Analysis of molecular packing and nanoscale atomic variation in polymer semiconductors

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Background incl. aims
Conjugated polymers are an important class of organic light emitting diodes (OLEDs) and organic solar cells (OSCs). These materials are predominantly semi-crystalline or amorphous with intricate molecular packing and mixed variety of structural orders and disorders [1]. The susceptibility of these materials to 'burn-in degradation' [2] can induce blend-demixing and photo-induced ordering/disordering [3], thereby resulting in the performance losses of the devices [4]. Controlling this performance degradation during operation necessitates an understanding in changes in chemical structures and structural disorders at the nanoscale – the length scale commensurate with the transport of charge carriers. Yet direct nanoscale characterisation is limited for polymer semiconductors and their associated devices due to the irreversible changes in these materials structure when exposed to high-energy ion and electron beam conditions [5]. Here, we advance the structural characterisation of polymer semiconductors, whether in the form of free-standing films or cross-sectioned lamella, using low-dose four-dimesion scanning transmission electron microscopy (4D-STEM), enabling the analysis of the molecular packing, crystallinity, and atomic arrangement in the polymer semiconductors in response to temperature and ion milling-induced damage.

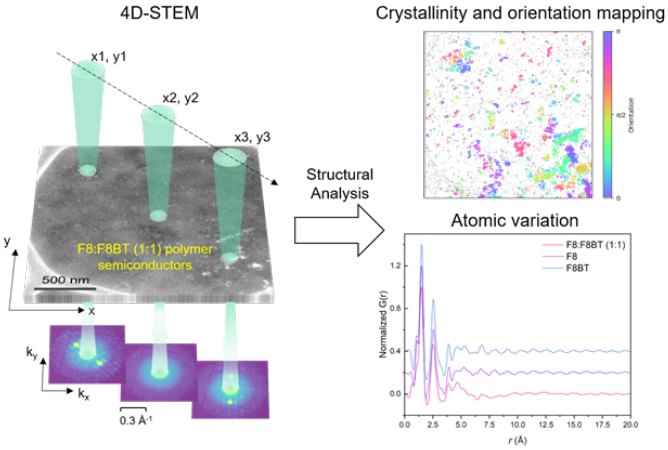
Methods
Low-dose 4D-STEM analysis was conducted using established nanobeam scanning electron diffraction alignment at electron Physical Science Imaging Centre (ePSIC), Diamond Light Source. In particular, Merlin-Medipix detector and <1 mrad convergence semi-angle with 1-2 pA in probe current at 300 kV were used to minimize radiolytic damage. We obtained data at a range of camera lengths to enable both mapping of crystalline domains from Bragg scattering as well as reciprocal space (variance measures) and real space electron Pair Distribution Function (ePDF) analysis of disordered and amorphous regions. The materials under examination were free-standing polymer films (F8:F8BT, 1:1), prepared by spin-coating onto PDOT:PSS/ITO/Glass substrates. Subsequently, the multi-layered sample was submerged in deionized water, and the F8:F8BT films were floated onto carbon support films for 4D-STEM analysis. Additionally, we developed cryo-Focused Ion Beam (cryo-FIB) protocols to facilitate the structural examination of the cross-sectioned device model, Glass/ITO/PDOT:PSS/F8:F8BT (1:1).

Results
The developed techniques reveal the formation of nano-crystalline domains in the F8:F8BT films after heat treatment. These domains are attributed to the crystallisation of F8 polymers, as evidenced by indexing some diffraction patterns aligning along the zone axis. Additionally, ePDF analysis allows us to characterise the atomic structures in amorphous areas with varying contrast. The analysis indicates that there were no chemical changes in the F8:F8BT blends induced by temperature. However, partial phase segregation occurred, as also supported by low-dose EELS analysis. We extended these analyses to a cross-sectioned device model prepared by cryo-FIB, and the findings demonstrate that our cryo-FIB protocol preserves the crystalinity of the polymer blends. ePDF shows that cryo-FIB milling does not alter the chemical structures of the films, i.e. intramolecular structure, but does affect the intermolecular arrangement.

Conclusion

The developed electron microscopy techniques enable the characterisation of microstructures and nanoscale atomic arrangements in beam-sensitive polymer semiconductors, paving a pathway for examining phase segregation and chemical changes resulting from the burn-in degradation. By doing so, effective strategies can be developed to minimise structural degradation in polymer semiconductors, thereby preventing performance losses during operation.

Graphic:



Keywords:

Polymer semiconductors, 4D-STEM, ePDF, cryo-FIB

Reference:

[1] L. Ding et al. Chemical Reviews. 2023, 123, 12, 7421–7497; [2] L. Duan et al., ACS Appl. Mater. Interfaces 2020, 12, 24, 27433–27442; [3] N. Li et al., Nat. Commun. 2017, 8, 14541; [4] L. G. Kaake et al. J. Phys. Chem. Lett. 2010, 1, 3, 628–635; [5] J. Donohue et al. iScience, 2022, 25, 103882.