

On the Unexpected Cation Exchange Behavior, Caused by Covalent Bond Formation between PEDOT and Cl⁻ Ions: Extending the Conception for the Polymer–Dopant Interactions

PS. Tóth, C. Janáky, O. Berkesi, T. Tamm, C. Visy

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Abstract

The ionic motion in connection with the redox transformation of poly(3,4-ethylenedioxythiophene) (PEDOT) conjugated polymer have been studied by both experimental: electrochemical (electrochemical quartz crystal nanobalance - EQCN), spectroscopic (Infrared spectroscopy - IR-ATR); and theoretical methods. The observations have been completed by direct, semiquantitative analytical data, provided by energy dispersive X-ray (EDX) microanalysis. The EQCN results suggested an anomalous behavior, since only cationic movements have been observed for films deposited from chloride solutions. Chloride ions were proved to be immobile also when bulky tetrabutylammonium (Bu₄N⁺) cations were substituted with even larger (hexadecyl-trimethylammonium) cations. Since PEDOT films synthesized in the presence of other spherical, not too large anions - such as perchlorate and tetrafluoroborate - endowed mixed ion exchange behavior together with the Bu₄N⁺ cation, the possibility of a special interaction between chloride and the polymeric chain has been assumed. Semi-empirical and DFT calculations indicated that chloride ions interact with the alpha carbon atoms of the thiophene rings of the oxidized EDOT oligomers, creating sp³ type perturbations in the polymer chain. FTIR-ATR spectra evidenced the appearance of C-Cl bonds. Elementary analysis, performed by EDX spectroscopy with 8 polymer samples at different doping levels clearly showed the permanent presence of constant amount of chlorine, independently of the oxidation state of the PEDOT layer. Finally, the presented observations call attention to the fact that unique dopant-polymer interactions during the electrochemical polymerization are of prime importance, being able to rule over conventions for the charge compensation of conjugated polymers, often solely based on steric parameters.