



Review

Recent advances in high performance donor-acceptor polymers for organic photovoltaics

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ABSTRACT

Organic photovoltaic cells made with semiconducting polymers remain one of the most promising technologies for low-cost solar energy due to their compatibility with roll-to-roll printing techniques. The development of new light-absorbing polymers has driven tremendous advances in the power conversion efficiency of these devices. In particular, the use of alternating electron rich (donor) and electron poor (acceptor) segments along the polymer backbone can produce low optical bandgap materials that capture more of the solar spectrum. As a result, power conversion efficiencies over 10% are increasingly common for this technology. This review summarizes the recent advances in donor-acceptor polymer design and synthesis, highlighting the structural features that are key to providing high efficiency, scalable and stable devices.

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1. Introduction

Organic photovoltaics (OPVs), which utilize light absorbing polymers or small molecules to generate an electrical current from light, have received significant attention in recent years as a form of highly scalable and inexpensive solar energy production. In contrast to the relatively heavy and brittle modules made with inorganic semiconductors such as silicon, OPVs offer the attractive prospect of low-temperature, solution processed fabrication such as roll-to-roll and inkjet printing, that have the potential to dramatically lower the cost of solar energy production. Furthermore, the potential for large-area, lightweight and mechanically flexible modules, with options for semi-transparent and colored films, opens up new opportunities for building-integrated photovoltaics among other applications [1–3]. The field of OPV has advanced enormously in the last few decades, with frequent reports now of lab-scale efficiencies >10%, which is often stated as the benchmark for commercial viability [4]. A large part of this progress can be attributed to the development of new light-absorbing polymers. From the simple homopolymers such as MDMO-PPV and P3HT that were popular in the early days of the field [5–7], hundreds of more complex polymer structures have since been introduced with improved light absorption, charge generation and charge transport properties [8–10]. Significant advances have also been made in other integral components of the device including the electron acceptor [11,12], electrodes and interfacial layers [13,14]. In this review, we will detail the recent advances made in donor-acceptor (D-A) copolymers for OPV applications, with particular focus on key polymer structural features that contribute to their high performance. As a rough benchmark for high performance, we have included only polymers demonstrating power conversion efficiencies of 8% or over in this review.

2. Working principles of OPV

2.1. Bulk heterojunction OPV

Organic materials, which are typically considered insulators, can become semiconductors when they possess sufficient conjugated π -bonding character. As the number of alternating single and double bonds in a π -bonded system is increased, such as in a highly conjugated (sp^2 hybridized) polymer or small molecule, the overlap of atomic orbitals increases and thus the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) becomes smaller. When this energy gap becomes small enough, the absorption of visible light can photo-excite an electron in the material across this gap, analogous to the band model of inorganic semiconductors. However, in contrast to inorganic semiconductors, in which free electron-hole pairs are produced upon photoexcitation, the photoexcitation of organic semiconductors produces bound electron-hole pairs, also known as excitons. These excitons have a large binding energy (typically 0.2–1.0 eV) that drives the electron and hole to recombine after photoexcitation [15]. A solution to this problem was proposed by Tang et al. in 1986 [16], which involves combining two organic semiconductors with slightly offset HOMO and LUMO energies, such that the photoexcited electron in the first material (the 'donor') is transferred to the second material ('acceptor'), allowing for the charges to be separated at the junction between these two materials.

Fig. 1 demonstrates a simplified energy diagram for the process of charge separation at this heterojunction. When the donor absorbs a photon, an electron is initially excited across the bandgap from the HOMO to the LUMO, forming an exciton (i). This exciton then diffuses towards the donor-acceptor interface, where the

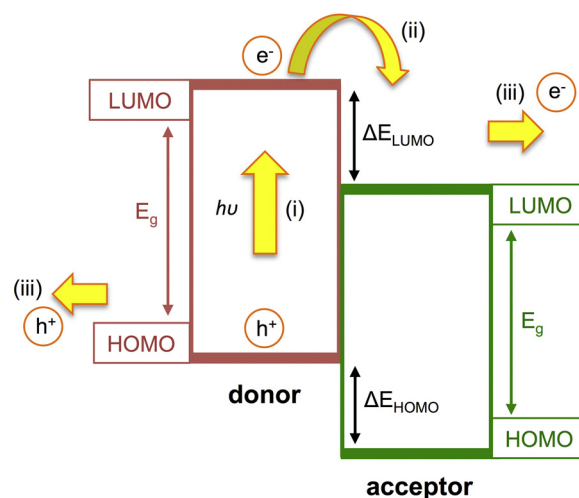


Fig. 1. Simplified energy level diagram for a donor-acceptor heterojunction in an OPV device with basic charge generation and separation processes indicated as follows: (i) absorption of a photon with energy $>E_g$, causing an electron to be excited in the donor to form an exciton; (ii) transfer of the electron to the acceptor; (iii) drift of electron and hole towards the electrodes.

electron can be transferred to the LUMO of the acceptor material, provided that the difference between the LUMO energies (ΔE_{LUMO}) of the donor and acceptor is greater than the exciton binding energy (ii). Likewise, for an exciton that is formed on the acceptor, hole transfer to the donor can occur if the energy offset between the HOMO energies (ΔE_{HOMO}) is sufficient. It is from this weakly bound charge transfer (CT) state that the free electron and hole can be generated, which can then drift towards their respective electrodes (iii). However, it is also possible that the exciton can recombine at the heterojunction prior to becoming free charges (geminate recombination), or alternatively recombine with other free charges generated from separate absorption events (non-geminate recombination), and both of these processes can result in significant efficiency losses in OPV devices [17].

The very short diffusion length of excitons (average length an exciton moves between generation and recombination) in most organic semiconductors (around 10 nm) adds a further challenge, as the donor and acceptor phases must be close enough for excitons to reach the interface in order to separate. For this reason, the donor and acceptor components are typically blended on the nanoscale to form a bulk heterojunction (BHJ). This morphological strategy was first proposed in the early 1990s [18,19], and has since remained the prevalent active layer structure in OPV research. Compared to a bilayer structure, the BHJ archetype allows relatively thick films of the active layer blend to be deposited so that more light can be absorbed, while maintaining a large number of donor-acceptor interfaces for efficient exciton dissociation. Such BHJ films are typically fabricated by co-depositing the two semiconductors from a mixed solution, and allowing the two materials to phase separate upon drying to form nanoscale domains of donor and acceptor. In practice, predicting and controlling the extent of this phase separation is extremely challenging, as will be discussed in Section 2.5.

2.2. Solar cell characterization

The photovoltaic performance of a solar cell can be characterized by illuminating the cell and obtaining the current density (J , output current divided by the device illuminated area) in response to an applied voltage (V). Several important parameters can be extracted from this J - V curve, including the current density at short circuit (J_{SC}), the voltage at open circuit (V_{OC}) and the fill factor (FF). The

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