



Water-related defects in PPV: effects on electronic and transport properties

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Abstract – We investigate the role of simple defects related to exposure to water in the transport and electronic properties of single-chain and herring-bone-structured poly-[para-phenylene-vinylene] PPV systems. We use for that state-of-the-art quantum approaches, coupled to classical molecular mechanics methods. Our results point to the serious impact of hydrogen and hydroxyl impurities, and to the particular nature of the keto-defect which can bring unexpected benefits for photoconductivity.

Polymer films are complex systems, with structural properties governed by supra-molecular interactions and, due to the usually adopted growth techniques, the “bulk” material is composed of crystalline grains, with overall structural disorder. In this way, inside the grain we must look at three-dimensional (3D) properties, while in the amorphous regions on-chain processes are possibly more relevant. Electronic and/or excitonic transport in polymer films must thus be studied from different viewpoints: disorder requires statistical modeling, but locally, inside crystallites, structure counts and there is a strong anisotropy [1] between on-chain and inter-chain transport. Furthermore, the open character of the assembly makes films more susceptible to contamination and environment conditions, and also the character of the incorporation and its final effect will depend on the nature of the affected region.

The role of defects can be intrinsically distinct in one-dimensional (1D) systems compared to its 3D counterparts, and in polymer films both extremes are present, and will be difficult to individuate in the experimental data. I will present our theoretical study of defects in poly-[para-phenylene-vinylene] (PPV). We focus on simple defects that can be introduced by exposure to water, and thus hydrogen defects, and oxygen and hydroxyl incorporations in the vinyl group are investigated [2,3] in different charge states. We investigate the impact on the electronic structure of the crystalline regions, and on the electron transport properties of 1D chains. The structural properties for isolated defects in the polymer crystal are first obtained through classical molecular mechanics, while electronic and in-chain transport properties are studied through state-of-the-art *ab initio* calculations [4,5]. Our results show that the most disruptive effect on carrier transport comes from conjugation breaking, imposed by the over-coordination of a carbon atom in the vinyl group, independently from the chemical nature of the defect. The particular case of the C=O keto-defect shows in addition unexpected electron-hole separation [2], suggesting that the experimentally detected photoluminescence bleaching and photoconductivity enhancement could be due to exciton dissociation caused by the spatial characteristics of the defect. The role of charged hydrogen and hydroxyl defects [3] will also be discussed.

References

- [1] A. Ferreti et al, Phys. Rev. Lett. 90, 086401 (2003); Phys. Rev. B 69, 205205 (2004).
- [2] L. Zoppi, et al, Phys. Rev. B 78, 165204 (2008).
- [3] A. Calzolari, A. Ruini, and M.J. Caldas, preprint (2009).
- [4] S. Baroni et al, (2001), <http://www.pwscf.org>.
- [5] A. Calzolari et al, Phys. Rev. B 69, 035108 (2004).