

Enabling Singlet Fission by Controlling Intermolecular Charge Transfer

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Singlet exciton fission (SF) in ensembles of molecular chromophores down-converts one singlet exciton (S_1) produced by single-photon absorption into two triplet excitons (T_1) provided that the overall process is exoergic, i.e. $E(S_1) > 2E(T_1)$. While there has been great interest in SF because of its potential for increasing the maximum efficiency of photovoltaics from the 32% Shockley-Queisser limit for single-junction devices to nearly 45%, important details of the SF photophysical mechanism remain unresolved. SF can occur by two general mechanisms: one that directly couples the initial $^1(S_1S_0)$ state to a multi-exciton $^1(T_1T_1)$ state by a two-electron process, and another that proceeds via a charge transfer (CT) state by two consecutive one-electron processes. In the latter process, photoexcitation of a chromophore that is electronically coupled to a second nearby chromophore creates an electronic superposition state involving $^1(S_1S_0)$, a virtual CT state, and $^1(T_1T_1)$. Electronic dephasing of this superposition state typically should occur on a sub-picosecond timescale leaving the spin-coherent $^1(T_1T_1)$ state, which is frequently referred to as a correlated triplet pair state. Spin dephasing is a much slower process, typically on the order of nanoseconds, so that spin dephasing in $^1(T_1T_1)$ may occur on a timescale comparable to spatial separation of the triplet states resulting in two independent triplet states.

We report here on a series of covalently-linked terrylene-3,4:11,12-bis(dicarboximide) (TDI) dimers in which triptycene spacers hold two TDI molecules in π -stacked geometries (Fig. 1A).^[1] When dimer **2** in which the TDI chromophores are slip-stacked by 7.6 Å is dissolved in polar CH_2Cl_2 , ultrafast symmetry-breaking charge separation occurs in $\tau = 8.1$ ps to yield $TDI^{+•}-TDI^{•-}$. In contrast, when the same dimer is dissolved in non-polar toluene, rapid singlet fission is observed in $\tau = 2.2$ ps, while the reverse triplet-triplet annihilation occurs in $\tau = 4.4$ ps resulting in an excited-state equilibrium giving an overall 133% triplet yield in steady state. Controlling the $TDI^{+•}-TDI^{•-}$ CT state energy relative to that of $^1(S_1S_0)$ results in the CT state

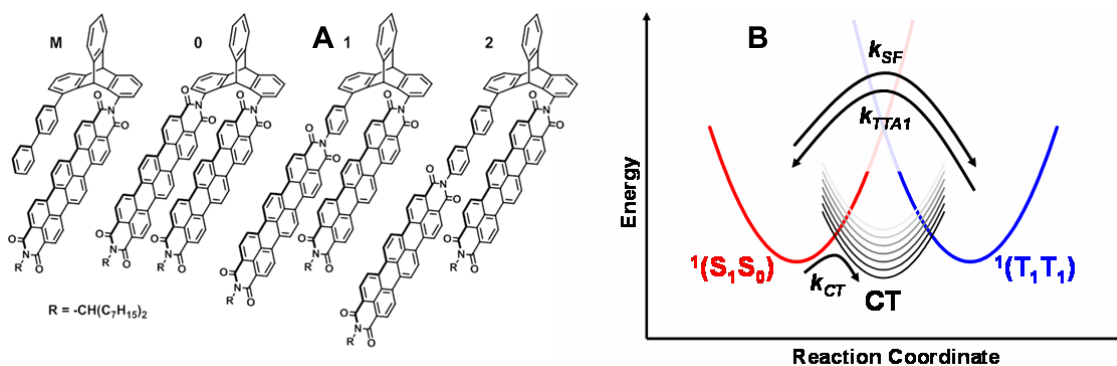


Figure 1. A) Structures of TDI derivatives. B) Proposed schematic potential energy surface of SF. The CT state serves either as a trap (k_{CT}) or as a virtual state through which SF (k_{SF}) or triplet-triplet annihilation (k_{TTA1}) may proceed along the reaction coordinate depending on how its energy level is affected by solvent polarity.

serving as either a virtual state promoting singlet fission or a trap state inhibiting it (Fig. 1B).

Extending this work to thin films of TDI derivatives, we will report on SF in thin polycrystalline films of two TDI derivatives **3** and **4**, which crystallize into two distinct π -stacked structures.^[2] Femtosecond transient absorption spectroscopy (fsTA) reveals a charge transfer state preceding a 190% T_1 yield in films of **3**, where the π -stacked TDI molecules are rotated by 23° along an axis perpendicular to their π systems. In contrast, when the TDI molecules are slip-stacked along their N-N axes in films of **4**, fsTA shows excimer formation followed by a 50% T_1 yield. The high SF yield observed in **3** highlights the broader scope of inter-chromophore geometries that can lead to favorable electronic couplings and CT state involvement in SF.

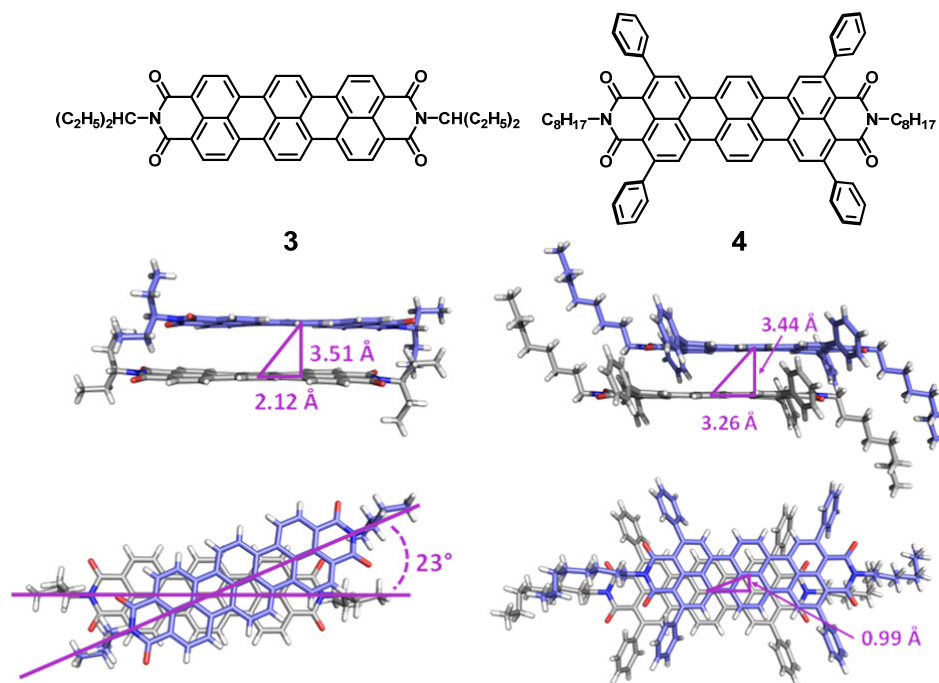


Figure 2. Chemical and single crystal X-ray diffraction structures of **3** and **4**.

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References:

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- [2] E. A. Margulies, C. E. Miller, L. Ma, E. Simonoff, G. C. Schatz, and M. R. Wasielewski, *J. Am. Chem. Soc.* **2017**, 139, 663.