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The modeling of the properties of dyes and electronic processes in photosensitizer-semiconductor complexes for selected anthocyanidins and tetrahydroquinoline derivatives regarding their use in dye-sensitized solar cells

Currently, one of primary problems considered by the scientific and technical community is the utilization of renewable energy sources. One proposed solution is the solar energy harvesting and its conversion into electric current by dye-sensitized solar cells (DSSC), which are considered as an alternative to conventional silicon devices. This work aimed to evaluate natural-origin compounds such as pelargonidin, cyanidin, delphinidin, and tricetinidin as DSSC photosensitizers. Theoretical modeling involved structural, thermodynamic, and spectroscopic properties. Additionally, an electron transfer from the photosensitizer to the semiconductor process (occurring as a result of light absorption) and factors affecting it were investigated. The current density-voltage characteristic of the proposed solar cells was simulated by utilizing the theoretical results. Quantum-chemical computations were conducted by applying the density functional theory and time-dependent density functional theory formalisms. The examined dyes were represented by their flavylium cations. The absorption and fluorescence process modelling revealed that cyanidin is the most efficient photosensitizer. However, the values of parameters of the potential DSSC obtained with the simulated current density-voltage characteristic were noticeably higher in comparison with the literature data. The charge transfer from the photosensitizer to the semiconductor was investigated applying models representing the systems as complexes of cations and $(TiO_2)_{18}\cdot 26H_2O$ or $(TiO_2)_{20}\cdot 28H_2O$ cluster. The analysis of absorption spectra and graphical representation of molecular orbitals for the studied systems revealed the incapability of flavylium compounds as photosensitizers in DSSC, leading to the conclusion which is inconsistent with the experimental findings. Therefore, to evaluate the validity of the applied theoretical model, several tetrahydroquinoline derivatives, which are known photosensitizers, were also modeled. Based on the obtained results, it was concluded that the theoretical model accurately reproduces trends of evolutions in spectroscopic properties occurring with an increasing spacer length for the examined dyes. However, it was noticed that the complex formation is responsible for the placement of dye frontier orbitals within the band gap of the semiconductor, regardless of TiO_2 crystal representation. This demonstrates that the conclusions derived from the relative positions of the orbitals HOMO and LUMO could be inadequate in the context of the analyzed process. Therefore, it is important to take special care during the analysis of orbital energy values.