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Singlet Fission and Multi-Exciton Generation in Organic Systems

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Multi-exciton generation (MEG) has been observed in a variety of materials and might be exploited in solar-cells to dramatically increase efficiency. In tetracene and pentacene MEG has been attributed to singlet fission (SF), however a fundamental mechanism for SF has not been previously described. Here, we use sophisticated ab initio calculations to show that MEG in pentacene proceeds by transition of the lowest optically allowed excited state S1 to a dark state (D) of multi-exciton character, which subsequently undergoes SF to generate two triplets (2×T0). D satisfies the energy requirement for SF ($E_D > 2E_{T0}$) and lies just below S1 in pentacene, but above S1 in tetracene, consistent with the observed thermally activated SF process in tetracene, but no thermal activation in pentacene. While S1 exhibits single exciton character, D shows multi-exciton character comprising two separated electron-hole pairs. Dimer simulations predict S1 excimer formation and that fission of D into triplets proceeds through the excimer. The predicted energetics, wavefunctions and excimer interaction support the proposed mechanism, which accounts for the observed rapid, unactivated SF in pentacene. Results for SF in polyacenes, grapheme nanoribbons, rubrene and carbon nanotubes will be presented.