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Effect of Stabilization and End Group Induced Charge Transfer on Frontier Molecular Orbital Reorganization - Applications to Molecular Thermoelectrics JANAKIRAMAN BALACHANDRAN, Graduate Student, Univ. of Michigan, Ann Arbor, MI, PRAMOD REDDY, Assistant Professor, Univ. of Michigan, Ann Arbor, MI, BARRY DUNIETZ, Assistant Professor, Kent State University, Kent, OH, VIKRAM GAVINI, Assistant Professor, Univ. of Michigan, Ann Arbor, MI — Endgroups play an important role in determining the thermopower and nature of transport across molecular junctions. In this work, we analyze the electronic structure of phenyl molecules coupled to gold electrodes through five different end groups. Accordingly we find that the direction of charge transfer is strongly correlated to the degree of reorganization of frontier molecular orbitals (FMOs) and in turn on the thermopower of molecular junctions. In particular, isocyanide, nitrile, and amine end-group molecular junctions, with charge (electron) transfer out of the molecule, exhibit a strong overall downward shift in the energies of frontier molecular orbitals, whereas thiol and hydroxyl end-group molecular junctions, with charge transfer into the molecule, exhibit a smaller overall downward shift. Two dominant factors namely (i)the stabilization effect due to contact with Au cluster and (ii) the change in electron-electron interactions due to charge transfer, determine the FMOs reorganization. We also provide a good estimate of the shift individually caused by each of these factors by performing a perturbation analysis.

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