Electronic structure contributions to molecular rectification

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Fundamental advances in our ability to design and construct electronic components at the nanoscale will require new design paradigms. One of the proposed electronic components is the molecular rectifier. The original concept of a molecular rectifier was proposed by Aviram and Ratner in 1974 by using a donor-insulator-acceptor (D-σ-A) type molecular construct. Molecular and molecule-based electronic components are advantageous to the ease of synthetic manipulation coupled with the fact that the size dimensions of molecules are inherently at the nanoscale (0.5 - 3nm). Here, we study donor-bridge-acceptor biradicals as first generation models for understanding electronic structure contributions to molecular rectification. Constitutional isomers of the donor-bridge-acceptor biradical (NN-Th-Py-SQ) (S=1/2 *ortho*-semiquinonate, **SQ**; A: S=1/2 nitronlynitroxide, **NN**; Th = thiophene; Py = pyridine) complexes serve as constant bias analogs for molecular current rectifying devices. The efficiency of rectification is given by the rectification ratio (RR = $g_{forward}/g_{reverse}$; where g = conductance). The experimental RR that we derive from measured magnetic exchange couplings ($J_{SQ\text{-}NN}$) is calculated to be RR = 1.58. The experimental RR shows good agreement with the computed RR of 1.24 at +/-2.56V. Spectroscopic studies and bonding calculations provide insight into the electronic origin of the RR, the effects of bond torsions on the RR, and the nature of the current carrying molecular orbitals. We will discuss our results in terms of newly developed molecular design rules for rectification and the roles of the bridge HOMO and LUMO in magnetic coupling and bias dependent rectification.