



# Fluorinated conjugated polymers in organic bulk heterojunction photovoltaic solar cells



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## ABSTRACT

The photovoltaic technology represents a major renewable energy source to harness the solar power. Over the last two decades, the development of solution-processed bulk heterojunction polymer solar cells has attracted a considerable interest. This has resulted in a significant efficiency improvement through innovation of device architectures and molecular structure design of donor polymers. In this regard, the introduction of fluorinated units along the conjugated backbone has emerged as a successful strategy for further fine-tuning the physical and chemical properties of conducting polymers. In this review, we highlight recent strategies aiming at improving the solar cell performance by variable fluorine substitution of repeating units. Fluorination was found to achieve a modulation of HOMO and LUMO energy levels and optical properties to some extent. Moreover, intermolecular interactions involving fluorine atoms have a significant influence on blend film morphology. The resulting organic photovoltaic solar cells endowed some of the highest power conversion efficiency values reported to date.

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## 1. Introduction

The development of new and renewable sources of energy has become a major concern and a requirement in today's world. In this regard, scientists' imagination proposed many different approaches to tackle these energy issues, among which is the conversion of solar energy into electricity. During the last two decades, spectacular advances have been made in the development and the improvement of the performance of photovoltaic (or solar) cells. According to the National Center for Photovoltaics, the best solar cell has reached a power conversion efficiency (PCE) of about 44% (multijunction cells) and emerging organic devices are close to 12% in 2014 [1]. Inorganic materials occupy the forefront of the technology presently, but their high manufacturing and raw material costs make organic photovoltaic (OPV) compounds highly attractive systems for future developments.

In the landscape of OPV materials, these organic semiconductors are divided into two main classes: small molecules and polymeric compounds. Both categories feature a distinct mode of preparation, purification and device fabrication. One significant difference lies in the deposition of the active constituents on the substrate. Small molecule semiconductors are mainly processed through vapor phase deposition under high vacuum. In contrast, conducting polymers are typically processed from solution in organic solvents. This aspect is of particular relevance since the nanoscale morphology of corresponding thin films can impact dramatically on the solar cell performance [2].

Polymer-based solar cells have stimulated broad interest owing to the combination of varied physical and chemical properties such as a light weight, an easy processability and a good mechanical flexibility [3–5]. The inherent economics of high-throughput manufacturing combined with these specific features are gaining a significant advantage in reducing installation costs and developing tailor-made photovoltaic installations [6].

## 2. Generalities

### 2.1. Bulk heterojunction (BHJ) solar cells

The most successful device architecture for polymeric photovoltaics is the bulk heterojunction (BHJ) solar cell. Typically, BHJ devices consist of a photoactive blend layer [7] composed of a conjugated polymer used as an electron donor, a soluble electron acceptor derived from fullerene [8] between a metal cathode electrode and an indium-doped tin oxide (ITO) anode electrode covered by a poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer (Fig. 1) [9].

As far as the polymer is concerned, different parameters are correlated with an efficient sunlight absorbing agent [10]. Thus, efficient photovoltaic cells are closely related to high charge carrier mobility. In this regard, a good

diffusion length of holes and electrons in the polymer layer is a key parameter to improve the charge transfer efficiency [11,12]. Moreover, a low band gap to absorb at long wavelength and a large absorption coefficient represent critical parameters [13]. Recently conjugated polymers comprised of donor (D) and acceptor (A) units along the backbone have been tailored to improve the performance of these parameters. The relative positioning of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) of the acceptor (PCBM) and the polymer play a crucial role in making a photovoltaic cell work successfully [14]. In principle, the LUMO of the polymer must be higher than the LUMO of the acceptor. An efficient charge transfer is correlated to large offsets between the LUMO (HOMO) of the donor and the LUMO (HOMO) of the acceptor. Further, a large open circuit voltage ( $V_{oc}$ ), namely the difference between the LUMO of the acceptor and HOMO of the polymer, is usually observed for low HOMO energy level of the donor [15]. As aforementioned, the morphology of the photoactive layer has a great influence on the solar cell performance. In general, alkyl pendant groups endow the polymers with good solubility and controlled morphologies of the blend can be achieved through an annealing step [16,17]. Finally, the air stability is also a crucial point for the device lifetime since these polymeric compounds can degrade under oxygen and humidity exposure. This can pose a challenge when compared to the relative stability of inorganic solar cells. With these data in mind, it appears that the careful design of molecular structures can influence the final properties of the polymeric system.

### 2.2. Intrinsic properties of fluorine

Owing to the inherent features of the fluorine atom, fluorination offers an appealing strategy to tune the physical and chemical properties of active ingredients [18]. Although the van der Waals radius of fluorine (1.47 Å) is slightly larger than hydrogen and similar to oxygen, the steric hindrance of the CF<sub>3</sub> group is similar to that of the isopropyl group. Further, a very low polarizability and high electronegativity, (3.98 on the Pauling scale) makes fluorine a strong electron withdrawing substituent. Also, the C–F bond is one of the strongest bonds known as determined by its short length of 1.39 Å. By comparison with their hydrocarbon counterparts, fluorinated compounds

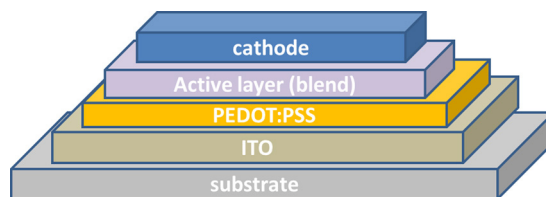


Fig. 1. Typical bulk heterojunction solar cell structure.

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