

## Description of Additional Supplementary Files

**Supplementary Movie 1.** Tilt series of X-ray images of a decahedral colloidal cluster consisting of 500 nm PS particles on solid substrate.

**Supplementary Movie 2.** Surface of 3D reconstruction of the decahedral colloidal cluster from X-ray tomography.

**Supplementary Movie 3.** Slices through the 3D reconstruction of decahedral colloidal cluster along the five-fold axis showing individual PS particles and defect plane.

**Supplementary Movie 4.** Simulation trajectory forming a decahedral cluster. Grains are shown with random color, fluid particles semi-transparent. Insets are the bond-orientational order diagram (bottom left) and the grain projection (bottom right). Three snapshots of this movie are analyzed in Figure 3a-c.

**Supplementary Movie 5.** Growth of decahedral colloidal cluster in emulsion droplet observed in real-time under optical microscope with 125x objective. Grains grow from one side to the other and form characteristic half-circle structural color pattern.

**Supplementary Movie 6.** Growth of decahedral colloidal cluster in emulsion droplet observed in real-time under optical microscope with 40x objective. Grains grow from one side to the other and form characteristic half-circle structural color pattern.

**Supplementary Movie 7.** Simulation trajectory forming an icosahedral cluster. Three snapshots of this movie are analyzed in Figure 3e-g.

**Supplementary Movie 8.** Simulation trajectory forming a defective cluster. The impossibility to form a complete icosahedron is not yet apparent, it affects only the final stage of droplet drying.

**Supplementary Movie 9.** Growth of icosahedral colloidal cluster in emulsion droplet observed in real-time under optical microscope with 125x objective. Individual grains grow sequentially to form characteristic bow-tie structural color pattern.

**Supplementary Movie 10.** Growth of icosahedral colloidal cluster in emulsion droplet observed in real-time under optical microscope with 40x objective. Individual grains grow sequentially to form characteristic bow-tie structural color pattern.