

RETHINKING THE IDEALIZED MORPHOLOGY IN HIGH-PERFORMANCE ORGANIC PHOTOVOLTAICS

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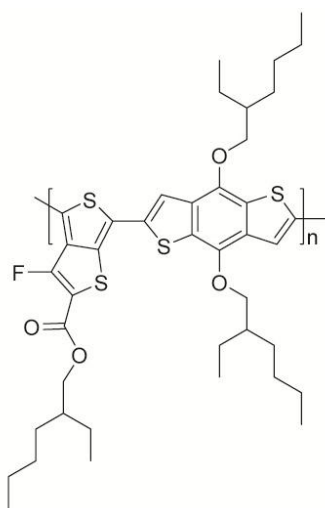
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Traditionally, the ideal morphology for organic photovoltaic (OPV) active layers is viewed as a bicontinuous network of pure donors and acceptors with a periodicity comparable to the exciton diffusion length. One approach used to target this morphology is through the self-assembly of block copolymers containing semiconducting polymer blocks.¹ Our efforts along these lines²⁻⁵ will be briefly discussed prior to presenting recent results that suggest the traditional idealized morphology may not be the only one worth pursuing.⁶



Scheme 1

PTB7 semiconducting copolymer comprising thieno[3,4-b]thiophene and benzodithiophene alternating repeat units (Scheme 1) set a historic record of solar energy conversion efficiency in polymer:fullerene bulk heterojunction solar cells. To further improve solar cell performance, a thorough understanding of structure–

property relationships associated with PTB7:fullerene and related OPV devices is crucial. A collection of x-ray scattering and neutron scattering techniques are applied to this system, supported by energy-filtered transmission electron microscopy (Figure 1). GIWAXS and XRR provide insight into molecular ordering while RSoXS reveals structures at larger length scales.

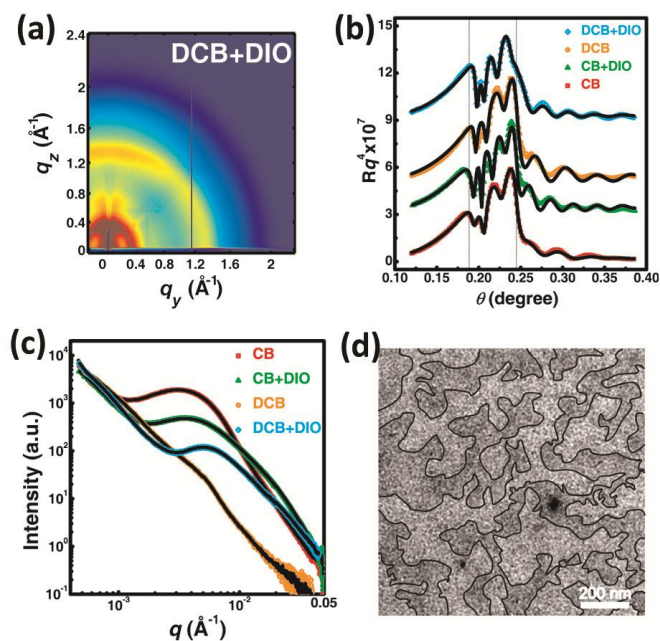


Figure 1. PTB7/PCBM film structural characterization. (a) Grazing incidence x-ray scattering (GIWAXS). (b) X-ray reflectivity (XRR) of films prepared from different solvent systems. (c) Resonant soft x-ray scattering (RSoXS) of films prepared from different solvent systems. (d) Energy-filtered TEM image. DCB is dichlorobenzene, CB is chlorobenzene, and DIO is diiodooctane.

Based on these data, we show that the OPV active layer of PTB7:fullerene OPV devices, contrary to the traditional picture, involves hierarchical nanomorphologies ranging from several nanometers of crystallites to tens of nanometers of nanocrystallite aggregates in PTB7-rich and fullerene-rich domains, themselves hundreds of nanometers in size (Figure 2).

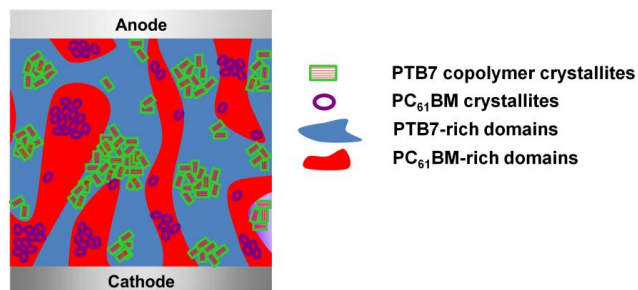


Figure 2. Schematic of hierarchical nanomorphologies in PTB7/PCBM OPV active layers.

Based on device measurements and correlations with structural analysis, these hierarchical nanomorphologies are coupled to significantly enhanced exciton dissociation, which consequently contribute to photocurrent, indicating that the nanostructural

characteristics at multiple length scales is one of the key factors determining the performance of PTB7 copolymer—and likely most polymer:fullerene systems—in OPV devices.

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