

Chemical doping based design of oligoacenes for tuning the biradical character and excitation properties

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Abstract: The idea of combining semiconducting and open-shell properties in organic materials has attracted the attention of many researchers towards the study of polyaromatic hydrocarbons (PAHs) [1]. In particular, the acenes are interesting models of PAHs that evolve towards polyradical structures with thermally accessible triplet excited states as the size increases [2,3]. From the theoretical viewpoint, this feature impose a significant challenge since the emergence of strong electron correlation in such larger acenes requires to go beyond the usual single-determinant mean-field approximations [3,4]. Recently, we have shown that doping acenes with boron (B) or nitrogen (N) atoms leads to a large modulation in its biradicaloid nature [5]. Here we extend the previous study to the case of asymmetric substitutions with a BN-pair and also explores the consequences of the chemical doping on the excitation properties of oligoacenes based on Time-dependent Density Functional Theory (TD-DFT) and multireference configuration interaction (MRCI) calculations. Moving the dopants from the terminal to the central benzene rings leads to a remarkable increase in the singlet-singlet and singlet-triplet (π - π^*) energy gaps that is also accompanied by a quenching of the acenes biradical character. These results are interpreted in terms of aromaticity changes and a π -charge transfer effect. Finally, through a rational molecular design, our study provides new insights towards developing high-spin organic materials with efficient singlet fission for solar cell applications.

Key-words: mutireference, biradical, unpaired electrons, excited states, acenes

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