

Search for New Classes of Structures for Efficient Singlet Fission Materials

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Singlet fission (SF) is a process in which a singlet excited chromophore and its ground-state neighbor are converted into two triplet excited chromophores. Its use in solar cell sensitizers promises to improve cell efficiency, but the number of known compounds that actually perform SF with a triplet quantum yield of 200% is less than half a dozen, and none are very practical. We have therefore embarked on a search for structural design rules that would allow the discovery of additional efficient SF materials. The first criterion that an efficient SF compound needs to fulfill is isoergicity or even slight exoergicity: twice the triplet excitation energy needs to be less than or equal to that of the first singlet and the second triplet excitations, $E(T_2) > E(S_1) \geq 2E(T_1)$.¹ Very few known chromophores meet this requirement, and it has been suggested that biradicaloids are good candidates.² The selection of suitable candidates for synthesis is guided by quantum mechanical calculations.³ We proceed in two steps. The first is a time-dependent density functional theory (TD-DFT) calculation of vertical excitation energies using long-range corrected functionals. The second is a multireference ab initio calculation of both vertical and adiabatic excitation energies of the lowest few singlet and triplet states with numerical gradient optimization in CASPT2 with a large active space. In order to facilitate a future high-level theoretical treatment of SF dynamics, we look for relatively small chromophores and report here the results for a series of heterocycles (Figure 1).

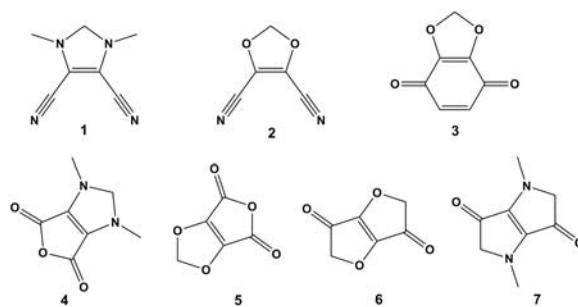


Figure 1. Chromophores examined for use in SF.

References

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