In situ spectroelectrochemical studies of radical reactions in new ladder type oligomers

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New unsaturated fluoranthene-type structures with ladder topologies [1] as molecules with two-dimensionally extended p-conjugation were investigated to study the influence of the oligomer length on dimerisation reactions in solution following an electron transfer step [2]. As they carry solubilizing chains, this enabled us to study single solvated molecules without interference of the dimerisation by ordering phenomena. Our main interest in the field of conducting oligomers and polymers is to investigate the driving force of dimerisation in such structures applying spectroelectrochemical techniques even at different temperatures using in situ ESR/UV-Vis-NIR spectroscopy [3] for structural studies of the reaction products at electrode surfaces. We report here on this spectroelectrochemical study of the oligomer length dependence of the dimerisation reactions and the stabilisation of charged states in conjugated p systems. We founded that radical ions of the short fluorantheno-pyracylene structures are in equilibrium with their s-dimers in solution: Radical ions of longer oligomers are already strongly stabilised and their dimerisation is negligible in the studied temperature range (290 K-260 K). In this case after an electron transfer the paramagnetic species fully dominate the reaction product in the solution. The extended p-conjugation in structures was found to be sufficient for stabilisation of charges in the molecule without dimerisation and an electron transfer results neither in a dimer nor a radical. A small intramolecular coupling of two charges leads to the stable doubly charged spinless structures within the chain which are similar to the electronic state of a bipolaron and a diion in a 1Ag singlet ground state carrying two individual polarons [4]. This finding is an indication that chemical dimerisation in organic conducting polymers may not be a necessary stabilisation mechanism of general validity.

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