

Electronic Supplementary Information

**Orientation Transitions during the Growth of Imine Covalent
Organic Framework Thin Films**

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Instruments and Methods. All of the chemicals were purchased from Sigma Aldrich. Scanning electron microscopy (SEM) images were recorded using a Zeiss Gemini Ultra-55 Analytical Scanning Electron Microscope using a beam energy of 1 kV. Grazing incidence wide angle X-ray scattering (GIWAXS) was conducted at Beamline 7.3.3 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, using an approximately 0.5 mm wide 10 keV X-ray beam. Near-edge X-ray absorption fine structure (NEXAFS) data were acquired at beamline 11.0.2.2 at ALS. Film thicknesses were determined on a Veeco Dektak 150 Surface Profilometer.

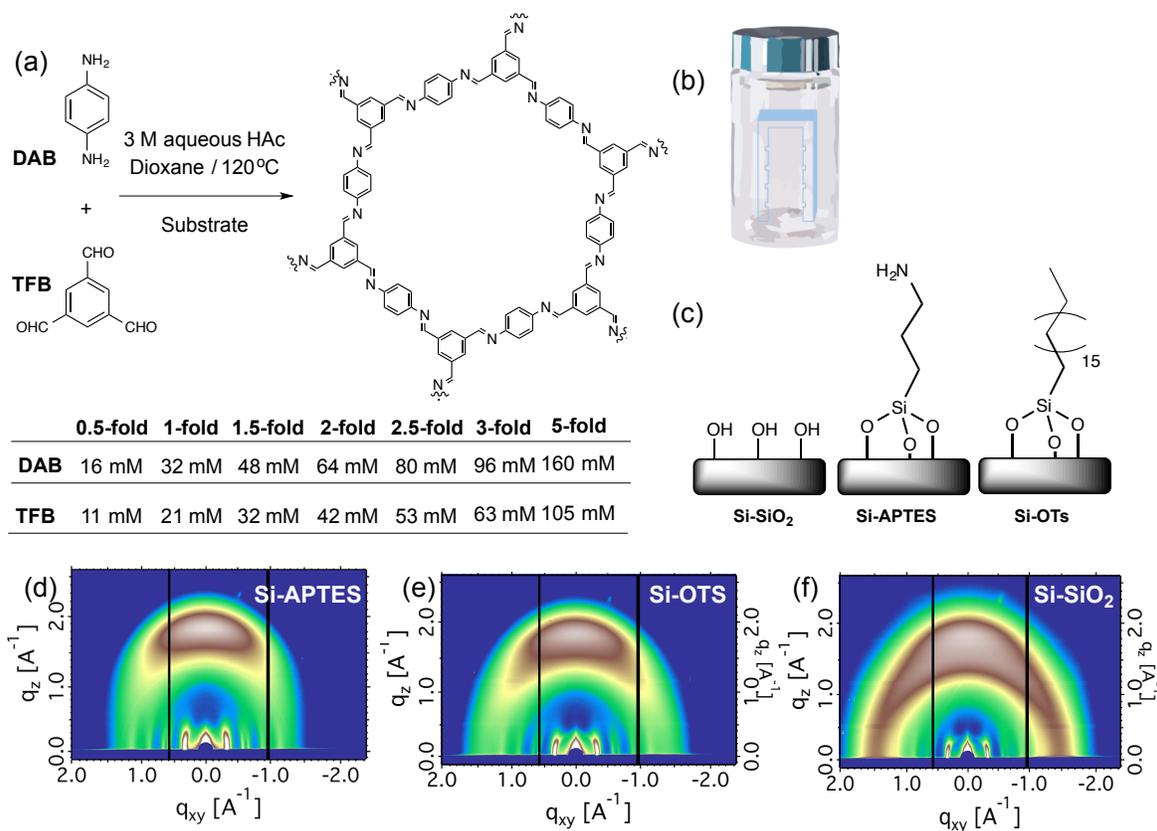


Figure S1. (a) Reaction scheme for the formation of COF-LZU1 at different concentrations. (b) Illustration of the reaction setup that involves a customized Teflon rack with four parallel slots enclosed in a sealed reaction vial. (c) Si surfaces functionalized with APTES and OTS SAMs and native oxide. GIWAXS patterns of thin films grown from (d) Si-APTES, (e) Si-OTS and (f) Si-SiO₂.

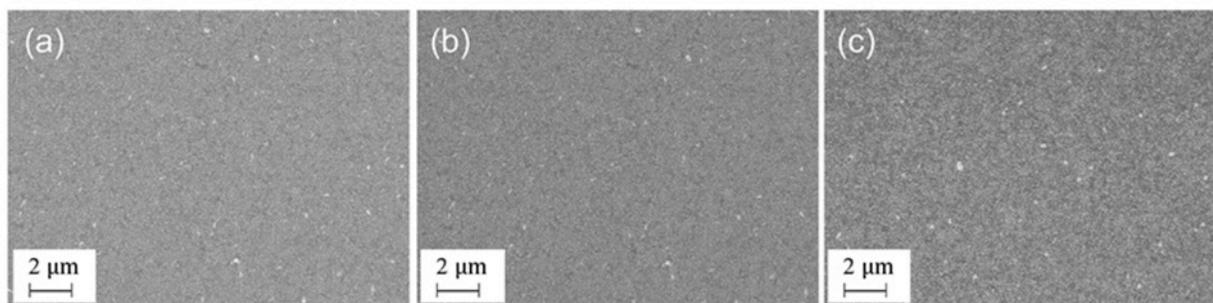


Figure S2. SEM images of continuous thin films grown on (a) Si-APTES, (b) Si-OTS, (c) Si-SiO₂ substrates showing good coverage after reacting the 1-fold mixture for 48 hours.

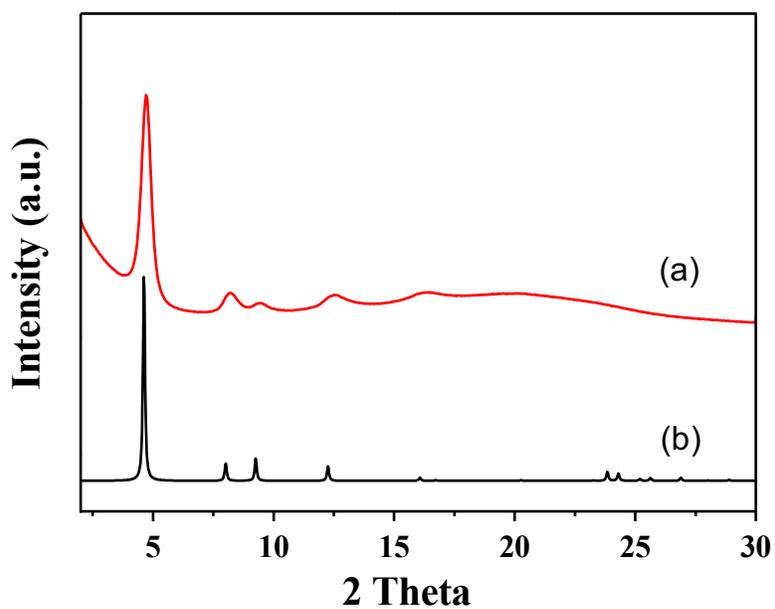


Figure S3. (a) The lateral linecut of the GIWAXS profile of the COF-LZU1 thin film from 1.5-fold mixtures after 84 h, (b) Simulated PXR D pattern for the COF-LZU1 powder.

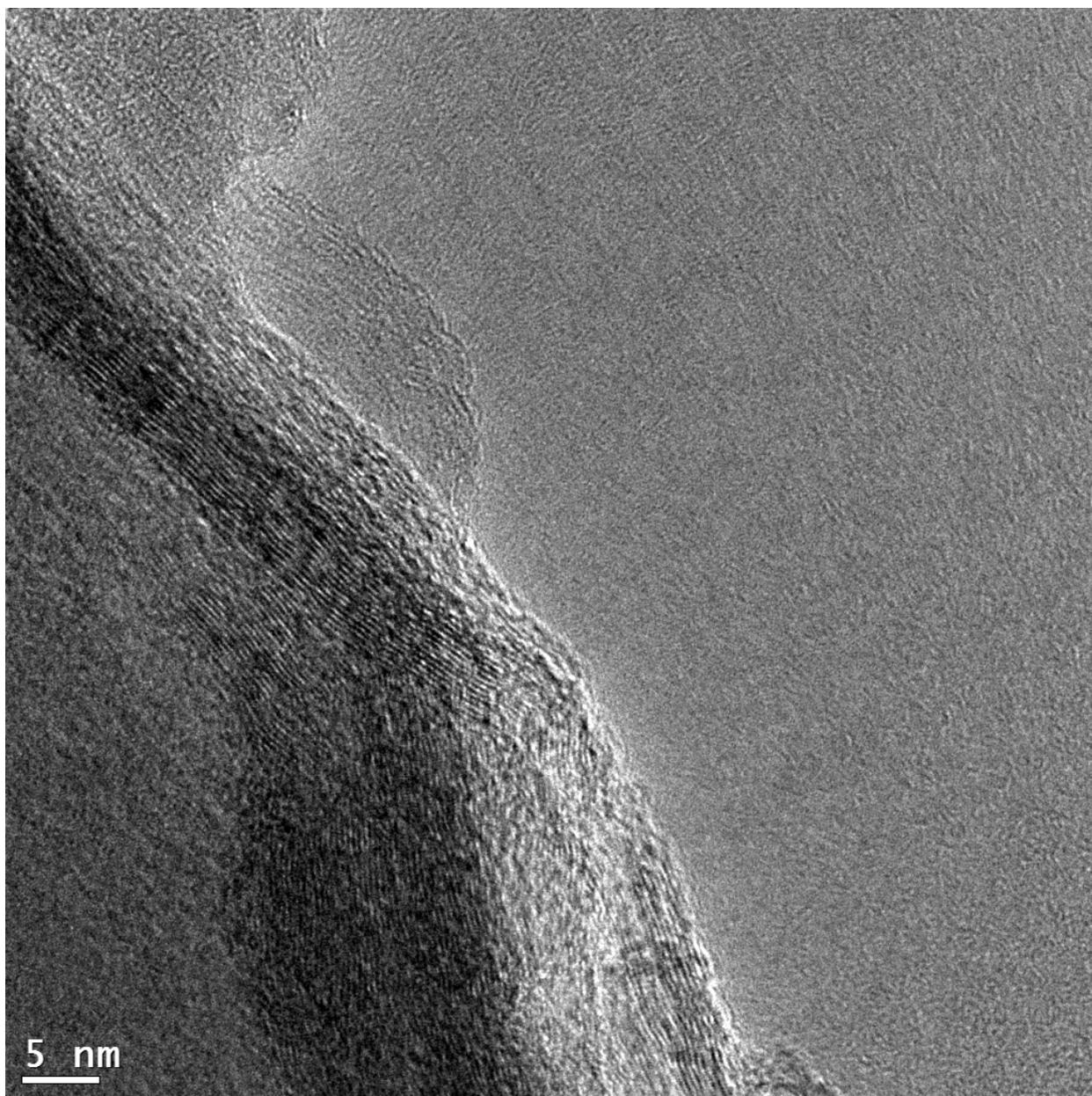


Figure S4. TEM image of a slice of COF thin film transferred onto a TEM grid, showing the layered stacking structure.

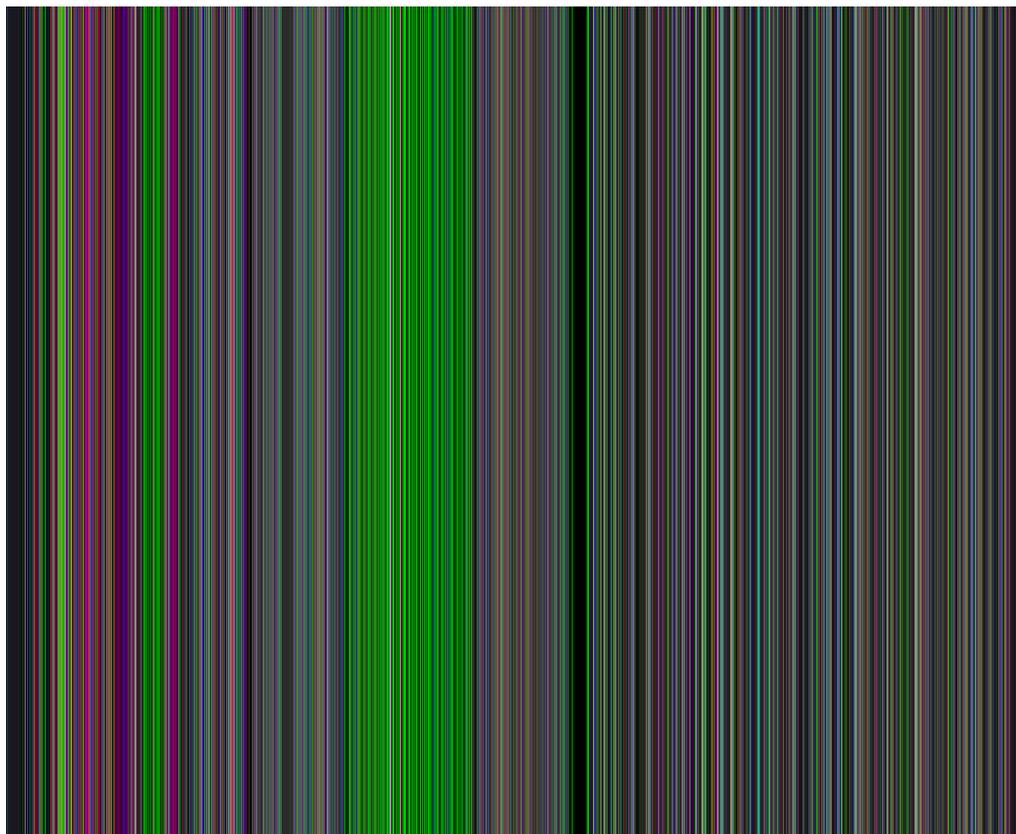


Figure S5. Cross-section SEM of COF thin films grown from different concentrations after 48 hours reaction on Si-APTES substrates. The white arrows indicate the COF layers. (a) 0.5-fold, (b) 1-fold, (c) 1.5-fold, (d) 2-fold, (e) 2.5-fold, (f) 3-fold, and (g) 5-fold mixtures.

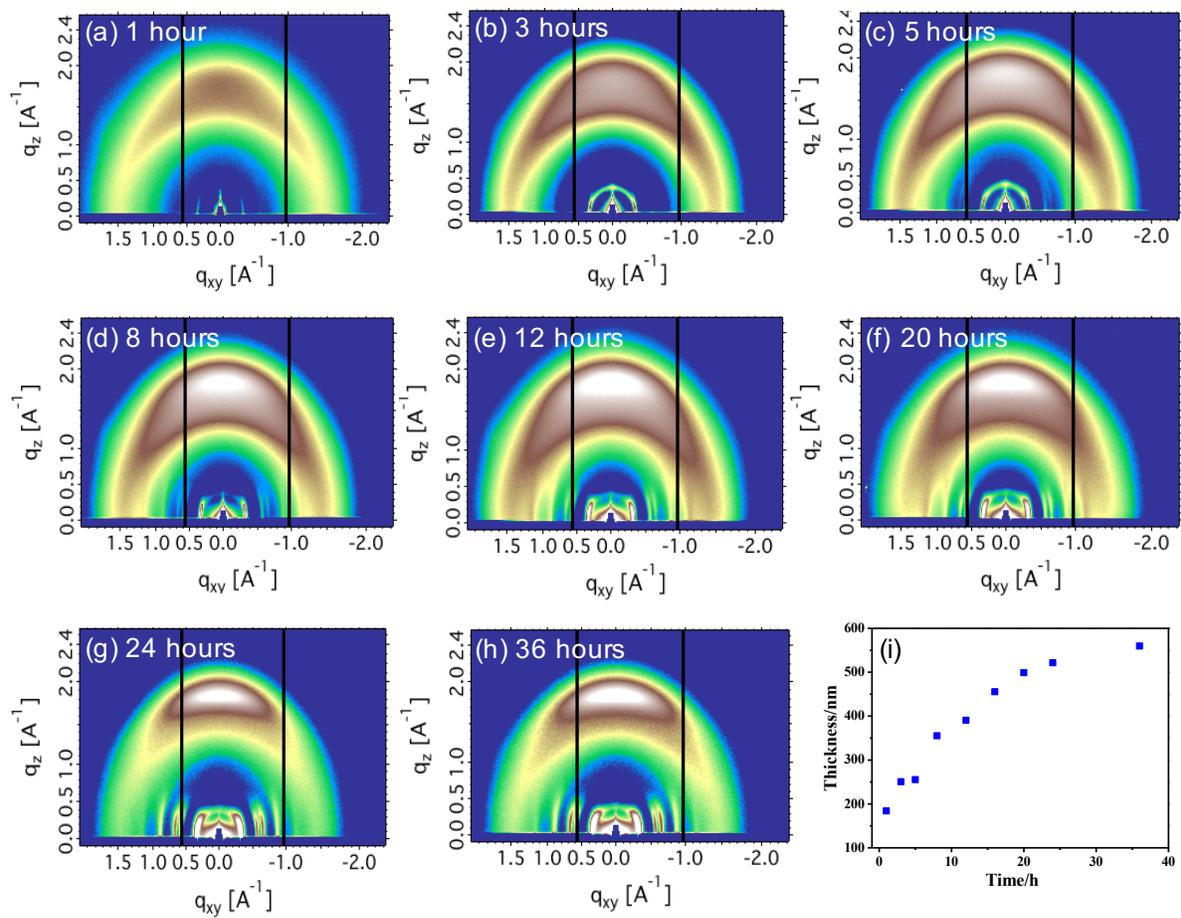


Figure S6. GIWAXS patterns of thin films grown on Si-SiO₂ substrates from 5-fold mixtures at (a) 1 hour, (b) 3 hours, (c) 5 hours, (d) 8 hours, (e) 12 hours, (f) 20 hours, (g) 24 hours, and (h) 36 hours. (i) The plot of film thickness against different reaction time.

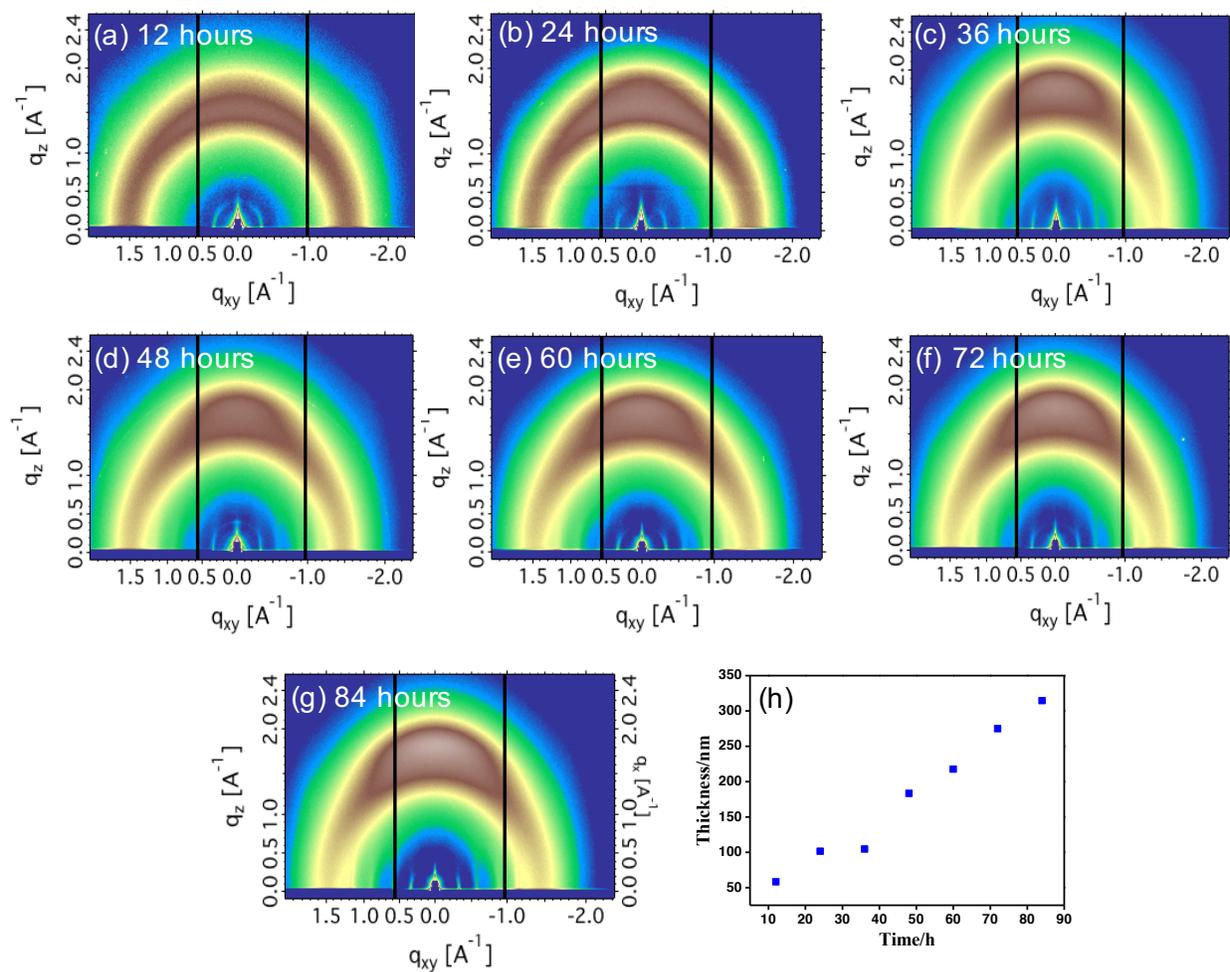


Figure S7. GIWAXS patterns of thin films grown on Si-SiO₂ substrates from 1.5-fold mixtures at (a) 12 hour, (b) 24 hours, (c) 36 hours, (d) 48 hours, (e) 60 hours, (f) 72 hours, and (g) 84 hours. (h) The plot of film thickness against different reaction time.

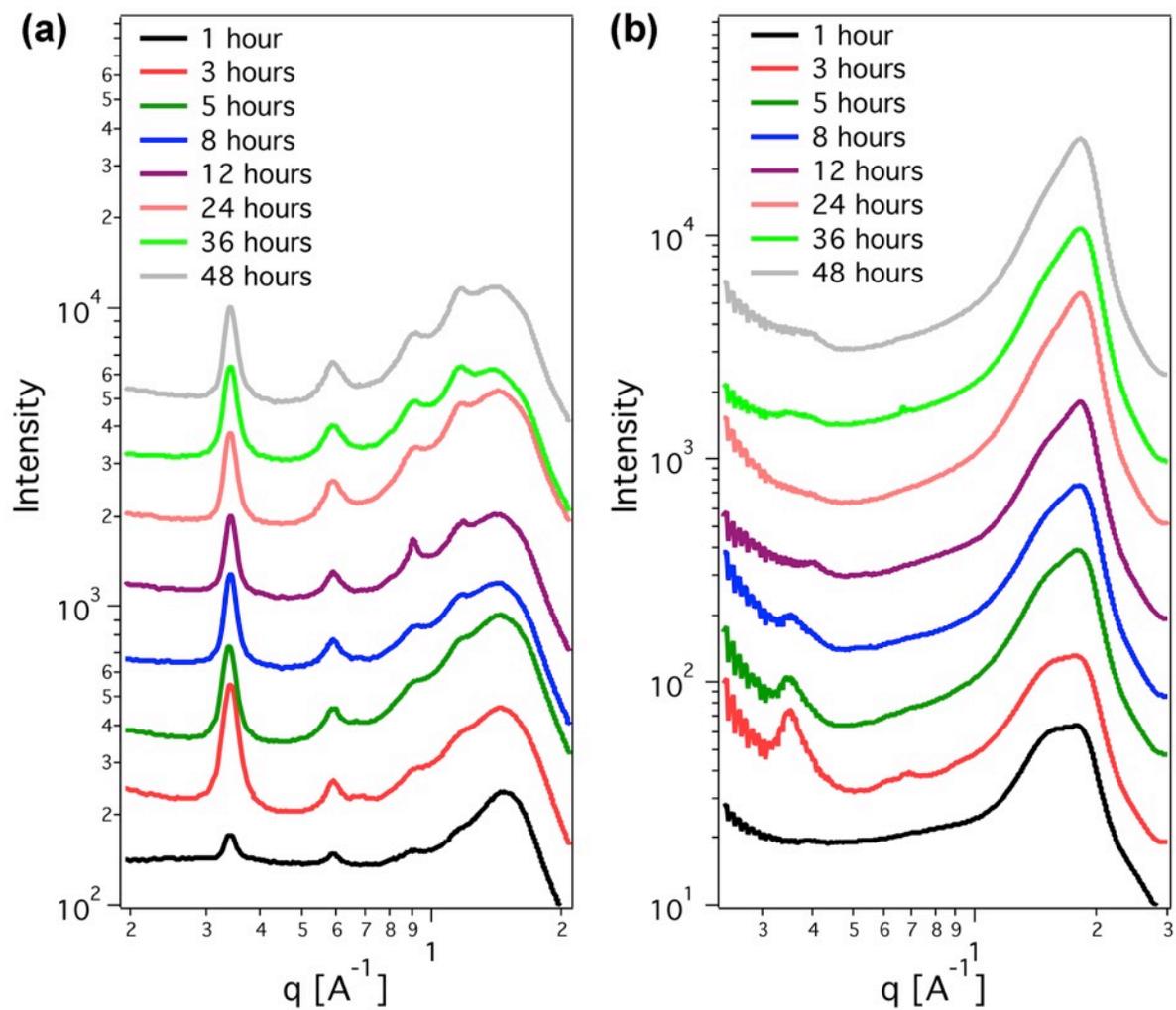


Figure S8. Stacked plots of (a) in-plane and (b) out-of-plane linecuts at different times for thin films grown from 5-fold reactions.

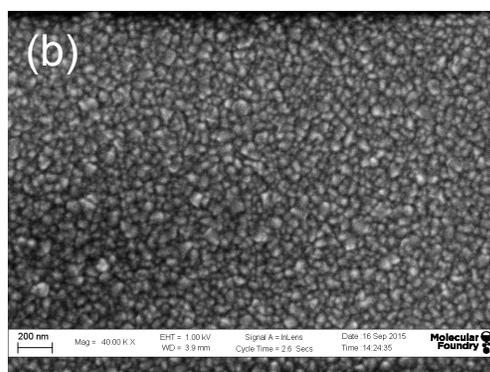
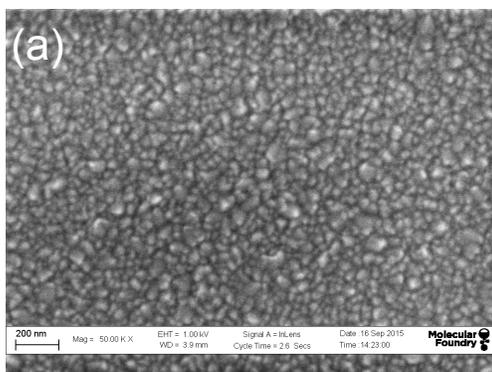


Figure S9. SEM images of thin films from the 1.5-fold reactions after (a) 24 h and (b) 48 h reaction time. The scale bar is 200 nm.