Charge Transport and Molecular Rectification in Donor–Acceptor Dyads

Svante Hedström, Adam J. Matula, Victor S. Batista

Department of Chemistry, Yale University, P.O. Box 208107, New Haven, CT 06520-8107, U.S.A.
svante.hedstrom@yale.edu

The intramolecular donor–acceptor (D–A) or push–pull motif, is a common strategy for narrowing the band gap of conjugated molecules. This is important e.g. in organic photovoltaics where small molecules, oligomers, or polymers of D–A type are typically responsible for light-absorption and hole-transport through the active layer to the anode.[1–3]

We present calculated charge transport properties of single molecule donor–acceptor dyads connected to semi-infinite gold electrodes, using a computational approach based on the nonequilibrium Green's function coupled to DFT,[4] as implemented in the TranSiesta software.[5] The conjugated donor and acceptor units under investigation are commonly used in organic photovoltaics and other molecular electronics applications.

Owing to left–right asymmetric distributions of the frontier MOs responsible for the transport, the calculated currents I are different for forward or reverse bias V, i.e. the molecules exhibit intrinsic rectification. We find rectification ratios RR=-I(-V)/I(V) of 1.1–6.5. The trends in calculated I and RR are put in relation to calculated frontier orbital energies, the HOMO–LUMO gaps, and asymmetry and character of the main transport channels.

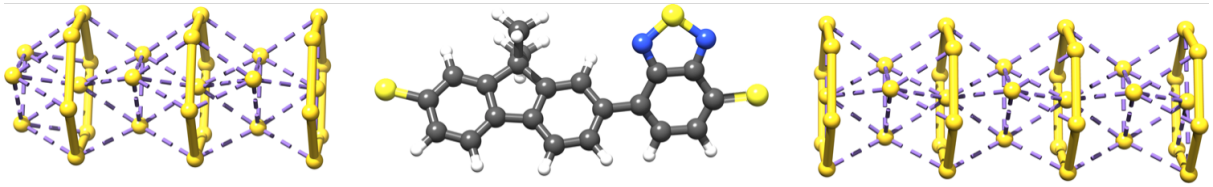

Figure 1. A fluorene–benzothiadiazole D–A molecule connected with sulfur anchors to two gold electrodes.

References

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