Electronic and optical properties of S,N-Heteroacenes from screened range-separated hybrid functionals

Reinaldo V. Dantas Filho[1], Thiago B. de Queiroz[1]

[1]Centro de Ciências Naturais e Humanas - Universidade Federal do ABC, Santo André, SP

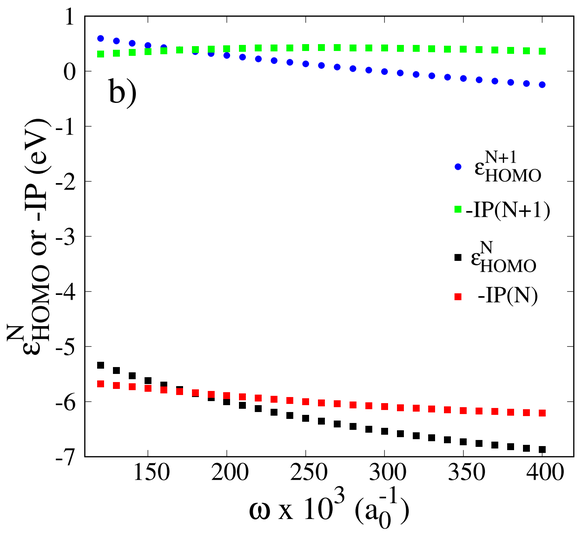
Introduction

Recent investigations demonstrated that organic photovoltaic (OPV) devices based on S, N-Heteroacenes (SN's) as acceptors shows excellent power conversion efficiencies [1]. This class of molecules are ideal alternatives to fullerenes since they are easy to design and synthesize from building blocks. In this study, we performed Time-Dependant Density Functional Theory (TD-DFT) calculations using the optimally tuned range-separated hybrid (OT-RSH) and screened OT-RSH (OT-sRSH) approaches to characterize the electronic and optical properties for a serie of S,N-heteroacenes. The latter approach includes the chemical environmental effects of the medium in the description, making possible to compare our results with experimental values.

Methodology

- Structures taken from [2] and [3];
- M06-2X functional used for optimizations;
- 6-31G(d,p) basis set used in all calculations;
- $\omega \rightarrow$ minimal diferences:

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



$$E^{sRSH}_{xc} = E^{SR}_{PBE_x} + (1 - \frac{1}{\epsilon})E^{LR}_{PBE_x} + \frac{1}{\epsilon}E^{LR}_{xx} + E_{PBE_c}$$

Figure 1: **a)** S, N–Heteroheptacene (SN7a) molecule [2] and **b)** it's ω tuning curves.

Results & discussions

Range separating parameter (ω)

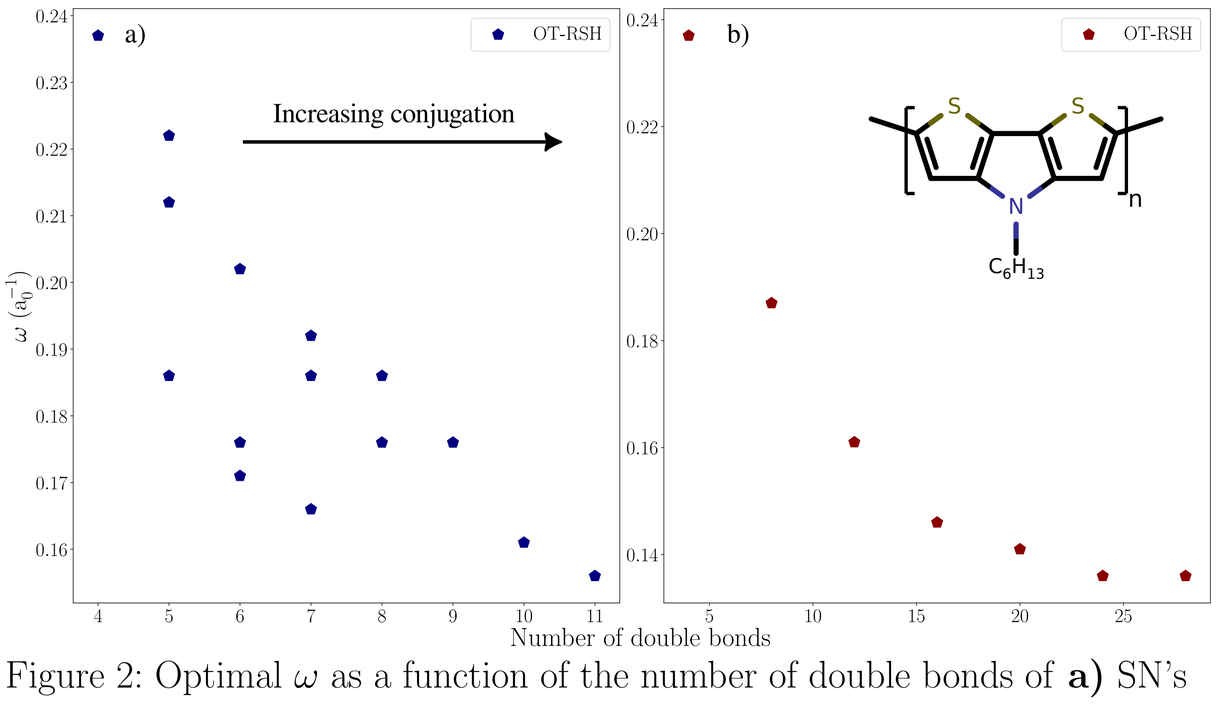


Figure 2: Optimal ω as a function of the number of double bonds of **a)** SN's and **b)** oligo-SN3.

S, N – Heteroacenes

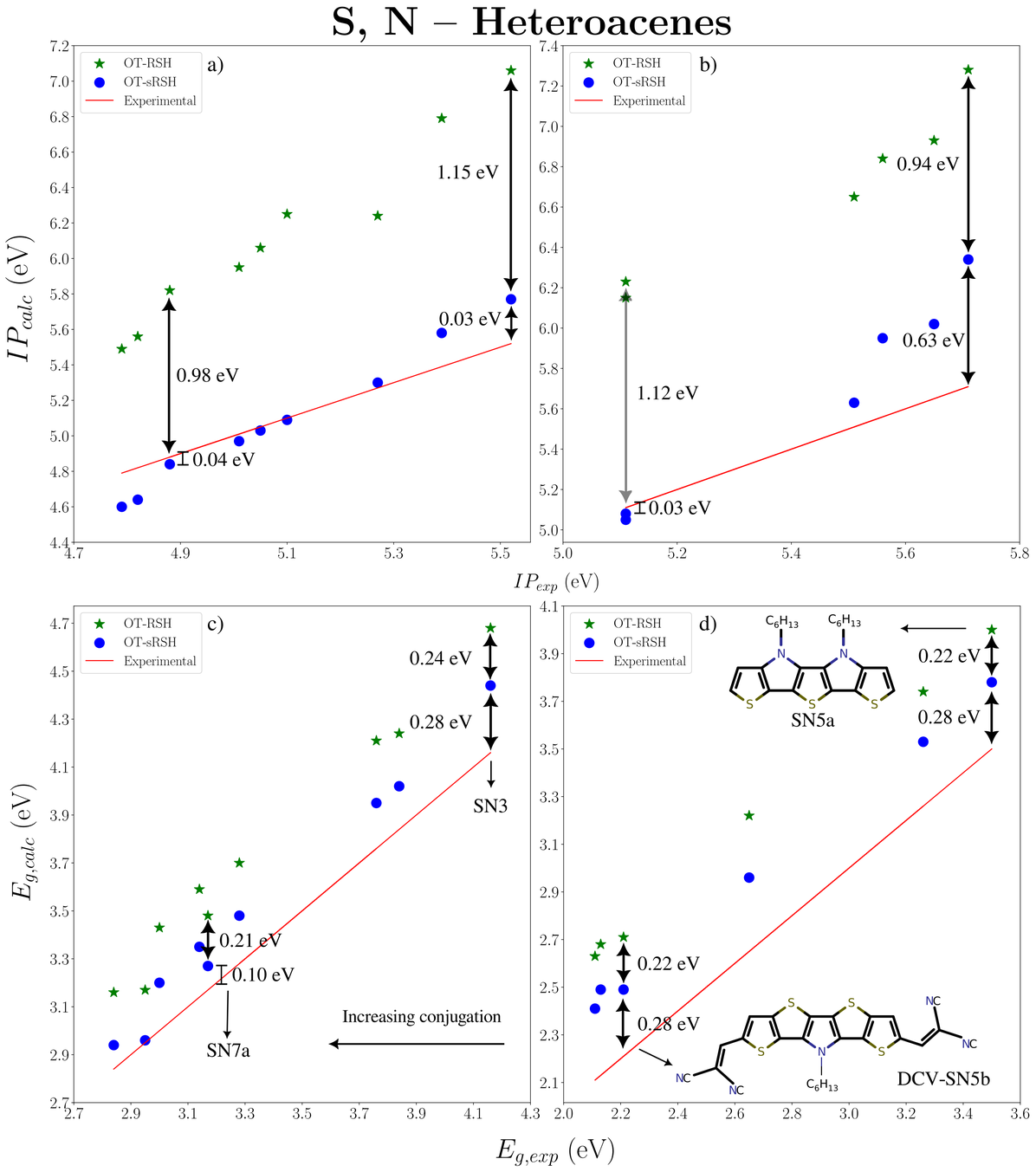


Figure 3: **a), b)** Ionization potentials (IP_{calc}) and **c), d)** optical gaps ($E_{g,calc}$) calculated with OT-RSH (green stars) and OT-sRSH (blue circles) functionals for molecules in **a), c)** tetrahydrofuran ($\epsilon_\infty = 1.95$) and **b), d)** dichlorometane ($\epsilon_\infty = 1.98$).

Oligo – SN3

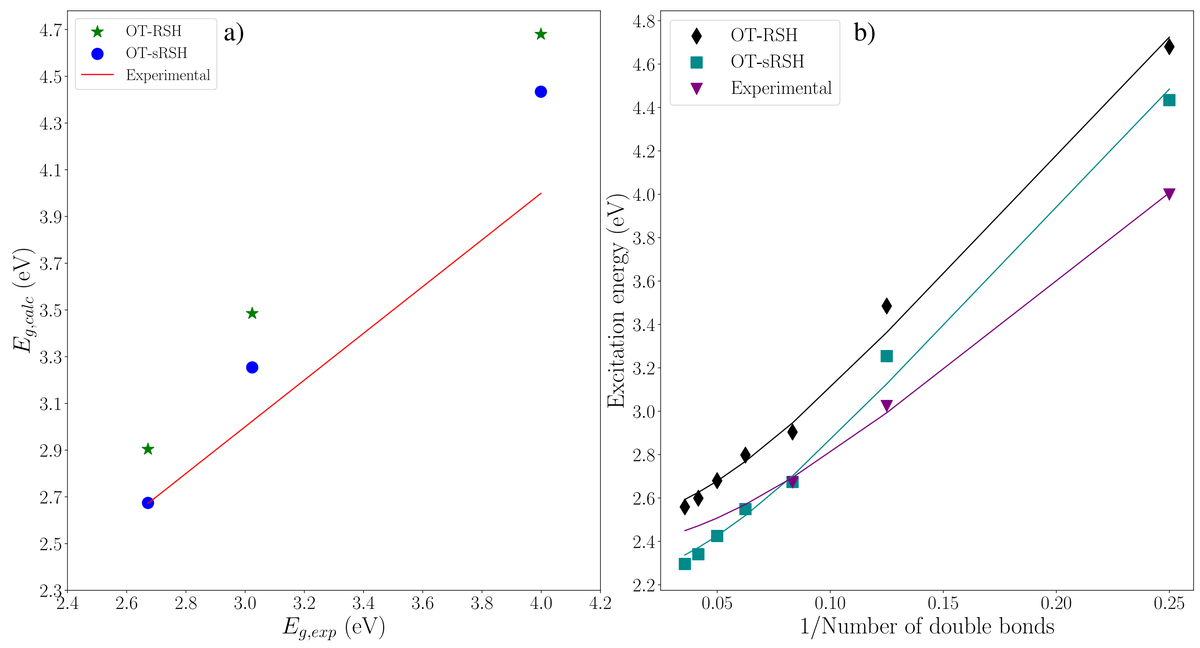


Figure 4: **a)** IP's and $E_{g,calc}$ calculated for oligo-SN3 molecules in dichlorometane solution and **b)** maximum absorption energy as the inverse number of double bonds. Solid lines are fits according to the Kuhn Model.

Conclusions & perspectives

		Medium	OT-RSH	OT-sRSH
IP (eV)	SN's	THF	1.04	0.11
		DCM	1.24	0.27
E_g (eV)	SN's	THF	0.39	0.16
		DCM	0.52	0.30
	Oligo-SN3	DCM	0.46	0.22

$\rightarrow$ Mean absolute errors obtained for the IP and E_g for each functional and chemical environment considered.

Acknowledgements

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References

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