Bond length alternation of π-conjugated polymers predicted by FLOSIC method

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The electron delocalization in π-conjugated polymers can be characterized by the difference between central multiple and single bond lengths (bond length alternation, BLA). The accurate determination of this parameter has been used to assess electron correlation effects and the removal of self-interaction error within electronic structure methods. Although density functional theory (DFT) can be considered the workhorse of electronic structure calculations, it typically fails to provide a correct description of the BLA in π-conjugated polymers. In this study, we computed the BLAs of five oligomers containing up to 16 repeating units using the Fermi-Löwdin orbital self-interaction correction (FLOSIC) method, recently proposed to remove one-electron self-interaction from approximate DFT. For comparison, DFT models (LDA, PBE, CAM-B3LYP) and MP2 were used to fully relax the structures of these oligomers. The polymeric BLA limits were obtained as extrapolations from BLAs of oligomers with finite chain lengths. Our results reveal that FLOSIC, when combined with local and gradient-corrected density functional approximations, improves BLAs compared to their pure DFT counterparts, but slightly overcorrects.