π-Dimerization of Oligothienoacene Radical Cations

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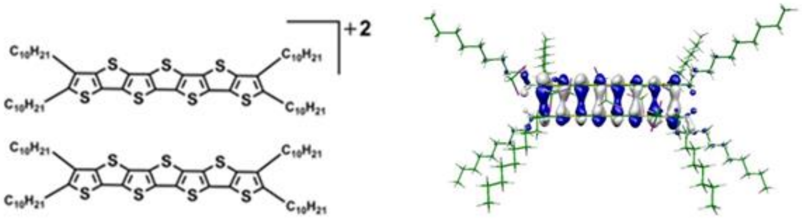
Oligothienoacenes, the fused-ring analog of α-linked oligothiophenes, belong to the most promising candidates for organic electronic applications. This is in part due to their densely packed solid-state structures resulting in high charge carrier mobilities.[1] In recent years, there has been a growing 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 π-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. In this work, the exceptional π-dimerization capability showed by radical cations of oligothienoacenes is investigated for the first time. To this end, we make use of a joint experimental and theoretical approach that combines different spectroscopic techniques with advanced DFT calculations. Our results evidence that the incorporation of bulky TIPS groups prevents the π-dimerization while the α,β-substitution with n-decyl groups in heptathienoacene or α-substitution with thienyl groups in tetrathienoacene favors the π-dimer formation.[3] The nature, structure and stability of the different aggregate structures formed in the course of the oxidation are rigorously analyzed with the help of exhaustive DFT and TD-DFT calculations.



Scheme 1: A -schematic structure of a heptathienoacene π-dimer dication and its HOMO orbital computed at the M06L/6-31G* level.

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