The Nature of the Donor Motif in Acceptor-Bridge-Donor Dyes as an Influence in the Electron Photo-Injection Mechanism in DSSCs

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The combination and balance of acceptor(A)-bridge-donor(D) architecture of molecules confer suitable attributes and/or properties to act as efficient light-harvesting and sensitizers in dye sensitized solar cells (DSSCs). An important process in a DSSC performance is the electron photoinjection (PI) mechanism which can take place either via type I (indirect), that consists in injecting from the excited state of the dye to the semiconductor, or type II (direct), where the PI is from the ground state of the dye to the semiconductor upon photoexcitation. Here, we present a computational study about the role of the donor motif in the PI mechanisms displayed from a family of 11 A-bridge-D structured dyes to a (TiO2)15 anatase cluster. To this end, different donor motifs (D1-D11) were evaluated while the A and bridge motifs remained the same. All the computations were carried out within the DFT framework, using the B3LYP, PW91, PBE, M06L and CAM-B3LYP functionals. The 6-31G(d) basis set was employed for nonmetallic atoms and the LANL2DZ pseudopotential for Ti atoms. The solvation effects were incorporated using the polarized continuum model (PCM) for acetonitrile. As benchmark systems, alizarin and naphthalenediol dyes were analyzed, as they are known to undergo Type I and Type II PI pathways in DSSCs, respectively. Donors in the studied family of dyes could influence to drive Type I or II PI since it was found that D2 could show some Type II PI route, showing a new absorption band, although with CAM-B3LYP this shows a very low oscillator strength, while the remaining dyes behave according to Type I photoinjectors. Finally, the photovoltaic parameters that govern the light absorption process were evaluated, as the use of these criteria could be applied to predict the efficiency of the studied dyes in DSSCs devices.