

Abstract Submitted  
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**A first-principles study of  $\pi$ -stacking in charged oligothiophenes in the presence of counterions** NICHOLAS MILLER, DMSE, Massachusetts Institute of Technology, DAMIAN SCHERLIS, Universidad de Buenos Aires, NICOLA MARZARI, DMSE, Massachusetts Institute of Technology — We investigate the structural and electronic properties of charged oligothiophenes and of their  $\pi$ -stacking interactions with extensive density-functional theory (PBE, B3LYP) and post-Hartree-Fock (MP2) calculations. We pay particular attention to the role of counterions and of the solvation medium in tuning the balance between electrostatic repulsion and chemical bonding, including explicitly hexafluorophosphate counterions, and exploring the role of polarizability and surface tension for different solvents. Our calculations show that Coulomb's repulsion of the charged oligothiophenes is rapidly screened by solvation, counterions, or both, leading to stable  $\pi$ -dimerized systems (or higher stackings) where binding is driven by  $\pi$ -bond hybridization. Furthermore, we studied the charge-transfer properties of the counterion-oligomer system, as well as site preferences for counterions, highlighting the relevance of a proper treatment of correlations and self-interaction in describing the electronic-structure of these systems.

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