

External electric field dependent photoinduced charge transfer in Donor-PC71BM system for an organic solar cell

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Received 15 February 2016; Accepted (in revised version) 22 April 2016

Published Online 25 May 2016

Abstract. We use time-dependent density functional theory together with a set of extensive multidimensional visualization techniques to characterize the field-dependent electronic structure and rate of photo-induced charge transfer in organic donor-acceptor dyad. External electric field is incorporated into the generalized Mulliken-Hush model and Marcus theory. We use these methods to evaluate the influence of the external electric field on the electronic coupling between donor and acceptor. We also calculate the reorganization energy and the free energy change of the electron transfer. These theoretical methods and calculation techniques proves that the external electric field has main effect on the electron transfer rate. More important, our results provide a new framework to understand charge transfer of organic systems under the external electric field.

PACS: 31.25.Jf, 82.39.Jn

Key words: external electric fields; light-induced charge transfer; electronic coupling; organic solar cell.

1 Introduction

Solution-processed bulk-hetero-junction photovoltaic cells were first reported in 1995 [1-2]. It took another 3-4 years until the scientific community realized the huge potential of

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this technology. And suddenly in 1999, the number of publications in that field started to rise exponentially [3]. Since then, organic materials are becoming more and more attractive due to their numerous advantages for cite an instance low cost, flexibility, large-area capability and easy processing [4]. They play an important role in fabricating of transistor, photodiodes, solar cells, and so on. From what has been discussed above and the current understanding, the photon-to-charge conversion in organic photovoltaic (OPV) devices can be described as a sequence of basic steps [1]. Therefore, charge transfer is the main aspect of the power conversion efficiency of OPV device.

In order to promote deeper understanding of the charge transfer, we pay more attention to investigate the dissociation of the photo-generated excitons into separate charges. The electron transfer rate can be estimated by Marcus theory as shown in following equation:

$$k = \sqrt{\frac{4\pi^3}{h^2 \lambda k_B T}} |V_{da}|^2 \exp\left[-\frac{(\Delta G + \lambda)^2}{4\lambda k_B T}\right] \quad (1)$$

where λ represents the reorganization energy, V_{DA} is the electronic coupling (charge-transfer integral) between donor and acceptor, ΔG is the Gibbs free energy change for the electron transfer reaction, k_B is the Boltzmann constant, h is the Planck constant, and T is the temperature, which is set as 300K in our calculations. PCE is dominated intricately by many factors on the mentioned electron processing, the effective coupling of donor and acceptor V_{DA} is a key parameter. Several years ago, Cave and Newton introduced the generalized Mulliken-Hush (GMH) method. The GMH method has been employed for estimating electronic coupling in various systems [5].

Among all kinds of OPVs, bulk heterojunction (BHJ) OPV is one of the best OPV device architectures so far, which composed of a blend of donor (D) and acceptor (A) components [6]. And in these paper, we chose a system with [6,6]-phenyl-C71-butyric acid methyl ester (PC₇₁BM) as acceptor material to obtain higher PCE. As for the donor, we had a strict comparison before deciding. We designed a series of D-A copolymers using BTI as acceptor unit with different donor units. Finally, we believe that cyanomethylene-CPDT-BT will be a promising candidate for superior performance BHJ OPVs using PC₇₁-BM as an acceptor material [6].

There are three elementary electronic processes photo-excitation. Firstly, active layer absorbs the solar photons to create electron-hole pairs; besides it will dissociating into free holes and electrons in the D/A interface; thirdly holes and electrons mobile through the donor and acceptor channels to anodes and cathodes respectively; then the charges will be collected by the electrodes [7]. Base on above, we found that electron-hole pairs play an important role in these processes. While, there is no answer to the specific impact of external electric field on electron-hole pairs. In this paper, we will discuss how the external electric field enables efficient long-range charge separation and the electron transfer rate in organic bulk heterojunction. The paper is organized as follows: Section 2 displays the theoretical methods used for the calculation external electric field dependent rate of electron transfer. We will consider the external electric field on the basis of