

## Abstract

Organic photovoltaic (OPV) cells based on semiconducting polymers are very appealing because they are light-weight and flexible. Ternary bulk heterojunction is an effective strategy to achieve high efficient organic photovoltaic devices. Understanding the relationship of the complex morphology and the fundamental physical processes in the ternary system plays a key role to realize efficient electron transfer and enhance the device efficiency.

The variation of vertical phase distribution significantly influences device performance because of its impact on the charge transport and charge recombination. In order to achieve favorable vertical phase distribution in OSCs based on PBDB-T:ITIC, PC71BM was incorporated into the binary system to fabricate ternary OSCs. In the ternary blend, PC71BM can effectively regulate the phase distribution of PBDB-T and ITIC in vertical direction, which provides favorable vertical phase distribution for charge transport. Moreover, the addition of PC71BM can also effectively increase the  $\pi$ - $\pi$  stacking coherence length of both donor and acceptor, which facilitates charge transport and reduces the bimolecular recombination.

Using ultra-low band-gap small molecule as a third component in ternary organic solar cells is a promising method to improve device efficiency by broadening their spectral response range and enhancing charge transfer and transport ability. IEICO-4F was used as a secondary acceptor in both fullerene (PTB7-Th:PC71BM) and non-fullerene based (PBDB-T:ITIC) ternary organic solar cells. A notable photocurrent and power conversion efficiency enhancement can be obtained by introducing an appropriate amount of IEICO-4F in ternary blends. A new model of a donor/acceptor "quasi-alloy" is proposed to describe the mechanism operating in the ternary systems. Various measurements suggest that IEICO-4F can enhance the crystallinity of polymer donors and provide additional channels for charge transfer and transport compared to binary systems, leading to an ultrafast charge transfer and a more effective charge transport process.