

## $\pi$ -Dimerization of Heptathienoacene Radical Cations

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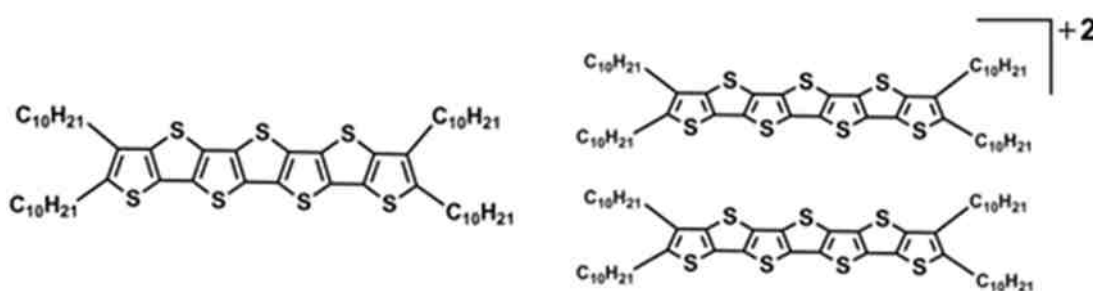
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Oligothienoacenes, the fused-ring analog of  $\alpha$ -linked oligothiophenes, belong to the most promising candidates for organic electronic applications. This is in part due to their fully planar structure that avoids conformational disorder and 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  $\pi$ -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, such as actuators. [2] However, the  $\pi$ -dimerization of planar conjugated radical cations in solution is scarce and usually encountered at low temperatures.[3] In this work, we investigate the exceptional  $\pi$ -dimerization capability showed by radical cations of a heptathienoacene  $\alpha,\beta$ -substituted with four n-decyl side groups (**D4T7**<sup>•+</sup>) by using a joint experimental and theoretical approach.[4-5] **D4T7** radical cations are found to exhibit an exceptional ability to form  $\pi$ -dimer dication even at ambient temperature.[4] Our results evidence the presence of two different transitory oxidized species formed during the course of the one-electron oxidation: (i) different conformations of the [**D4T7**<sup>•+</sup>]<sub>2</sub>  $\pi$ -dimer dication and (ii) the intermediate [**D4T7**]<sub>2</sub><sup>•+</sup>  $\pi$ -dimer radical cations.[5] The nature and structure of these transitory species and ultimate  $\pi$ -dimer dication are rigorously analyzed with the help of the DFT and TD-DFT calculations. Our study would provide valuable guidance for the further development of  $\pi$ -dimer based supramolecular architectures.



**Figure 1.**- A molecular structure of **D4T7** (left) and a schematic structure of [**D4T7**<sup>•+</sup>]<sub>2</sub>  $\pi$ -dimer dication (right).

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