Singlet Fission

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Singlet fission is a little known and usually inefficient form of multiple exciton generation from a single photon. It is a spin-allowed process in which a chromophore excited into its singlet state shares energy with a nearby ground state chromophore, producing a pair of triplet excited chromophores coupled into an overall singlet. Singlet fission has been observed in a very small number of aromatic hydrocarbons, particularly tetracene and pentacene, and also in a few conjugated polymers and carotenoids, starting half a century ago. It had received little attention until very recently, when it was pointed out that if it were fully efficient, and if it were possible to achieve charge separation from both resulting triplets, the limiting theoretical efficiency of a simple photovoltaic cell would be increased from 1/3 to nearly 1/2. In order to explore the potential of the phenomenon in solar cells, a much wider selection of structures for which singlet fission is efficient is needed.

We shall describe a first-principles approach to the problem of designing molecular structures for which singlet fission is efficient. This involves developing three sets of structural design rules: (i) for finding chromophores in which the conditions $E(S_1) \geq 2\,E(T_1)$ and $E(T_2) \geq 2\,E(T_1)$ are satisfied, making singlet fission exoergic and triplet annihilation endoergic, (ii) for finding chromophore coupling that maximizes the rate of singlet fission relative to all other possible decay processes in a dimer, oligomer, or crystal, and (iii) for finding arrangements that maximize the likelihood of two independent charge separation events from a triplet pair in competition with all other decay modes. The first application of the rules produced a material that exhibited a 2005 triplet yield.