

Revisiting the structural and photophysical properties of 3-hexylthiophene (P3HT): a combined experimental and theoretical study

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The context of our work is to design a lab-on-chip based on the luminescence properties of a micro-algae: *Chlamydomonas reinhardtii*. The algae luminescence is collected thanks to an organic photodiode (OPD) based on a low band gap polymer, PTB7 (high external quantum efficiency of 80% when mixed with PC71BM) [1]. Before ab-initio calculations simulating those systems, we perform these calculations (TD-DFT and DFT) on the experimentally and theoretically extensively studied P3HT in order to identify the best-adapted simulation's methodology. We will demonstrate here how modern ab-initio methods are able to describe with good precisions vibrational and optoelectronic properties of those polymers chains and particularly to estimate the impact of the chain-length of oligomers (eight units to twenty units). Raman (figure 1), infrared, vibrationally resolved UV-visible absorption (figure 2) and photoluminescence (PL) spectra have been simulated. Their comparison with their respective experimental spectra shows a perfect agreement. We demonstrate that the vibronic structure is due to a collective mode, dominated by inter-ring C-C bond stretching, coupled to alkyl chains vibration mode. By optimizing and describing the lowest excited states of these oligothiophenes (singlet S1 and triplet states T1), we find that S1 and T1 present a quinoidal structure with a spin distribution localized on the central part of the chain. Relative energies of the two lowest excited states provide the possibility to these systems to be involved in singlet exciton fission process. As a result of this work, we have checked that our method is able to predict P3HT photophysical properties. Further theoretical and experimental efforts are now focus on PTB7 studies, and we are confident on our calculation method for various polymers.

[1] C. M. Lochner, Y. Khan, A. Pierre and A. C. Arias, *Nature communications*, p.1-7, 2014.

