Energetics and Kinetics Requirements for High efficiency Organic Solar Cells

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The efficiency of solar cells is fundamentally constrained by thermodynamic limits set by the semiconductor band gap. In organic solar cells (OSCs), however, efficiency is governed by a more complex interplay between the energetics and kinetics of three key species: excitons, charge-transfer (CT) states, and free charge carriers. Here, we develop an analytical framework based on detailed balance to elucidate how the relative energetics and kinetic rate constants of these species collectively determine photocurrent generation, recombination losses, and the open-circuit voltage in OSCs. The framework provides explicit relationships between charge generation yield (CGY), charge-carrier recombination coefficients, and photovoltaic parameters, enabling a rigorous assessment of the conditions under which mutual equilibrium between excitons, CT states, and free carriers can be established.

Our analysis reveals that while relative energetic offsets between excitons and CT states are important, device performance critically depends on kinetic factors, particularly exciton recombination rates. In low-offset systems, slow exciton recombination emerges as a key requirement for maintaining high charge generation and suppressing recombination losses. Depending on the kinetic parameters, we predict an optimal power conversion efficiency (PCE) exceeding 20% at energetic offsets as small as ~0.1 eV, providing a theoretical basis for the high efficiencies observed in state-of-the-art non-fullerene OSCs.

Experimental validation is provided using PM6:Y6-based solar cells, which exhibit a near-unity CGY of 98.4%, further improved to 99.3% by employing the Y6 derivative BTP-eC9. Notably, small differences in CGY are shown to have a disproportionate impact on free-carrier recombination and overall device performance, particularly in industrially relevant thick-junction devices. Importantly, we demonstrate that efficient CT-state dissociation and charge generation do not necessarily require favorable energetics but are predominantly kinetically driven. Systems such as PM6:BTP-eC9 achieve the highest CGY despite larger activation energies, in agreement with our theoretical predictions. Together, these findings provide critical insights into the design principles for high-efficiency, low-offset organic solar cells.

References:

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