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Impact of Backbone Fluorination on π -Conjugated Polymers in Organic Photovoltaic Devices: A Review

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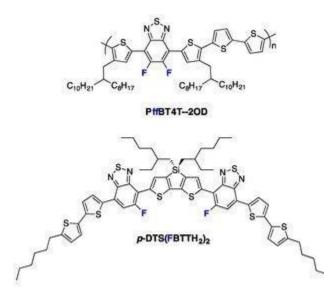
ABSTRACT

Solution-processed bulk heterojunction solar cells have undergone remarkable output acceleration over the past two decades, achieving power conversion efficiencies above 10%. This remarkable advancement is the product of a simultaneous production of more sophisticated system architectures and engineered polymers in semiconduction. Recently, fluorination of the conjugated polymer backbone has appeared to be a particularly promising approach for developing effective semiconducting polymers. As a matter of fact, most currently best-performing semiconducting polymers are using fluorine atoms in their conjugated backbone. Solar cells based on polymer composite active layers were first identified in 1995 as Solution-processed bulk heterojunction (BHJ). These devices have recently experienced a remarkable acceleration in efficiency after a slow initial increase in power conversion efficiencies (PCEs), hitting PCE values above 10 per cent. This remarkable progress is the product of the simultaneous development of more sophisticated system architectures and engineered polymers with semiconduction. As the physical mechanisms underlying a BHJ solar cell's activity have been increasingly clarified, the specifications for a highly performing photoactive polymer have been better established. As a result, numerous polymers have been engineered with continuously improving optoelectronic properties, and have contributed significantly to this very positive evolution. For example, the synthesis of pro-quinoidal copolymers or of

alternating electron-donor (D) and electronacceptor (A) moietieshas proved especially useful. Both chemical strategies allowed many research groups to fine-tune the energy levels of the frontier molecular orbital (FMO) by choosing the constitutive moieties accordingly. Many chemical and structural parameters were also shown to have a significant effect on the optoelectronic properties of polymers. These parameters include the structure and position of the solubilizing alkyl side chains, the planarity of the backbone (which can be increased by using coplanar monomers of the ladder-type) and the molecular weight of the polymer.

More recently, the fluorination of the conjugated polymer backbone has proven to be a particularly promising approach to the production of effective polymers. Many currently best performing semiconducting polymers typically use fluorine atoms in their conjugated backbone. For example, this is the case for the PffBT4T-2OD polymer recently published by Yan and his colleagues holding the PCE record for single junction solar cells. The PDTP-DFTBT copolymer is a further illustrative example having a band gap as low as 1.38 eV and achieving nearly 8% PCE in single junction devices. In addition, the PTB7 polymer series fluorinated derivatives which were engineered according to the pro-quinoid method, achieved PCE above 10 per cent. Jenekhe et al. demonstrated an 8 per cent PCE in all polymer solar cells using PTB7 as substrate for electron donors. Last but not least, fluorination has also

proven successful in the design of high performance molecular semiconductors. For example, the fluorinated p-DTS(FBTTH2)2 derivative currently ranks among the best performing small molecules for BHJ devices.



Chemical structures of highly efficient fluorinated materials for organic photovoltaics (OPV)

In this study, we attempt to provide an up-to date overview of the latest results achieved for solar cells on fluorinated polymers and to highlight the evolutionary patterns of general polymer properties relevant to the fluorination of their conjugated backbone. Keywords: conjugated polymer; fluorine; optoelectronic; organic photovoltaics