PÔSTER - RESUMO - MATERIAIS E BIOMATERIAIS

ROTATIONAL BARRIERS AND FRONTIER ORBITALS OF NDI AND DPP-BASED DONOR-ACCEPTOR POLYMERS: A THEORETICAL STUDY ON THE EFFECT OF POLAR SIDECHAINS

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Semiconducting polymers are key materials for emerging electronic applications, including organic electrochemical sensors and thermoelectric devices. Optimizing their performance requires a detailed understanding of their molecular geometry and electronic properties. For this, density functional theory is a valuable tool to assess these features on the molecular scale which enables the study of both the structural properties such as steric hindrance and conformation locking as well as electronic features such as the energetic position of the frontier orbitals and their delocalization. This work investigates donor-acceptor polymers composed of naphthalene diimide (NDI), thiophene, thiazole, and diketopyrrolopyrrole (DPP) [1] using Density Functional based Tight Binding (DFTB), [2] a computationally efficient quantum-chemical approach. In this study, we present our results on the structural and electronic properties of small oligomer models of these polymers, focusing on rotational potentials and frontier orbitals. The former is a very simple and efficient method to assess not only the planarity of the polymer, but also to determine whether or not barriers can be overcome, e.g. due to thermal effects or energy gain due to p-p stacking. Furthermore, a detailed knowledge of the rotation barriers allows us to understand local interactions such as steric hinderance or hydrogen

bonding that can affect the polymer's charge mobility [3]. On the other hand, considering the frontier orbitals allows to analyze to what extent functionalization impact features that determine electronic transport properties such as localization or energetic position. The results presented here include analyses of two- and three-unit rotational barriers and how their results impact the shape of the polymer formed. The characterization of the frontier orbitals is quantitatively described through the Mulliken population, an intrinsic tool of SCC-DFTB capable of analyzing the delocalization and charge transfer of the polymer. By analyzing the impact of side chains on molecular conformation and charge distribution, our work aims to identify key trends that influence material properties. We verified that the influence on the electronic structure is mainly due to the polarity of the side chain through analyses of the inclusion of polar and non-polar side chains (e.g., oligo(ethylene glycol)) in the system, as well as equivalent charge models for comparison, which represent the same polarity (and orientation) through simple point charges or dipoles, considerably reducing the computational effort.

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References

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