TDDFT Assessment for the Calculation of Electronic Vertical Excitation Energies of cNDIs
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Abstract

The main goal of this study is to develop a TDDFT protocol for the accurate estimation of the vertical excitation energies of core-substituted naphthalene diimides (dNDI). To do so, functionals of multiple families have been tested in both gas phase and condensed phase, namely BLYP and OLYP (GGA), B3LYP and PBE0 (Global Hybrid) and CAMY-B3LYP and LC-BLYP (Range Separated Hybrid). Also, the range separated hybrid functional LC-BLYP has been optimally tuned to better reproduce the experimental excitation energy. After the calculations, simple linear regression (SLR) is used to complete the protocol. It is eventually concluded that calculations in dichloromethane are systematically better for all functionals. Without any statistical treatment, the GH functional B3LYP shows the best accuracy in gas phase (MD = -0.03 eV, MAD = 0.14 eV) and the GH functional PBE0 in condensed phase (MD = 0.01 eV, MAD = 0.09 eV). The RSH functional LC-BLYP shows the best systematic trend with an R²-value of 0.96 and 0.98 in the gas phase and condensed phase, respectively. The tuning of the functional greatly improves the accuracy since the MD and MAD drop in both gas and condensed phase. SLR improves the accuracy in all cases. Eventually, the most accurate protocol is decided to be LC-BLYP in condensed phase, using SLR as an statistical operator, resulting in an accuracy of ± 0.04 eV. Prediction of a new cNDI can thus be made with significant accuracy with SLR treated LC-BLYP.