Petascale Simulations Expose a Rational Tunability of Bulk Heterostructure Morphology and the Molecular Interfaces

**Achievement:** Petascale molecular dynamics, atomistic, and density functional computation reveal the evolution of internal mixing of poly(3-hexylthiophene) (P3HT) and phenyl-C_{61}-butyric acid methyl ester (PCBM) allowing comparison with neutron-reflectivity-derived density profiles.

**Significance and Impact:** Controlling nanoscale mixing of organic photovoltaic (OPV) donor and acceptor materials is key to optimizing their performance. This work serves as a roadmap for rational design of conjugated-polymer based composite materials.

**Research Details:**

- High performance computing enables description of structure on multiple length scales.
- Neutron reflectivity measurements provide nanoscale view of interfacial mixing.

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Overview:
Understanding how additives interact and segregate within bulk heterojunction (BHJ) thin films is critical for exercising control over structure at multiple length scales and delivering improvements in photovoltaic performance. The morphological evolution of poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) blends that are commensurate with the size of a BHJ thin film was examined using petascale computational simulations. Comparisons between two-component and three-component systems containing short P3HT chains as additives undergoing thermal annealing demonstrated that short chains alter the morphology in useful ways: they efficiently migrate to the P3HT/PCBM interface, increasing the P3HT domain size and interfacial area. Simulation results agree with depth profiles determined from neutron reflectometry measurements that reveal PCBM enrichment near substrate and air interfaces but a decrease in that PCBM enrichment when a small amount of short P3HT chains are integrated into the BHJ blend. Atomistic simulations of the P3HT/PCBM blend interfaces show a non-monotonic dependence of the interfacial thickness as a function of number of repeat units in the oligomeric P3HT additive, and the thiophene rings orient parallel to the interfacial plane as they approach the PCBM domain. Using the nanoscale geometries of the P3HT oligomers, LUMO and HOMO energy levels calculated by density functional theory are found to be invariant across the donor/acceptor interface. These connections between additives, processing, and morphology at all length scales are generally useful for efforts to improve device performance.