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## **Model Calculations of Optical Properties of Azobenzene Photoswitches**

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### Abstract:

Molecular photoswitches, capable of light-driven reversible shift between at least two (meta)stable states, attract considerable attention due to potential applications in nanotechnology. One of the most widely studied molecular photoswitches is azobenzene, composed of two phenyl rings linked by an azo group. Azobenzene can be reversibly switched between the more thermodynamically stable *trans* isomer and the less stable *cis* one upon irradiation with appropriate wavelengths. To implement functionality, molecular photoswitches should be placed on a substrate to keep a fixed position in a space. However, the isomerization ability can be affected when photoswitches are situated on a surface by means of interactions with the surface as well as neighboring molecules. An example is non-switchable densely packed self-assembled monolayers of certain azobenzene-containing thiols formed on a gold surface, for which exciton coupling between molecules was assumed to be a reason that prevents isomerization besides a possible steric hindrance.<sup>1</sup> The exciton coupling, in turn, appears as a change in optical absorption when

comparing to the spectra of molecules in gas phase or solution.

In this work by means of quantum chemical calculations we considered the optical absorption of model systems consisting of 4-nitroazobenzene photoswitches and a silicon nanocluster. The low-lying singlet excited states in isolated monomer and dimer (composed of *trans* isomers) as well as their composites with a silicon pentamantane nanocluster were examined. We assessed the performance of linear response time-dependent Hartree-Fock (TD-HF) and density functional theory (TD-DFT), namely two hybrid (B3LYP, BMK) and one range-separated (CAM-B3LYP) density functionals, comparing the results to each other and to ones obtained with the approximate coupled cluster CC2 method. Further, based on natural transition orbital (NTO) analysis, we determined the delocalized exciton transitions in dimer and calculated corresponding exciton splitting associated with the lowest bright transition; the dependence of exciton splitting on monomer separation was also tested. We found the redshift of absorption upon attachment of the molecular photoswitch monomer to the silicon nanocluster. The exciton splitting in the dimer attached to the silicon nanocluster is similar to one obtained for the dimer itself, without cluster, at the same monomer separation.

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#### References

(1) Gahl, C.; Schmidt, R.; Brete, D.; McNellis, E. R.; Freyer, W.; Carley, R.; Reuter, K.; Weinelt, M. Structure and Excitonic Coupling in Self-Assembled Monolayers of Azobenzene-Functionalized Alkanethiols. *J. Am. Chem. Soc.* **2010**, *132*, 1831–1838.