

Time-Dependent Density Functional Theory (TD-DFT) Calculations of the Chiroptical Properties of CdS Nanoparticles Functionalized with Cysteine

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INTRODUCTION

One of the most important properties of chiral materials, whether natural or synthetic, is their optical activity. Although it is well established that chiroptical responses depend on geometric properties of the chiral units comprising the material, a full understanding of the factors affecting them are still missing. In order to fill some of these information gaps, we have performed an extensive series of electronic circular dichroism (ECD) calculations using time-dependent density functional theory (TD-DFT) for CdS nanoparticles (NPs) with cysteine molecules as stabilizers.

METHODS

The model systems consisted of truncated tetrahedral NPs ($\text{Cd}_{31}\text{S}_{40}^{-18}$) functionalized with 24 cysteine molecules. Geometry optimization was performed with the semiempirical Hamiltonian PM7 (as implemented in MOPAC2012) and TD-DFT calculations were performed at the B3LYP/LANL2DZ level (as implemented in Gaussian 09, revision C.01). We defined a representative set of structural and environmental features whose effects on the ECD spectra are not known yet. Among many possibilities, we have chosen to study in this preliminary investigation the two cysteine enantiomers (either D or L), their arrangement on the NPs faces (either clockwise or counterclockwise), their protonation state (anionic, neutral, zwitterionic or cationic), the solvent effect and the distribution of counterions.

RESULTS AND DISCUSSION

The most difficult and tricky part of the investigation was the evaluation of the

electrostatic screening of the counterions around the NPs. We sampled the sodium cations distribution around a negatively charged NP using a Metropolis sampling Monte Carlo to place the ions at physically meaningful positions, and performed the TD-DFT ECD calculation for 400 excited states (Fig. 1). The band just below 300 nm was the most conserved ECD signal, with negative peaks for all configurations, whereas other spectral regions presented bands of varying intensity and algebraic signal.

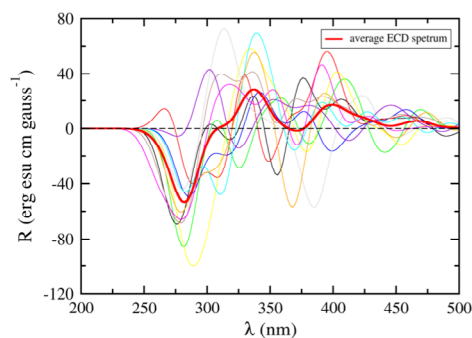


Figure 1. ECD spectra (counterclockwise anionic L-cysteine). Thin lines stand for spectra with 10 different arrangements of sodium cations around the NP.

CONCLUSIONS

The TD-DFT ECD calculation yielded spectra in excellent agreement with experimental results. Chiroptical properties are responsive to changes in the chirality and arrangement of the organic ligands, as well as to the protonation state of ligands and the electrostatic screening of the environment.

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