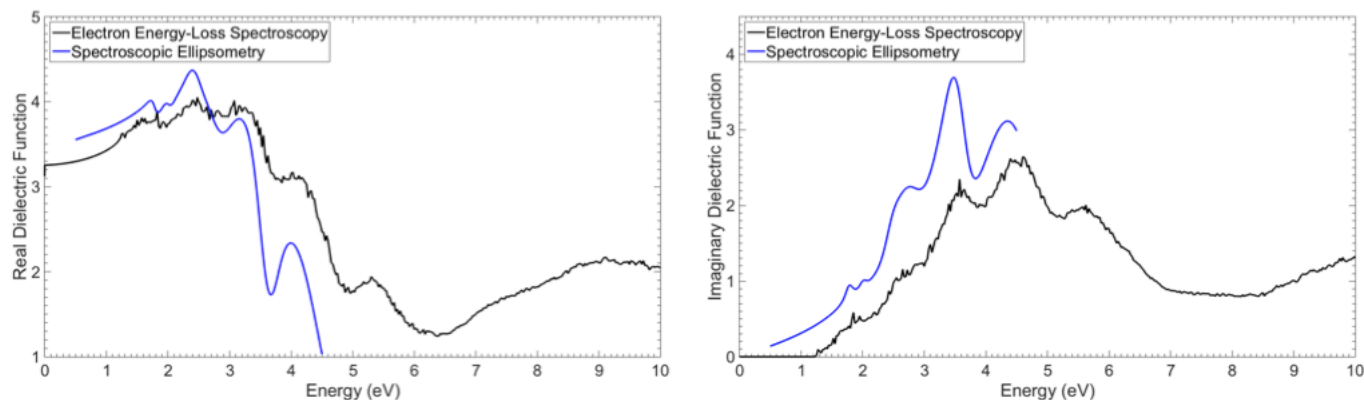
Once these measurements were completed, thus proving that monochromated EELS spectra could be collected for these easily beam damaged materials, the conditions for collecting spectrum images of monochromated EELS spectra were also optimized, and the donor/acceptor interface of actual devices were studied resulting in the first monochromated EELS measurements at the donor/acceptor interface in OPV devices. Furthermore, as the EELS spectra correlating to the pure donor and acceptor materials have been measured, the identification of peaks that are due solely to the interface has been completed.

## References

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- [7] The authors acknowledge the Air Force Office of Scientific Research and the Air Force Research Laboratory (AFRL) Materials and Manufacturing Directorate, the Dayton Area Graduate Studies Institute (DAGSI), and The Ohio State University for funding; Kurt Eynik and Luke Bissel from AFRL for technical support; and The Ohio State University Center for Electron Microscopy and Analysis for technical support.



**Figure 1:** Valence-loss spectra collected for CuPc. The electron dose for each spectrum is indicated relative to the dose of the first exposure (1x).



**Figure 2:** Comparisons of the real and imaginary dielectric functions for C<sub>60</sub>, showing good agreement between the EELS and VASE data.