

Fig. S1. Bragg rod profiles of the first three Bragg rods integrated along  $q_p$  (from 1.317 Å<sup>-1</sup> to 1.38 Å<sup>-1</sup> for the first, from 1.62 Å<sup>-1</sup> to 1.70 Å<sup>-1</sup> for the second, and from 1.94 Å<sup>-1</sup> to 1.99 Å<sup>-1</sup> for the third rod) for 1 monolayer (1 ML), 2 ML, 3 ML and 50 nm thin pentacene film. Lab measurements (red lines) are compared to synchrotron measurements (black lines); the intensities at the Yoneda peak are scaled to each other. The evolution of a 3 dimensional structure is clearly observed in the 2 ML and 3 ML samples by the emergence of Bragg peaks at out-of-plane  $q_z$  values corresponding to them of the thin film phase.