



DFT investigation of self-assembling, light-responsive azobenzene dithiol ligands

Ram Singh, Prateek K. Jha^{*}

Department of Chemical Engineering, IIT Roorkee, Uttarakhand 247667, India

ARTICLE INFO

Keywords:
Azobenzene
DFT
Interaction energy
Light-responsive
Self-assembly

ABSTRACT

Azobenzene dithiol (ADT) ligands that exhibit *trans-cis* conversion when exposed to UV light are sometimes used in the light-induced self-assembly of nanoparticles. In this work, we perform density functional theory (DFT) calculations to study the ligand–ligand interactions that drive this self-assembly process. The dipole moment of individual ADT molecules and interaction energy between a pair of ADT molecules are computed for *cis* and *trans* states in various compositions of methanol-toluene mixture used as the solvent. *Cis*-ADT is found to possess substantially higher dipole moment than *trans*-ADT. Dipole moment of the mixture increases with methanol % up to 20% methanol, followed by lesser change on further addition of methanol. *Trans-cis* isomerization results in a shift of the position of energy minimum on the interaction energy against separation curve. The scaling of effective interaction between nanoparticles against separation for different ADT loading are also estimated from the results of DFT calculations.

1. Introduction

Light induced self-assembly (LISA) refers to the use of light as the stimulus to drive self-assembly of nanoparticles functionalized with photo-switchable ligands.[1] Some of the most studied systems [2–6] employ light of different wavelengths to drive *trans-to-cis* isomerization of ligands at nanoparticle surface. This results in an emergence of effective dipolar attractions between nanoparticles due to a large difference in dipole moments (μ) of *cis* and *trans* ligand conformations. Unlike covalent linkage that gives rise to irreversible self-assembled structures, the structures formed using switchable dipolar attractions are reversible and results in precise dynamic control of formed structures. Further control of self-assembly is attained by the use of mixed solvents of variable polarities [5], use of different metal cores², and the size and shape of primary nanoparticles. LISA strategy has been successful in synthesizing nanoparticles for many applications such as tunable catalysts [7] and self-erasing paper [8].

From a fundamental perspective, the success of LISA strategy depends on the ability to achieve precise control of the strength and range of effective interaction between the nanoparticles and its tunability by using light of different wavelengths. Generally speaking, attractive part of the interaction energy between nanoparticles at separation d may be represented as $\mathcal{W}(d) = Bd^{-\gamma}$. The exponent γ depends on the type of

interaction and characterizes the interaction range with larger γ value indicating shorter interaction range. The prefactor B may be controlled by varying the number density of ligands on the nanoparticle surface, nanoparticle size, and the choice of solvent. In addition to interparticle interactions, nanoparticles suspended in solution also possess thermal energy of an order of $k_B T$, where k_B is the Boltzmann constant and T is the absolute temperature. Assuming that gravity does not play a significant role, $\overline{\mathcal{W}}(d) = \mathcal{W}(d)/k_B T$ dictates the self-assembling behavior of nanoparticles. Naturally, self-assembly may occur when $\overline{\mathcal{W}}(d) < -1$ but the approach to equilibrium self-assembled structures may be slower for much more negative values of $\overline{\mathcal{W}}$ or for smaller range of interactions due to diffusive limitations. This simplified picture has been used in particle simulations of a generic coarse-grained model in an earlier work [9], wherein ligand-functionalized nanoparticle are represented as spheres and the interaction between nanoparticles is considered using a model potential that switches from repulsive to attractive interaction on exposure to UV light. This approach is quite simplistic and does not capture the effects of ligand configurations on the nanoparticle surface and the effects of metal core. Thus, while this approach captures the qualitative features of LISA, it does not provide quantitative prediction of LISA behavior or facilitate prediction of self-assembly behavior of different ligand–metal combinations. In general, $\mathcal{W}(d)$ is a sum of interaction energy between all pairs of ligand (i, j) on the surface of two

^{*} Corresponding author.

E-mail address: prateek.jha@ch.iitr.ac.in (P.K. Jha).