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Nonadiabatic dynamics of cycloparaphenylenes

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We implemented and applied the fewest switches surface hopping method based on time-dependent density functional tight binding (TD-DFTB) to study the gas-phase relaxation dynamics of two cycloparaphenylene molecules, [8]CPP and [10]CPP. TD-DFTB based on DFTB3 model provides a qualitatively correct description of excited-state dynamics, as compared to experimental and other theoretical results. According to the dynamics, both molecules remain in their excited states during 3 ps of dynamics. The long fluorescence lifetimes originate from the slow radiative relaxation from the S_1 state. The trend of increasing the fluorescence rate with the molecule size is explained by an increase of the energy gap and oscillator strength for the S_1-S_0 transition in the larger molecule. The analysis of the charge transfer and spatial localization properties of the S_1 states shows that these states have charge transfer characters. In the case of [8]CPP, the S_1 state is delocalized over the whole molecule, whereas in [10]CPP it comprises both localized and delocalized excitons. Even though the TD-DFTB method underestimates the excitation energies of the S_1 states, the charge-transfer character and the types of the excitations occurring during dynamics are well described, when compared to results of TD-DFTB with long-range corrected functional.

Cycloparaphenylenes, Surface hopping dynamics, TD-DFTB