

## Supplementary Information

# Ultrafast Crystallization Dynamics at an Organic–Inorganic Interface Revealed in Real Time by Grazing Incidence Fast Atom Diffraction

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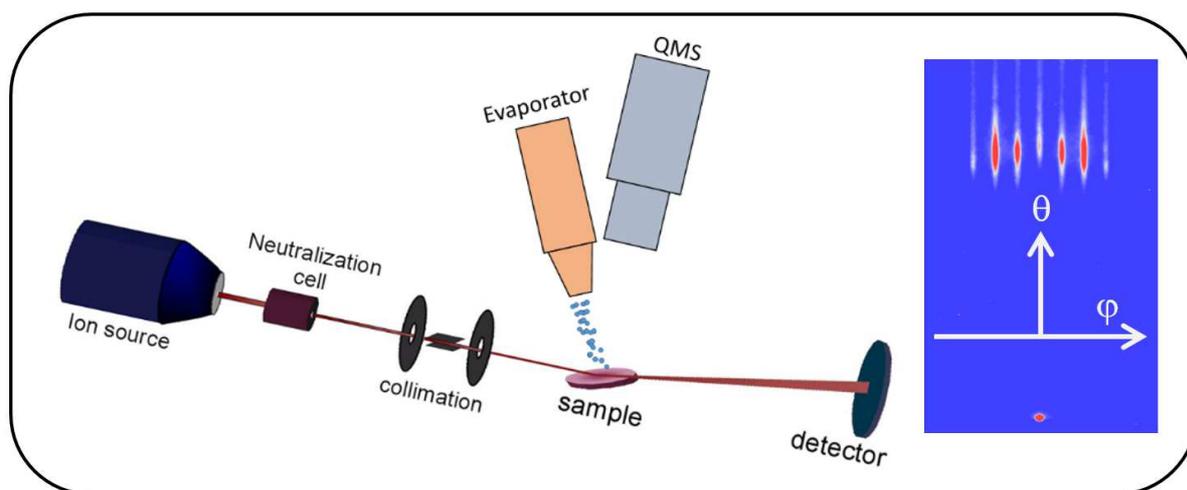
## Experimental method

The experimental scheme (see figure S1) consists in observing the scattering pattern of fast He atoms scattered off the Ag(110) surface during the deposition process. The probe beam is prepared as follows: He<sup>+</sup> ions are extracted from an ion source at energies typically in the range 300 -1000 eV. Following neutralization in a He gas cell, a nearly parallel neutral beam is produced by a set of collimating apertures with a size lower than 0.1 mm and directed to the sample surface at grazing angles that can vary between 0.3 and 1.2°; the probed sample area varies between 5x0.1 and 8x0.1 mm<sup>2</sup>. Reflected atoms are collected on a position sensitive detector made of Microchannel plates and a phosphor screen, and images captured by a CCD camera. A quadrupole mass spectrometer (QMS), with mass range of 300 a.m.u., is facing the sample; it is used to collect species desorbing during deposition.

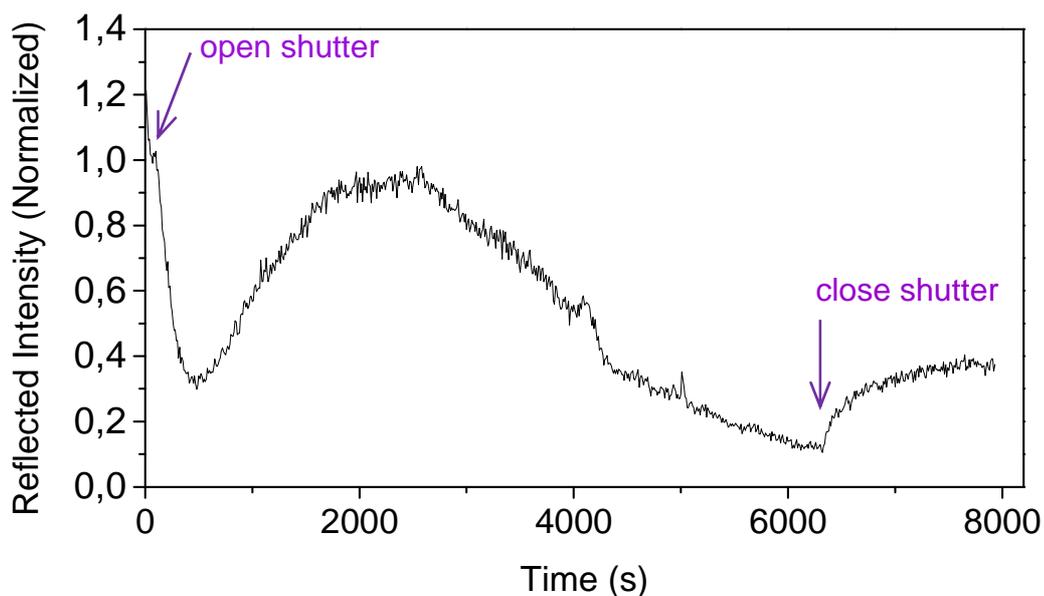
The Ag(110) substrate has been prepared very carefully by cycles of ion sputtering at 1 keV and annealing at 700°K. A good quality GIFAD pattern (see insert in figure S1) could only be observed after a much larger number of sputter/anneal cycles than typically required for a good LEED pattern. Although a well resolved diffraction pattern may initially be obtained by GIFAD, the reflectivity curve may only show a weak fluctuation at the transition (see figure S2), translating the reduced size of the domains adopting the S1 structure. The ultra-fast transition shown in both reflectivity and mean exit angle is only visible on a very well prepared substrate.

Perylene deposition is made from commercial powder by thermal evaporation in a Mo crucible at temperatures varying between 80° and 100°C; the results reported here were obtained with a constant temperature closer to 80°C. Although the evaporation rate could not be measured directly, a good estimate can be made from the time required to reach half a monolayer, which corresponds to the first minimum in the reflectivity curve. According to figure 1a, the deposition rate is on the order of 0.047 ML/min, this figure is higher than the rate used by Gao et al.

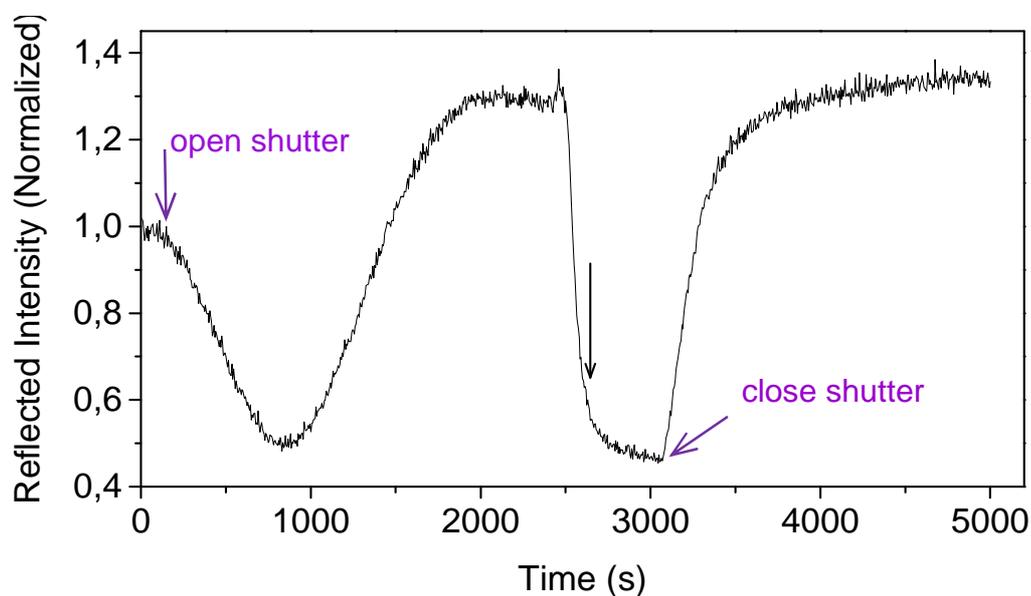
(reference 17 in the manuscript). The deposition rate is kept constant by stabilization of the crucible heating power. During deposition, made with the sample kept at room temperature, a sequence of images, with exposure time between 3 and 15 s, is acquired. Simultaneously, the QMS is run in the trend mode in which the intensities of the intact perylene molecule (masse 252) as well as the most intense fragments (masses 125 and 126) produced in the ionization zone of the QMS are recorded as a function of time.



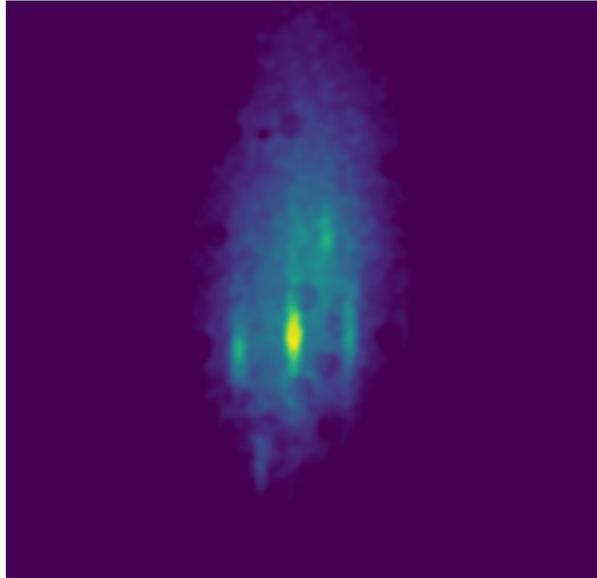
**Figure S1.** Experimental scheme showing the different parts of the GIFAD apparatus. The insert shows a diffraction pattern measured from a well prepared Ag(110) with a 500 eV He beam parallel to the [110]. The polar ( $\theta$ ) and azimuthal ( $\phi$ ) scattering angles are also represented; note that  $\phi$  is proportional to the exchange of wave vector parallel to the surface. The small spot at the bottom is part of the direct beam.



**Figure S2.** Normalized reflectivity curve recorded in conditions close to those of figure 2, but with a lower quality substrate. Note that the transition near 4000 is barely visible.



**Figure S3.** Normalized reflectivity curve recorded in conditions close to those of figure 1 (the molecular flux is slightly lower) with an extended deposition time. One can notice the change of slope right after the sharp rise and drop, this is indicated by the black arrow. At this point, crystallization of the first layer is complete and additional molecules continue to adsorb in the second layer.



**Figure S4.** Image recorded after the growth sequence described in figures 2 and 3 of the manuscript, but at a slightly larger incidence angle ( $0.6^\circ$ ) than used during the growth ( $0.5^\circ$ ). Here, the left-hand side first-order peak from S2 (missing in figure 2b) is clearly visible.