Controlled Symmetry Breaking in Colloidal Crystal Engineering with DNA

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The programmed crystallization of particles into low-symmetry lattices represents a major synthetic challenge in the field of colloidal crystal engineering. Herein, we report an approach to realizing such structures that relies on a library of low-symmetry Au nanoparticles, with synthetically adjustable dimensions and tunable aspect ratios. When modified with DNA ligands and used as building blocks for colloidal crystal engineering, these structures enable one to expand the types of accessible lattices and to answer mechanistic questions about phase transitions that break crystal symmetry. Indeed, crystals formed from a library of elongated rhombic dodecahedra yield a rich phase space, including low-symmetry lattices (body-centered tetragonal and hexagonal planar). Molecular dynamics simulations corroborate and provide insight into the origin of these phase transitions. In particular, we identify an unexpected asymmetry in the DNA shell, distinct from both the particle and lattice symmetries, which enables directional, nonclose-packed interactions.

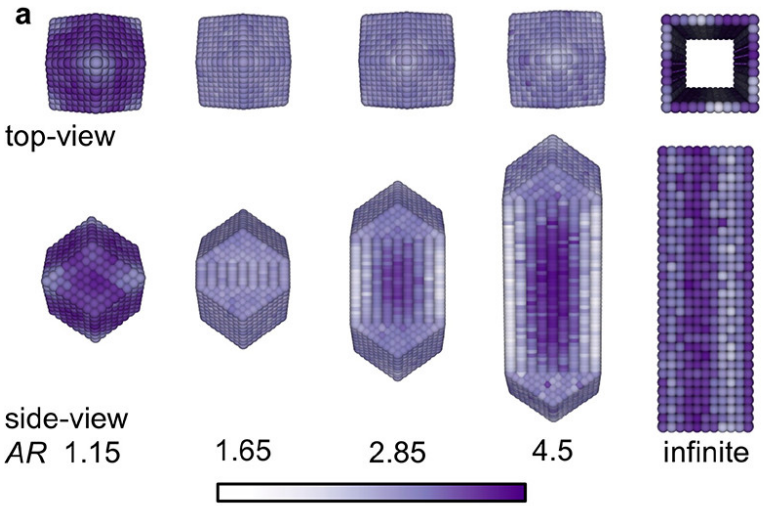

Figure: Elongated rhombic dodecahedra building blocks crystallized into multiple lattice symmetries. (a) As the AR of building blocks increases, the surface area (and thus number of DNA molecules) on elongated (green) facets increases, while the surface area of the tip (purple) facets remains the same.

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