Interplay Between π-Conjugated Polymer Donors and Acceptors Determines Crystalline Order of Their Blends and Photovoltaic Performance

([1]*Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Kodai Yamanaka[1], Masahiko Saito[1], Itaru Osaka[1]

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Organic photovoltaics (OPVs) have been paid significant attention because they allow us to produce them on flexible and lightweight plastic substrates through the solution process. The development of new semiconducting materials has markedly improved the efficiencies of OPVs such as over 18%. Although fullerene derivatives have long been used as the n-type semiconducting (acceptor) material, nonfullerene compounds (NFAs) have recently been mainly used as the acceptor material. Whereas, for fullerene-based cells, high-crystalline π-conjugated polymers are typically used as the p-type semiconducting (donor) materials,[1)] NFA-based cells, low-crystalline polymers typically provide better efficiencies.[2)] However, we envisage that if higher crystalline polymers can function well in NFA-based cells, further improvement in efficiency could be realized.

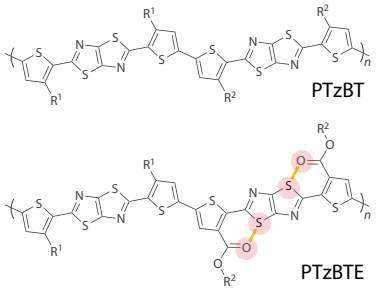

Figure 1. Chemical structures of thiophene-thiazolothiazole copolymer.

In this work, we prepared a series of thiazolothiazole (TzTz)–thiophene copolymers named PTzBT and PTzBTE (Figure 1) and systematically studied how the polymer crystallinity and aggregation properties impact the performance of OPV cells based on NFAs such as IT-4F, Y6, and Y12 as well as a fullerene material $PC_{71}BM$ as the acceptor (Figure 2). PTzBT has alkyl groups (2-butyloctyl and 2-hexyldecyl groups) as the side chains, whereas PTzBTE has alkyl (2-butyloctyl) and ester (2-hexyldecyl ester) groups as the side chains. In PTzBTE, the sulfur atom in the TzTz ring and the carbonyl oxygen can induce a noncovalent intramolecular interaction (S···O interaction) to interlock the linkage between the ester-substituted thiophene and TzTz rings, suppressing the backbone torsion.

Interestingly, whereas PTzBTE exhibited crystalline structures in the blend film regardless of the acceptor materials, PTzBT exhibited crystalline structures only when blended with acceptors showing relatively high aggregation properties and crystalline order. Notably, such crystalline order in the blend films was correlated closely with the OPV performance. This study demonstrates how the interplay between the polymer donor and acceptor plays a crucial role in determining the crystalline order in the bulk heterojunction systems and thereby high photovoltaic performance.

Reference

1) *Nat. Photon.* **2015**, *9*, 403. 2) *Joule* **2019**, *3*, 1140.