Directed assembly of tetrahedral DNA-origami patchy colloids into diamond cubic, hexagonal diamond and S-II clathrates

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Understanding and controlling the self-assembly of colloidal building blocks into open crystal lattices remains a central challenge in colloid science. In particular, accessing distinct polymorphs from the same building block requires precise control over directional interactions and assembly conditions. DNA origami provides a powerful platform for this because it enables colloidal units with well-defined geometry and programmable binding.[1]
Carbon is a classic example of how one building block can generate multiple crystal structures. Through different relative rotations and stacking via tetrahedral bonds, it forms diamond cubic, hexagonal diamond (lonsdaleite), and other polytypes. Tetrapod DNA-origami building blocks were recently shown to assemble into a diamond cubic structure through single-stranded DNA binding extensions at their four tips with threefold symmetry.[2] Extending this concept to a two-component system allows the relative rotation between neighboring monomers to be programmed through the binding pattern. A 60° relative rotation favors diamond cubic formation, whereas enforcing a 0° rotation on one arm biases the system toward hexagonal diamond. To introduce competing pathways within one system, a mixed binding-extension design was implemented that allows neighboring monomers to adopt either the 60° or the 0° configuration.
This competition between local binding geometries, together with variations in crystallization conditions such as temperature and salt concentration, produces rich structural phase behavior. Depending on the assembly conditions, diamond cubic and hexagonal diamond stacking variants, interpenetrating lattices, and S-II clathrate lattices form. The clathrate phase is particularly notable because its energetic minimum is reached when all monomers adopt the 0° configuration, despite the distortions required to stabilize this structure (Fig. 1A).
The resulting clathrate has a lattice constant of about 440 nm and a unit cell containing 136 monomers. After stabilization by SiO2 growth via a sol-gel process[3], this structural length scale gives rise to an optical response in the visible range. After drying, the crystals exhibit blue or green structural reflections under dark-field illumination, depending on crystal orientation and angle of incidence (Fig. 1B).
These results establish DNA origami as a model platform for controlling polymorphism and phase selection in programmable tetrahedral patchy colloids, while opening a route toward the bottom-up assembly of open photonic materials.

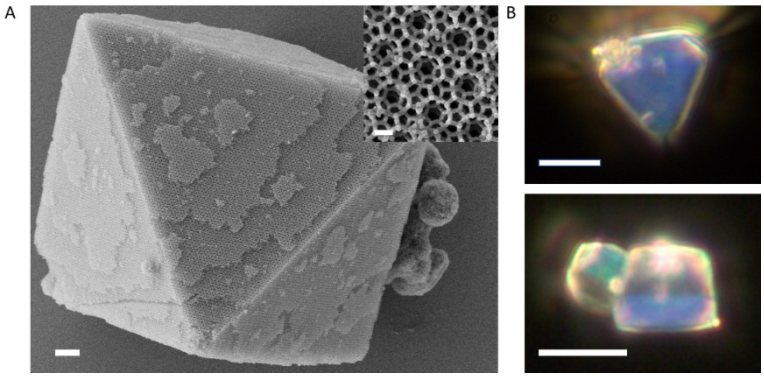

Fig 1. (A) SEM image of clathrate lattice with zoomed in image of its (111) plane (top right inset). Scale bars: 2 µm, inset: 200 nm. (B) Reflection-mode dark-field microscope image of clathrate single crystal (up) and twinned crystals (bottom). Scale bars: 10 µm (up), 15 µm (down).

References:

[1] Paul WK Rothemund. "Folding DNA to create nanoscale shapes and patterns." *Nature* 440.7082 (2006): 297-302.
[2] Gregor Posnjak, **Xin Yin** , et al. "Diamond-lattice photonic crystals assembled from DNA origami." *Science* 384.6697 (2024): 781-785.
[3] Linh Nguyen, et al. "DNA - origami - templated silica growth by sol–gel chemistry." *Angewandte Chemie International Edition* 58.3 (2019): 912-916.
[4] **Xin Yin** , et al. “Directed assembly of DNA origami-based tetrahedral patchy particles into diamond and clathrate structures.” In preparation.