Modeling of 5,6-dihydroxyindole and caffeic acid on TiO_2: direct electron injection in Dye-Sensitized Solar Cells

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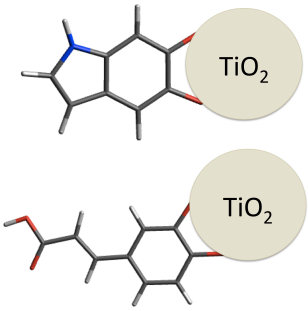
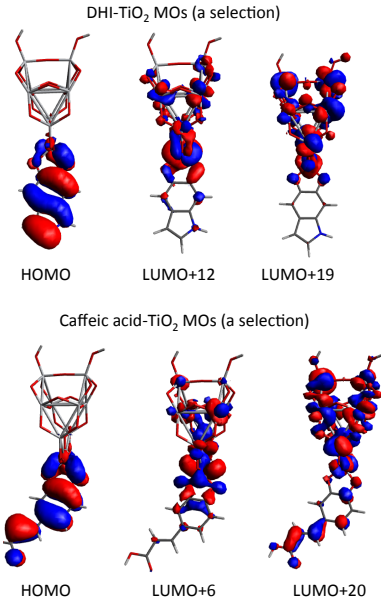
Catechol-based sensitizers have been indicated as light-harvesting molecules for Dye-Sensitized Solar Cells (DSSC). Upon binding TiO_2 they exhibit broad photoabsorption dye-to-TiO_2 charge transfer (DTCT) bands, in the longer wavelength region, whose photoexcitation leads to a direct electron injection in the TiO_2 semiconductor [1,2]. In order to identify novel sensitizers for DSSC employing such a direct mechanism, we model the electron injection mechanism of 5,6-dihydroxyindole (DHI) and caffeic acid on $(TiO_2)_9$ using density functional theory (DFT) methods, as successfully applied in a previous study [3]. The calculation of excitation energies at the time-dependent DFT level show that for both sensitizer/TiO_2 systems it is possible to identify a broad DTCT band along with the absorption of the isolated chromophore. The inspection of the wavefunction plots of the molecular orbitals reveals that the transitions governing the DTCT excitation include the HOMO, localized on the sensitizer, and several unoccupied orbitals whose electron density is mainly localized on the TiO_2 cluster with a non-negligible contribution on the TiO_2-bonding oxygens of the sensitizers. These features indicate a strong electronic coupling for both TiO_2-absorbed sensitizers, which is in favor of a direct mechanism of injection. The strong coupling is also confirmed by a Density of States (DOS) and partial DOS analysis. In conclusion, our results strongly suggest that a direct electron transfer mechanism applies for both DHI and caffeic acid when adsorbed on TiO_2 and used as sensitizers for DSSC.





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