# Electronic Supplementary Information

# A Controlling Parameter of Topological Defects in Two-Dimensional Covalent Organic Frameworks

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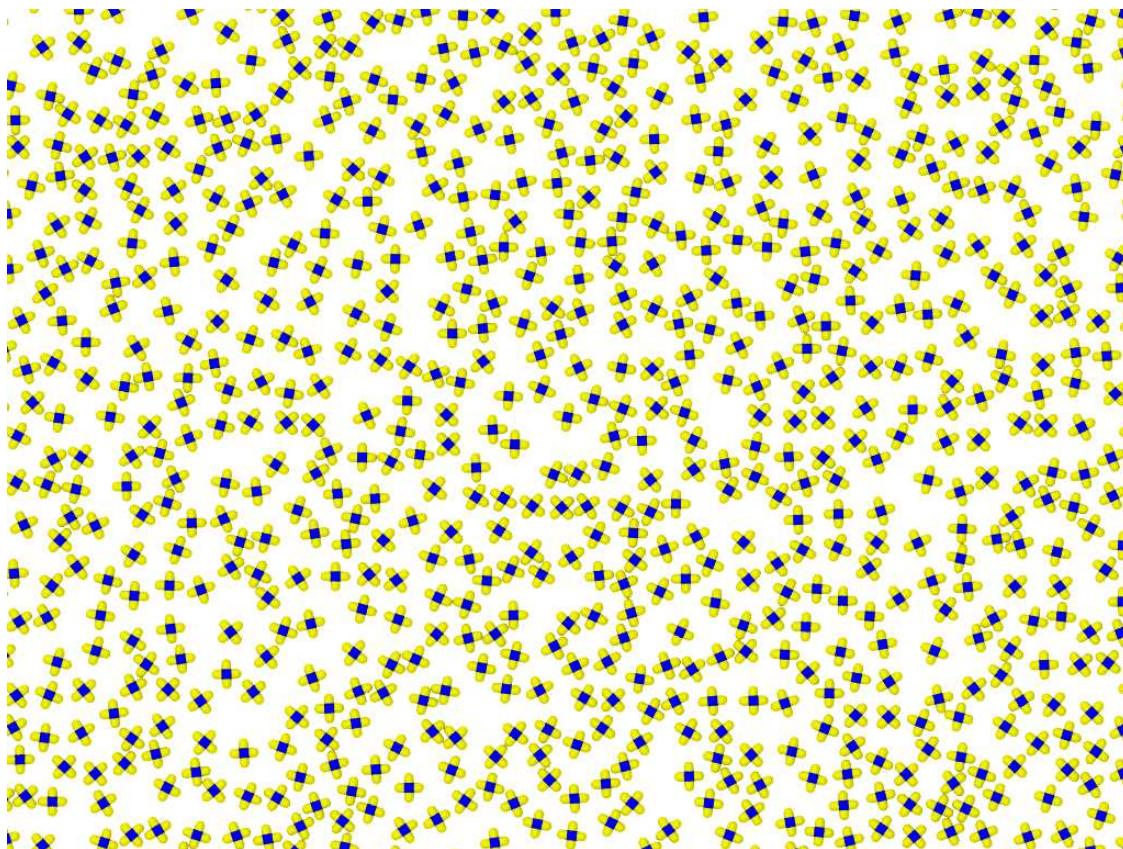# (S1) Snapshots of polymerization process of $[C_4 + C_4]$



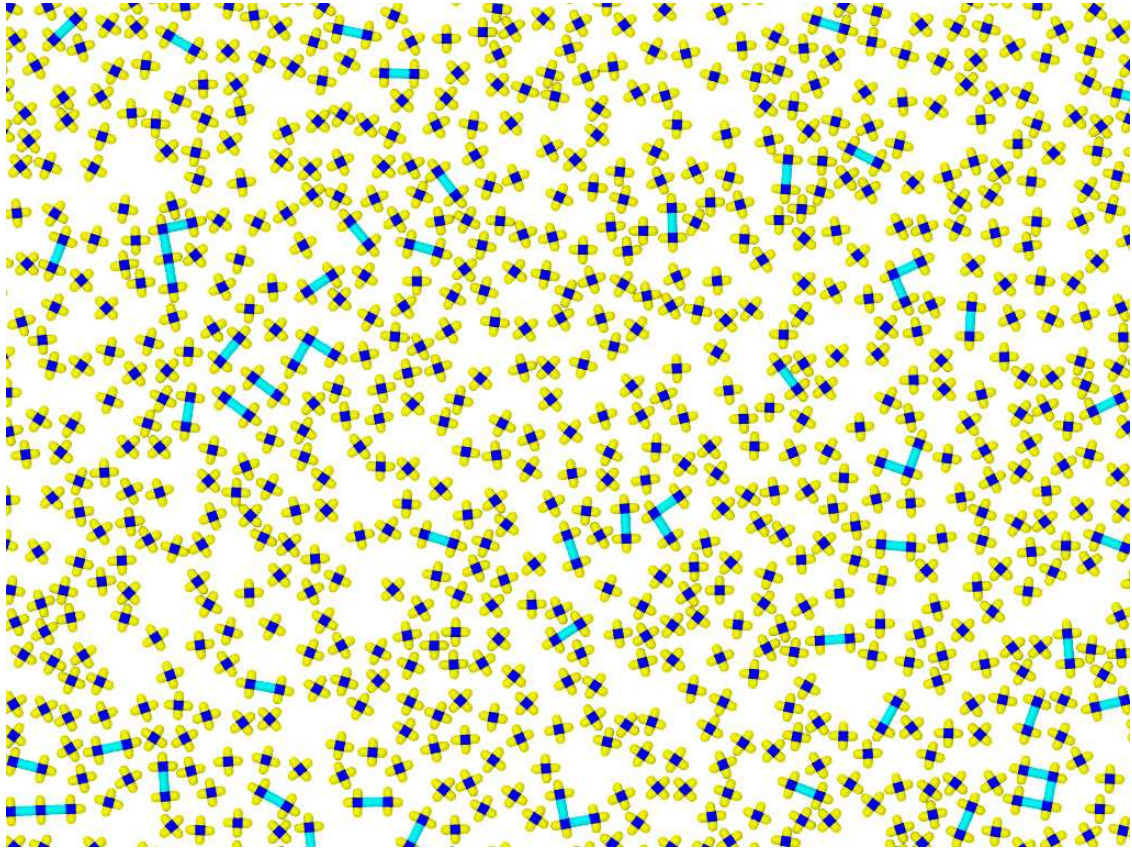Figure S1: Snapshot of polymerization at time $t = 0$.

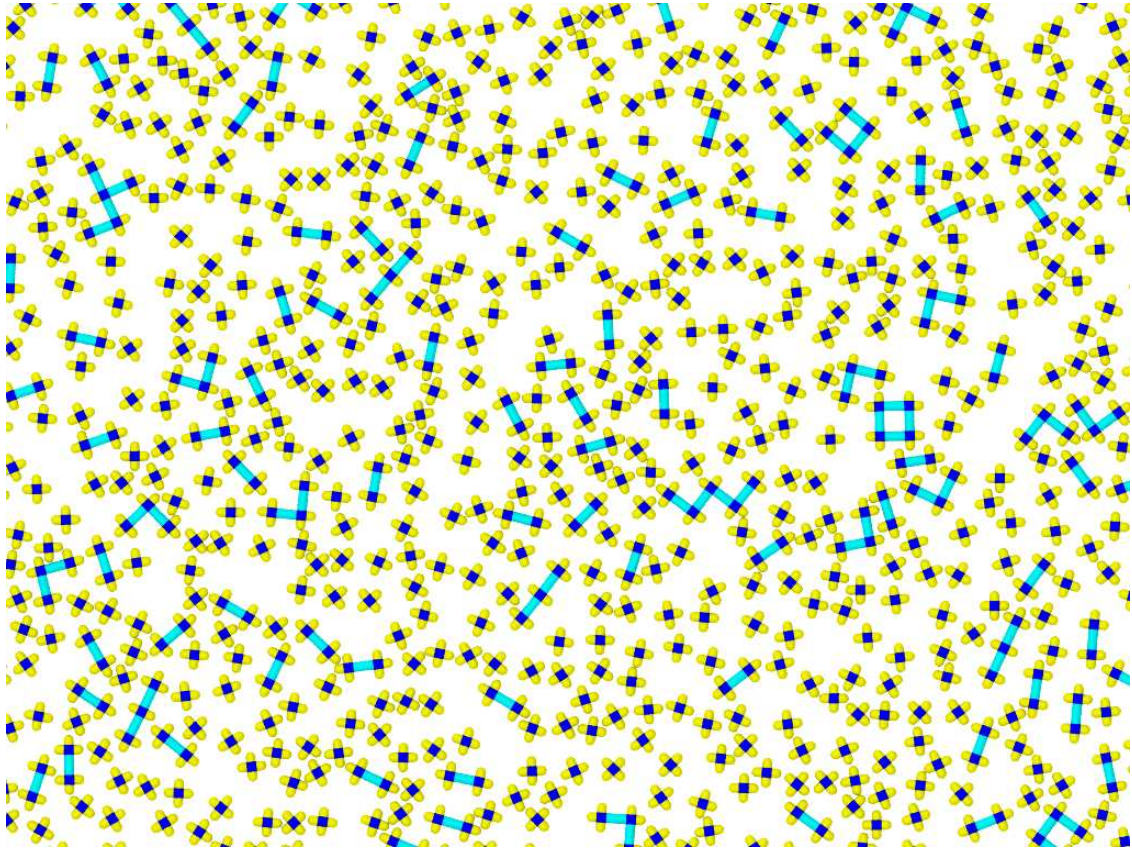Figure S2: Snapshot of polymerization at time $t = 1,000$.

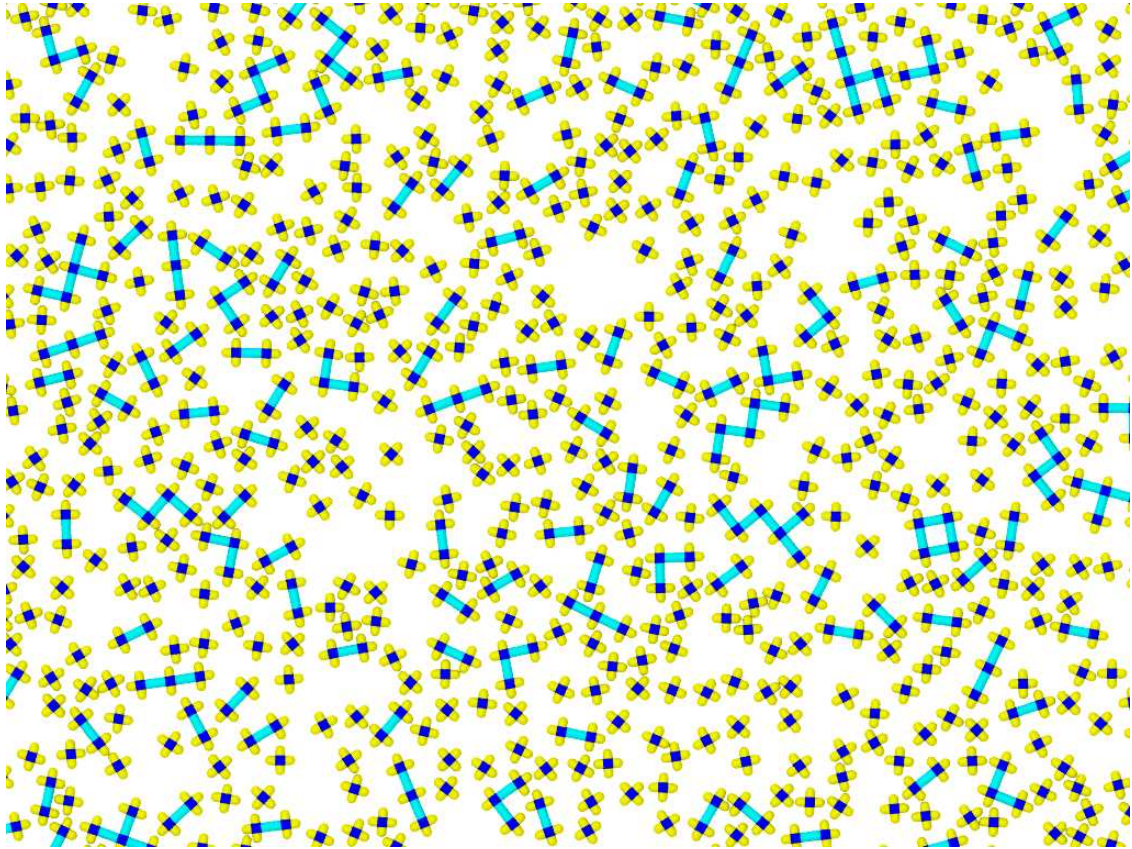Figure S3: Snapshot of polymerization at time $t = 2,000$.

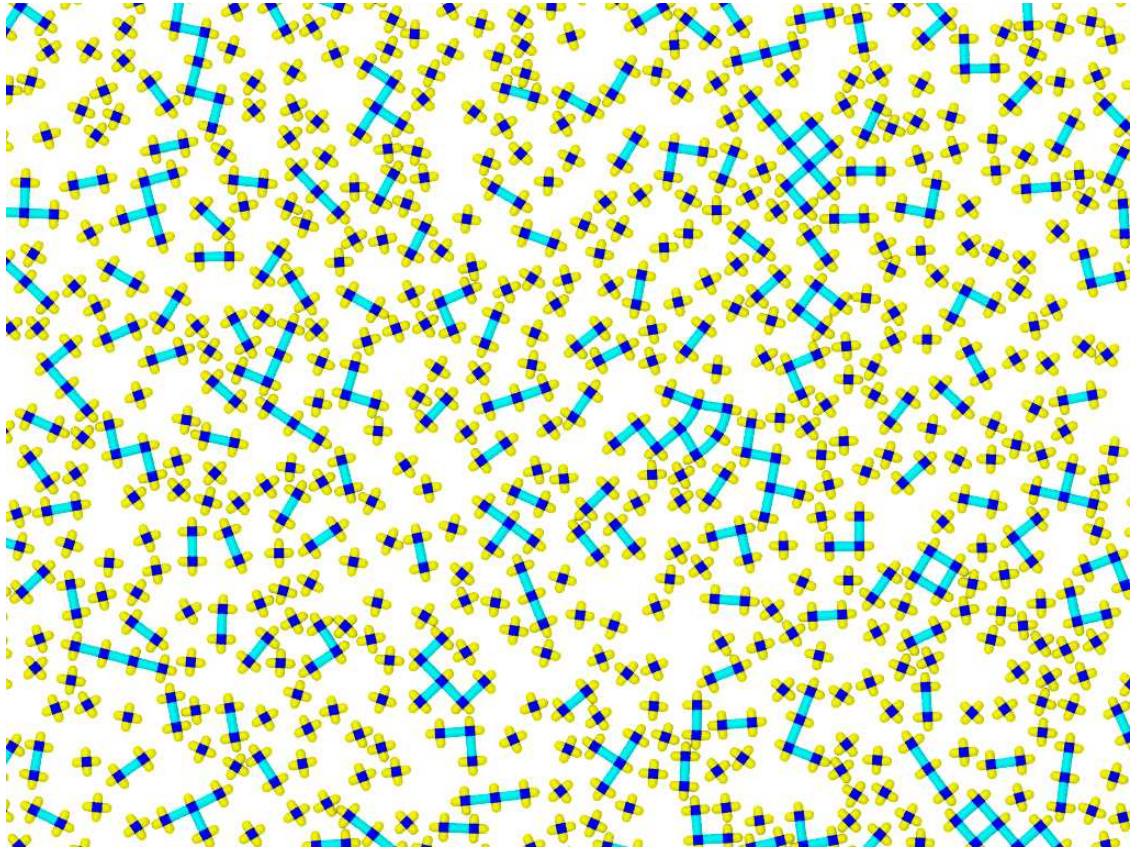Figure S4: Snapshot of polymerization at time $t = 3,000$.

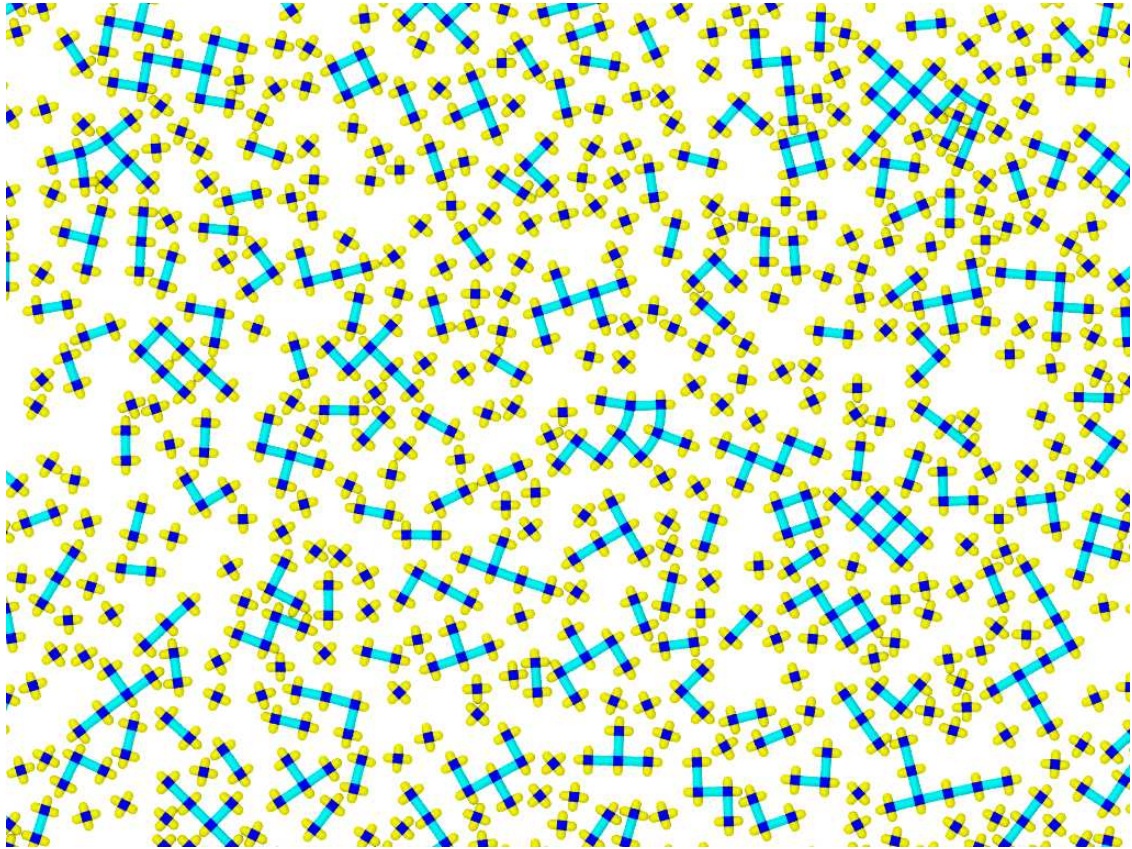Figure S5: Snapshot of polymerization at time $t = 4,000$.

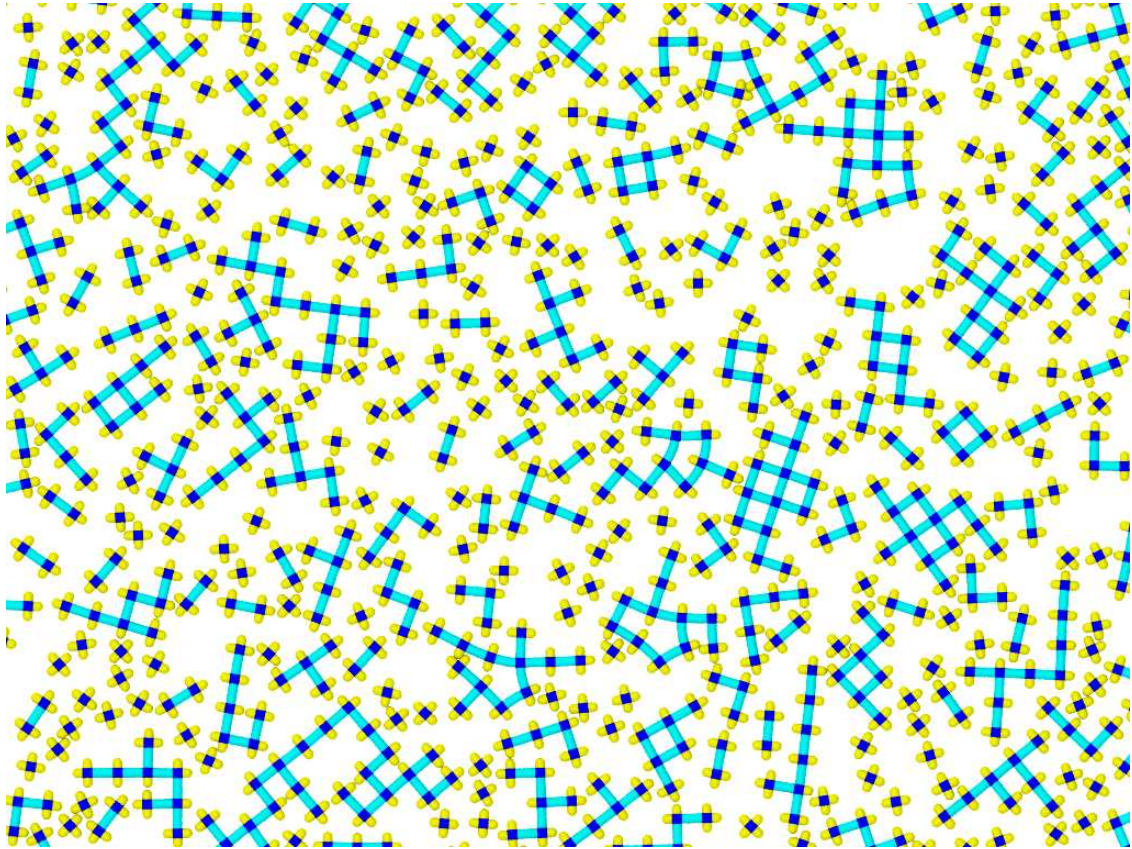Figure S6: Snapshot of polymerization at time $t = 6,000$.

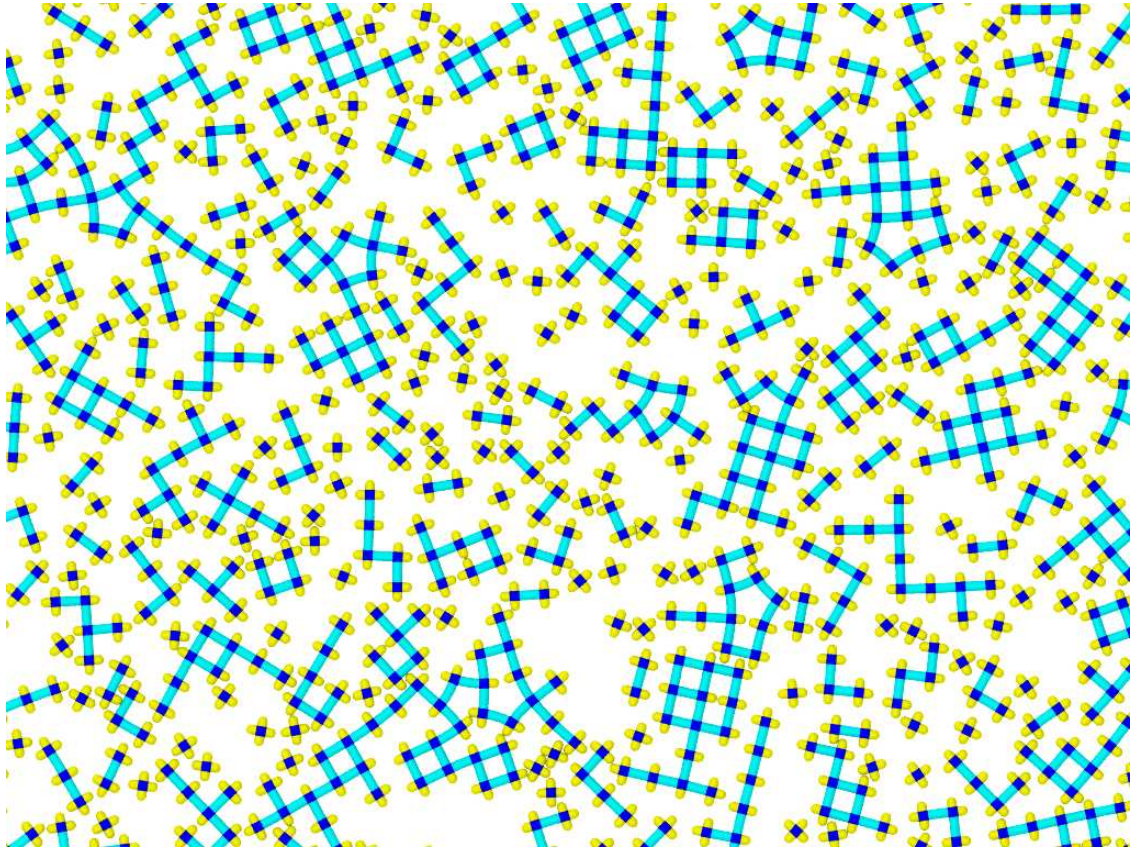Figure S7: Snapshot of polymerization at time $t = 8,000$.

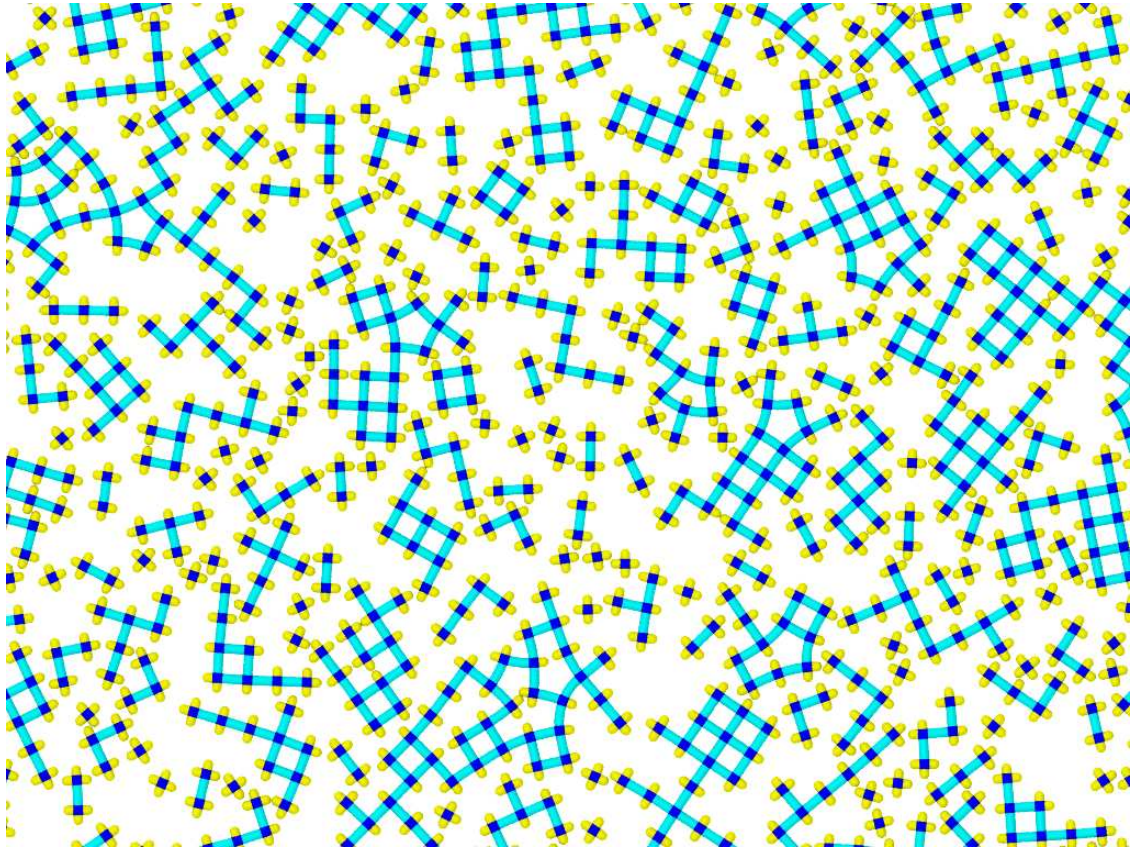Figure S8: Snapshot of polymerization at time $t = 10,000$.

Figure S9: Snapshot of polymerization at time $t = 12,000$.
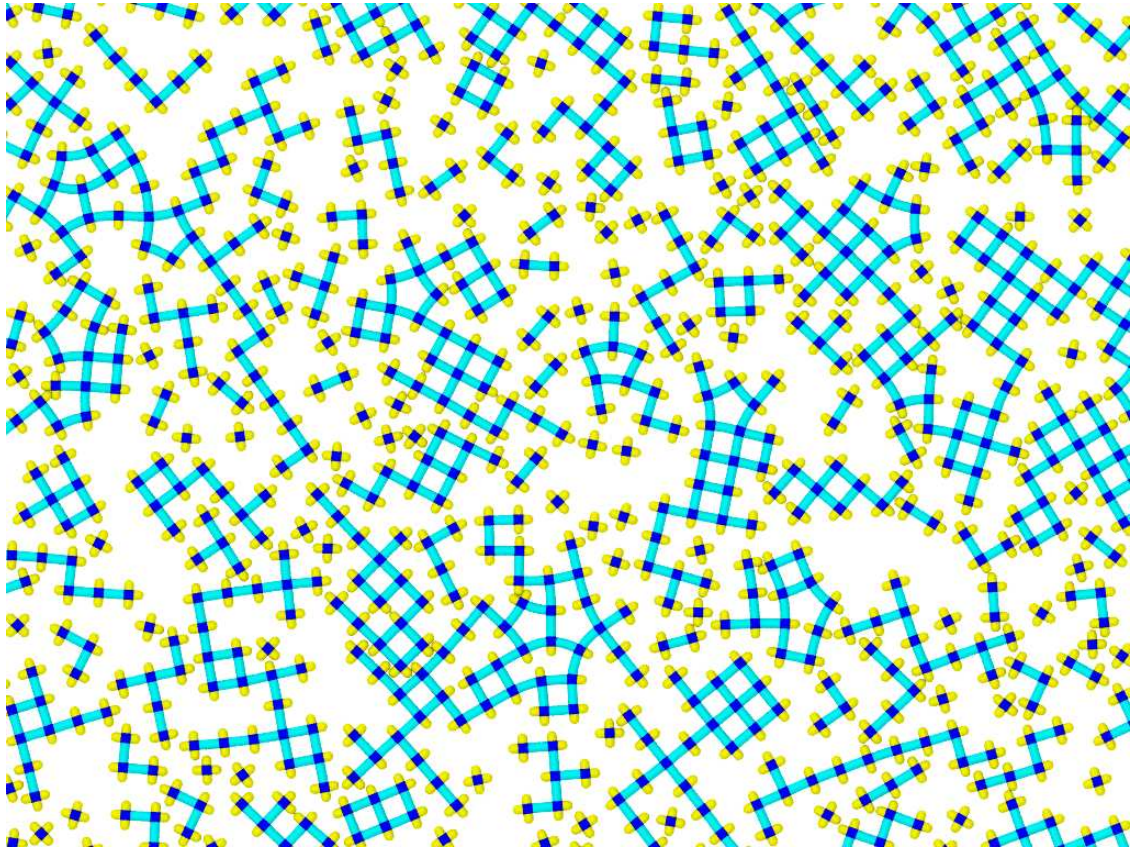
Figure S10: Snapshot of polymerization at time $t = 14,000$.
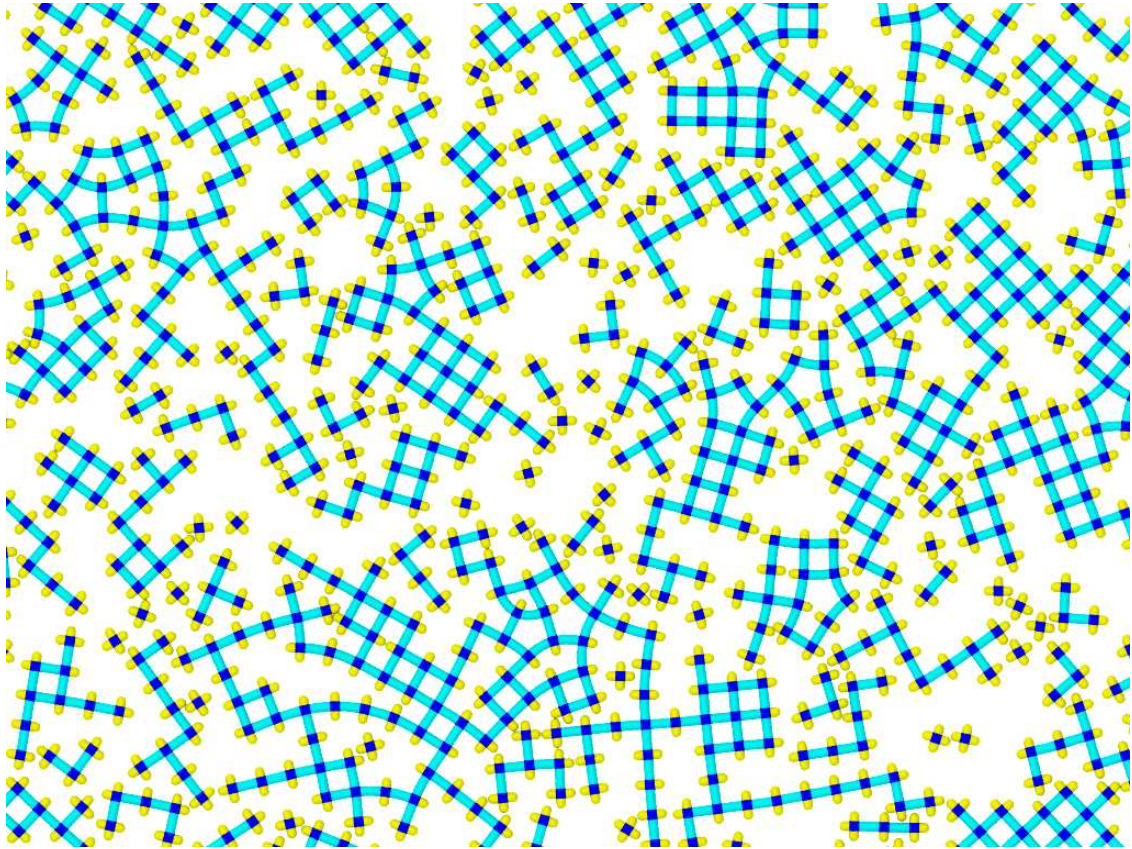
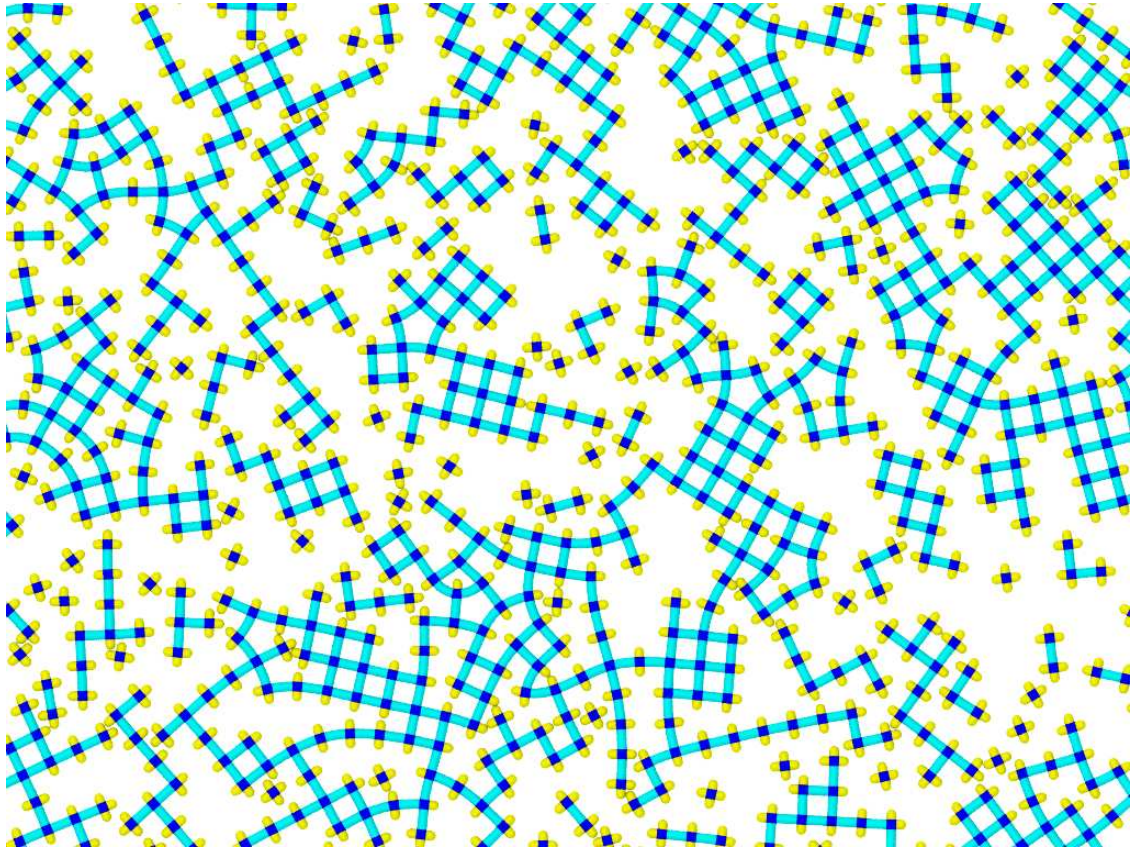Figure S11: Snapshot of polymerization at time $t = 16,000$.

Figure S12: Snapshot of polymerization at time $t = 18,000$.

Figure S13: Snapshot of polymerization at time $t = 20,000$.
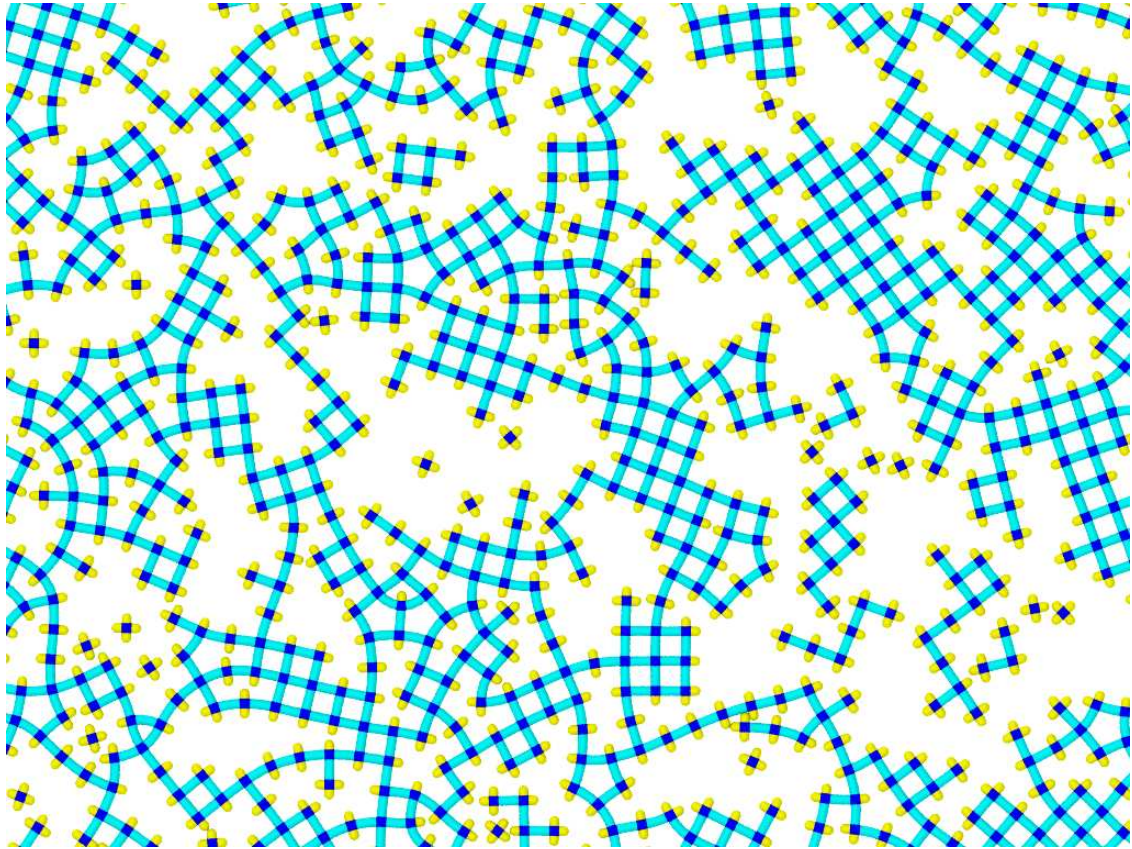
Figure S14: Snapshot of polymerization at time $t = 30,000$.
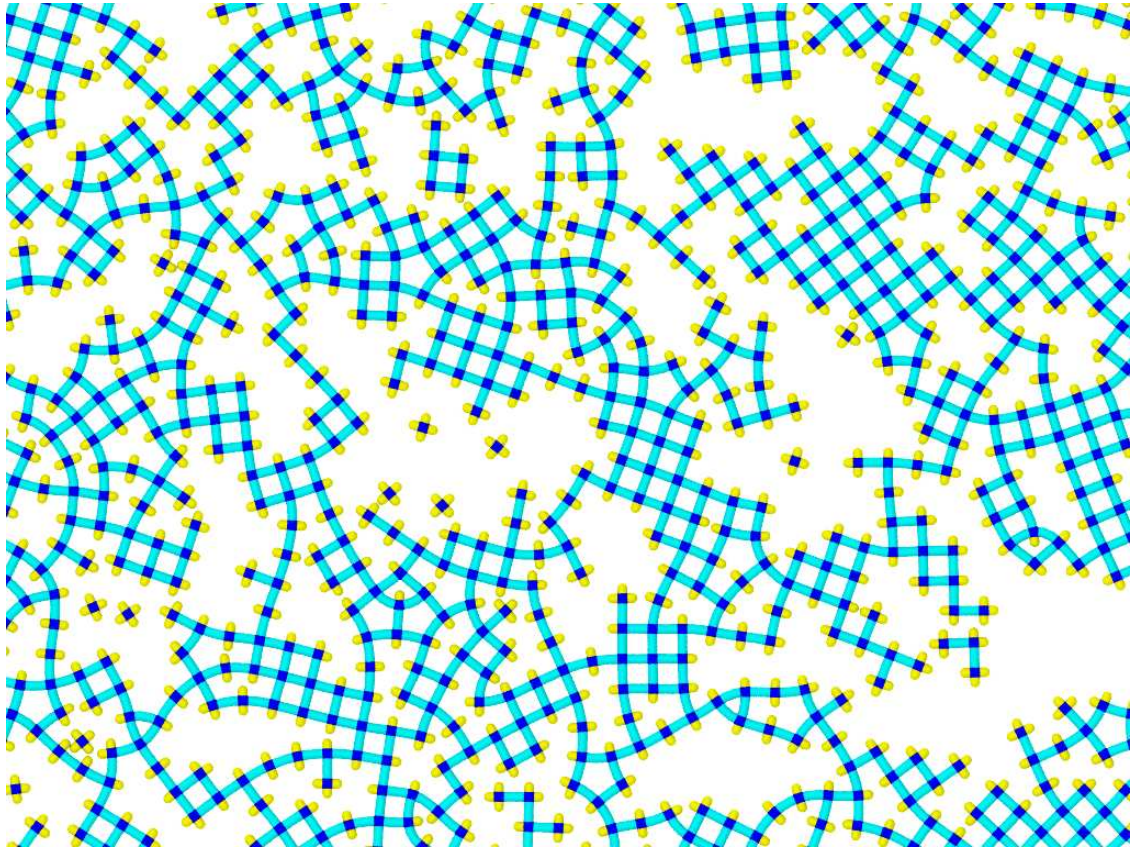
Figure S15: Snapshot of polymerization at time $t = 40,000$.
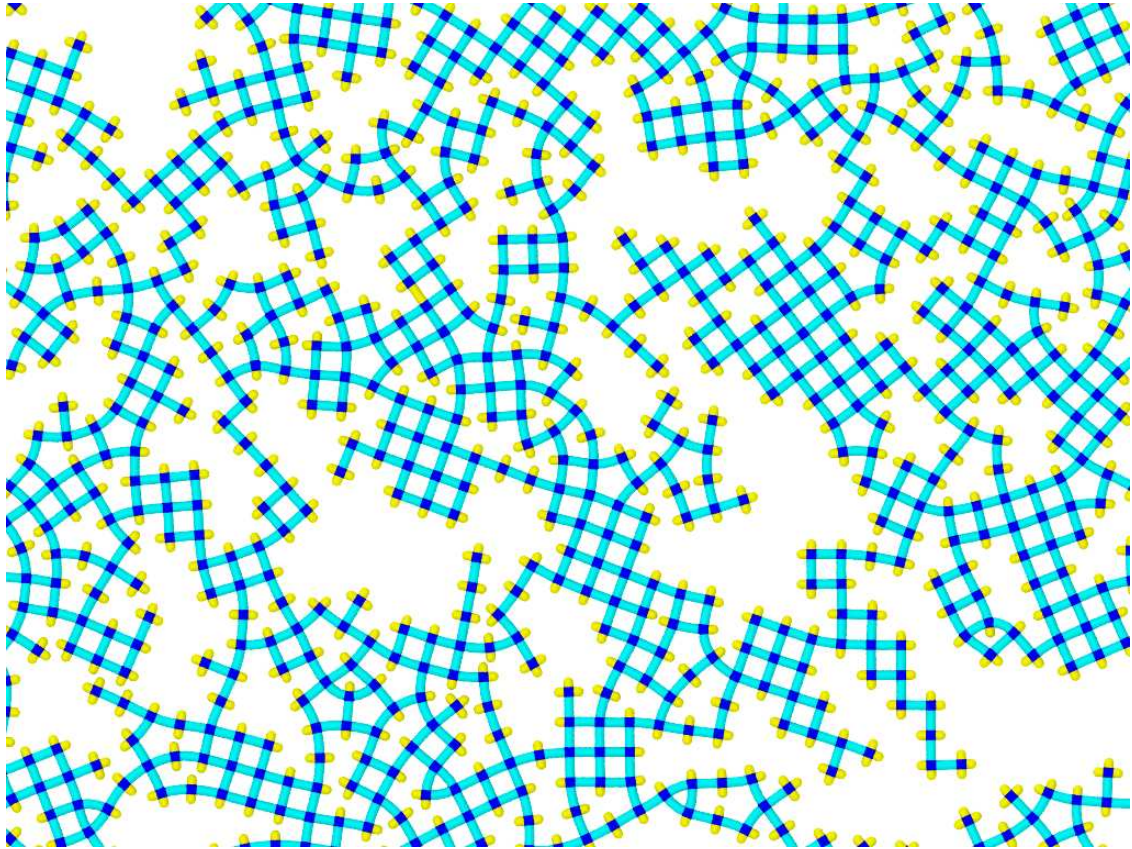
Figure S16: Snapshot of polymerization at time $t = 1,000,000$.
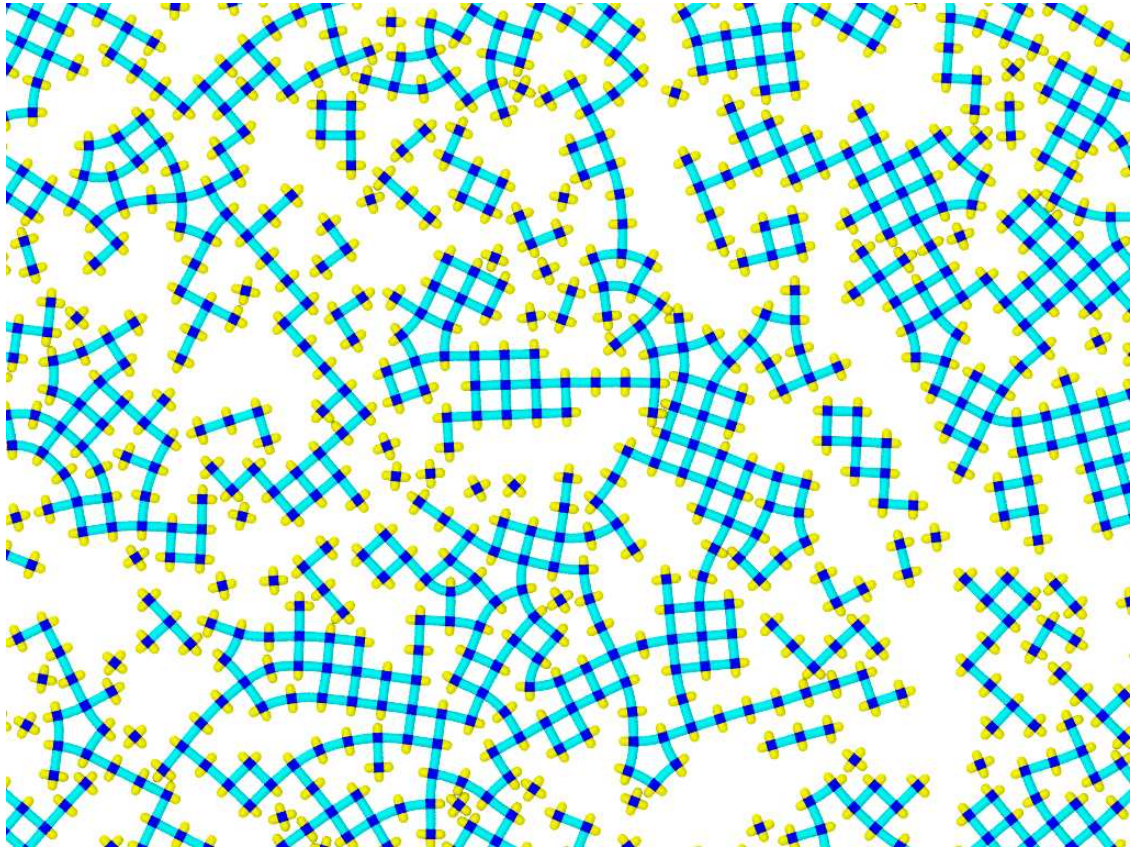
# (S2) Snapshots of 2D COFs with initial defects
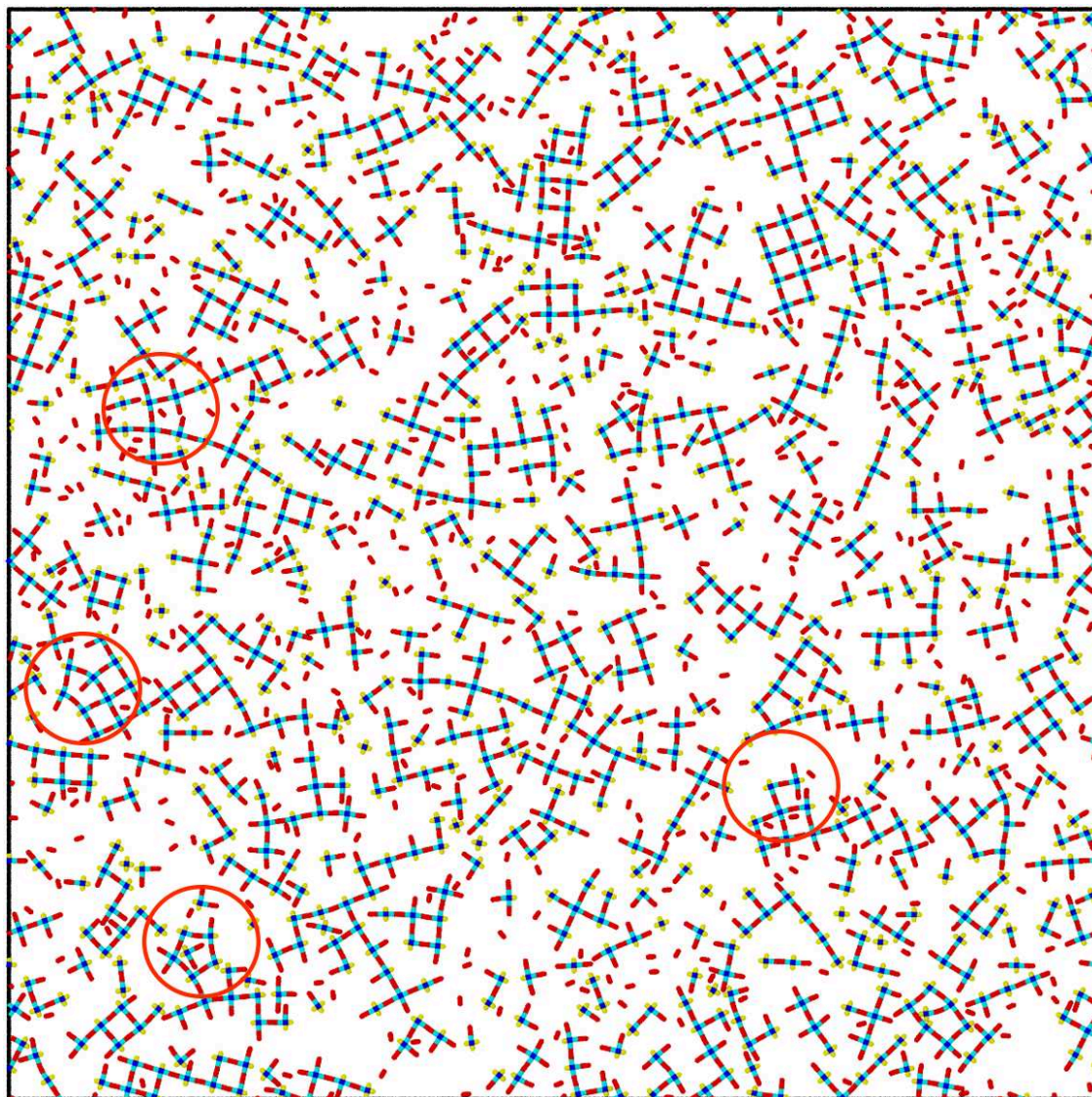


Figure S17: Snapshot of $[C_4 + C_2]$ with uncontrolled nucleation and $\varphi = 180$ degrees, when the initial defects of five-member ring that are circled by red circle, emerge.
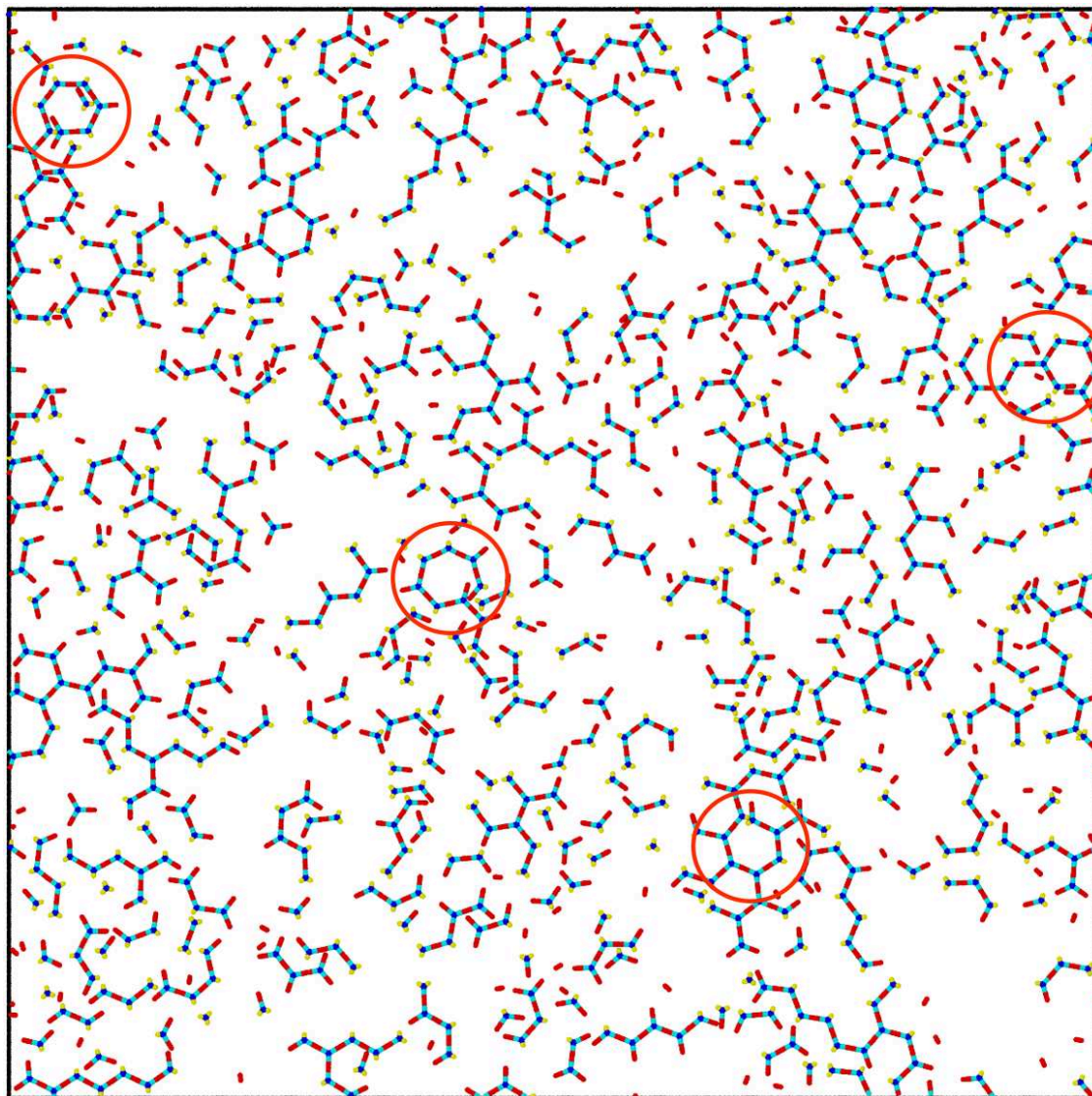
Figure S18: Snapshot of $[C_3 + C_2]$ with uncontrolled nucleation and $\varphi = 180$ degrees, when the initial defects of seven-member ring that are circled by red circle, emerge.
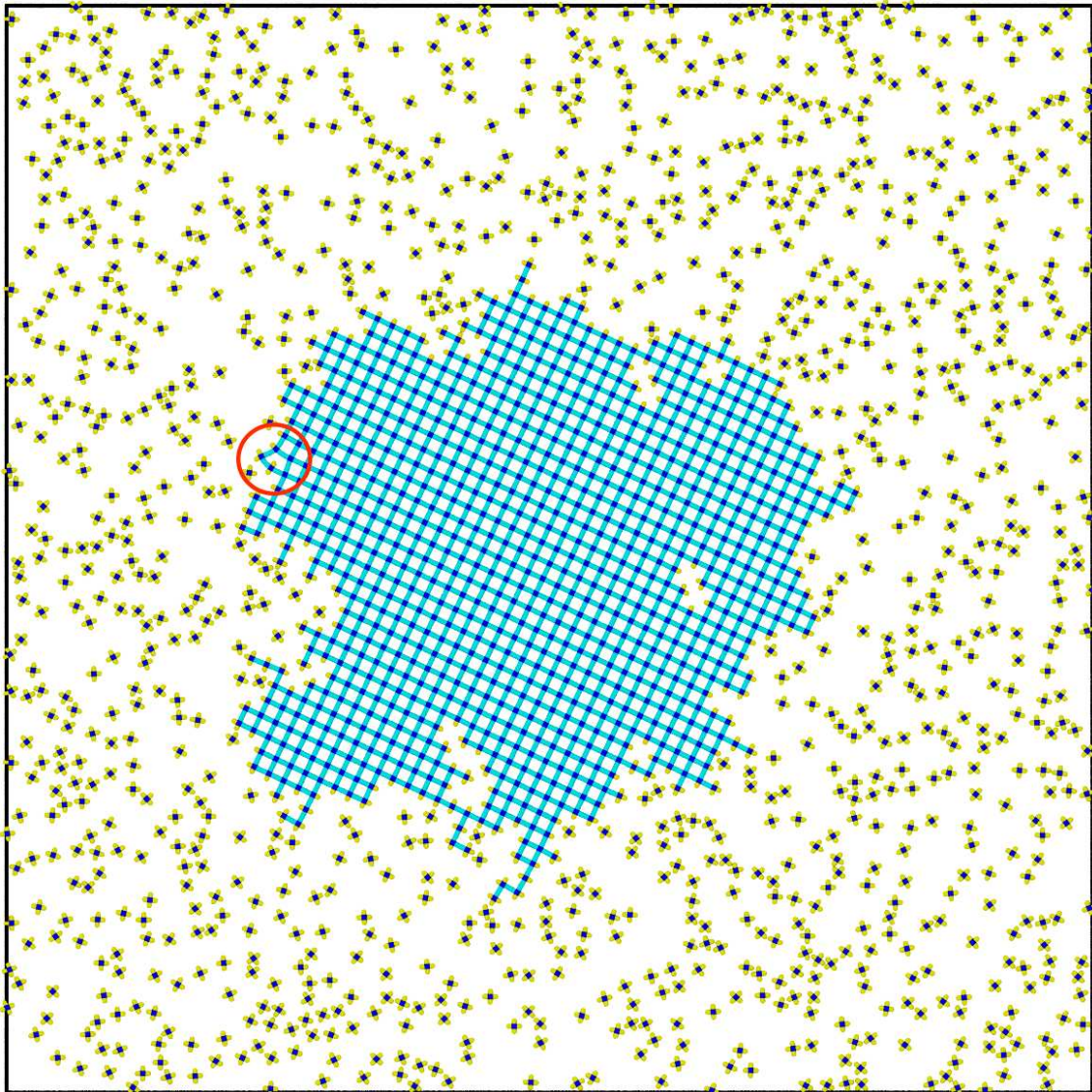
Figure S19: Snapshot of $[C_4 + C_4]$ through the seeded growth with suppressed nucleation and $\varphi = 180$ degrees, when first defect of five-member ring that are circled by red circle, emerges.
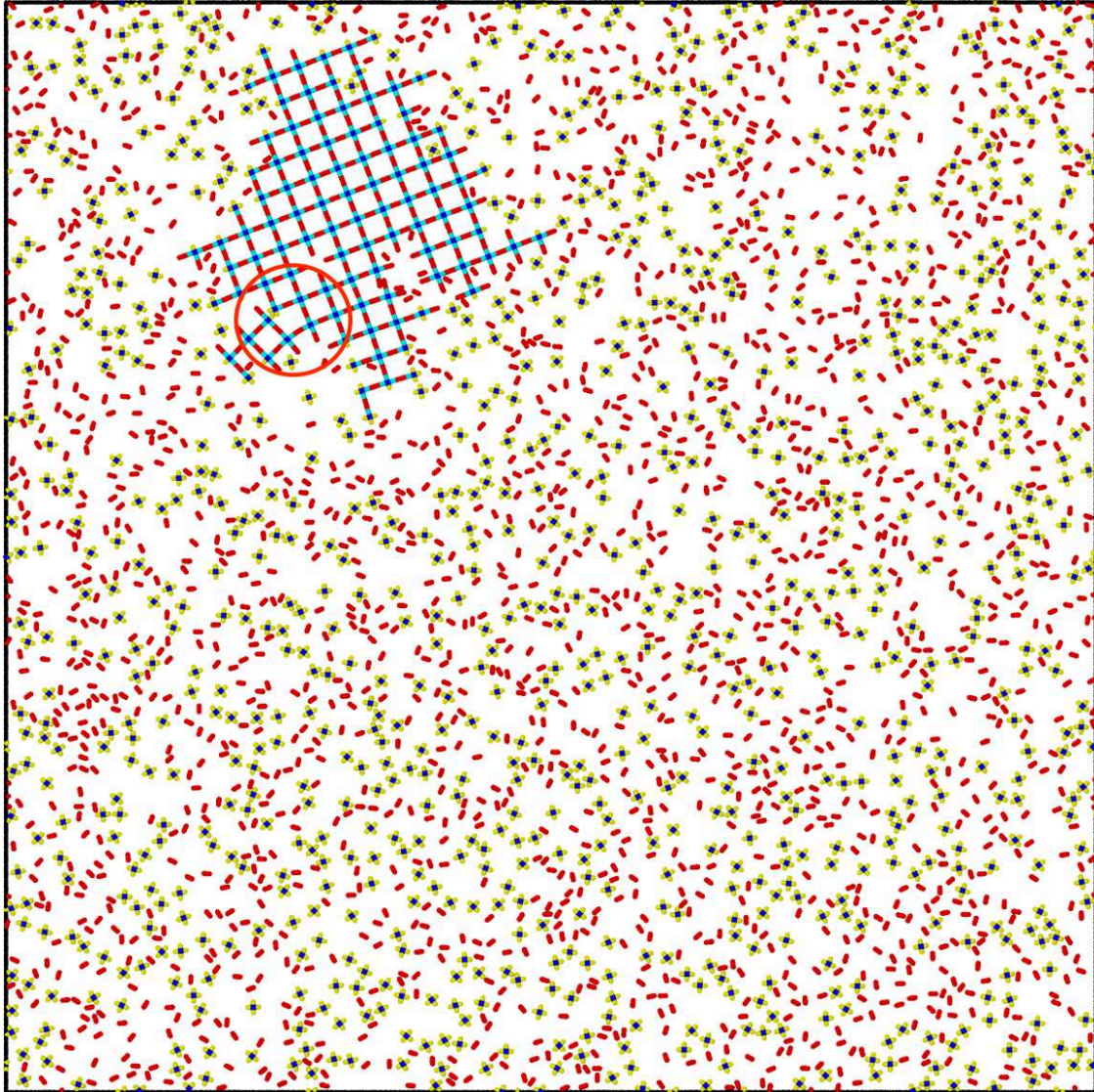
Figure S20: Snapshot of $[C_4 + C_2]$ through the seeded growth with suppressed nucleation and $\varphi = 180$ degrees, when first defect of five-member ring that are circled by red circle, emerges.

Figure S21: Snapshot of $[C_3 + C_3]$ through the seeded growth with suppressed nucleation and $\varphi = 180$ degrees, when first defect of seven-member ring that are circled by red circle, emerges.

Figure S22: Snapshot of $[C_3 + C_2]$ through the seeded growth with suppressed nucleation and $\varphi = 180$ degrees, when first defect of seven-member ring that are circled by red circle, emerges.
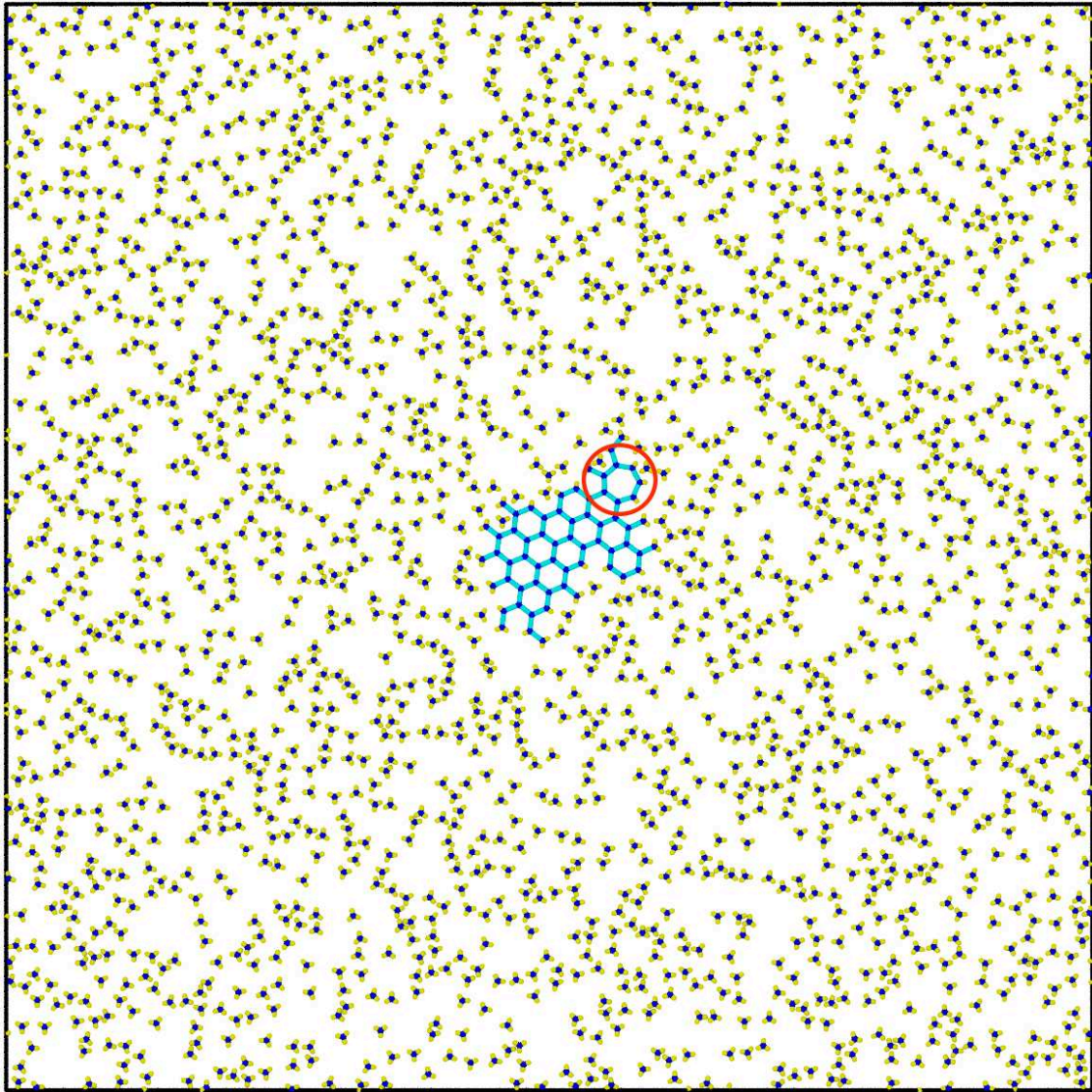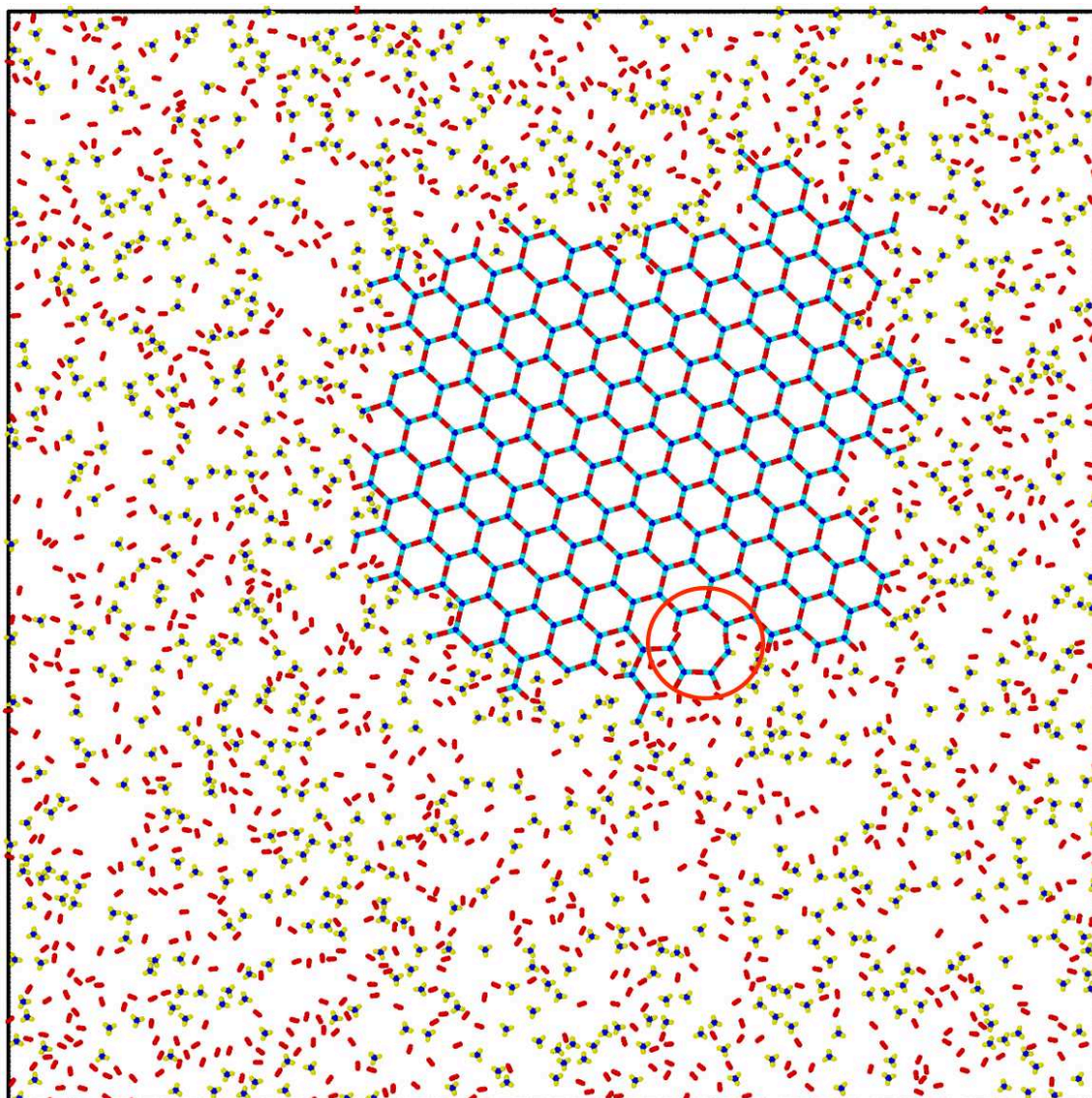
# (S3) Pore size analysis algorithm

For the convenience of reading, we rewrite the description of this algorithm that is the same as the one in the Supporting Information of our previous work.[1] To analyze the structure of two-dimensional covalent organic frameworks, we employ a move-and-grow algorithm to measure the distribution of pore sizes, which has been successfully applied in the detection of porous aromatic framework systems.[1-3] In this method, testing particles are randomly placed in box starting with a diameter $d = 0.01$. The testing particles interact with surrounding particles with a potential form, $V(r) = dr^2(\frac{1}{r} - \frac{1}{d})^2, r < d$, where $d$ is the diameter of testing particle. The testing particles move under the forces of surrounding particles by $d\vec{s} = dt \sum \vec{F_j}$. And at same time, the diameter of testing particles grows with $d = d + \gamma dt$. The growth of diameter stops when the potential exceeds a threshold $V_0$ vale. A modest growth rate is chosen for the measurement of the distribution of pore size. We use $10^6$ testing particles with $V_0 = 6$, $dt = 0.02$, and $\gamma = 0.1$ for the calculation. When the testing particle stops growing, its diameter could be larger than the size of pore. Then we calculate the pore size by averaging the distance of the surrounding particles from the testing particle or counting the number of the surrounding particles. In this work, we present the pore size by the number of monomer units, each having four particles, around the pore.

# References

(1) Zhu, Y.-L.; Fu, C.-L.; Li, Z.-W.; Sun, Z.-Y. Building Block Design for Minimizing Defects in the Construction of Two-Dimensional Covalent Organic Frameworks. *J. Phys. Chem. Lett.* **2019**, *11*, 179–183.

(2) Li, M.; Ren, H.; Sun, F.; Tian, Y.; Zhu, Y.; Li, J.; Mu, X.; Xu, J.; Deng, F.; Zhu, G. Construction of Porous Aromatic Frameworks with Exceptional Porosity via Building Unit Engineering. *Adv. Mater.* **2018**, *30*, 1804169.

(3) Tian, Y.; Song, J.; Zhu, Y.; Zhao, H.; Muhammad, F.; Ma, T.; Chen, M.; Zhu, G. Understanding the desulphurization process in an ionic porous aromatic framework. *Chem. Sci.* **2019**, *10*, 606–613.