

## Engineering Aggregation for High-performance Non-fullerene Organic Photovoltaics

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Intimate  $\pi$ -stacking in organic semiconductors is known to form aggregates, which drive dissociation of photogenerated excitons through delocalization of exciton wavefunctions [1-3]. In particular, the onset of non-fullerene acceptors (NFAs) such as Y6 has seen a dramatic rise in discussion of exciton delocalization and its relation to (acceptor-donor) hole transfer [4-6]. Here, we revisit the concept of exciton delocalization in organic semiconductors and show that such a treatment is necessary to accurately describe electron and hole transfer in high performance OPV blends. Specifically, we evaluate how  $\pi$ -interactions in aggregates contribute to delocalization strength, revealing that the formation of delocalized excitons in strongly  $\pi$ -interacting materials opens a new pathway for free carrier generation. As a result, the charge transfer pathway partially bypasses the formation of performance-limiting singlet and triplet charge-transfer states in OPV blends. This pathway improves the internal quantum efficiency in OPVs to realize power conversion efficiencies of >19%. [7, 8] Moreover, triplet states in OPVs based on NFAs are known to mediate instability, either through formation of singlet oxygen ( $^1\text{O}_2$ ) [9], or through anhydrous degradation pathways [10]. We find that in aggregated films, triplet states are transferred to local excitons, which improves the stability by several orders of magnitude [11].

Ultimately, we provide an insight into overcoming the fundamental limits of OPVs associated with aggregation. Designing materials with stronger aggregation should increase the exciton dissociation efficiency and limit terminal back recombination, pushing OPVs towards theoretical efficiency limits. Simultaneously, aggregation can also de-activate triplet states and drastically improve stability.

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