Assessing the dynamics of hemithioindigo-based photoswitches using multi-state molecular mechanics

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In the realm of nanotechnology and molecular engineering, photoswitches play a key role as structural elements converting light into mechanical work. In particular, switchable chromophores embedded in complex molecular environments – such as molecular machines and self-assembled monolayers on surfaces – offer unique opportunities for the precise control of material properties and molecular motion. [1] A relatively new but emerging class of photoswitches is based on hemithioindigo (HTI) chromophores, which feature high thermal bistability, bright absorption bands in the visible region of the electromagnetic spectrum, and chemical durability. Upon photon absorption, HTIs readily undergo double bond isomerization, resulting in the formation of either *Z*- or *E*-isomers. By using HTI photoswitches as core structures, future photoresponsive (nano-)devices are accessible via HTI functionalization to tailor the light-induced motion, aggregation, and self-assembly on substrate surfaces. [2]

Excited state dynamics simulations are powerful tools to investigate the photoinduced processes in individual photoswitchable molecules [4-6]. However, in most light-responsive devices, the motion of the photoswitch is strongly coupled to a complex environment – e.g. explicit solvent shells or ensembles of photoswitches – requiring an atomistic treatment of 1000s of molecules paired with ns-scale dynamics. While this presents a significant challenge for fully *ab initio* treatment, an approximate approach, as suggested by Duchstein et al. for azobenzene chromophores, involves multiple molecular mechanics models, each describing a separate electronic state under consideration. [3] Here, we present an adaption of this methodology to the widely employed HTI chromophors. For this, we revisit the static theoretical description of the excited states of HTI [7-8] using high-level multireference calculations and investigate the role of the triplet state in *E-Z* (photo-) isomerization. The multi-state molecular mechanics are demonstrated for the exemplary case of photoswitching on the first triplet (T_1) surface applying dynamics in different explicit solvation environments and gaining atomic-scale insight into energetic and kinetic effects.

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