Light-induced electron spin resonance as a probe for charge separation and recombination in hybrid donor:acceptor systems

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A B S T R A C T

Donor:acceptor systems are the core of many concepts for photovoltaic devices, because they provide a mean to separate photo-generated electron-hole pairs into extractable charge carriers. In organic photovoltaics, donor:acceptor systems consist of two different organic semiconductors. Alternatively, inorganic semiconductor nanocrystals are also suitable materials. Their use in combination with an organic material gives rise to hybrid systems. Charge separation being a key step in the energy conversion process, suitable methods are required to study this physical process. The present review article provides an overview on the use of light-induced electron spin resonance as a powerful method to investigate charge separation in donor:acceptor blends. Thereby, organic and hybrid material systems are compared. Furthermore, detailed investigations of recombination processes are considered as well.

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1. Introduction

Solar cells with photoactive layers made of materials which can be processed from solution are a promising alternative to classical photovoltaic devices. Key features of this approach are the possibility to deposit the active layer by printing technologies and the compatibility with roll-to-roll production [1–3]. Deposition of the absorber layer from a liquid medium is possible in different types of photovoltaic devices, among them organic bulk heterojunction (BHJ) solar cells [4–7], hybrid BHJ solar cells [8–11], quantum dot solar cells [11–13], and perovskite solar cells [14–16]. Even in the case of thin film solar cells with absorber layers composed of $Cu(In,Ga)(S,Se)_2$ (CIS/CIGS) or Cu_2ZnSnS_4 (CZTS), strategies to produce these semiconductors from solution-cast precursor layers are subject of current research [17–20].

A concept intensively studied in the past is the BHJ approach, which relies on the combination of two materials in the absorber layer that form a donor:acceptor system. Basically, due to an offset between the energy levels of the donor and acceptor material, photo-generated electron-hole pairs are supposed to be split at the interface [4,5]. The involved transfer of charge across the donor: acceptor interface is an important elementary step in the energy

conversion process. However, the creation of a large interfacial area between the donor and acceptor materials enables not only efficient separation of electron-hole pairs, but gives also rise to recombination of positive and negative charge carriers diffusing or drifting through the composite active layer, the recombination rate having a strong impact on the device performance [4,21,22].

In order to achieve a deep understanding of the functionality of donor:acceptor solar cells, methods to investigate the steps of charge transfer and recombination processes are required. A widely used and comparably simple approach to study charge transfer in donor: acceptor systems is steady-state photoluminescence (PL) quenching [23,24]. If the donor material alone exhibits a pronounced PL signal, the reduction of its intensity in a blend with an electron acceptor provides a first indication for successful charge transfer. In time-resolved PL measurements, quenching of the photoluminescence results in a reduction of the decay time [24,25]. However, PL measurements are not always sufficient as a probe for charge transfer, because other processes like Förster resonance energy transfer (FRET) can cause PL quenching as well. Alternative methods are for example, photo-induced absorption (PIA) spectroscopy [11,25–28] or light-induced electron spin resonance (L-ESR) [11,29,30]. Both, PIA and L-ESR are not only useful to study charge transfer, but enable also obtaining valuable information about the recombination of charge carriers [26,30–32].

The present review article is devoted in particular to the L-ESR technique as a probe to study charge transfer at donor:acceptor interfaces as well as recombination processes. In Chapter 2, a more

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detailed description of charge separation and recombination in donor:acceptor systems as well as an introduction to the L-ESR technique are given. Chapter 3 provides an up-to-date overview on applications of L-ESR measurements in the fields of organic and hybrid solar cells. Chapter 4 finally shows up perspectives and conclusions.

2. Fundamentals

2.1. Charge carrier generation in donor:acceptor systems

In every solar cell, light absorption leads in a first step to the generation of Coulomb bound electron-hole pairs, so-called excitons. In many inorganic semiconductors, the exciton binding energy is low so that the thermal energy is sufficient to split the excitons into free charge carriers which can travel through the device and finally be extracted at the electrodes. For example, the exciton binding energy in silicon is as low as 14.7 meV [33]. In contrast, organic semiconductors exhibit exciton binding energies which are typically of the order of several hundreds of meV. By consequence, photo-generated excitons will not easily split at room temperature into free carriers. A strategy to split the electron-hole pairs is the creation of donor:acceptor systems.

In a donor:acceptor system, two materials with different energy levels are combined. The electron donor has its frontier orbitals (both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)) closer to vacuum than the acceptor. This configuration, sketched in Fig. 1a, is called a type II heterojunction and creates a driving force for electrons excited to the LUMO level of the donor to be transferred to the lower-lying LUMO level of the acceptor. This charge transfer process is an essential step in the energy conversion process in a donor:acceptor solar cell. However, directly after charge transfer, the charge carriers are not yet free, but still Coulomb bound. Thus, the picture in Fig. 1a is a very simple one.

The Coulomb bound electron-hole pair with the electron on the acceptor moiety and the hole on the donor moiety is called a charge transfer (CT) state [34,35]. Fig. 1b illustrates CT states formed by electron transfer from the excited donor to the LUMO level of the acceptor. After creation, there are different pathways to decay for the CT state. The desired pathway in a solar cell would be the separation of the electron and hole into extractable carriers. Therefore, the charge carriers must be displaced from the donor: acceptor interface. This can for example happen by diffusion and relaxation of the electrons (holes) into lower-lying (higher-lying) energy levels which usually exist, because the energies of the HOMO and LUMO levels of organic semiconductors exhibit a broadened density of states [22,36]. The energetic width of the density of states, sometimes called disorder parameter, is typically of the order of ~50–150 meV [36], so that relaxation of the carriers into the tails of the density of states can provide sufficient energy to overcome the Coulomb binding energy. With increasing distance from the material interface, the Coulomb attraction becomes less, and finally, the electron and hole become independent of each other, which is often referred to as the charge-separated state [35]. However, as also illustrated in Fig. 1b, there are concurring processes, among them geminate recombination which means the recombination of the electron and hole originating from the same photo-generated exciton. Fig. 1c shows the processes of charge transfer, CT state formation, charge separation and geminate recombination in another schematic representation.
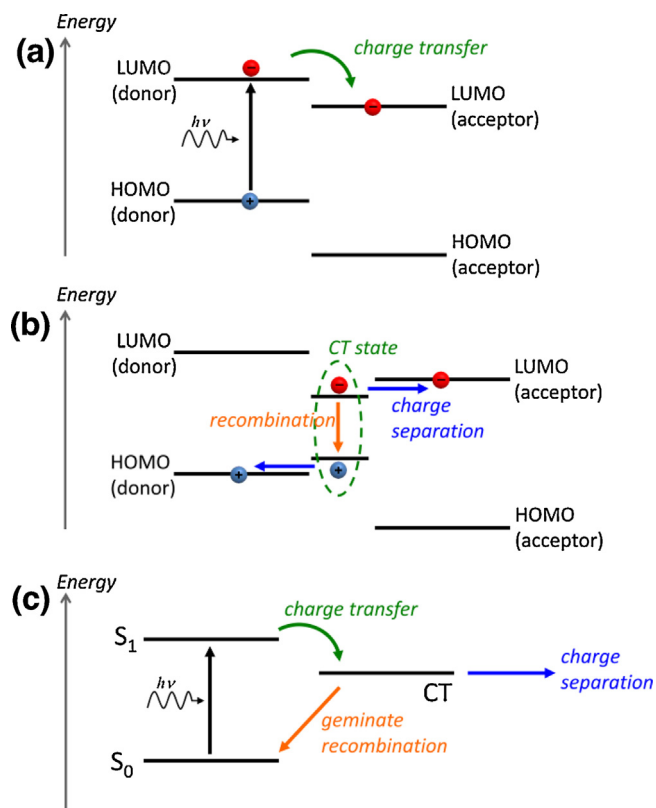

Fig. 1. Schematic illustrations of the charge transfer process and charge transfer (CT) states. (a): In the simplest picture, the offset between the HOMO and LUMO levels in a type II heterojunction creates a driving force for electrons excited in the donor material to be transferred to the electron acceptor material. (b): In more detail, a CT state is formed which can be considered as a Coulomb bound electron-hole pair located at the interface, with the hole on the donor and the electron on the acceptor material, respectively. To achieve charge separation, the Coulomb binding energy must be overcome. (c): An alternative schematic representation of the involved processes. First, light absorption by the donor material leads to an excited singlet state (S_1). By electron transfer to the acceptor, the CT state can be populated. The CT state can decay either by charge separation or by geminate recombination. (For simplicity, concurring processes like triplet state population are not included into this figure.).

2.2. Recombination in donor:acceptor systems

After charge separation, charge carrier recombination can occur. This recombination process between opposed charge carriers can either be geminate, between electrons and holes originating from the same photo-generated exciton, or non-geminate, between separated charge carriers. The geminate recombination of a polaron pair is monomolecular and therefore a first order process. The non-geminate, bimolecular recombination following Langevin theory is of second order. The Langevin recombination rate is given by [4]:

$$R = \gamma(np - n_i^2) \tag{1}$$

with n and p being the electron and hole concentration, respectively, n_i the intrinsic carrier concentration, and γ the Langevin recombination prefactor. The recombination rate is limited by the velocity electron and hole find each other and thus dependent on the sum of their mobilities:

$$\gamma = \frac{q}{\varepsilon}(\mu_e + \mu_h) \tag{2}$$

Therein q is the elementary charge, ε the dielectric constant and μ_e and μ_h are the electron and hole mobility, respectively.