

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

V. Janković<sup>1,2</sup> and N. Vukmirović<sup>2</sup>

<sup>1</sup>*Institute of Physics, Faculty of Mathematics and Physics, Charles University in Prague,  
Ke Karlovu 5, 121 16 Prague 2, Czech Republic*

<sup>2</sup>*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].

### REFERENCES

- [1] G. Grancini et al., *Nat. Mater.* 12, 29 (2013).
- [2] K. Vandewal et al., *Nat. Mater.* 13, 63 (2014).
- [3] A. Grupp et al., *J. Phys. Chem. Lett.* 8, 4858 (2017).
- [4] V. Janković, N. Vukmirović, *Phys. Rev. B* 95, 075308 (2017).
- [5] V. Janković, N. Vukmirović, *J. Phys. Chem. C* 121, 19602 (2017).
- [6] V. Janković, N. Vukmirović, *J. Phys. Chem. C* 122, 10343 (2018).