A Theoretical Study on Highly Efficient Triplet Harvest in Selone Analogs of Perylenediimide

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ABSTRACT

Visible-light absorbing metal-free organic molecules are potential candidates for efficient triplet harvesting applications. The highly fluorescent perylenediimide (PDI) has been one such attractive molecule owing to its diverse chemical functional space and structural rigidity. Incorporating chalcogens (S, Se, Te) to improve the inherently small spin-orbit coupling (SOC) of PDI via heavy-atom effect and orbital symmetry modifications is a novel molecular-scale design strategy. Several thione analogs of PDI were recently reported to show remarkably high intersystem crossing (ISC) rates with a complete fluorescence turn-off due to substantially large SOC. [1,2] This motivates to develop other chalcogen analogs of the PDI. Herein several selone analogs of PDI denoted as mSe-PDIs (m=1-4) with varied Se content and positions are investigated to provide a comprehensive and comparative picture down the group-16 using density functional theory (DFT) and time-dependent DFT implementing optimally tuned range-separated hybrid (OT-RSH) in toluene dielectric. [3] All the proposed mSe-PDIs are shown to be thermodynamically synthetically feasible from their oxygen and thione congeners. mSe-PDI with m = 1, 2 possess a first excited-state singlet (S_1) of $n\pi^*$character with an expected fluorescence turn-off while 3Se-PDI and 4Se-PDI have a S_1 of $\pi\pi^*$ state with a possible fluorescence turn-on in absence of any other active nonradiative deactivation pathways. Nevertheless, all mSe-PDI have ~4-6 orders greater ISC rates (~10^{12}-10^{14} s^{-1}) than the fluorescence ones (~10^8 s^{-1}), signifying highly efficient triplet harvest. Importantly, significantly larger SOC and corresponding ISC rates for these mSe-PDIs than their thione congeners render them to serve as better triplet photosensitizers.

References

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