

## PHOTOCHEMICAL DYNAMICS OF INTRAMOLECULAR SINGLET FISSION

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Singlet fission (SF) converts a singlet exciton ( $S_1$ ) into a pair of triplet ones ( $T_1$ ) via a “multi-exciton” (ME) intermediate:  $S_1 \longleftrightarrow {}^1\text{ME} \longleftrightarrow {}^1(T_1T_1) \longrightarrow 2T_1$ .<sup>a</sup> In exothermic cases, *e.g.*, crystalline pentacene or its derivatives, the quantum yield of SF can reach 200%. With SF doubling the electric current generated by an incident high-energy photon, the solar conversion efficiency in pentacene-based organic photovoltaics (OPVs) can exceed the Shockley–Queisser limit of 33.7%.<sup>b</sup> The ME state is popularly considered to be a dimeric state with significant charge transfer (CT) character that is strongly coupled to both  $S_1$  and  ${}^1(T_1T_1)$ ,<sup>c</sup> while this local model lacks strong support from full quantum dynamics studies. Intramolecular SF (ISF) occurring to covalently-bound dimers in the solution phase is an excellent model for a straightforward dynamics simulation of local excitons. In the present study, we investigate the ISF mechanisms for three covalently-bound dimers of pentacene derivatives, including *ortho*-, *meta*-, and *para*-bis(6,13-bis(triisopropylsilyl)ethynyl)pentacene)benzene, in non-protic solvents. Specifically, we propagate the real-time, non-adiabatic quantum mechanical/molecular mechanical (QM/MM) dynamics on the potential energy surfaces associated with the states of  $S_1$ ,  ${}^1(T_1T_1)$  and CT.<sup>d,e</sup> We explore how the energies of these ISF-relevant states and the non-adiabatic couplings between each other fluctuate with time and the instantaneous molecular configuration (*e.g.*, intermonomer distance and orientation). We also quantitatively compare Condon and non-Condon ISF dynamics with solution-phase spectroscopic data. Our results allow us to understand the roles of CT energy levels in the ISF mechanism and propose a design strategy to maximize ISF efficiency.

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<sup>b</sup>W. Shockley and H. J. Queisser, *J. Appl. Phys.* **32**, 510 (1961).

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