Supplementary Material for

Entropic Colloidal Crystallization Pathways via Fluid-Fluid Transitions and Multidimensional Pre-Nucleation Motifs

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This contains only supplementary figures. For the descriptions of simulation and analysis methods, please see the method section at the end of the main article.

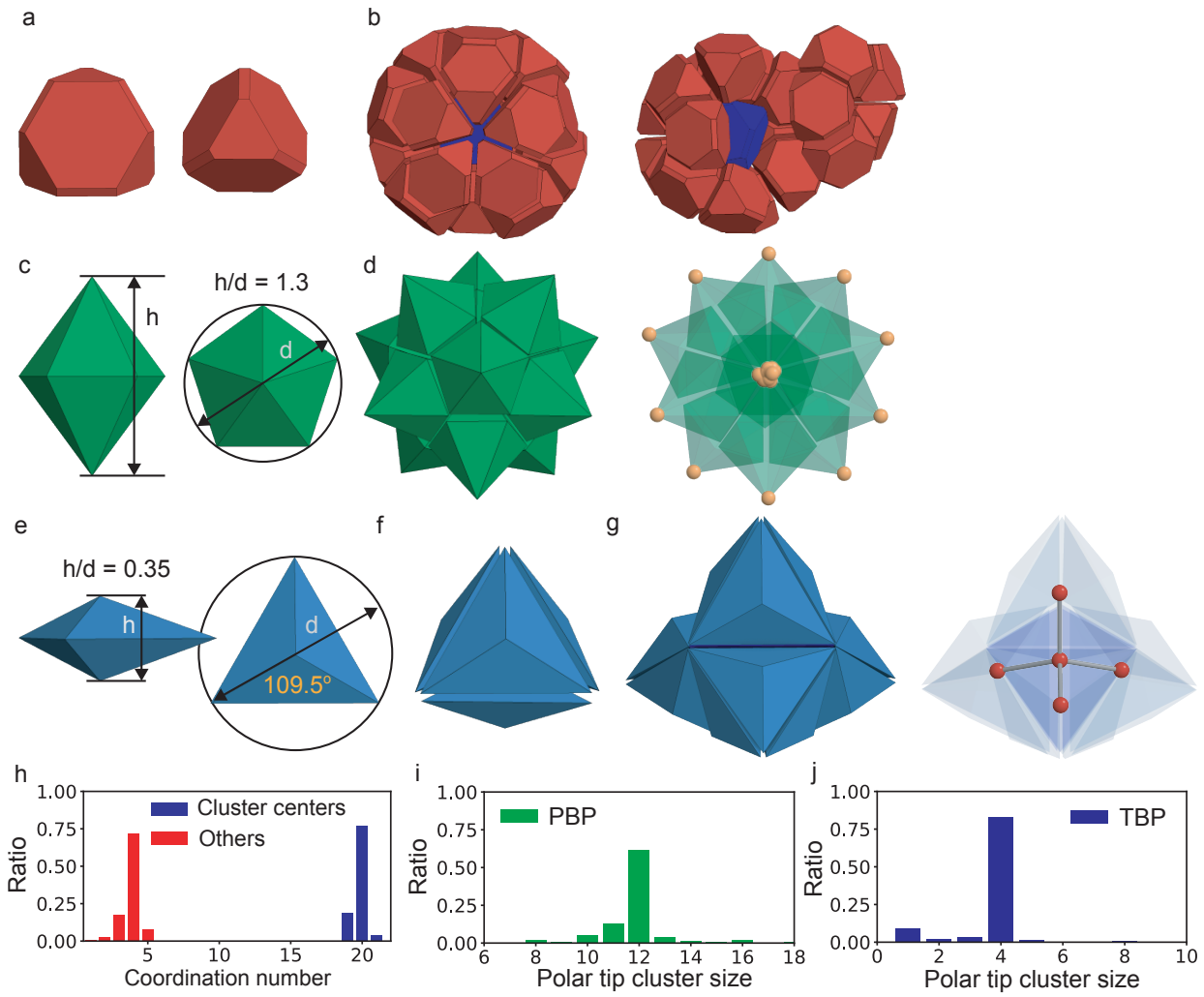

Figure S1. Particle geometry and local motifs. a, A single TT with truncation parameters(1) $(a, b, c) = (1.10, 1.00, 1.44)$ from side view (left) and top view (right). **b,** A cluster-type motif of $N = 20$ TTs (red) with one additional TT in the center (blue). **c,** A single PBP with aspect ratio 1.3 from side view (left) and top view (right). **d,** A small stellated dodecahedron (SSD) of $N = 12$ PBPs (green), a unit of fiber-like local motifs in the PBP system. One polar tip (yellow sphere) of each PBP points toward the SSD center. **e,** A single TBP with 109.5° edge angle from side view (left) and top view (right). **f,** A tetramer of $N = 4$ TBPs that is a node of the network-type motif in the TBP system. **g,** When five tetramers assemble (left), a unit of the tetrahedral network can be mapped by connecting the locations of polar tip groups (red spheres on the right). **h**, The coordination number distribution of the TT cluster centers (blue shown in b) and the other TTs (red shown in b) calculated from nearest neighbors in the HDF phase ($P^* = 18.0$). **i**, Distribution of polar tip cluster size of PBPs in the HDF phase ($P^* = 16.35$), which shows a peak at 12. **j**, Distribution of polar tip cluster size of TBPs in the HDF phase ($P^* = 9.13$), which shows a peak at 4.

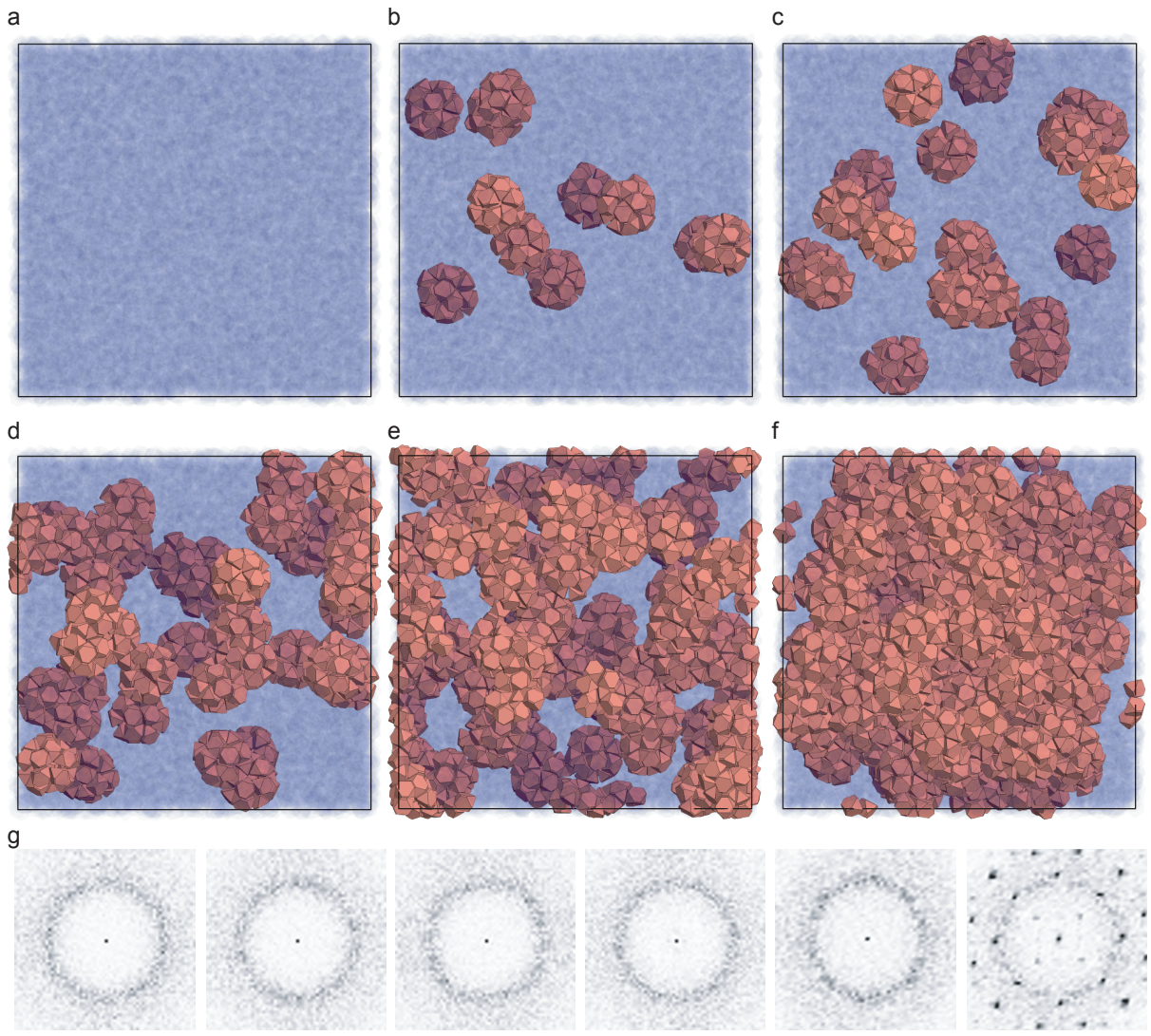

Figure S2. Crystallization process of *cF*432. Snapshots of TTs colored by the cluster-type prenucleation motif (pink) after **a**, 3×10^6, **b**, 27×10^6, **c**, 40×10^6, **d**, 70×10^6, **e**, 340×10^6 and **f**, 1481×10^6 Monte Carlo sweeps. Simulation parameters are identical to those in Fig. 2a and b. When the HDF forms in the first step, individual clusters first appear (a-c), and then aggregate (**d, e**) as the number of clusters increases. In the second step, the *cF*432 phase crystallizes (**f**). **g**, Diffraction patterns that correspond to each snapshot in **a-f**. The diffraction pattern of the HDF (**a-e**) is isotropic, while that of the *cF*432 (**f**) shows clear peaks along the four-fold axis. See Movie S1 for the complete crystallization process.

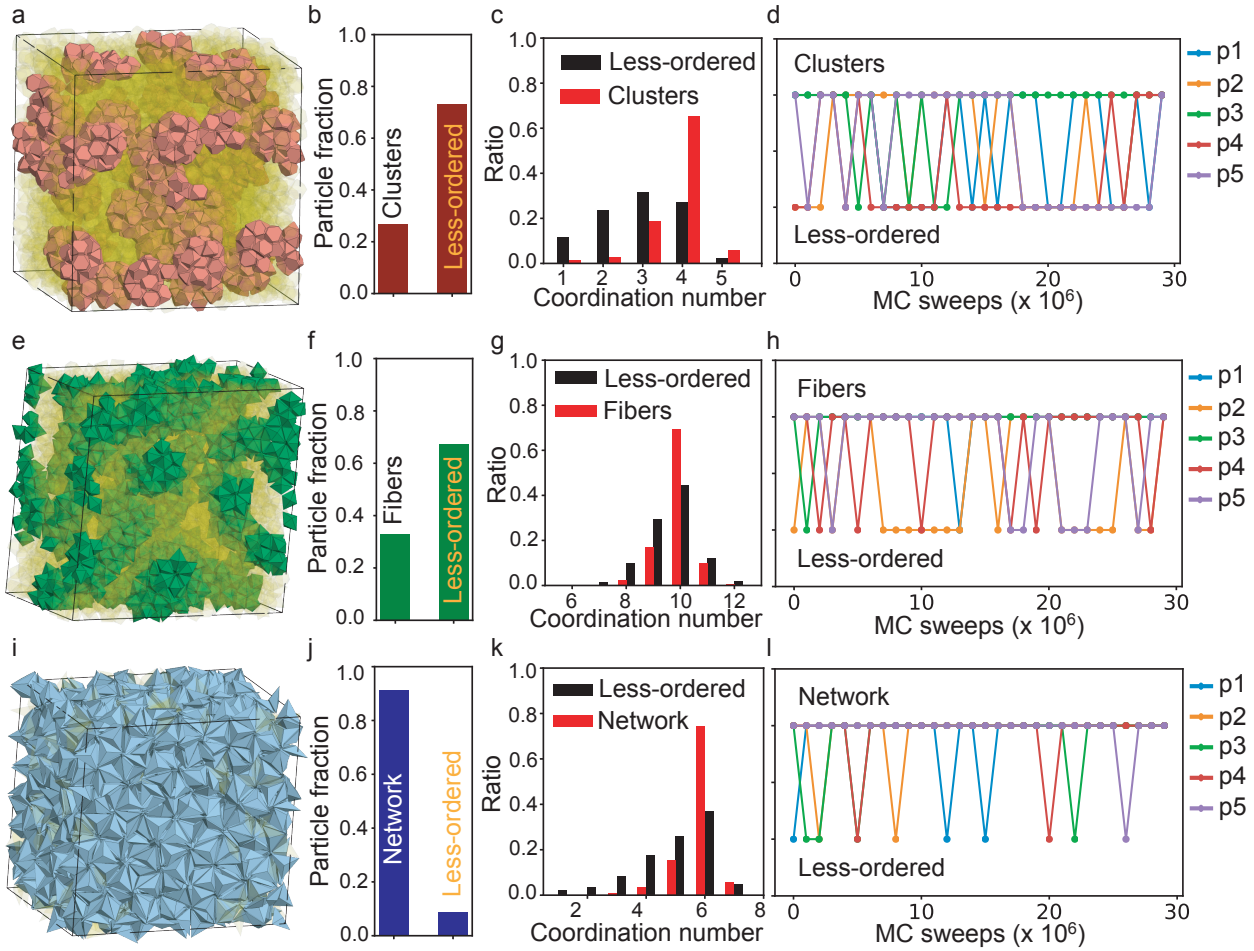

Figure S3. Highly ordered and weakly ordered regions of the HDF. a, e, i, Snapshots of the HDF prepared under isobaric conditions at $P^* = 18.0$ and $N = 3{,}456$ for TTs (a), $P^* = 16.35$ and $N = 4{,}000$ for PBPs (e), and $P^* = 9.13$ and $N = 4{,}000$ for TBPs (i). Particles in prenucleation motifs are colored pink for cluster-type motifs (a), dark green for fiber-type motifs (e), and light blue for network-type motifs (i). Particles in the weakly ordered region are transparent yellow. **b, f, j**, The fraction of particles that participate in the prenucleation motifs is 27% for TTs (b), 33% for PBPs (f) and 91% for TBPs (j). **c, g, k**, The coordination number distribution of particles in the prenucleation motif (red) shows a peak at 4 for TTs (c), 10 for PBPs (g) and 6 for TBPs (k), while that of the weakly ordered region (black) shows a relatively broad distribution. **d, h, i**, When tracking five randomly selected particles (p1 – p5) in the HDF during 30×10^6 Monte Carlo sweeps, all three systems show particle exchange between the highly ordered region and the weakly ordered region

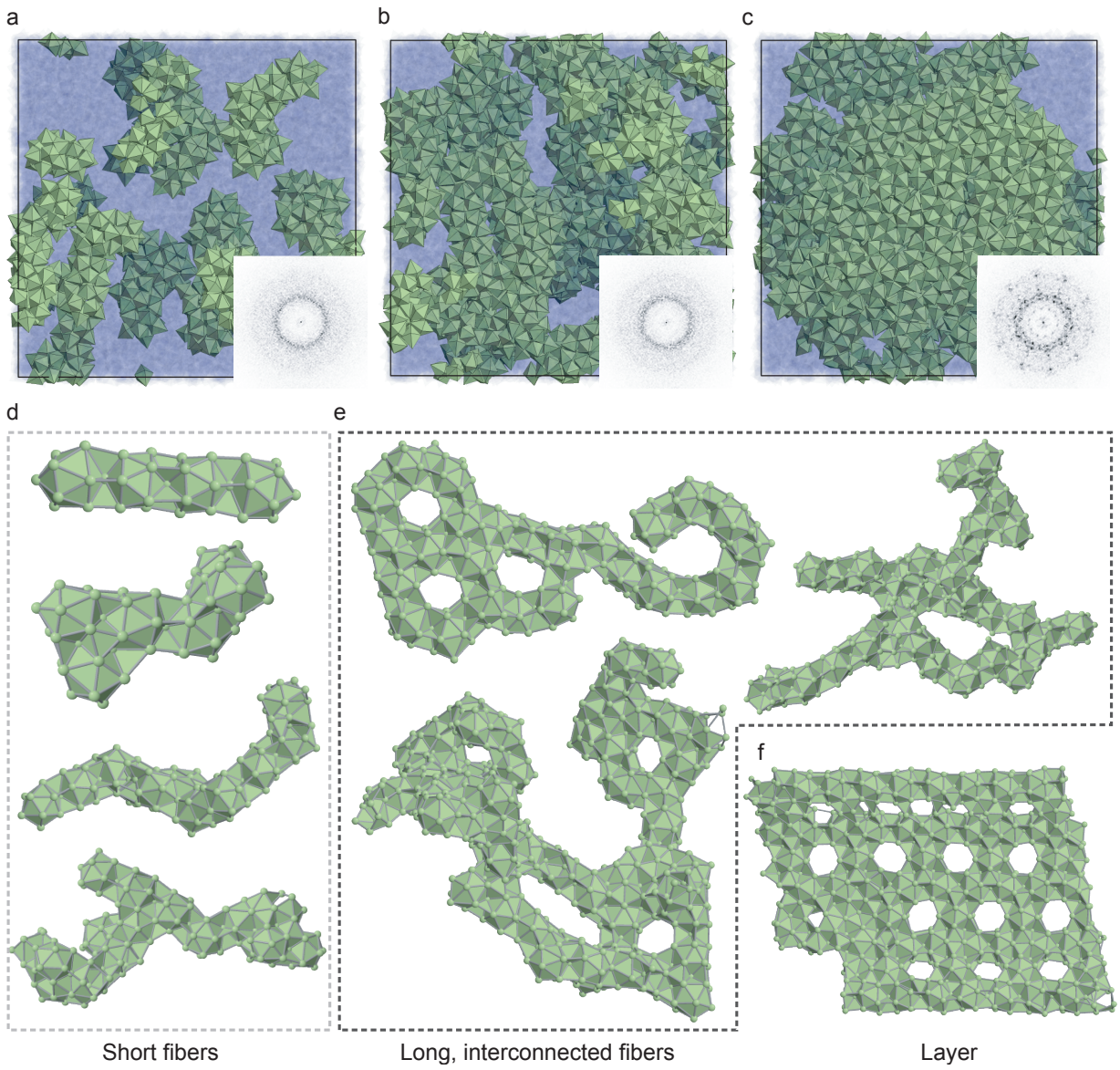

Figure S4. Various fiber-type local motifs of PBPs. Simulation snapshots of the PBP system colored by the fiber-type prenucleation motif (light green) after **a,** 7×10^6, **b**, 77×10^6 and **c**, 1105×10^6 Monte Carlo sweeps. Simulation parameters are identical to those in Fig. 3a, b. Various morphologies of **d, e**, fiber-type prenucleation motifs and **f**, a crystal layer that are observed during the crystallization process. Light green spheres represent PBP centers. They are connected to nearest neighbors by grey bonds.

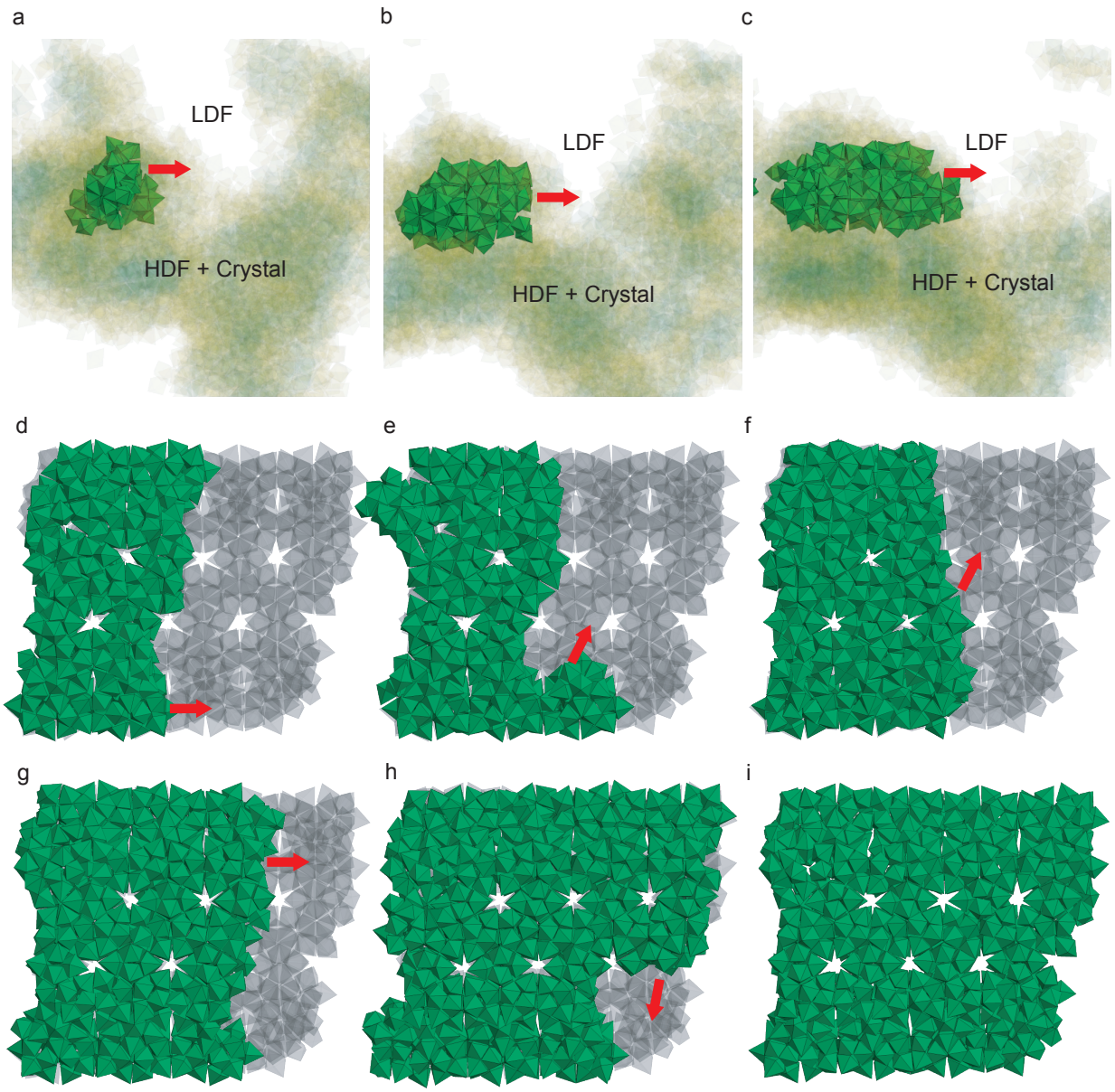

Figure S5. Growth of one layer of the PBP crystal. Simulation snapshots (side view of a crystal layer) of the PBP system after **a**, 115×10^6, **b**, 334×10^6 and **c**, 475×10^6 Monte Carlo sweeps. Only one layer of crystal is colored dark green, and particles in the dense phase (HDF and the other layers of crystal) are colored transparent yellow and green. Particles in the LDF are not shown. Red arrows indicate the growth direction. **d-i**, Growth of the crystal layer from top view. Transparent gray particles in the background are the final state of the crystal layer shown for reference. All snapshots correspond to the same system as that in Fig. 3a, b. See Movie S2 for the complete growth process of a layer.

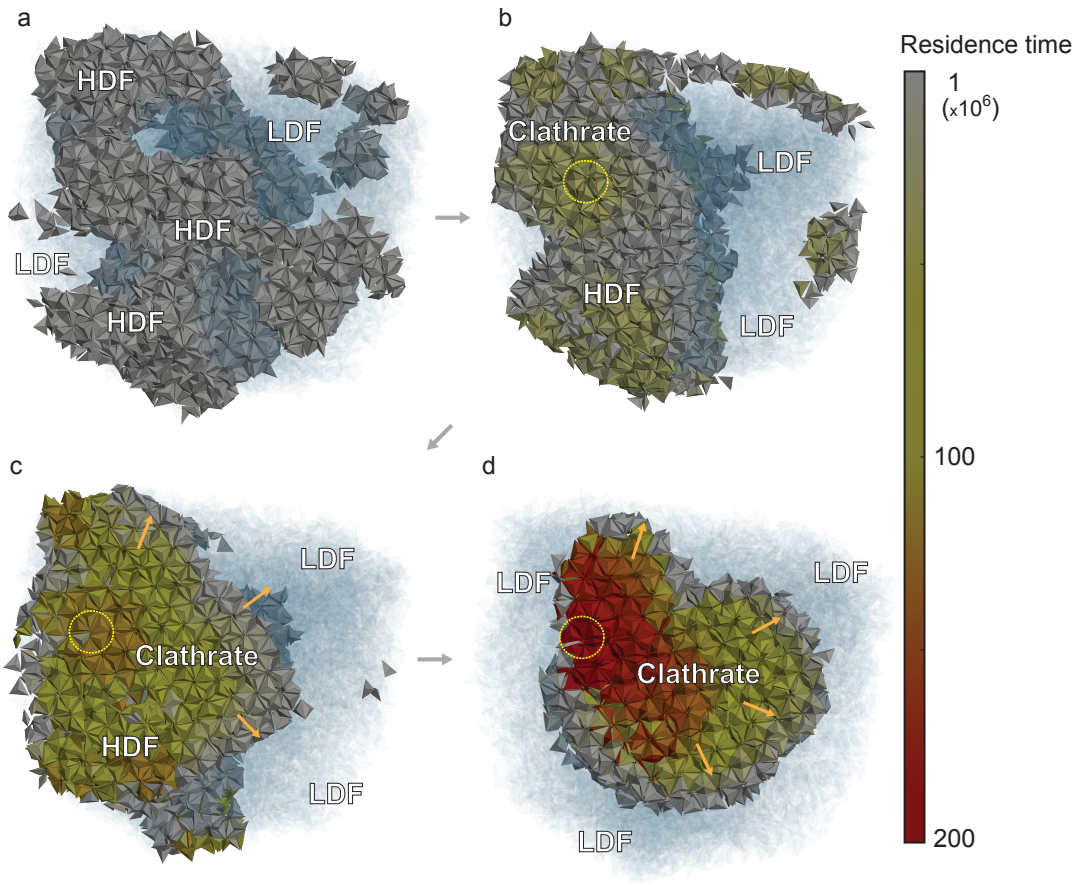

Figure S6. Growth direction of the TBP crystal. A system of hard triangular bipyramids (TBPs) self-assembles into a clathrate colloidal crystal at packing density $\phi = 0.5$ after **a**, 7×10^6, **b**, 40×10^6, **c**, 120×10^6 and **d**, 200×10^6 Monte Carlo sweeps. We color each TBP in the high-density region (HDF or crystal) by the residence time in the high-density region. If crystallization occurs inside the HDF precursor then only TBPs already existing in the high-density region are involved in crystallization and the color should be uniform. If instead the crystal grows by incorporating TBPs from the LDF then the color should follow a gradient in the direction of growth. A gradual change of the residence time in the clathrate demonstrates growth toward the LDF (indicated by arrows). A fixed position in the clathrate is marked (dashed yellow ring) as a guide to the eye.

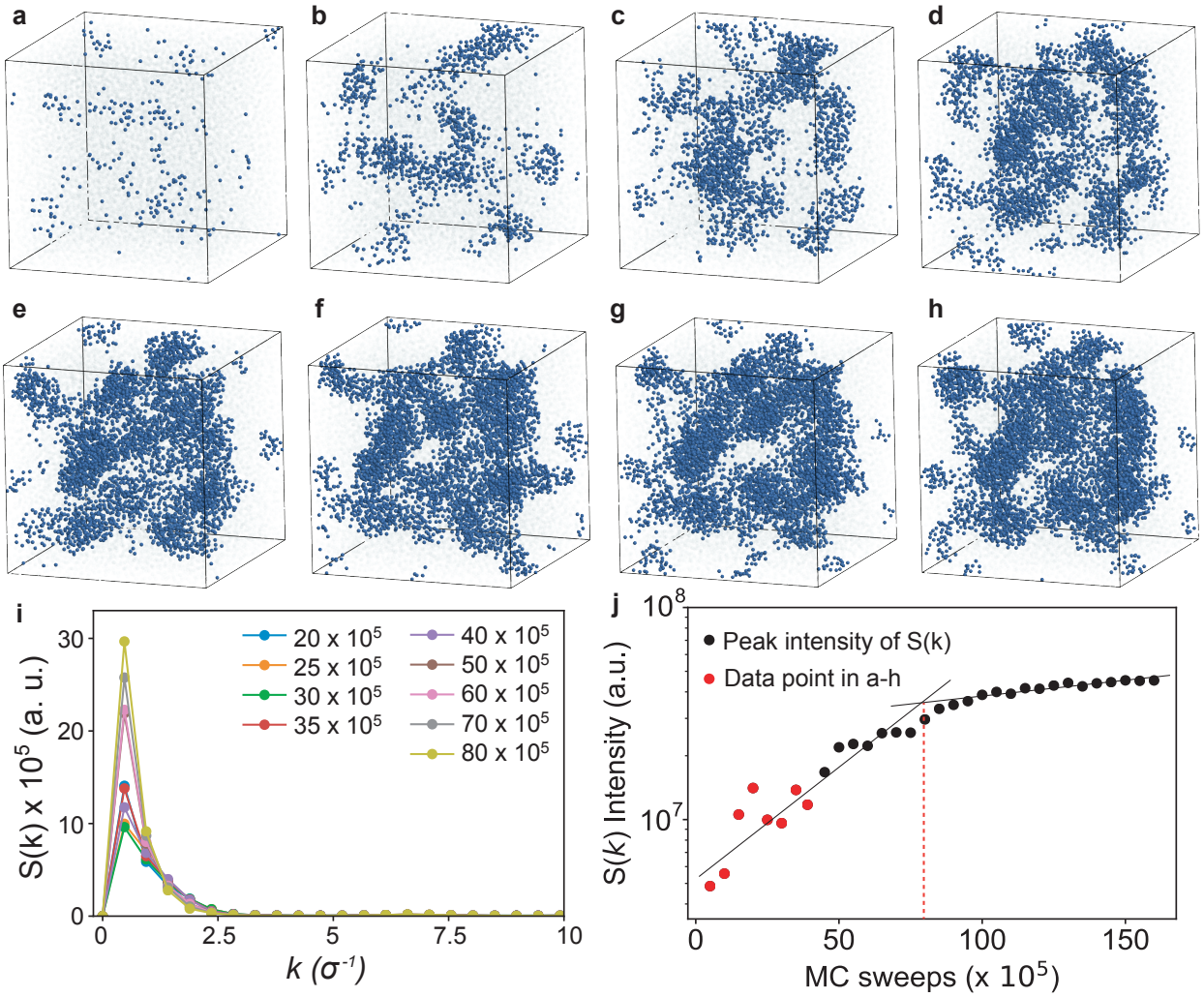

Figure S7. HDF precursor formation in the TBP system. Snapshots in the TBP center representation after **a**, 0.5×10^6, **b**, 1.0×10^6, **c**, 1.5×10^6, **d**, 2.0×10^6, **e**, 2.5×10^6, **f**, 3.0×10^6, **g**, 3.5×10^6, and **h**, 4.0×10^6 Monte Carlo sweeps. The HDF forms without delay and gradually coarsens. **i**, Time evolution of the first peak of the structure factor $S(k)$ between 2.0×10^6 and 8.0×10^6 Monte Carlo sweeps. **j**, The peak height increases exponentially at constant wavevector during HDF precursor formation (left side of the dashed red line). This observation agrees with behavior expected for the early stages of spinodal decomposition (2).

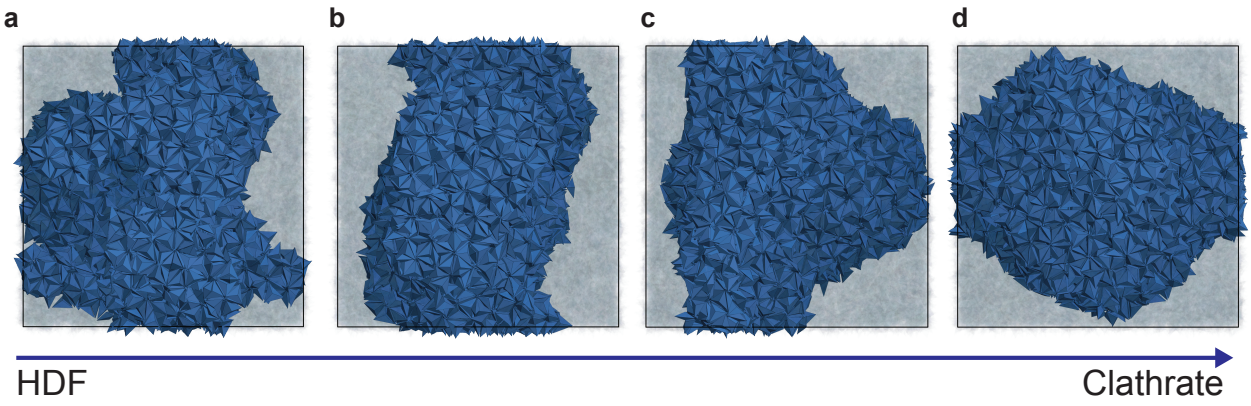

Figure S8. Shape change of the high-density region in the TBP system. Snapshots after **a**, 20×10^6, **b**, 60×10^6, **c**, 150×10^6, and **d**, 200×10^6 Monte Carlo sweeps. The high-density region has a non-spherical shape during the first part of the simulation run where the HDF dominates (a-b). As the volume of the clathrate grows and the volume of the HDF shrinks, the shape of the high-density region becomes more spherical (c-d).

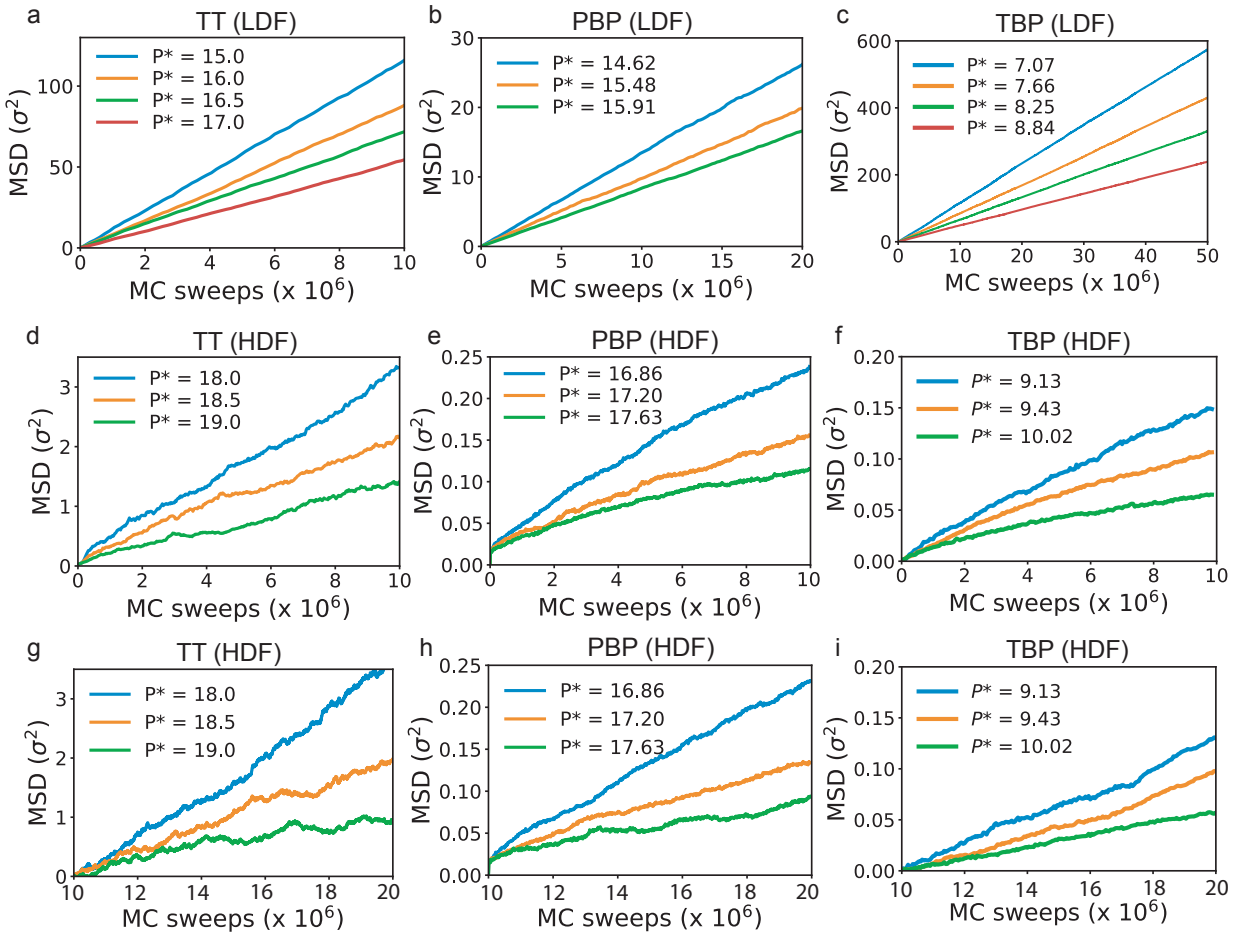

Figure S9. Mean-squared displacement (MSD). The MSD of TTs (**a**, **d, g**), PBPs (**b**, **e, h**), and TBPs (**c**, **f, i**) in LDF and HDF at different values of pressure. The MSD of HDF **d-f**, between 0 and 10×10^6 MC sweeps shows similar behavior with the MSD **g-i**, between 10×10^6 and 20×10^6 MC sweeps. The consistency of the MSD for different aging times provide further evidence that the HDF phase is equilibrated. We calculated the MSD of the HDF only when crystallization did not occur during the simulation. For all three systems, both fluids show diffusive motion.

References

1. Chen ER, Klotsa D, Engel M, Damasceno PF, Glotzer SC (2014) Complexity in surfaces of densest packings for families of polyhedra. *Phys Rev X* 4(1):011024.

2. Bates FS, Wiltzius P (1989) Spinodal decomposition of a symmetric critical mixture of deuterated and protonated polymer. *J Chem Phys* 91(5):3258–3274.

Legend of Movies

Movie 1. Crystallization of TTs. Evolution of a Monte Carlo simulation of 8,000 TTs at constant packing density $\phi = 0.615$ initialized from a disordered starting configuration. **a**, Whole view with simulation box. **b**, Zoom-in around the nucleation spot. Particle colors are identical to Fig. 2a,b.

Movie 2. Growth of a layer of PBP crystal. Evolution of a Monte Carlo simulation of 10,000 PBPs at constant packing density $\phi = 0.58$ initialized from a disordered starting configuration. To visualize the growth of a crystal layer, a subset of PBPs that form the layer at the end of the simulation are colored based on their location in the system: fiber-like motifs (green), the weakly ordered region of the HDF (transparent yellow) and the LDF (transparent blue). **a**, Top view and **b**, side view of the layer.

Movie 3. Particle movements within two different layers of PBP crystal. Ten selected PBPs in **a**, the highly ordered layer and **b**, the weakly ordered layer are shown during 2×10^8 Monte Carlo sweeps. The PBPs in the highly ordered layer (a) only exhibit local thermal vibration, while those in the weakly ordered layer (b) show significant translational and orientational movement.

Movie 4. Crystallization of TPBs. Evolution of a Monte Carlo simulation of 20,000 TBPs at constant packing density $\phi = 0.5$ initialized from a disordered starting configuration. **a**, Polyhedron representation of the high-density region ($\phi_{\mathrm{loc}} > 0.52$). **b**, Polyhedron representation of the clathrate phase (red) colored by clathrate order parameter ($\mathrm{CPN} = 3$) within the HDF (transparent blue). **c**, The tetrahedral network representation obtained by connecting tetramer centers. Growth of the clathrate crystal proceeds dominantly towards the top right, into the LDF. The high-density phase is automatically centered in each frame.