New lights on Dihydropyrene systems photoisomerization process with theoretical study.

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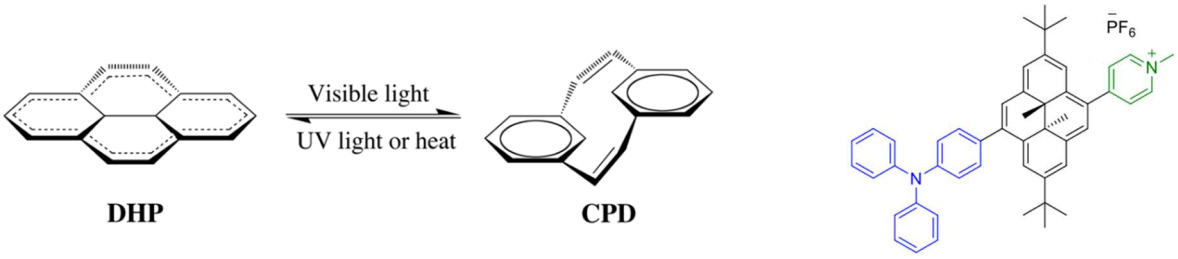

Figure 1. Photoisomerization of the DHP/CPD photochromic couple (left), push-pull DHP (right).

Dihydropyrene (DHP) is a negative photochromic system which turns into its open-ring cyclophanediene (CPD) form upon light absorption (Figure 1 left).[1] A mechanism for the photoisomerization of DHP was first proposed using a CASPT2//CASSCF computational strategy, relying on CASPT2 energy calculations performed at CASSCF optimized geometries.[2] This strategy suffers from the poor description of the effects of dynamic electron correlation on the optimized structures and on the photochemical reaction path. It is also limited by the system size and the underlying active space required to describe the photoisomerization process.

An alternative way is to use the computationally efficient Spin-Flip Time Dependent Density Functional Theory (SF-TDDFT) method which describes the electronic states of interest and their coupling.[3] A comparative study of the photoisomerization mechanism between CASPT2//CASSCF and SF-TDDFT will be discussed, highlighting some of the differences found. The results obtained by SF-TDDFT calculations are consistent with CASPT2 calculations performed along the SF-TDDFT photochemical reaction path. The application of this method on an extended substituted DHP (Figure 1 right) leads to a new understanding on the more efficient photoconversion of this push-pull system over the bare dihydropyrene.[4]

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[4] Zakaria Ziani, Frédérique Loiseau, Elise Lognon, Martial Boggio-Pasqua, Christian Philouze, Saioa Cobo, and Guy Royal, Chem. Eur. J., 2021, 10.1002/chem.202103003.