Epitaxial Growth of π-Stacked Perfluoropentacene on Graphene-Coated Quartz

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Chemical-vapor deposited large-area graphene is employed as coating of transparent substrates for the growth of the prototypical organic n-type semiconductor perfluoropentacene (PFP). The graphene coating is found to cause face-on growth of PFP in a yet unknown substrate-mediated polymorph (SMP), which is solved by grazing-incidence X-ray diffraction reciprocal space mapping (GIXRD-RSM) and a direct fit of the molecular orientation against the experimental intensities [1]. This approach became feasible owing to the large number of reflections in the corresponding map on the (fiber-textured) PFP/HOPG reference. In contrast to the otherwise common herringbone arrangement of PFP in single-crystals and "standing" films, we report a π-stacked arrangement of coplanar molecules in "flat-lying" films, which exhibit an exceedingly low π-stacking distance of only 3.07 Å. The experiments were carried out at DORIS beamline W1 using a MYTHEN 1D detector in He-atmosphere.

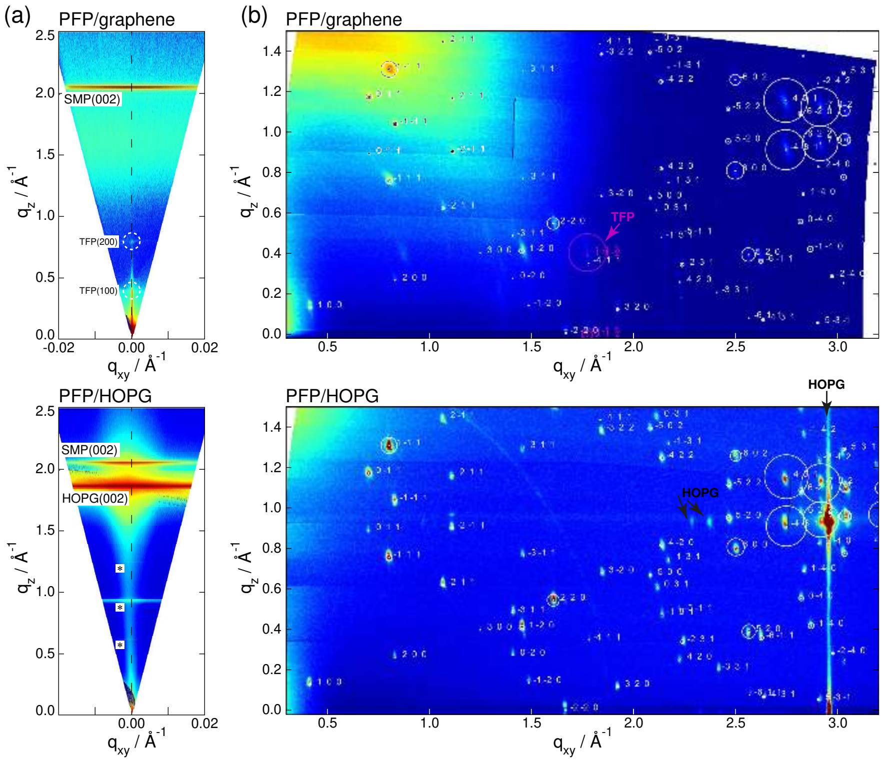

Figure 1: (a) Specular XRD scans of 30 nm PFP on single-layer graphene (top) and that of a 50 nm PFP film on highly-oriented pyrolytic graphite (HOPG) as reference (bottom) both showing the SMP(002) reflection. In contrast to PFP/HOPG, where the HOPG(002) reflection dominates the spectrum (higher harmonics of the substrate marked by stars), no diffraction from the substrate is observed for PFP/graphene; there, minor contributions of standing PFP grown in a thin-film polymorph (TFP), likely related to nucleation on substrate defects, are found. (b) GIXRD-RSM on PFP/graphene (top) PFP/HOPG (bottom), which yield the SMP unit-cell dimensions and allowed carrying out a full structure solution by fitting the experimental intensities [1].

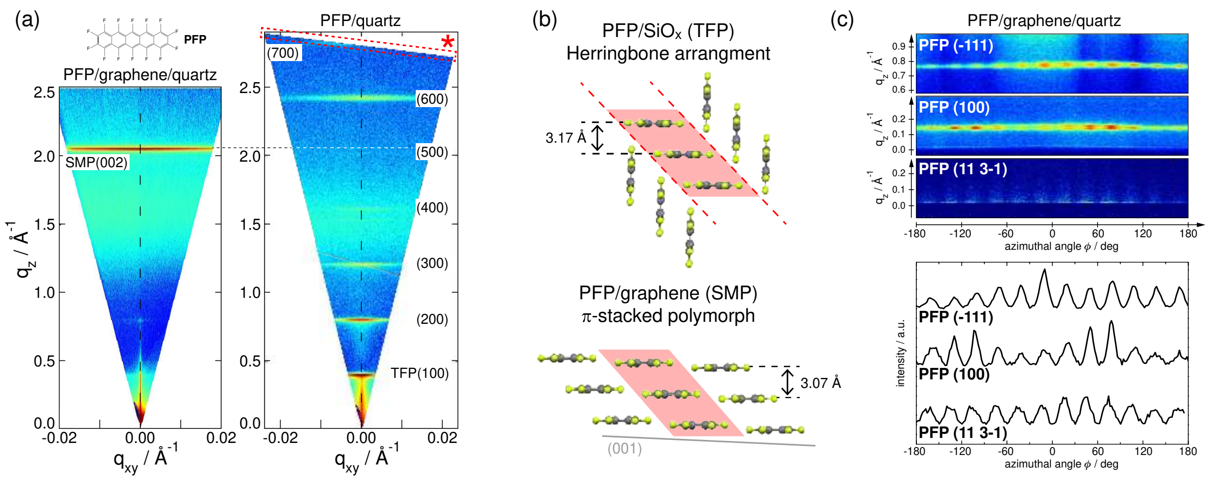

Figure 2: (a) Specular XRD on PFP/graphene-coated quartz (left) compared to nominally 30 nm PFP on pristine quartz (right), showing growth of lying and standing PFP, respectively. The horizontal dotted line indicates the position on the lying π-stacked SMP(002) reflection dominant on graphene coated quartz and absent on the bare quartz substrate. ***The red star marks the signature of the last photons diffracted at beamline W1 during the final shutdown of the storage ring DORIS on October 22, 2012.*** (b) The herringbone arrangement of the TFP on SiO_x (top) compared to the π-stacked arrangement of the SMP (bottom); similar π-stacked motifs are shaded in red, π-stacking distances are indicated. (c) GIXRD texture analysis performed around the azimuthal angle ϕ for the three strong reflections (-111), (100), and (11 3-1) of the PSP, each showing 12 maxima (top). Integration of the data along the out-of plane component of the scattering vector (q_z) yields line-scans (bottom).

Coating transparent quartz substrates with graphene induces lying and coplanar π-stacked growth in thin PFP films, as shown in Fig. 2b by a comparison of specular scans on PFP films on the bare and graphene-coated substrates. The packing motifs of PFP on these two substrates is rationalized by intramolecular electrostatics: PFP exhibits strong intramolecular polar bonds between the highly electronegative fluorine atoms carrying a negative partial charge F[δ^-] and the backbone carbon atoms C[δ^+] stabilizing the parallel-displaced π-stacked arrangement of PFP both present in the TFP and SMP (see Fig. 2b). In contrast to standing PFP on quartz, where a herringbone arrangement is found (Fig. 2b), the formation of a flat-lying PFP monolayer on graphene kinetically stabilizes subsequent π-stacked multilayer growth in the SMP.

Graphene as substrate not only induces growth in the π-stacked polymorph, but further leads to three-dimensional *epitaxial* growth of uniaxially aligned, flat-lying PFP molecules. This is envisioned employing GIXRD texture-analysis *via* sample rotation around the texture axis (sample normal) by $\phi = 360°$, as illustrated in Fig. 2c. There, modulations in peak intensity for given net planes appear in ϕ-scans if the crystallites exhibit a preferential azimuthal orientation around the texture axis instead of a perfect fiber texture ("2D-powder") that would occur as homogeneous intensity distribution instead. For PFP/graphene we find a strong intensity modulation with 12 equidistant maxima for three selected strong PFP reflections [(-111), (100), and the strong in-plane reflection (11 3-1)], which exhibit an angular relation in ϕ that perfectly agrees with the SMP unit-cell.

References

[1] I. Salzmann, A. Moser, M. Oehzelt, T. Breuer, X. Feng, Z.-Y. Juang, D. Nabok, R. Della Valle, S. Duhm, G. Heimel, A. Brillante, E. Venuti, I. Bilotti, C. Christodoulou, J. Frisch, P. Puschnig, C. Draxl, G. Witte, K. Müllen, and N. Koch, "Epitaxial growth of π-stacked perfluoropentacene on graphene-coated quartz," *ACS Nano*, vol. 6, no. 12, pp. 10874–10883, 2012.