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### **Expanded Morphological Paradigm of Polymeric Solar Cells: Contributions by Soft X-ray Methods<sup>1</sup>**

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The complex three dimensional morphology of polymeric/organic donor:fullerene bulk heterojunction solar cells and the structure of the discrete and recently inferred dispersed interfaces are critical to performance, yet have been very difficult to study due to a paucity of adequate characterization methods. Recently developed soft X-ray microscopy and scattering tools and methods can provide new avenues and contribute substantially to infer the number of phases present in a device, determine the minimum fullerene content in mixed domains and to provide a quantitative statistical measurement of the composition variations and size distribution. This contributed to the realization that mixed domains are prevalent and rather than just being detrimental can have important beneficial contributions for charge generation and charge transport as such mixed domains represent a special form of hierarchical structures (E.g. [1-3]). Furthermore, polarized x-ray scattering can reveal preferential orientation of the donor polymer/small molecule (edge-on or face-on) relative to the fullerene aggregate interface. Such ordering has previously not been observed nor controlled in fullerene-based solar cells and is shown here to be a critical factor for high performance in a number of systems.

[1] Collins, B. A. *et al. Nat. Mater.* **11**, 1–8 (2012).

[2] Collins, B. A. *et al. Adv. Energy Mater.* **3**, 65-74 (2013).

[3] Ma, W. *et al. Adv. Energy Mater.*, **3**, 864 (2013).

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