Transient phases as a route to self-assembly of organic semiconductor thin films

Supplementary information

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Estimation of X-ray penetration depth

The penetration length Λ is estimated from the transmitted angle α'.[1]

$$\Lambda = \frac{1}{2kIm(\alpha')} \quad \text{and} \quad \alpha^2 = \alpha'^2 + \alpha_c^2 - 2i\beta$$

k is the wavevector calculated by $\frac{2\pi}{\lambda}$, β is the imaginary part of the index of refraction given the chemical formula and density of Chlorobenzene and photon energy of the X-ray beam.

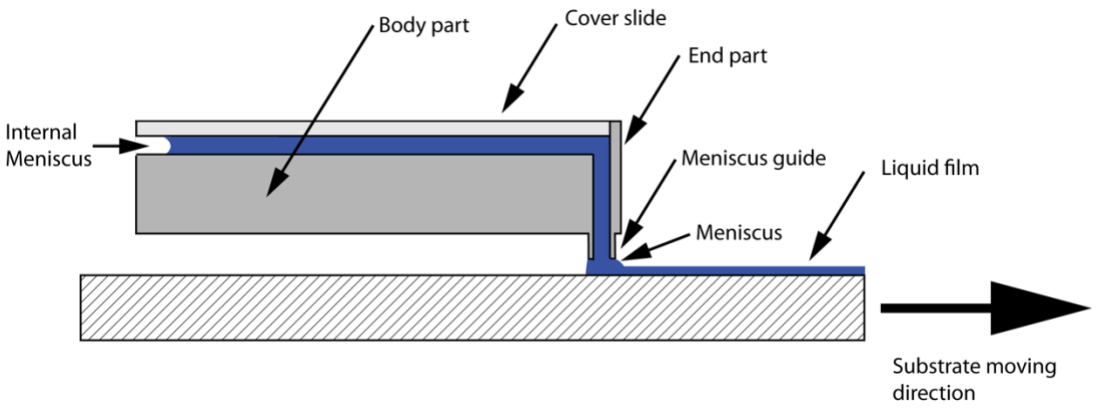

Figure S1. Schematic of the writing process showing internal details of the channel and the reservoir. The internal meniscus creates a capillary force that prevents the solution from running out of the writing head under its own weight when no deposition is occurring.

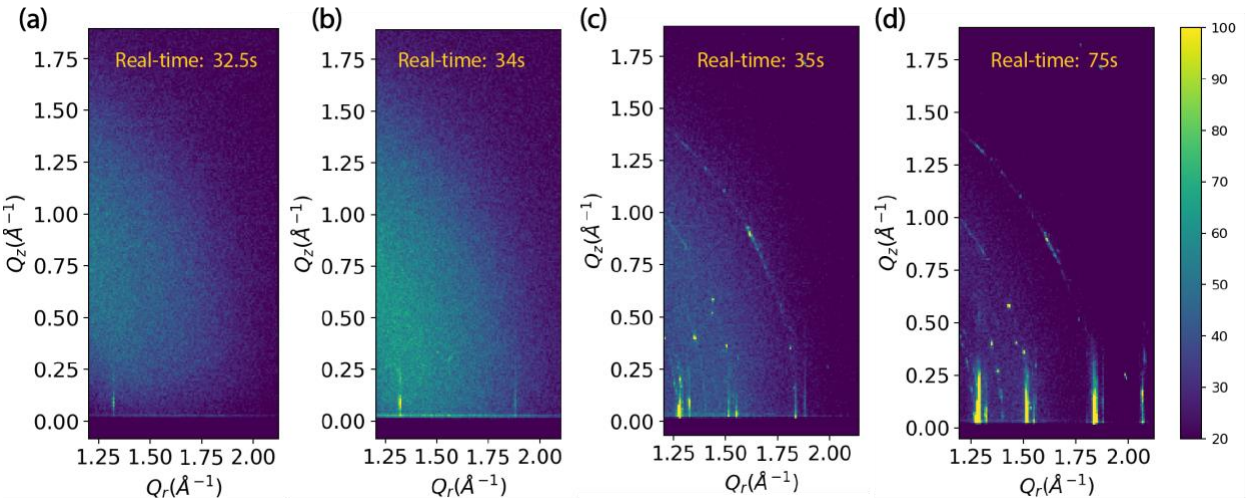

Figure S2. Frames from the real-time deposition of Ph-BTBT-C_{10} written at 0.2mm/s and 90°C to show the solution ring and peaks, which is supplementary for Figure 3 in the paper. GIWAXS image of the films at (a) 32.5s with solution ring showing up. (b) 34s with intense solution ring and a peak at Q_r = 1.32 $Å^{-1}$. (c) 35s with solution ring just gone. (d) 75s at the end of the time series.

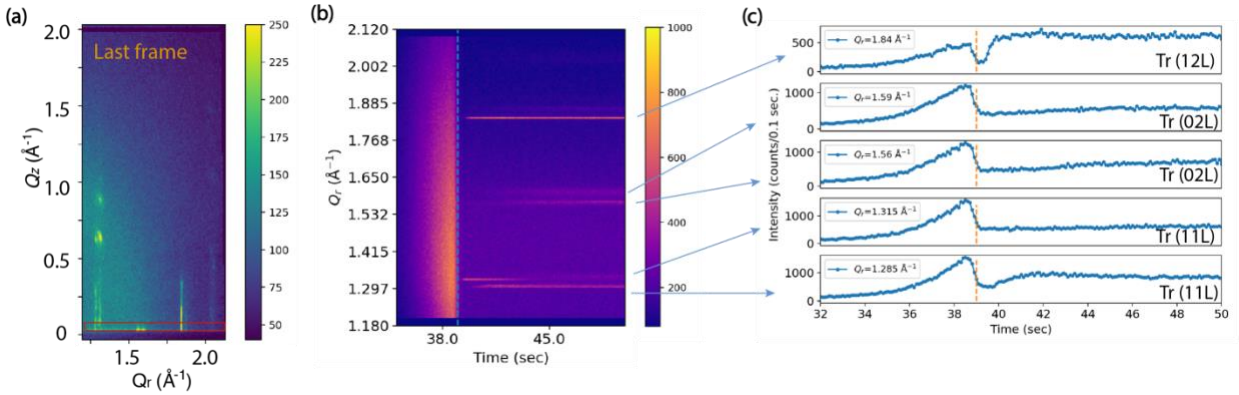

Figure S3. Observation of real-time deposition for Ph-BTBT-C_{10} solution in chlorobenzene written at 0.2mm/s and 80°C. The film thickness (a) GIWAXS image of the films at the end of the time series. (b) A sum of intensities of the interested region indicated in the red box at Q_z = 0.03-0.05 $Å^{-1}$, over the time of deposition process. (c) The corresponding intensity plot over time for certain Q_r positions as the arrows point to. The vertical dash lines in (b,c,e,f) indicate the time when the writer passes the X-ray beam, and thus the newly deposited film is being detected.

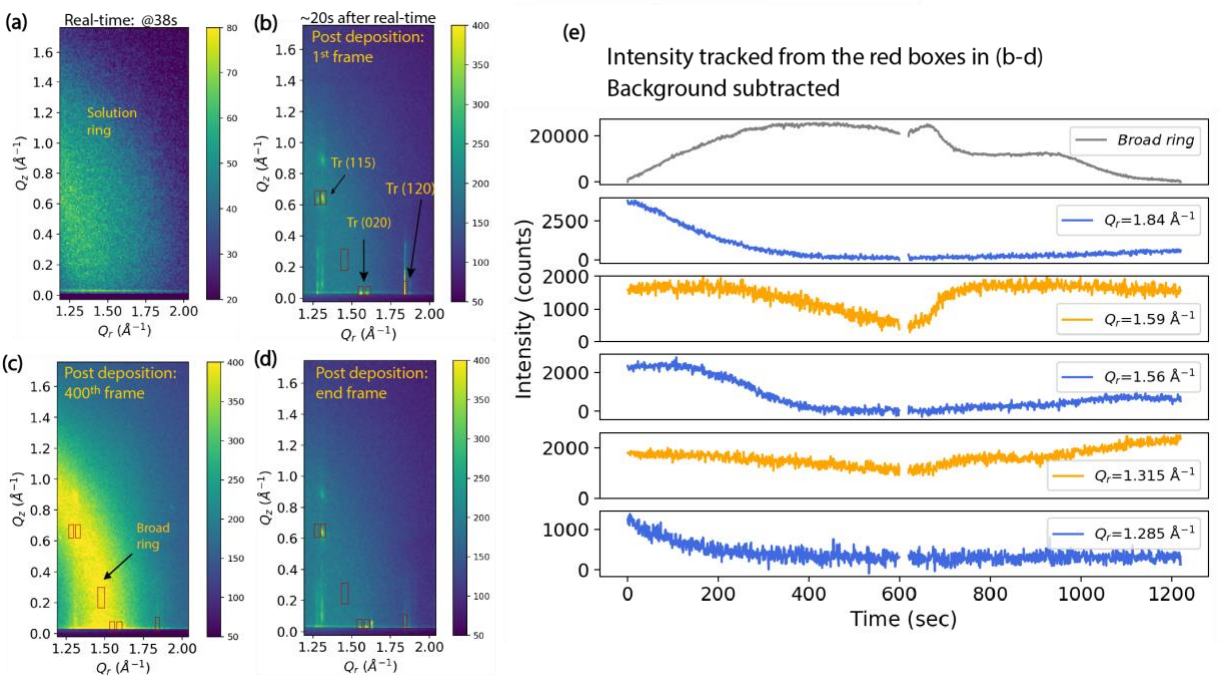

Figure S4. Observation of post deposition film at 1 frame/sec for two 10-min sections, starting around 60 seconds after the film is being detected in the real-time series. (a) An image of solution ring at 38 second of the real-time series before film is written, served as a comparison of the ring in (c). (b) The first frame of the post deposition series, which starts around 20s after the real-time movie is finished. The red boxes indicate the peak intensities being traced in (e). (c) The 400th frame shows a broad ring feature shown up for about 10 minutes. (d) The last frame of the post deposition series. (e) The major intensity track of the peaks and the ring feature. In-situ time is not counted.

Figure S3 shows the intensity fluctuations happening in a 20 minutes post deposition period, which involves self-assembly of molecules. As shown in Figure S3(c), an unusual feature of a broad ring showed up and was tracked in Figure S3(e) in grey, which is clearly different from the solution ring in Figure S3(a). The solution ring is more scattered, suggesting the molecules are in an isotropic state. The ring in Figure 3(c) has a width about 0.2 Å^{-1}, which corresponds to a domain size around 31 Å. It looks like the small domains were going through a highly disordered process. At the end of the post deposition period, the peaks or rods at Qr~1.28 Å^{-1}, 1.56 Å^{-1} and 1.84 Å^{-1} have much less intensity from the beginning. These transient positions lead to lattice constants closer to SmE phase. On the other hand, the peaks closer to the crystalline phase (Qr~1.32 Å^{-1}, 1.59 Å^{-1}) have the same or slightly more intensity comparing with the beginning. It is possible the film is still undergoing some slow transformation to crystalline phase.

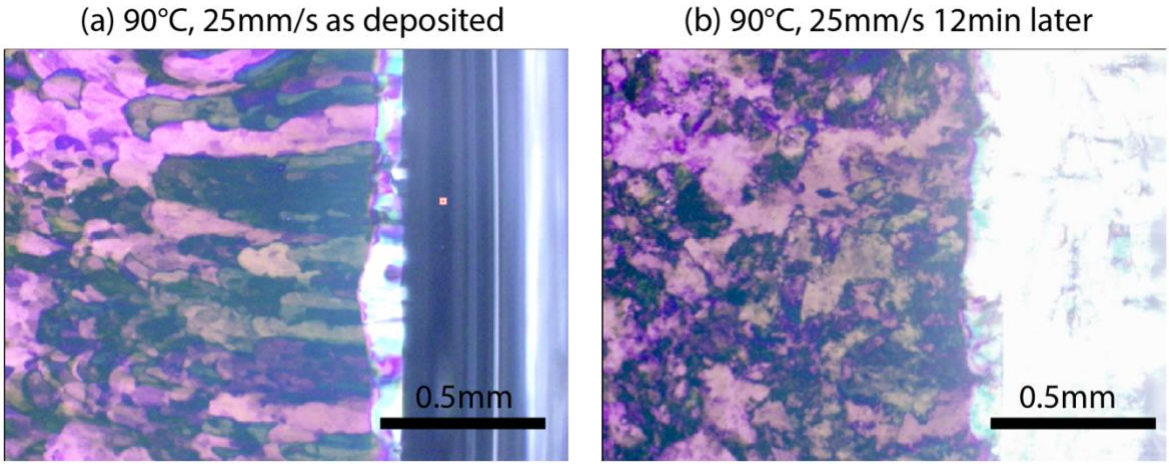

Figure S5. Frames from a polarized optical microscopy video during deposition at 90°C with solution in chlorobenzene and 25 mm/s writing speed. (a) The initial film right after the translational stage stops. (b) The re-nucleated film after 12 minutes when temperature was held at 90°C. The initial grain structure has been replaced.

Reference

1 Jens Als-Nielsen and Des McMorrow, *Elements of modern X-ray physics*. (John Wiley & Sons, 2011).