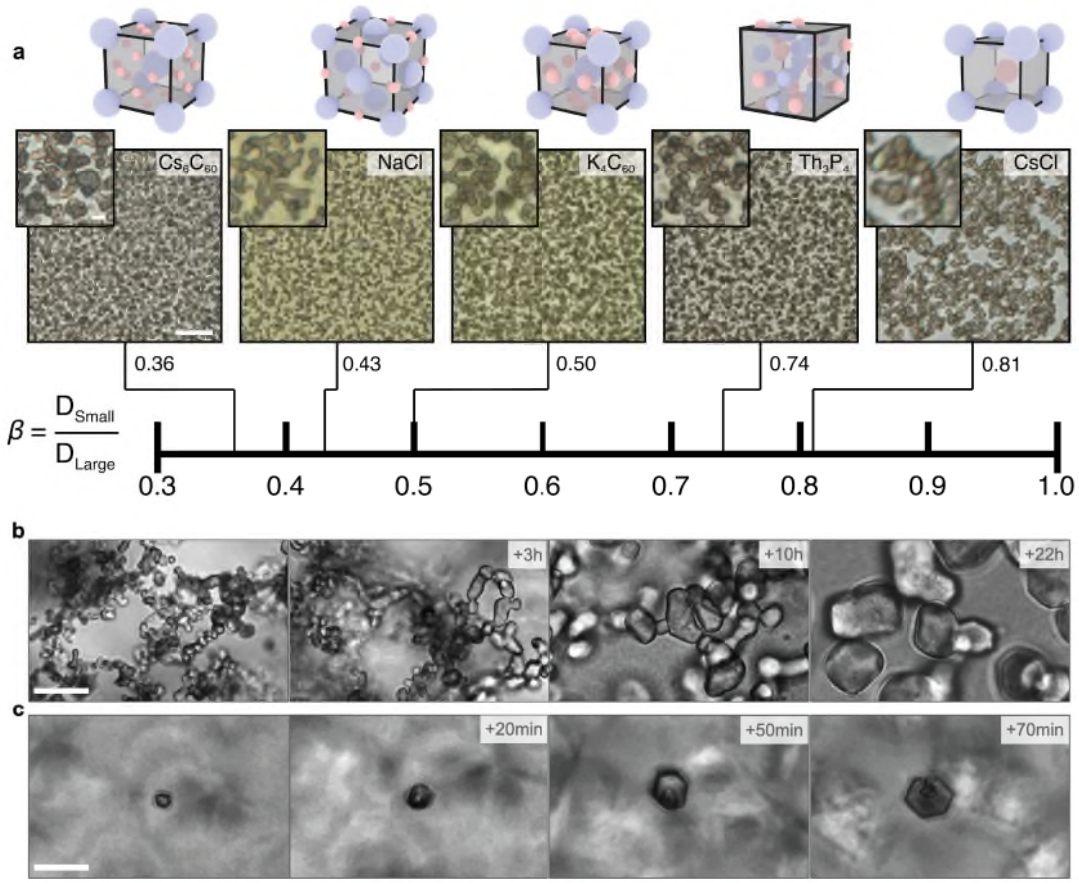
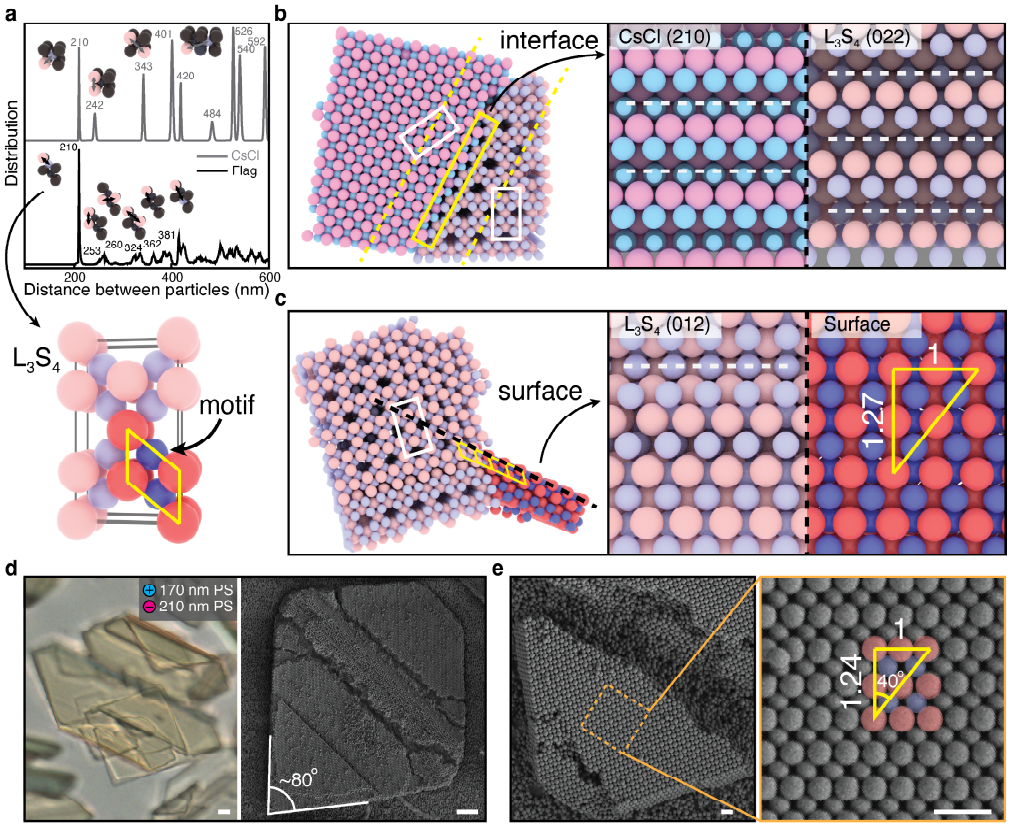
Direct observation and control of non-classical crystallization pathways in binary colloidal systems

Shihao Zang[1], Sanjib Paul[1,†], Cheuk W Leung[1,†], Michael S Chen[1,2], Theodore Hueckel[1,3], Glen M Hocky[1,2,*], and Stefano Sacanna[1,*]

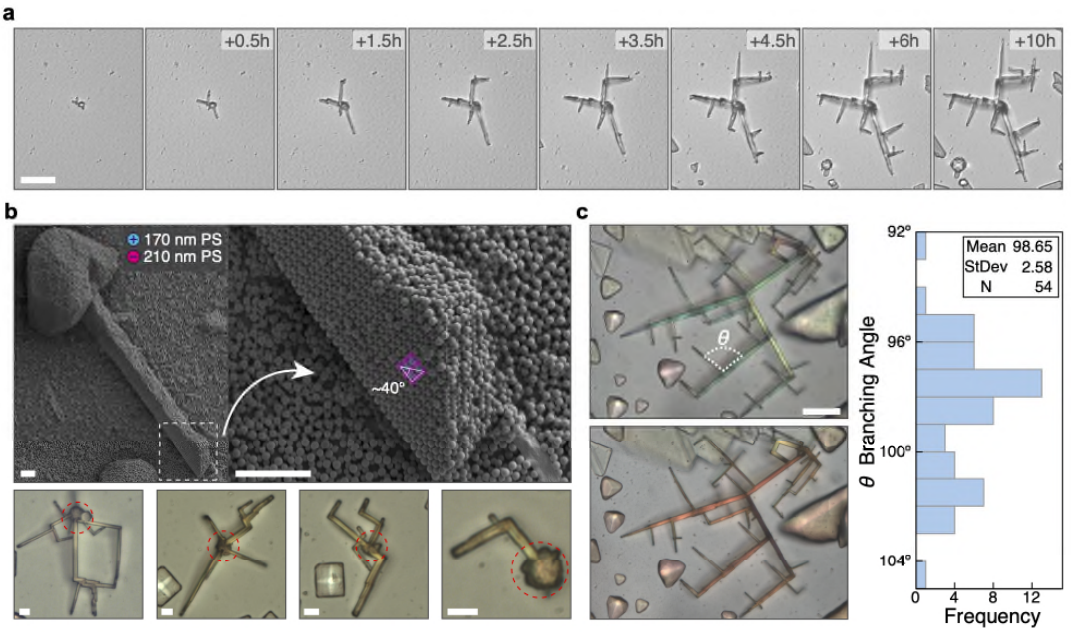
[1]Department of Chemistry, New York University, New York, NY, USA
[2]Simons Center for Computational Physical Chemistry, New York University, New York, NY, USA
[3]Present address: Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA
[†]These authors contributed equally to this work
[*]Corresponding authors: GMH: hockyg@nyu.edu, SS: s.sacanna@nyu.edu



Supplementary Figure 1: **Generalization of two-step crystallization behavior.** **a**, Bright-field microscopy images showing snapshots taken during the crystallization of binary mixtures with various values of β. The images capture the transient state where crystals grow by blob absorption, eventually resulting in Cs_6C_{60}–, NaCl–, K_4C_{60}–, Th_3P_4–, and CsCl–like crystals. Scale bars, 50 μm for overall view and 5 μm for insets. **b**, A typical two-step crystallization process of ionic colloidal crystals in a sealed capillary, involving diameter 185 nm negatively charged spheres and 200 nm positively charged spheres in 2.2 mM NaCl and 57% D_2O. The sequence shows the transformation from amorphous blobs to well-defined, faceted crystals. **c**, The same colloidal system as in (**b**) undergoing classical nucleation and growth under dialysis conditions (Fig.4). Both samples were imaged in the bulk, away from the glass wall. Scale bar, 20 μm.



Supplementary Figure 2: **Heteroepitaxy.** **a**, Distance distributions of the particles in epitaxial crystal A and B (Fig.8d) showing that A has a CsCl–like structure and B share at least one particle motif (yellow) with the L_3S_4 unit cell. **b**, The interface between L_3S_4 and epitaxial crystal A shows a similar particle arrangement between the (022) plane of L_3S_4 and the (210) plane of the CsCl-like structure, which might explain the epitaxial growth. **c** Cross-section of the interface between L_3S_4 and epitaxial crystal B showing the motif duplication along the (012) plane (black line) of L_3S_4, resulting in the epitaxial growth of thin crystal sheets. **d**, Bright-field (left) and SEM (right) images showing epitaxial crystal B formed with approximately 4-6 layers and a characteristic vertex angle of approximately 80 degrees. Scale bar, 3 μm. **e**, SEM images showing the surface plane of epitaxial crystal B with a length-to-width ratio of 1.24 for the right triangle (yellow), consistent with the simulation result in (**c**). This specific ratio confirms that the surface is not the (110) plane of CsCl (length-to-width ratio of 1.41) and also accounts for the vertex angle in (**d**). Scale bar, 0.5 μm.



Supplementary Figure 3: **Branched crystals.** **a**, Time-lapse bright-field microscopy images showing the nucleation and growth of branched crystals from a central seed (see also Supplementary Movie 7). This sample consists of a 1:1 mixture of 170 nm (+) PS and 210 nm (−) PS particles in a dialysis setup. Scale bar, 50 μm. **b**, (Top) SEM image showing a fragment of a crystal that survived the fixing process. This image suggests that these branched structures may form via heteroepitaxial growth from a central seed crystal. While the central seed's habit resembles the Th_3P_4 structure, the rest of the crystal appears to share the same structure as the flag-like crystal shown in Supplementary Figure 2e. Scale bar: 2 μm. (Bottom) Bright-field images showcasing various branched crystals, all featuring a central seed crystal circled in red. Scale bar: 10 μm. **c**, (Left) Polarized light microscopy images of a branched crystal extending over hundreds of micrometers and exhibiting strong color birefringence. (Right) Measurements of the branching angles θ reveal a relatively constant value of 98.6°, suggesting anisotropic growth due to facet-controlled growth or twinning. Scale bar: 50 μm.