Predicting the bandgap of donor-acceptor conjugated polymers

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Donor-acceptor (DA) organic semiconductors (OSC), predicated upon extended π-conjugation, with open-shell diradical character (*y*) are sought after for their unique quantum phenomena and magnetic interactions where they often serve as the active component in a wide array of next-generation devices. Functionality and utility of OSCs is often defined by the topological arrangement of the electronic structure and configuration of the frontier molecular orbitals (FMOs) (e.g. bandgap). This structure-function-performance relationship highlights the importance of rapid, but accurate, predictions of bandgap (E_g) energies for high-*y* OSCs in the polymeric state towards guiding synthesis. Current computational methods for determining the E_g of a DA conjugated polymer (CP) involve iterative, computationally expensive calculations while only indicating the properties of well-defined structures, requiring extrapolation to describe properties of the polymer. Here, an efficient method was developed to accurately determine the electronic configuration of DA CPs. The E_g values at varying polymer chain lengths were computed using density functional theory (DFT) at the unrestricted-B3LYP/6-311G** level and the trend was used to predict the narrowing E_g expected of an open-shell polymer. These results were used to develop and benchmark the performance of a protocol using periodic boundary conditions (PBC) to describe the electronic configuration along a one-dimensional cell forming an infinite lattice. While many systems were accurately described with PBC, results typically underestimated E_g compared to extrapolated values. Though early results are promising, systems with nearly degenerate FMOs can result in an overpredicted E_g, indicating that further development into the exchange, correlation, and mixing parameters is needed.