

Novel pCCD-based methods for designing efficient OPV materials: electronic structures and properties of BN-embedded PAHs

Ram Dhari Pandey, Matheus M. F. Moraes, and Pawel Tecmer

*Institute of Physics, Faculty of Physics, Astronomy, and Informatics,
Nicolaus Copernicus University in Toruń, ul. Grudziądzka 5, 87-100 Toruń, Poland*

Doping is a versatile strategy for enhancing the properties of organic compounds, making it attractive for the development and optimization of organic electronics. Incorporating boron and nitrogen atoms into a molecule allows for adjustable bandgap tuning, either increasing or decreasing. This tunability is crucial for designing materials with desired optical and electronic properties [1]. The boron and nitrogen atoms, forming an isoelectronic pair resembling two carbon atoms, have been utilized to replace carbon-carbon units with boron-nitrogen units in naphthalene [2]. Advanced theoretical approaches are needed to model desired properties accurately while maintaining relatively minimal computational expenses. One such example is the orbital optimized pair coupled-cluster doubles (oo-pCCD) and techniques based on it, including the IP variant of the equation-of-motion frozen-pair (fp)CC methods (IP-EOM-fpCCD and IP-EOM-fpCCSD), implemented in the PyBEST software package [3]. Some of these computationally effective models show accuracy comparable to CCSD(T) for properties such as ionization potential [4]. However, verifying their accuracy for other properties (e.g., singlet-triplet gap) is crucial to testing and establishing their reliability in modeling the excited structure of conjugated organic systems.

The current study focuses on the impact of BN doping on the ionization potential, electronic affinity, and low-lying singlet and triplet excitations of all twenty-three BN-naphthalene isomers. Our results demonstrate good agreement among the fpCCD, fpCCSD, and CCSD(T) methods, which closely align with experimental values. Additionally, the comparisons among systems reveal, among other trends, that the BN-doping effect strongly correlates with whether the positioning of heteroatoms is in the same ring or not. The calculation results show higher ionization potential and singlet-triplet gap values for systems with both heteroatoms in the same ring compared to those in different rings. This study emphasizes the significance of heteroatoms (boron and nitrogen) as a donor and acceptor in electronic properties, which can guide the synthesis of Organic Photovoltaic (OPV) materials with desired photoelectric properties.

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