

## Introduction

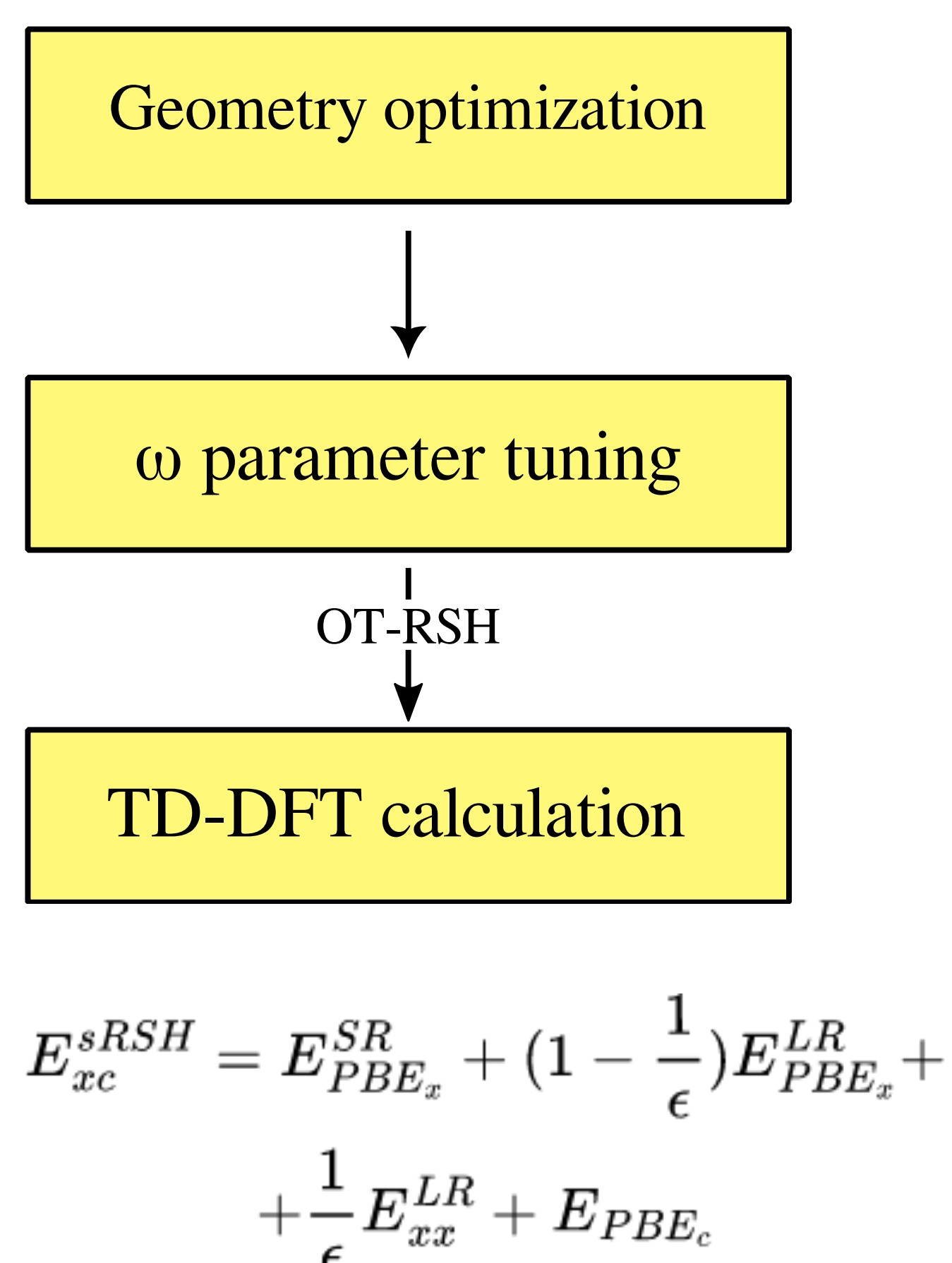
Low-bandgap organic molecules are key actors in organic photovoltaic (OPV) devices, in which an electron donor molecule (D) is coupled with an electron acceptor (A), forming a D-A heterojunction. S,N-Heteroacenes (SN's) are an emerging class of acceptor molecules due to its high electron affinity and enhanced conjugation<sup>1</sup>. In this study we verified how functionalization can be used to tune the optical and transport gap in such molecules. We performed time-dependent density functional theory (TD-DFT) calculations using the optimally tuned range-separated hybrid functionals (OT-RSH).

## Methodology

- Structures obtained via DFT optimizations;
- 6-31G(d,p) basis set used in all calculations;
- $\omega \rightarrow$  minimizing  $J2(\omega)$ :

$$J2(\omega) = \sqrt{\sum_{i=N}^{N+1} [\varepsilon_{HOMO}^i(\omega) + IP^i(\omega)]^2}$$

$$\frac{1}{r} = \frac{\alpha + \beta \text{erf}(\omega r)}{r} + \frac{1 - [\alpha + \beta \text{erf}(\omega r)]}{r}$$



## Results & discussions

### Motivations

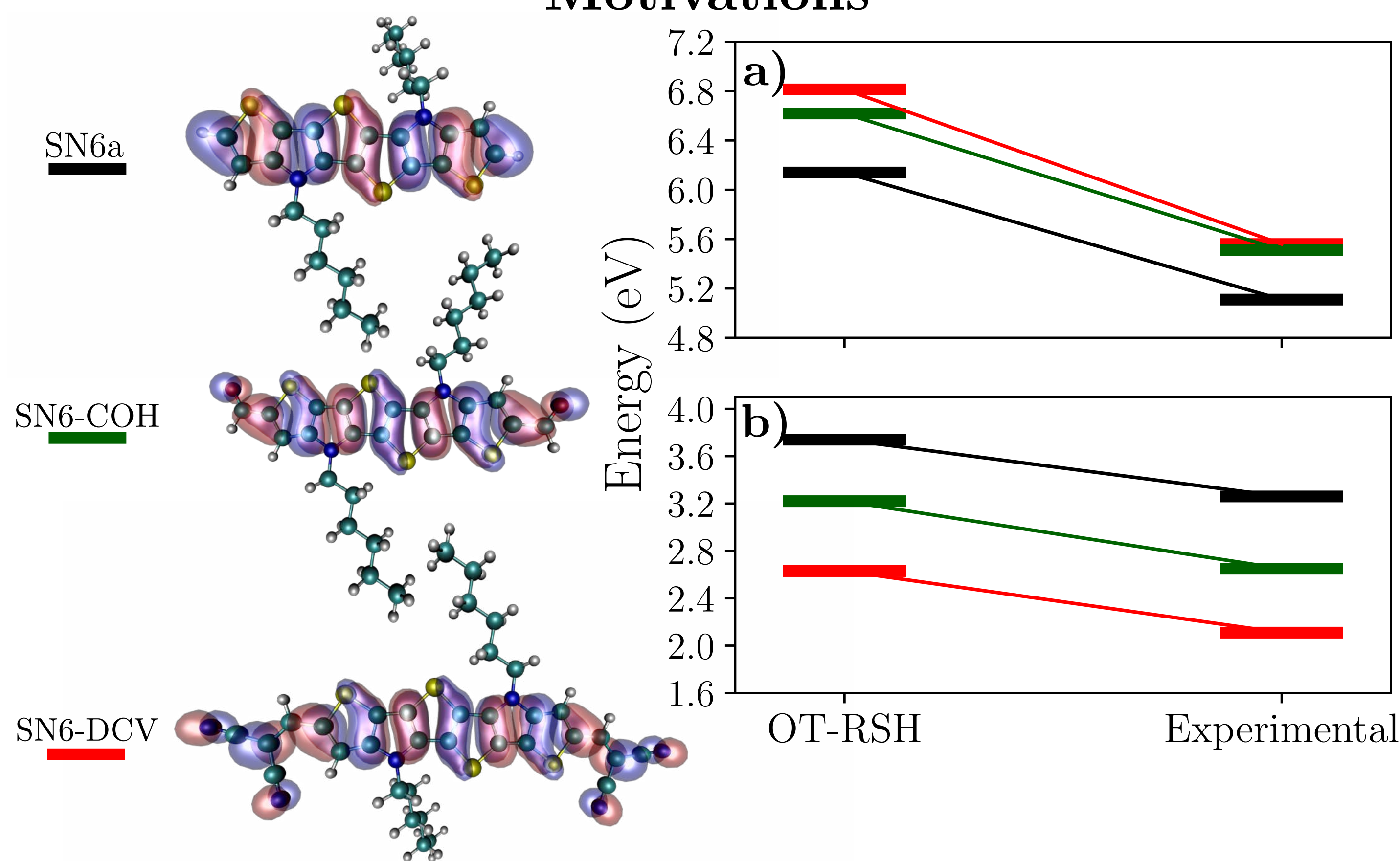


Figure 1: Example on how functionalization can change the **a)** ionization potential and **b)** optical gap for S,N-Heterohexacenes (SN6) molecules.

### Range separating parameter ( $\omega$ )

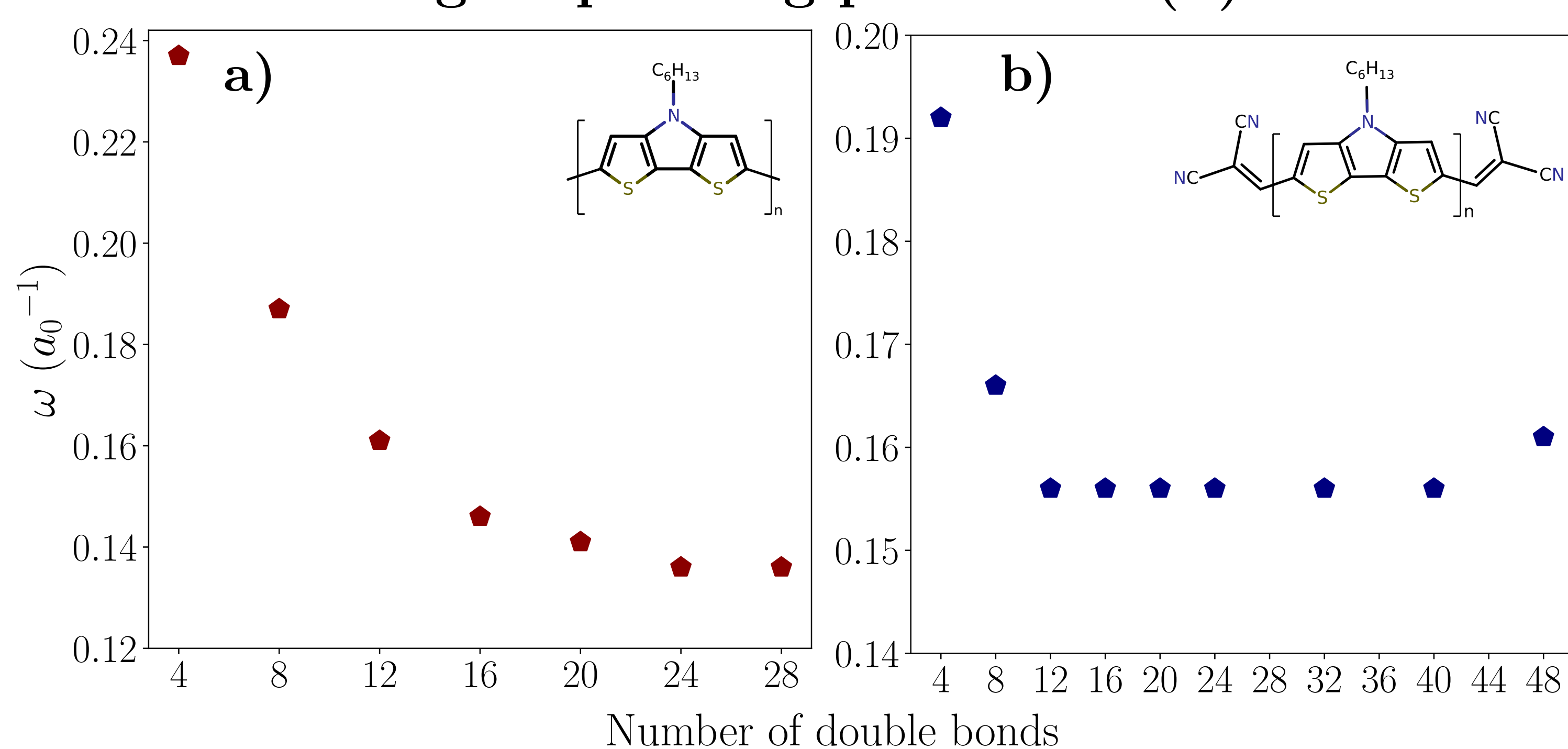


Figure 2: Optimal  $\omega$  as a function of the number of double bonds of **a)** oligo-SN3 and **b)** oligo-SN3-DCV.

### Electronic and optical properties

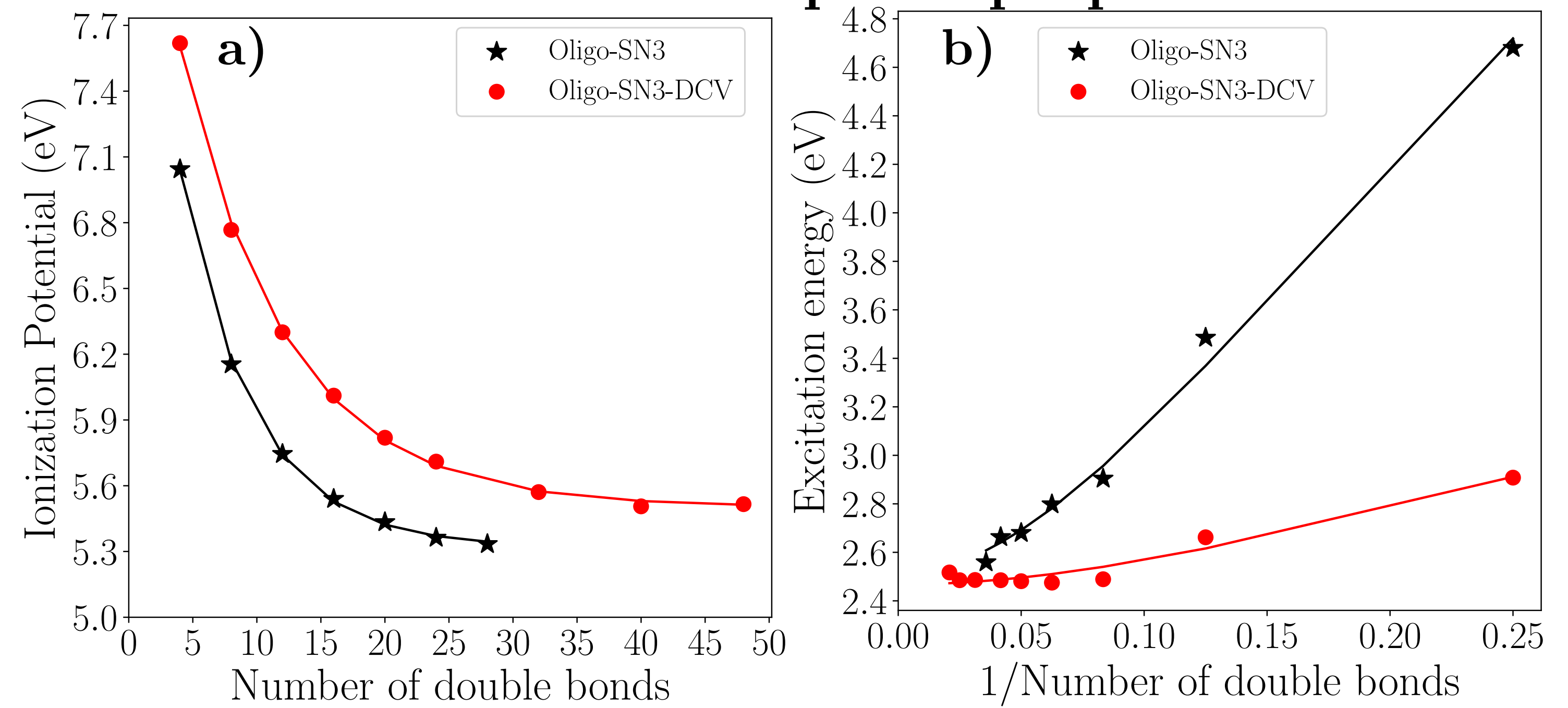


Figure 3: **a)** Ionization potential as a function of the number of double bonds and **b)** optical gaps as a function of the inverse of double bonds of oligo-SN3 and oligo-SN3-DCV calculated with OT-RSH approach.

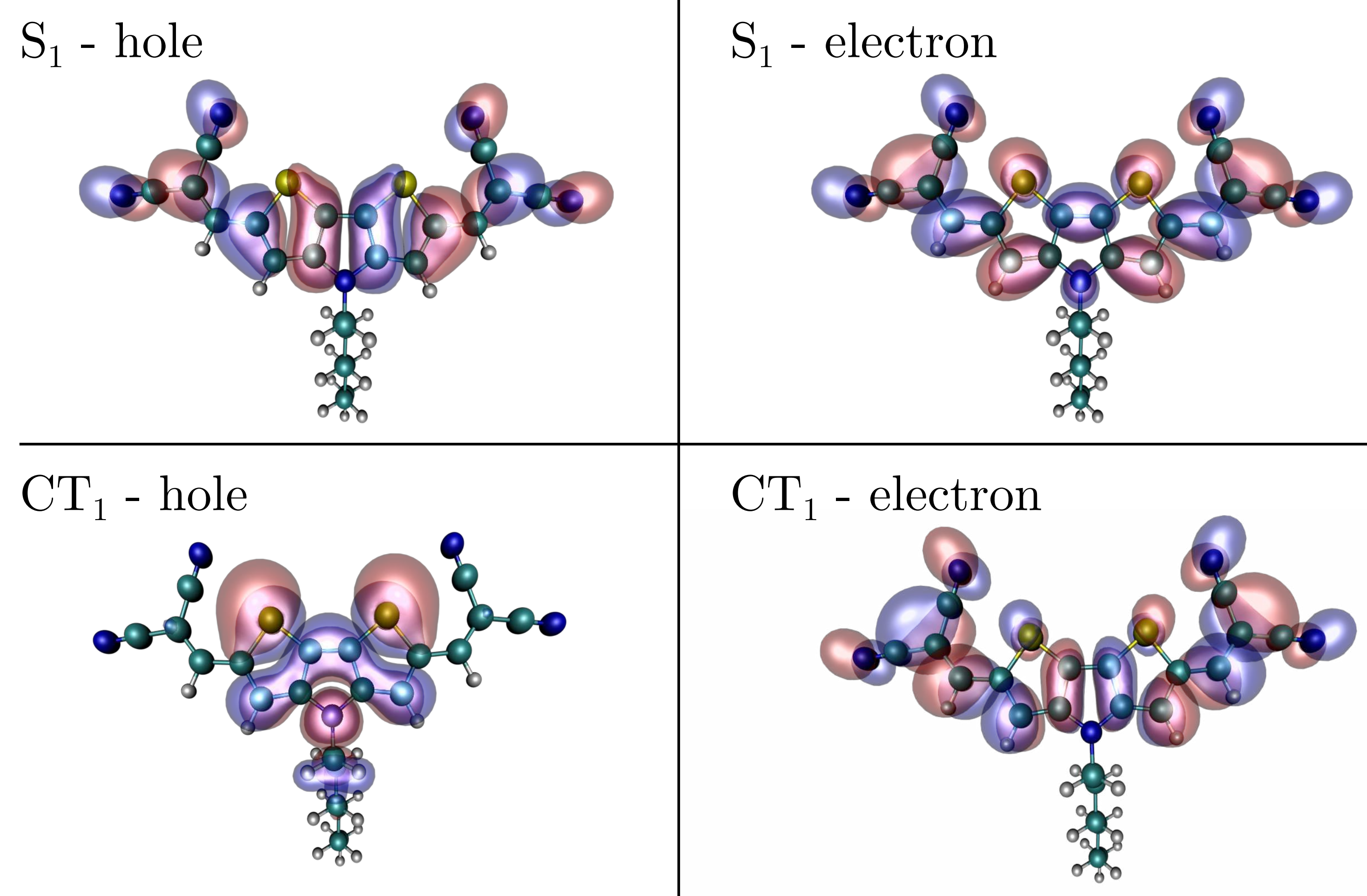


Figure 4: Natural transition orbitals (NTO's) for the first singlet and the first intramolecular charge-transfer state of SN3-DCV monomer.

### D/A systems design

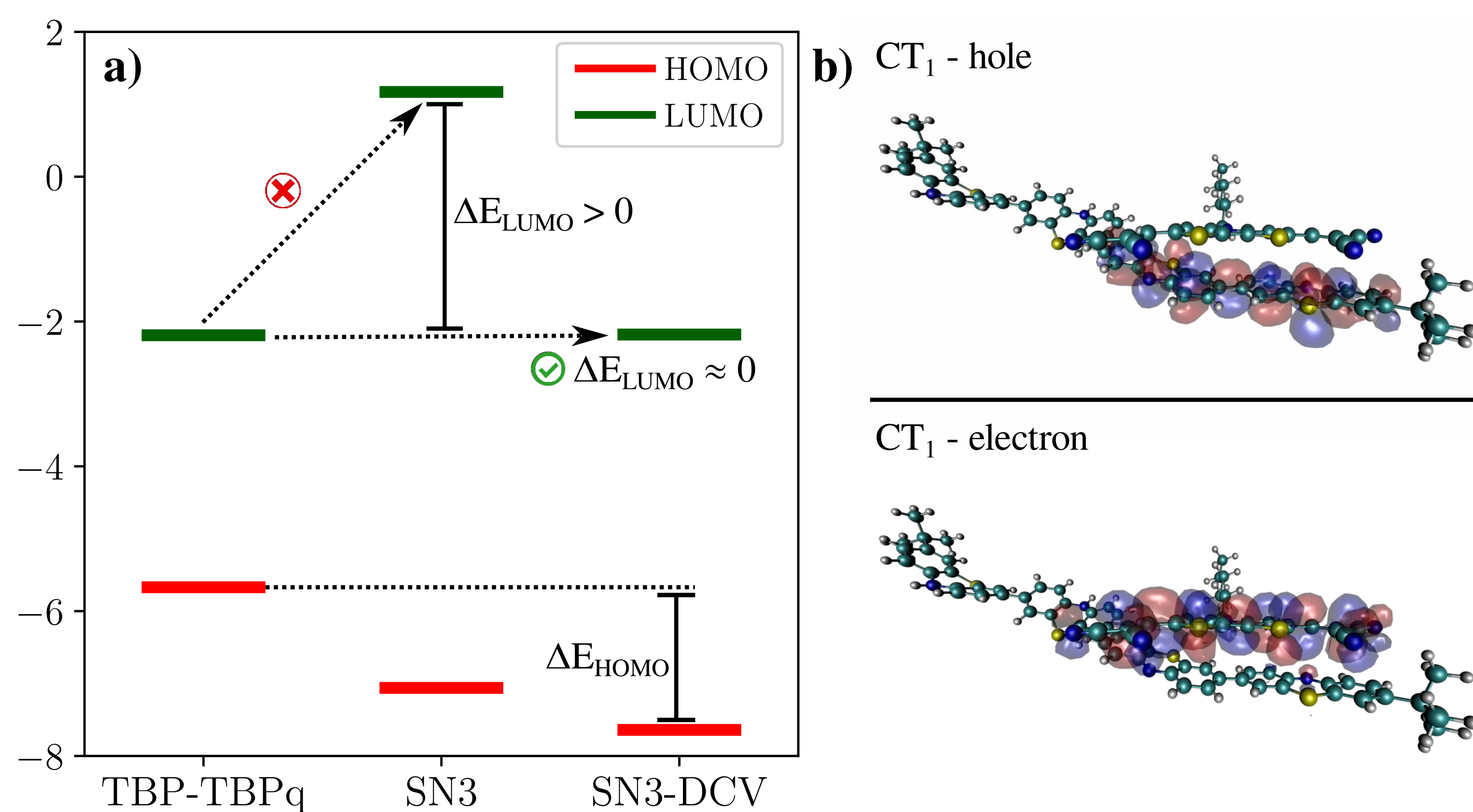


Figure 5: **a)** Frontier orbitals energy diagram for TBP-TBP<sub>q</sub> and SN3 molecules. **b)** NTO of the first charge-transfer state for the coupled TBP-TBP<sub>q</sub>:SN3-DCV molecular system.

## Conclusions & perspectives

The results indicates that we can engineer electronic and optical properties of the S,N-heteroacene class of molecules via functionalization. This is a powerful strategy to theoretically design novel donor/acceptor molecular systems for organic photovoltaics.

## Acknowledgements

We acknowledge FAPESP for financial support through projects DD 2022/03461-8 and JP 2020/13466-1.

## References

1. C. Huang et al., Chem. Mater., 30(15), 5429-5434 (2018). 10.1021/acs.chemmater.8b02276.