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Multiple Photoinduced Charge Separation in Covalent Molecular Triads: Insights from DFT

Multiple Photoinduced Charge Separation in Covalent Molecular Triads: Insights from DFT

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Efficient solar energy conversion is a major challenge in relation with climate change, which requires to stop using fossil fuels as primary energy sources. One solution to this problem is the development of solar fuels, among which, dihydrogen can be obtained through water photolysis[1].

Scheme 1: molecular D-PS-A triad and its Charge Separated States (CSS1 and CSS2) populated through sequential PETs

A key concept in this reaction, which requires the formal exchange of four electrons, is photoinduced electron transfer (PET). While this process is well understood for a single charge separation in donor-photosensitizer-acceptor (D-PS-A) triads[2], systems allowing the separation of two charges are uncommon[3], and no covalent non biological D-PS-A triad able to undergo double PET has been yet reported in the literature. The current challenge and the purpose of our work is to better understand multi-electron processes in these systems. The initial design of covalent molecular triads D-PS-A takes advantage of potential inversion[4], a phenomenon that is observed only with certain types of two-electron donors and acceptors, for which the second redox process is less demanding than the first one, mostly due to structural variations. The photosensitizers used are earth-abundant high-potential molybdenum complexes[5]. The desired double photoinduced charge separation process is shown on Scheme 1.

Our theoretical analysis of these systems is based on thermodynamic data, such as standard potentials or Gibbs energies obtained through DFT-based methods, as well as on the determination of reaction pathways for charge separation and recombination, both thermal and photochemical, using Nudged Elastic Band (NEB), time-dependent DFT (TD-DFT), and spin-flip TD-DFT calculations. This poster discusses about initial triad designs and future guidelines established during my first and second years of PhD.

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[5] W. R. Kitzmann et al, J. Am. Chem. Soc., 2023, 145, 16597–16609.$

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