

Interplay Between Triplet-, Singlet-Charge Transfer States and Free Charge Carriers Defining Bimolecular Recombination Rate Constant of Organic Solar Cells

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Despite the myriad of organic donor:acceptor materials, only few systems have emerged in the life of organic solar cells to exhibit considerable reduced bimolecular recombination with respect to the random encounter rate given by the Langevin equation. Monte Carlo simulations have revealed that the rate constant of the formation of electron-hole bound states depends on the random encounter of opposite charges and is nearly given by the Langevin equation for the domain sizes relevant to efficient bulk heterojunction systems. Herein we explain the reduced bimolecular recombination by solving kinetic rate equations for a BHJ system with realistic rates. We demonstrate that both singlet and triplet CT states can act as loss channels and suppression of both of the parallel loss channels can be achieved through increasing the dissociation rate of the charge transfer states; a crucial requirement to achieve a high charge carrier extraction efficiency (Figure 1).

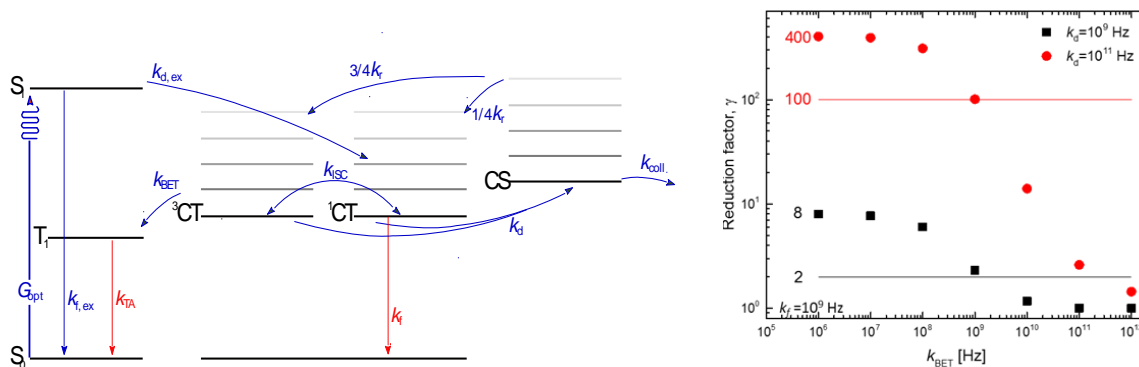


Figure 1. (left) State diagram of the BHJ solar cells considering the role of spin. The two main loss pathways of the CT states to the ground states are the decay of singlet CT states at the rate k_f to the ground state and the loss of the triplet CT states through back electron transfer to triplet excitons at rate k_{BET} . (right) The calculated reduction factor based on k_{BET} . The solid lines show the expected reduction factor without considering the role of triplet CT states. In absence of back electron transfer ($k_{BET} \ll k_d$) taking triplet CT states into account results in 4 times larger reduction factor compared to a cases in which triplets are ignored. When $k_{BET} \gg k_d$, even when $k_d \gg k_f$ the bimolecular recombination is diffusion-controlled with the reduction factor $\gamma \approx 1$. The reduced factor is given by $\gamma_{CT} = \frac{k_d}{0.25k_f + 0.75k_{BET}}$

In organic solar cell, charge collection efficiency is the result of the competition between bimolecular recombination of the charge carriers and their extraction rate at the electrodes; In junctions with active layer thickness on the order of several hundreds of nanometer – favourable for scaling up and large scale fabrication – the built-in electric field is smaller than that of thin (<100 nm) devices whilst the travel distance for the charge carriers is larger. This typically slows down the charge extraction rate and results in inefficient charge carrier collection. To improve charge collection efficiency and thereby power conversion efficiency of organic donor:acceptor (D:A) bulk heterojunctions (BHJ),

either the charge extraction rate must be improved or the bimolecular recombination has to be suppressed.

Improving charge extraction rate has proved to be challenging due to the limitations in charge carrier mobility. As such reducing bimolecular recombination can be a key for achieving high charge collection efficiencies. In systems with reduced recombination rate constant, the photogenerated carrier lifetime is long enough in order for them to be collected at the electrodes, even when their transit time is long due to the limited carrier mobility or large thickness.

Bimolecular recombination of free charges in low-mobility disordered systems, with short hopping distance compared to the Coulomb radius, has been considered to be given by the random encounter rate of opposite charges in the same manner as ions in an ionized gas or an electrolyte. Such a system can be described by the Langevin equation. However, Arkhipov realised that the kinetic of photoinduced charge carrier density in few examples of disordered dielectrics does not follow Langevin model.^[1] He proposed that the spatial separation of electrons and holes in a non-uniform and fluctuating potential landscape is the cause of the observed non-Langevin behaviour in disordered systems.

Although many BHJ systems exhibit slightly reduced recombination rate constants, significantly reduced recombination (reduction factors >100) has been reported only in very few systems in the life history of organic solar cells.^[3,4] In this work, we examine the previous proposals and investigate their limitations.^[4-6] We show that if fast dissociation of CT states relative to their decay rate and small rate of back electron transfer to triplet excitons – bimolecular recombination can be reduced. The simultaneous requirement of both conditions can also justify as to why the recently reported NT:PCBM system is 800 times non-Langevin (Figure 2). We also show that in the absence of direct singlet to triplet intersystem crossing, the triplet loss pathway has no influence on the charge generation efficiency, rather only on the onset of bimolecular recombination. Our experimental results also provide clues on how charge generation yield, and dissociation and decay rate of the CT states can be quantified. We find that whilst the decay rate constant is almost independent of the blend ratio and density of the CT states, the dissociation rate constant of the CT state is extremely sensitive to the blend ratio and possibly morphology. These are key steps towards material design for non-Langevin systems.

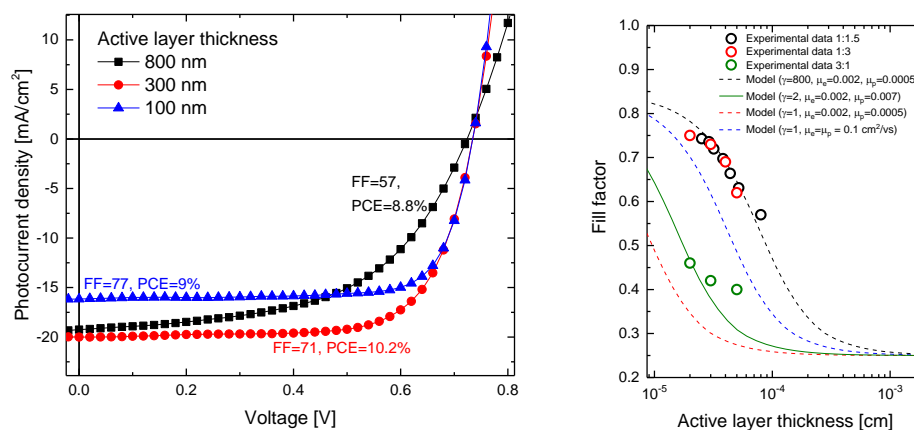


Figure 2 (left) J-V plots of typical NT812:PC71BM solar cells with different thicknesses. Comparison of experimental FF of the devices and prediction of modified Shockley model.

References: [1] V. I. Arkhipov, et al, *J. Phys. D: Appl. Phys.* **1993**, *26*, 1301. [2] L. J. A. Koster, et al, *Appl. Phys. Lett.* **2006**, *88*, 52104. [3] A. Armin, et al, *Adv. Energy Mater.* **2017**, *7*, 1701450. [4] A. Armin, et al, *Adv. Energy Mater.* **2016**, *6*, DOI 10.1002/aenm.201600939. [5] A. Rao, et al, *Nature* **2013**, *500*, 435. [6] T. M. Burke, et al, *Adv. Energy Mater.* **2015**, *5*, 1.