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Molecular Wires Formed from Polypyrroles and β-Cyclodextrins: A Theoretical Investigation.

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Abstract: A theoretical investigation using semi-empirical and DFT calculations was performed in order to obtain structural and electronic properties for native and derivatives polypyrroles (PPys). The band gap energies for PPys before and after the formation of β-Cyclodextrin-based molecular wires were estimated at the B3LYP/6-31G(d,p)//PM3 level of theory. For the isolated PPys, the results showed that after the replacement of PPy by the OCH_3 and NO_2 push-pull groups, it presented a significant decrease in the band gap value, which implies a supposed improvement in the polymer conductivity. Moreover, considering the β-Cyclodextrin-based molecular wires, after the introduction of the same OCH_3 and NO_2 push-pull group, it was observed a small decrease in band gap value in caparison to the isolated OCH_3-PPy-NO_2 specie, thus maintaining the polymer conductivity.

Key-words: Polypyrroles, band gap energy, molecular wires.

The fundamental requirement for processing and application of any conjugated polymer (PC) as molecular electronic device is its solubility. Polypyrrole (PPy) belongs to the class of PC, however, one of the main issues concerning the use of PPy as conductive material is due to its poor water solubility [1]. In this context, an alternative and viable strategy to improve the water solubility of PCs is the formation of inclusion complexes with cyclodextrins (CDs), also called CD-based molecular wires (MWs) [2]. In this context, the main goal of this work was to evaluate the molecular structure and electronic properties of native and derivatives PPys as well as a possible MW formed by cross-linked dimeric β-cyclodextrin (β-CD). The central idea was to analyze the encapsulation effect on the structural and electric properties of the PPys guest molecules. The PPys derivatives were substituted at the both ends by electron donors and withdrawers groups (*push-pull groups*) such as: NH_2, OCH_3, OH, SO_3H, NO_2, CF_3. The calculation methodology used was the sequential via B3LYP/6-31G(d,p)//PM3 level of theory which has been successfully used for CD inclusion compounds in our group [3]. As known, the ability of PCs to conduct electricity is fundamentally related to the energy difference between the HOMO / LUMO frontiers orbitals, which is known as band gap energy (Eg). Thus, initially an Eg analysis of native and derivatives PPys with four monomeric units $(PPys)_4$ was carried out and the results are shown in Table 1. It is

clear to notice that the $(PPy)_4$ substituted by the OCH_3 and NO_2 push-pull group shows de lowest Eg value. Afterwards, the OCH_3-$(PPy)_4$-NO_2 were added to the β-CD dimeric tube in the TT orientation with 3 cross-linking, which was chosen based on our previous work [4], in order to evaluate a supposed increase or decrease in conductivity after the formation of a MW. As can be seen in Table 1, after the inclusion process, the OCH_3-$(PPy)_4$-NO_2 molecular wire presented a slight decreasing in Eg in comparison to the OCH_3-$(PPy)_4$-NO_2 isolated polymer, which supposedly implies that the formation of a MW could maintain the conductive properties of the polymer now trapped inside the β-CD dimeric tube. In Figure 1, the optimized structure of OCH_3-$(PPy)_4$-NO_2 molecular wire is shown. Therefore, in the present work we have shown in molecular level that the use of PPys in the form of encapsulating conducting material, which is an interesting alternative to improve the solubility of organic polymers, can be very useful and should be considered in further experimental investigations.

Table 1 – Band gap energies (Eg) for isolated PPys and for a β-CD-based molecular wire calculated at the B3LYP/6-31G(d,p)//PM3.

Specie	Eg (eV)
$(PPy)_4$ (native)	3,48
$(PPy)_4$ - push-pull (NH_2 -SO_3H)	3,21
$(PPy)_4$ - push-pull (OCH_3 -NO_2)	2,55
$(PPy)_4$ - push-pull (OH - CF_3)	3,30
Molecular Wire - $(PPy)_4$ - push-pull (OCH_3 -NO_2)	2,49

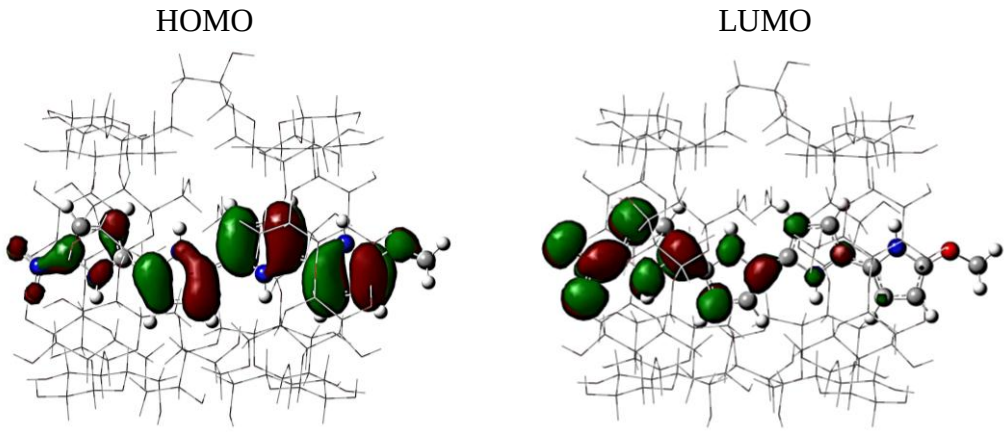

Figure 1 – Optimized geometry for OCH_3-$(PPy)_4$-NO_2 molecular wire along with HOMO/LUMO orbitals for $(PPy)_4$.

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