

Description of Additional Supplementary Files

Supplementary Movie 1: The early stages of binary ionic colloidal crystal nucleation, observed through bright-field microscopy, confocal microscopy, and molecular dynamics (MD) simulations, reveal a distinct two-step crystallization pathway. Initially, a colloidal gas condenses into metastable amorphous clusters, which then undergo a transition into an ordered crystalline state.

Supplementary Movie 2: The movie shows the growth of colloidal cesium chloride-like crystals through monomer-by-monomer addition, as captured by bright-field microscopy.

Supplementary Movie 3: The movie captures the growth of colloidal cesium chloride-like crystallites through the absorption of amorphous particle blobs, as observed via bright-field microscopy.

Supplementary Movie 4: The movie showcases the fusion of two cesium chloride-like crystallites via oriented attachment, as observed through bright-field microscopy.

Supplementary Movie 5: Video demonstrating a typical crystallization experiment under dialysis conditions. Thin capillaries, filled with binary colloidal mixtures at high ionic strength, are immersed in a deionized water reservoir. The resulting crystallization front is observed in real-time using a bright-field microscope, allowing visualization at both the macroscopic and microscopic levels.

Supplementary Movie 6: Video rendering of molecular dynamics simulations depicting the nucleation and growth of L_3S_4 crystals, including a demonstration of heteroepitaxial growth.

Supplementary Movie 7: Video microscopy capturing a crystallization experiment performed under dialysis conditions in which multiple crystal structures nucleate within the same sample.