Bottom-Up Colloidal Crystal Assembly with a Twist

Nathan A. Mahynski[1], Lorenzo Rovigatti[2], Christos N. Likos[2], Athanassios Z. Panagiotopoulos[3]

[1]Chemical Informatics Research Group, Chemical Sciences Division, National Institute of Standards and Technology, USA
[2]Faculty of Physics, University of Vienna, Boltzmanngasse 5, A-1090 Vienna, Austria
[3]Department of Chemical and Biological Engineering, Princeton University, USA

*lorenzo.rovigatti2@physics.ox.ac.uk

Globally ordered colloidal crystal lattices have broad utility in a wide range of optical and catalytic devices, for example, as photonic bandgap materials. However, the self-assembly of stereospecific structures is often confounded by polymorphism. Small free energy differences often characterize ensembles of different structures, making it difficult to produce a single morphology at will. Current techniques to handle this problem adopt one of two approaches: that of the "top-down," or "bottom-up" methodology, whereby structures are engineered starting from the largest or smallest relevant length scales, respectively. However, recently a third approach for directing high fidelity assembly of colloidal crystals has been suggested which relies on the introduction of polymer co-solutes into the crystal phase [1]. By tuning the polymer's morphology to interact uniquely with the void symmetry of a single desired crystal, the entropy loss associated with polymer confinement has been shown to strongly bias the formation of that phase. However, previously this approach has only been demonstrated in the limiting case of close-packed crystals. Here we show how this approach may be generalized and extended to complex open crystals, illustrating the utility of this "structure-directing agent" paradigm in engineering the nanoscale structure of ordered colloidal materials [2]. The high degree of transferability of this paradigm's basic principles between relatively simple crystals and more complex ones suggests this represents a valuable addition to presently known self-assembly techniques and opens new avenues to better engineer the structure of these materials.

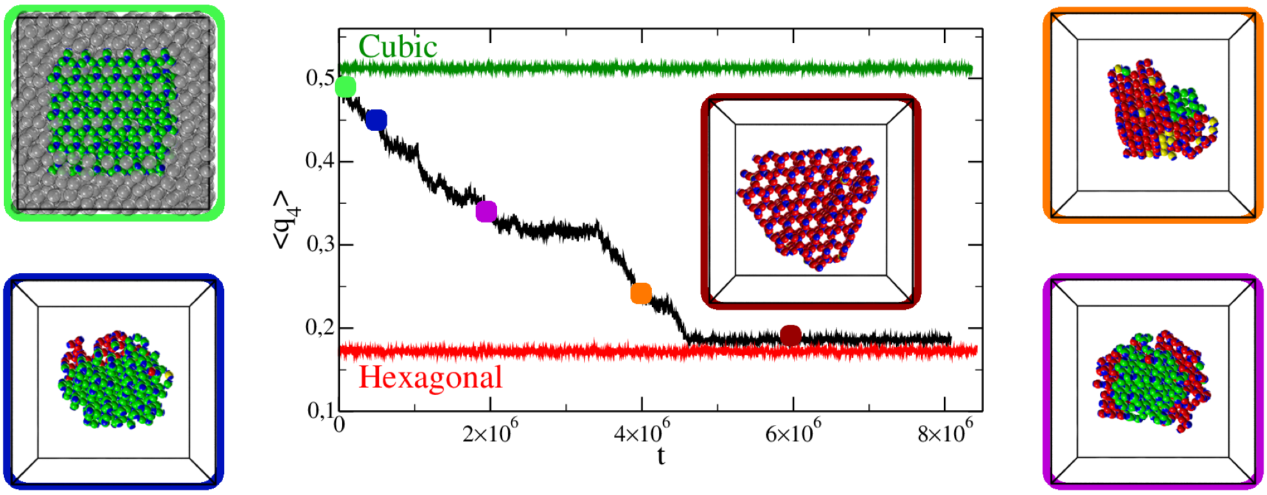

Figure 1 By employing star polymers with the right functionality, size and charge it is possible to anneal a cubic tetrastack crystal (green particles) into a hexagonal one (red particles).

[1] N. A. Mahynski, et al., *Nat. Commun.*, 2014, **5**, 4472.
[2] N. A. Mahynski, L. Rovigatti, C. N. Likos, A. Z. Panagiotopoulos, *ACS Nano*, 2016.