Abstract

An understanding of the effect of molecular structure on physicochemical properties of organic semiconducting polymers requires a proper method of preparation during which it is possible to obtain a polymer with a well-defined chemical structure. Therefore, in this work three methods of preparation of poly(3,4-ethylenedioxythiophene) (PEDOT), such as chemical oxidation, electrochemical polymerization, and a new method, namely acid-assisted polymerization, were utilized. Using chemical oxidation polymerization, it was investigated the effect of ions from Hofmeister series, specifically formate ion, on PEDOT physicochemical properties. In particular, it was shown the formation of hydrated oligomer chains which assemble into semicrystaline structure. Moreover, it was demonstrated that hydrated oligomers undergo rearrangement of its chains during the electrochemical treatment with the formation of anisotropic structure, and unique photoluminescence properties. Next method for PEDOT preparation, which was for the first time introduced by us, is acid-assisted polymerization. It was shown that it is possible to prepare, by using polar Brønsted acid, the PEDOT solution without applying oxidant at room temperature. Moreover, we have shown a way to control the optical properties of PEDOT, by the mean of a correlation between the process of self-assembly of PEDOT chains. The fundamental understanding the nature of the formation of charge carriers in energy storage devices sheds a light on the proper and precise way of their design. It was shown, during the electrochemical polymerization of PEDOT, the effect of the nature of supporting electrolyte, namely formic acid, on the formation of cation radicals in PEDOT structure. It was demonstrated the ability of formic acid to H-bonding formation with PEDOT monomer units with further formation of localized cation radicals. This knowledge, in turn, was applied for the construction of symmetrical PEDOT based supercapacitors and showed the major role of H-bonding formation on charge storage ability. Particularly, it was shown the device, made up from a dried and wet, prior to soaking in formic acid, electrodes show stable in time 900 mV open-circuit potential. The wide demand for semiconducting polymers, as ion-to-electron transducers, for analytes detection requires a material with reasonable properties. For that purpose, PEDOT with covalently bonded hydroquinone group was used. Thanks to the high redox capacitance of solid contact, based on PEDOT-HQ, it was constructed as the solid contact ion selective electrode with high potential reproducibility in relevant range of analyte concentrations.

Keywords: PEDOT, formic acid, hydrated chains, H-bonding, acid-assisted polymerization, supercapacitor, open-circuit potential, PEDOT-HQ.