

# **A Nonequilibrium-Thermodynamics Perspective on Charge Separation in Organic Solar Cells**

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**Abstract.** The operation of donor/acceptor (D/A) organic solar cells (OSCs) leans on the separation of the strongly bound charge transfer exciton (CTE) localized at the D/A interface into free charges [1]. Kinetic considerations suggest that CTE separation is facilitated by a combination of charge delocalization and moderate disorder [2], while it is hampered by strong disorder [2] and/or strong interaction with phonons [3]. From the standpoint of equilibrium thermodynamics, the charges in the CTE are thermodynamically free because its large binding energy is generally outweighed by the entropic contribution. While strong disorder and enhanced spatial connectivity eliminate the separation barrier [4], charge delocalization may increase it [5]. Such trends contradict the intuitive trends emerging from kinetic considerations.

We employ nonequilibrium thermodynamics to reconcile the kinetic and thermodynamic perspectives on charge separation in OSCs [6]. Within our one-dimensional model of a D/A interface [2, 3], we compute steady-state populations of interface states, which emerge from a competition between incoherent-light excitation, phonon-induced relaxation, and recombination. We then evaluate the nonequilibrium free-energy profile for charge separation and compare it to its equilibrium counterpart for different disorder strengths and delocalization extents. We find that the difference between the two profiles is maximized (minimized) when the separation efficiency is the largest (smallest). Our nonequilibrium profiles show that better delocalization suppresses the entropic contribution at small distances and enhances it at larger distances, meaning that charge delocalization promotes long-range separation. Despite the reduced dimensionality of our model, which is deleterious to the spatial connectivity of interface states, our nonequilibrium entropic contributions are consistently larger than the equilibrium ones because the former take into account the connectivity by phonon-assisted processes. Overall, we conclude that charge separation in the most efficient OSCs proceeds through a nonequilibrium pathway involving both the strongly bound CTE and higher-energy interface states.

## **REFERENCES**

1. Baessler, H., and Koehler, A., *Phys. Chem. Chem. Phys.* **17**, 28451 (2015).
2. Janković, V., and Vukmirović, N., *J. Phys. Chem. C* **122**, 10343 (2018).
3. Janković, V., and Vukmirović, N., *J. Phys. Chem. C* **124**, 4378 (2020).
4. Hood, S. N., and Kassal, I., *J. Phys. Chem. Lett.* **7**, 4495 (2016).
5. Gluchowski, A., Gray, K. L. G., Hood, S. N., and Kassal, I., *J. Phys. Chem. Lett.* **9**, 1359 (2018).
6. Kaiser, W., Janković, V., Vukmirović, N., and Gagliardi, A., *J. Phys. Chem. Lett.* **12**, 6389 (2021).