First-Principles Elucidation of Conducting Mechanisms in OligoEDOT Complexes: Towards Molecular Design Guidelines for High Conductivity

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Organic conductors are broadly divided into two categories: low-molecular-weight materials and polymers. Low-molecular-weight materials possess well-defined structures but offer limited control over their conductivities. Conductive polymers, on the other hand, feature highly conjugated systems but are challenging to control due to their structural inhomogeneity. To bridge this gap, oligomer-based conductors have been developed as intermediate materials. These conductors, based on oligo(3,4-ethylenedioxythiophene) (oligoEDOT), are modeled after the doped PEDOT family [1–5].

In this study, we systematically investigated the influence of end-cap substituents [6] and the stacking structure in donor–acceptor alternatingly mixed-stack complexes [7]. The effects of these structural factors were quantitatively evaluated using first-principles calculations (QUANTUM ESPRESSO, RESPACK, and H-wave packages; performed at Ohtaka, Supercomputer Center, ISSP). Our calculations revealed that the magnitude of the Coulomb repulsion between carriers, $\boldsymbol{U_{\mathrm{eff}}}$, is the dominant factor determining conductivity. Based on these theoretical findings, we provided electronic insights explaining the superior conductivity of mixed stack complexes compared to previously reported complexes [7]. This work thereby offers a new molecular design guideline for developing highly conducting charge-transfer salts and mixed-stack complexes.

References

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