



Time Dependent Density Functional Theory applied to study the optical absorption of PPP and PT oligomers

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Abstract – Time Dependent Density Functional calculations were employed to study the optical absorption of both the PT and PPP oligomers in order to obtain the exciton binding energy of these polymers. Our obtained results are in good agreement with the experimental data, whenever the comparison is possible. From the obtained preliminary results, we have found that by using molecular approaches to obtain the polymer exciton binding energy, we will get overestimated values for this property.

The interaction between the electromagnetic field and the matter is one of the interesting subjects of Modern Physics. In the absorption process, the energy of the incoming photons is sufficient to promote an electron excitation from a determined occupied state to an unoccupied one with higher energy. In both case of π -conjugated polymers, as well as one-dimensional molecular chains, these excitations can generate excitons, which are classified as in the intermediate case of the definition of the Wannier and Frenkel ones. In this case, these excitons are confined in the atomic chains formed in these materials.

In this work, we will show our preliminary results for the structural aspects, the electronic structure, as well as the electronic excitations for the biphenyl, terphenyl and quaterphenyl molecules, which are some of the PPP oligomers, as well as for the bithiophene, terthiophene and quaterthiophene ones, which are some of the PT oligomers, by using the Time Dependent Density Functional Theory (TDDFT), which is designed to calculate *ab initio* the energy of the excited states, as implemented in the Octopus code [1]. In the calculations, we have used the Troullier-Martins pseudopotentials and all the integrals involved were evaluated in the real space.

Our results are in good agreement with both the available experimental data (as shown in Fig. 1 for the terphenyl) and other theoretical calculations, whenever these comparisons are possible. Based on our results, we have analyzed the energy evolution of the calculated first peak in the optical absorption spectra as a function of the molecular chain increasing (as show in Fig. 2 for the PPP oligomers), and we have speculated about the observed energy of the excitons of PPP, as well as their nature. Finally, our results show that, by using molecular approaches to obtain the exciton binding energy, we will get overestimated values for them (from Fig. 2, for instance, the linear fit gives 2.13 eV for the PPP exciton, which is around the double of the experimental data, 1.06 eV).

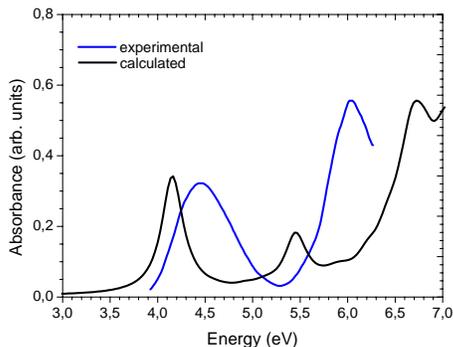


Figure 1: Calculated UV-Vis. Absorption of terphenyl compared with the experimental data from NIST database.

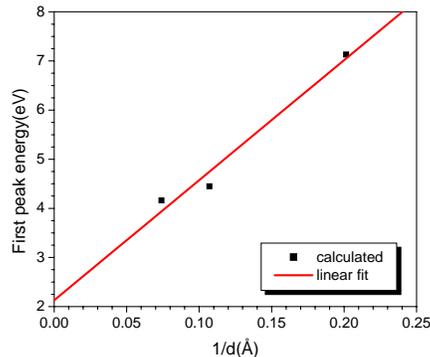


Figure 2: Calculated first absorption peak dependence with the inverse of the conjugation distance for the PPP oligomers.

References

- [1] A. Castro *et al.*, *phys. stat. sol. (b)* 243 (2006) 2465–2492.