

π -Dimerization of Oligothienoacene Radical Cations

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Oligothienoacenes, the fused-ring analog of α -linked oligothiophenes, belong to the most promising candidates for organic electronic applications. This is in part due to their fully planar structure that avoids conformational disorder and allows for densely packed solid-state structures resulting in high charge carrier mobilities.[1] In recent years, there has been a growing interest in the study of the π -dimerization of conjugated radical cations with a dual purpose: (i) elucidation of the nature of the charge-transport phenomena in p-doped semiconducting polymers and (ii) development of supramolecular bonding ideas for applications in material science. [2] However, the π -dimerization of planar conjugated radical cations in solution is scarce and usually encountered at low temperatures.[3] In this work, we investigate the influence of periphery substitution and conjugation length on the π -dimer formation of oligothienoacene radical cations.[4-5] Among all the systems studied, radical cations of a tetrathienoacene α,β -substituted with four n-decyl side groups (**D4T7^{•+}**) are found to exhibit the most exceptional ability towards the π -dimerization even at ambient temperature.[4] Our results evidence the presence of different transitory oxidized species formed during the course of the one-electron oxidation. [5] The nature and structure of these transitory species and ultimate π -dimer dications are rigorously analyzed with the help of the DFT calculations. Our study would provide valuable guidance for the further development of π -dimer based supramolecular architectures.

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