



# High-resolution monochromated electron energy-loss spectroscopy of organic photovoltaic materials



Jessica A. Alexander<sup>a</sup>, Frank J. Scheltens<sup>a</sup>, Lawrence F. Drummy<sup>b</sup>, Michael F. Durstock<sup>b</sup>, Fredrik S. Hage<sup>c</sup>, Quentin M. Ramasse<sup>c</sup>, David W. McComb<sup>a,\*</sup>

<sup>a</sup> Center for Electron Microscopy and Analysis, Department of Materials Science and Engineering, The Ohio State University, Columbus, OH, United States

<sup>b</sup> Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, WPAFB, OH, United States

<sup>c</sup> SuperSTEM Laboratory, SciTech Daresbury Campus, Daresbury, United Kingdom

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(PCBM)

## ABSTRACT

Advances in electron monochromator technology are providing opportunities for high energy resolution (10 – 200 meV) electron energy-loss spectroscopy (EELS) to be performed in the scanning transmission electron microscope (STEM). The energy-loss near-edge structure in core-loss spectroscopy is often limited by core-hole lifetimes rather than the energy spread of the incident illumination. However, in the valence-loss region, the reduced width of the zero loss peak makes it possible to resolve clearly and unambiguously spectral features at very low energy-losses (<3 eV). In this contribution, high-resolution EELS was used to investigate four materials commonly used in organic photovoltaics (OPVs): poly(3-hexylthiophene) (P3HT), [6,6] phenyl-C<sub>61</sub> butyric acid methyl ester (PCBM), copper phthalocyanine (CuPc), and fullerene (C<sub>60</sub>). Data was collected on two different monochromated instruments – a Nion UltraSTEM 100 MC ‘HERMES’ and a FEI Titan<sup>3</sup> 60–300 Image-Corrected S/TEM – using energy resolutions (as defined by the zero loss peak full-width at half-maximum) of 35 meV and 175 meV, respectively. The data was acquired to allow deconvolution of plural scattering, and Kramers–Kronig analysis was utilized to extract the complex dielectric functions. The real and imaginary parts of the complex dielectric functions obtained from the two instruments were compared to evaluate if the enhanced resolution in the Nion provides new opto-electronic information for these organic materials. The differences between the spectra are discussed, and the implications for STEM-EELS studies of advanced materials are considered.

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## 1. Introduction

Organic photovoltaics (OPVs) have garnered research interest as an alternative to traditional inorganic solar cells due to their light weight, flexibility, and low manufacturing costs [1]. Although improvements in device technology has led to OPVs with power conversion efficiencies approaching 10%, extending their efficiency beyond this 10% barrier has proved challenging [2]. One cause for this stagnation is that little is known about the electronic structure and bonding of the donor/acceptor interface in OPV devices. While much work has been done to correlate device performance with the morphology of the donor/acceptor interface, [3–12] it is challenging to measure directly the opto-electronic properties of the donor/acceptor interface. This information is critical as current generation within OPVs is contingent upon *both* the morphology and the electronic structure of this interface. This knowledge, cou-

pled with what is already known about the interface morphology, could lead to designing better performing OPVs.

We have recently demonstrated how the opto-electronic structure of OPV related materials can be probed via valence electron energy-loss spectroscopy (EELS) measurements made in a scanning transmission electron microscope (STEM) [13]. The complex dielectric function,  $\epsilon(E)$ , which can be utilized to determine single electron transitions and collective excitations, is calculated from the valence-loss spectrum ( $\Delta E < 50$  eV) [14]. The spatial resolution of valence-loss spectra is on the order of a few nanometers, depending on both the incident electron energy and the actual energy-loss [15,16]. Thus, by identifying which single electron transitions between bonding and anti-bonding sites are excited, it is possible to extract information about the local chemical environment in the material [17].

In EELS, the zero loss peak (ZLP) is associated with electrons that have lost no energy (or very small amounts of energy) as they have passed through the sample, and the full-width at half-maximum (FWHM) of the ZLP is normally used as a measure of the

\* Corresponding author.

E-mail address: [mccomb.29@osu.edu](mailto:mccomb.29@osu.edu) (D.W. McComb).

**Table 1**  
Growth parameters used for CuPc, C<sub>60</sub>, and PCBM thin films.

Material	Growth Rate (nm/min)	Pressure (torr)
CuPc	~ 1.7	~ $3 \times 10^{-7}$
C <sub>60</sub>	~ 0.6	~ $6 \times 10^{-7}$
PCBM	~ 0.5	~ $4.5 \times 10^{-6}$

spectral resolution. The implementation of electron monochromators in the scanning transmission electron microscope (STEM) has enabled EELS measurements to be performed with an energy resolution that matches, or improves on, the resolution that can be obtained using synchrotron-based X-ray absorption spectroscopy [18]. While this has benefits for core-loss spectroscopy, in particular for discrimination between energy-loss near-edge structure in mixed phase materials, the ionization edges are often limited in resolution by the core-hole lifetime rather than the energy resolution of the incident electron beam. However, the energy resolution of the incident beam has a much larger role in the analysis of valence-loss EELS data. The intensity of the ZLP at 1/10th, 1/100th and 1/1000th of the maximum is important as the intensity of the “tail” can mask spectral features at low energy-losses. By reducing this ZLP tail intensity, it is possible to measure, unambiguously, features at very low energy losses, including vibrational peaks in EEL spectra, as Krivanek et al. [18] have recently shown utilizing a Nion high-energy resolution monochromated EELS system (HERMES) STEM [19–21].

We have previously reported the results of our investigation of OPV materials using valence loss spectroscopy [13]. In this contribution, the effects of the tails of the ZLP on the energy-loss spectra of beam sensitive organic materials were studied to determine if additional information about the electronic structure of common OPV materials could be obtained using instruments with very high energy resolutions. EELS measurements made on a Nion UltraSTEM 100 MC HERMES have been compared with those from a FEI Titan<sup>3</sup> 60–300 Image-Corrected S/TEM. EELS data were collected for 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) films. The goal was to establish the potential of monochromated STEM-EELS at the highest energy resolution for experiments measuring the complex dielectric function at the acceptor/donor interface of OPV devices.

## 2. Materials and methods

Four organic materials were studied in this work: 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). Thermal vapor deposition methods were utilized to prepare thin films (with thicknesses less than 50 nm) of CuPc, C<sub>60</sub>, and PCBM (see Table 1 for growth parameters) on room temperature freshly cleaved rock salt substrates (NaCl and KCl with (100) orientation). The evaporation chamber was located within an argon-filled glove box. Thin films of P3HT were prepared by spin-coating a solution of P3HT in dichlorobenzene onto room temperature KCl substrates. These thin films were collected onto lacey carbon-coated TEM grids after they were floated off by dissolution of the substrates in distilled water.

EELS measurements were acquired using similar beam conditions for two different microscopes: (1) a FEI Titan<sup>3</sup> 60–300 Image-Corrected S/TEM and (2) a Nion UltraSTEM 100MC ‘HERMES’. STEM-EELS experiments were conducted at 60 keV, in conjunction with procedures minimizing the amount of electron beam exposure, as these organic materials were susceptible to electron beam damage [13]. All of the microscope alignments and optimization of

the EELS acquisition parameters were conducted on an area of the TEM grid that was not adjacent to any of the regions of interest on the grid. This ensured that the samples were not pre-exposed to the electron beam before collection of the data. Next, the edge of the thin film was brought into the field of view (~ 1 μm<sup>2</sup>) for any final beam adjustments, after which the electron beam was blanked. The sample position was blindly adjusted to bring an area of the sample that had not been previously scanned into the field of view. While set to continuously scan the sample, the electron beam was unblanked, and the EELS acquisition was started. After conclusion of the EELS acquisition, the beam was blanked. EEL spectra acquired utilizing the FEI Titan<sup>3</sup> 60–300 Image-Corrected S/TEM (hereafter referred to as ‘Titan’) and the attached Gatan Quantum spectrometer were collected in single-EELS mode with short acquisition times (2 – 4 ms). The convergence and collection semi-angles were 5 mrad and 15 mrad, respectively. This data were collected with a dispersion of 0.025 eV/channel, and the measured energy resolutions were in the range of 0.17 – 0.20 eV. These short acquisition times resulted in noisy data, so multiple individual spectra were collected and summed together to improve the signal-to-noise ratio (SNR). The EELS spectra collected on the Nion UltraSTEM 100 MC HERMES (hereafter referred to as ‘Nion’) were acquired in dual-EELS mode using convergence and collection semi-angles of 34 mrad and 44 mrad, respectively. In this mode, two spectra were sequentially acquired at each pixel. The first spanned the range (–1–9 eV) that encompassed the ZLP (5 ms acquisition), and the second (~0.05–10 eV) covered the low energy-loss region (100 to 300 ms acquisition). By using a starting energy of ~0.05 eV for the second spectra, the most intense part of the ZLP was not collected to ensure that the ZLP did not saturate the detector during this data acquisition. These spectra were collected with a dispersion of 0.005 eV/channel, while the monochromator was adjusted to provide an acceptable compromise between beam current (and therefore signal-to-noise ratio) and energy resolution, resulting in a measured energy resolution of approximately 35 meV. Again, multiple spectra were summed together to improve the SNR. To enable the analysis required for obtaining the optoelectronic properties, single EELS spectra were also collected for the extended energy range of –5–35 eV. The effective energy resolution of these data sets was ~60 meV as they were limited by the point-spread function (PSF) of the detector as a result of the reduced energy dispersion (0.02 eV/channel) necessary to collect data for desired energy range.

## 3. Results and discussion

In Fig. 1, the ZLPs collected through the CuPc specimen as well as a table comparing their widths at FWHM, FWQM (full-width at quarter-maximum) and FWTM (full-width at tenth-maximum) are shown. The energy resolution on the Nion (best reported is 9–10 meV, 35 meV for the beam settings used for these experiments as measured through the specimen) is better than on the Titan (best observed in our microscope is 50 meV, 175 meV for the beam settings used for these experiments as measured through the specimen) by a factor of five. This improvement in energy resolution makes it realistic to observe peaks at energy-losses below 1 eV.

In order to compare the shape of the ZLP on both instruments, the Nion ZLP was numerically broadened to match the FWHM of the ZLP from the Titan (shown as the dashed green line on Fig. 1). There is very good agreement between the shapes of the ZLPs on the two instruments. A small difference between this simulated ZLP and the ZLP from the Titan instrument is observed as a 10% change at FWQM and 15% at FWTM (Fig. 1). Although the instruments have different monochromator designs – the Titan utilizes a Wien filter [22] and the Nion utilizes an alpha filter [19] – it is not obvious that this would contribute to this

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