Coarse-Grained Simulations of Ligand-Tethered Nano-Tripods

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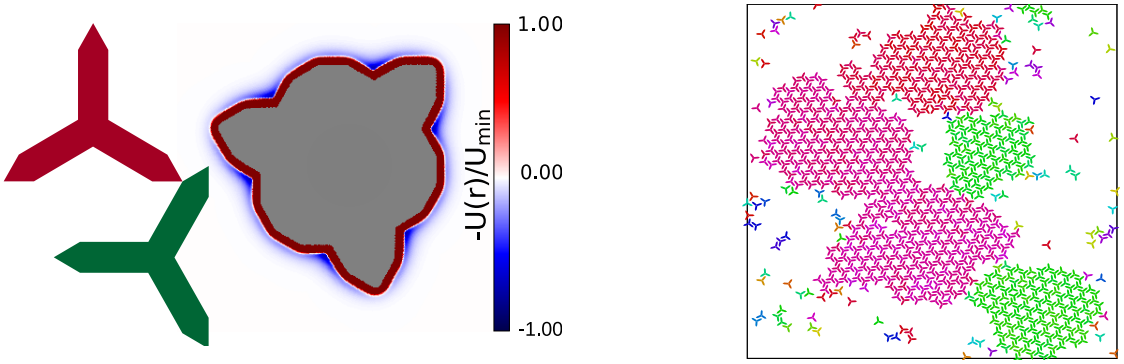
Ligands play important roles in nanocrystal assembly: they control the shape of nanocrystals, function as stabilizers, and determine the structure of the self-assembled superlattice. Two-dimensional nanocrystals, so-called nanoplates, are ideal model systems to study the effect of ligands as they can be synthetized with a range of aspect ratios and be functionalized highly controllably by ligands of different chemical species, molecular weight, and densities. Here, we present coarse-grained molecular dynamics simulation model to predict the self-assembled superlattices of nanoplates functionalized with ligands. We apply this framework to tripods, where we predict a number of distinct superlattices, among them chiral ones and with regular and controllable porosity. The coarse-grained simulation model describes the van der Waals interaction of the tripods that accounts for relative orientations via a generalized Derjaguin approximation by Monte Carlo integration over the nanocrystal surfaces. [1] The Monte Carlo results for the interaction potential are precalculated and tabulated for use in coarse-grained molecular dynamics simulations. We study the effect of tripod aspect ratio, ligand molecular weights and grafting densities, and thermodynamic conditions on the geometric structure of the self-assembled superlattices.



Our simulation results agree with experimental observations of rare earth oxide tripod particles and shade light on the complex superlattice formation pathways. Such pathways are not directly accessible by experiment. Our coarse-grained model and its predictions can be generalized to other convex and concave nanoplates and nanocrystals in three dimensions to evaluate the interplay of particle shape and patchy, directional ligand-induced interactions for the synthesis of functional nanostructures.

[1] Y. Liu et al., *J. Am. Chem. Soc.,* **2021**, *143*, 16163.