Influence of the Oligomer Chain-Length on the Optical Properties of Emeraldine Salt

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Conjugated organic polymers can be doped (via oxidation/reduction chemistry, or acid/base chemistry) to induce high electrical conductivity. After proton-acid doping polyaniline (PANI) increases remarkably its conductivity reaching values of the order of 10^2 S/cm [1]. This makes PANI particularly prospective for molecular-based electronics applications in electronic and opto-electronic devices. The conversion between the neutral semioxidized (emeraldine base) and the doped (emeraldine salt) form is a reversible and easily controllable process. Alongside with conductivity change, it is accompanied by notable variations of color and magnetic susceptibility. PANI allows a number of other applications and focuses incessantly the scientific interest. Major attention receive investigations searching for correlation between molecular geometry and electronic structure of the ground and excited states. However, the unambiguous interpretation of the emeraldine salt (ES) properties at the molecular level is still incomplete.

This study addresses the optical properties of model HCl-doped ES oligomers. The polaron and bipolaron configurations [2] at each chain length are considered. CC2/TZVP (Turbomole 6) and CIS/6-31G* (Gaussian 09) are employed. The choice of protocol is based on earlier findings [3], proving its potential for adequate description of the structure and electron distribution of ES. All calculations are carried out in implicit aqueous medium (COSMO/PCM). Parallel CC2/TZVP simulations in vacuum are performed in order to estimate the solvent effect on the electron spectra.

The results provide detailed information about the possible electron transitions in ES. The MO analysis affords description of the polaron/bipolaron states. The nature of the molecular orbitals involved in the electron transitions is discussed. The size dependence of the optical spectra is commented. The simulated spectra are compared to the available experimental data.

References

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