Mechanisms and time scales of free-charge generation in organic photovoltaics: hot and fast or cold and slow

V. Janković[1,2] and N. Vukmirović[2]
[1]*Institute of Physics, Faculty of Mathematics and Physics, Charles University in Prague, Ke Karlovu 5, 121 16 Prague 2, Czech Republic*
[2]*Scientific Computing Laboratory, Center for the Study of Complex Systems, Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia*
e-mail:veljko.jankovic@ipb.ac.rs

The physical mechanisms and time scales of light-to-charge conversion in photoexcited donor/acceptor organic solar cells have recently been heavily debated. The interpretation of experimental signals stemming from ultrafast spectroscopic experiments suggests that free-charge generation mainly occurs on a subpicosecond time scale following the excitation by virtue of high-energy ("hot") delocalized interfacial charge transfer (CT) states [1]. On the other hand, there is experimental evidence that free carriers are predominantly generated on time scales ranging from tens to hundreds of picoseconds out of the lowest-energy ("cold") CT state, which is strongly bound and localized [2,3].

We study charge separation in a one-dimensional model of an interface between two organic semiconductors, both on ultrashort and on much longer time scales. We obtain that free charges present on a subpicosecond time scale following the photoexcitation are mainly directly optically generated from the ground state thanks to the resonant mixing between states of donor excitons and free charges [4]. However, on the same time scale, we find that the majority of photogenerated charges still remain bound in form of donor or CT excitons [5]. We obtain that their further separation on longer time scales is weakly electric field- and temperature-dependent and is enabled by the synergy between carrier delocalization and moderate disorder [6].

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