
Modelling the electronic states of polyphenylene-ethynylene

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Résumé

Hydrocarbon dendrimers are macromolecules experimentally well-known for their interesting optoelectronic properties[1]. Phenylene-ethynylene (PE) dendrimers behave as light-harvesting antennae in which unidirectional exciton transfer occurs along a series of linear, conjugated building blocks connected *via* the *meta*-substitution of phenylene rings. Thus, PE dendrimers have received much interest as artificial photosynthetic systems. Recent theoretical investigations based on semi-classical dynamics simulations[2] have indicated that the unidirectional energy transfer involves a cascade of conical intersections between excited states localized on different linear fragments. Yet, the calculations of potential energy surfaces (PES) remains out of reach for any level higher than semi-empirical, due to the size of the systems.

Previous investigations using TD-DFT calculations showed that the electronic states involved in the energy transfer are almost pure single excitations localised on linear fragments, which allows a first-order description in terms of near-frontier π -orbitals. Calculations based on the extended Hückel approach confirmed that the frontier molecular orbitals (FMOs) of linear PEs (i) are dominated by the interaction between the FMOs of the fragments of benzene and acetylene (ii) bear some similarity with polyene chains when the number of units increases. In addition, we analysed the dependence of the FMOs on the main geometrical deformations occurring during electronic transitions. This work is the basis for a semi-empirical-type model to be used ultimately in quantum dynamics simulations of energy transfer processes.

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