

Abstract

Tetrathiafulvalene derivatives are remarkable molecules, with various applications, reported relatively recently. The radical cation of these compounds has very interesting optical, electronic, electrocatalytic superconducting and magnetic properties that have been intensively studied recently. Quantitative in-situ EPR voltammetric spectroelectrochemistry studies of 2-(2-hydroxyethylsulfanyl)-3-(benzylsulfanyl)-6,7-bis(octadecylsulphanyl)tetrathiafulvalene (TTF-Der3) have been carried out with the aim to confirm the oxidation sites, follow-up reactions (after the first electron transfer), and electrochemical behaviour. The diffusion process was confirmed by the dependence of current on the square root of the scan rate. It was claimed that the ratio of the number of generated radicals to transferred charge (electrons) for two representative TTF derivatives was determined to 5.5:500 for and 7:500 for TTF, indicating the follow-up reactions. Experiments were performed using the commercially available EPR standards, calibrated for this method (experimental setup). The latter was validated by quantitative EPR with standard 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl radical concentration ($1 \cdot 10^{-4} \text{ mol dm}^{-3}$). For the ratios the confidence interval was reported for the first time for TTF-Der3 it was 0.011 ± 0.001 and 0.014 ± 0.001 for TTF. For the future experiments different solvents, test concentration dependencies and additional substituents with donor/acceptor features related to TTF-core, will be used in order to study the follow-up reactions and intramolecular reactions more deeply. Finally, the concentration of paramagnetic centers in the manganese standard should be discussed with the manufacturer of the EPR standard to match lower analyte concentrations.

Keywords

Quantitative EPR (ESR) spectroelectrochemistry, Cyclic voltammetry, Charge transfer complexes, Tetrathiafulvalene