Effects of small octahedral mono, di, and trivalent hexafluoroanions on electronic and molecular structures of polypyrrole monitored by*in situ* UV-vis-NIR and resonance Raman spectroelectrochemical measurements.

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Streszczenie

In situ UV–vis–NIR and Raman spectra were recorded for three polypyrroles of different compositions established by the specific redox responses of the polymers. Polypyrrole has been electrodeposited in the reversibly oxidized state and concomitantly doped with a small octahedral counterion from aqueous solution of sodium hexafluorophosphate, sodium hexafluorosilicate or sodium hexafluoroaluminate. The dopant anions differ from each other by the charge valency, having at the same time very similar ionic radii. The spectra of the resulting three polypyrroles were found to differ noticeably. An origin of the differences was discussed. The doping level and/or structure of a polymer phase can be invoked to explain the observed spectral changes of the polymer due to the anion dopants. As expected, the most counterion sensitive are the N–H bond and the polaron and bipolaron electronic levels. Polypyrrole doped with hexafluoroaluminate has generated the spectra that differ markedly from that recorded for polypyrrole hexafluorosilicate and polypyrrole hexafluorophosphate. The spectroscopic results are in agreement with earlier findings concerning electrochemical properties of polypyrrole hexafluoroaluminate and polypyrrole hexafluorosilicate. Raman bands that are usually assigned to the ring deformation vibrations were shown to decrease significantly in energy on oxidation of polypyrrole (900–1000 cm^{-1}). Raman bands intensities are complex function of laser energy and electrode potentials so their analysis on the anion effects should be performed rather at a constant length of laser excitation.

Słowa kluczowe

UV–vis–NIR spectroelectrochemistry, Raman spectroelectrochemistry, Polypyrrole in aqueous environment, Hexafluoranions of Al(III), Si(IV), and P(V))

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