ESRF	**Experiment title:** Bonding Distances of π-Conjugated Molecules on Ag(111): From physisorption to charge transfer	**Experiment number**: SI-1819
Beamline: ID 32	**Date of experiment**: from: 31/10/2008 to: 11/11/2008	**Date of report**: 05/07/2009
Shifts: 18	**Local contact(s)**: Dr. J. Zegenhagen	*Received at ESRF:*

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Report:

1. Introduction

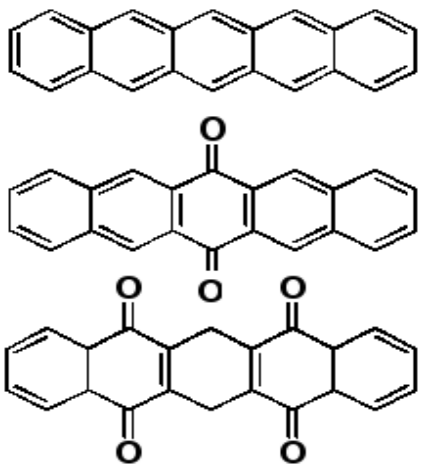

Figure 1: Chemical structure of (from top to bottom) pentacene (PEN), pentacenequinone (PQ) and pentacene-tetraone (PT).

As described in the proposal, the purpose of the experiments at ID32 was to measure the bonding distances and possible conformations of pentacene (PEN) and its oxo-derivatives pentacenequinone (PQ) and pentacene-tetraone (PT) on Ag(111). The X-ray standing wave (XSW) measurements were performed to complement existing experimental and theoretical studies on the electronic structure of these conjugated molecules and to establish a fundamental understanding of the three different systems. In particular we were interested in the interplay between the observed charge transfer and adsorption geometry of the molecules.

After preparation of the UHV chamber for our X-ray standing wave experiments we were able to take high quality XSW data on Ag(111). Below we give a short summary of results from the beamtime (SI-1819) at ID32.

2. XPS measurements on monolayers of PEN, PQ and PT on Ag(111)

Several films of PEN, PQ, and PT with coverages between the sub-monolayer and monolayer were prepared and characterized in detail by XPS and XSW. For PQ/Ag(111) and PT/Ag(111) we measured the carbon C(1s) and the oxygen O(1s) core-level signals; for PEN/Ag(111) we acquired the C(1s) signal only. To characterize our samples before the XSW measurements high-resolution XPS spectra were taken after each deposition, see Fig. 2 .

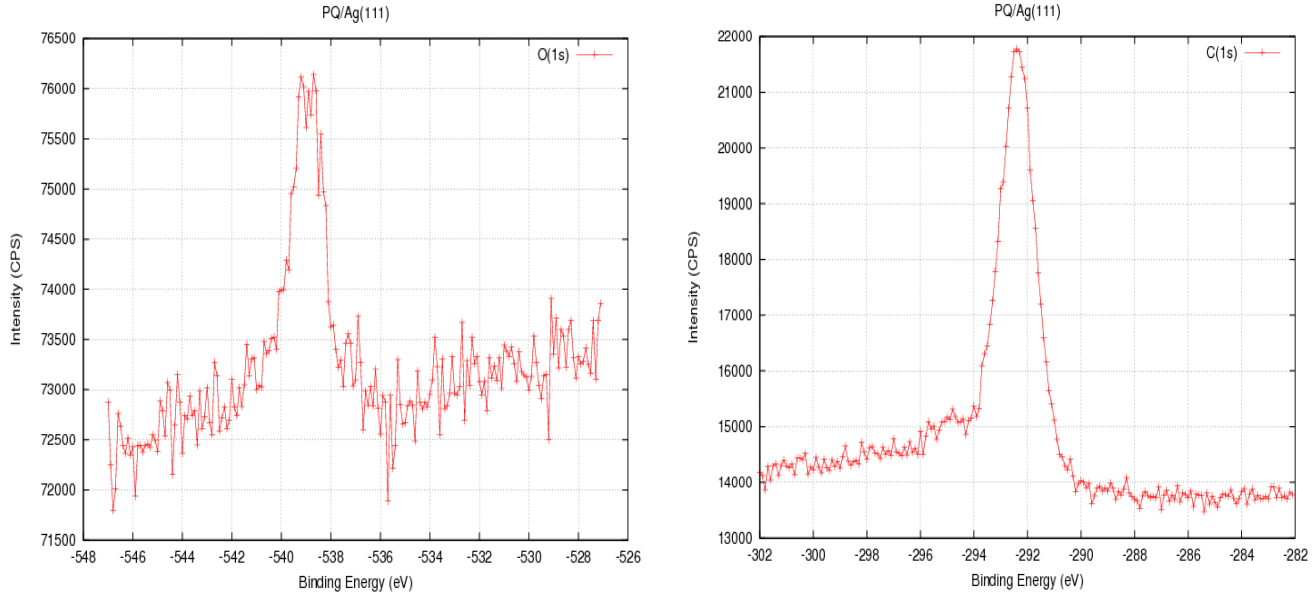

Figure 2: High-resolution XPS spectra from a sub-monolayer of PQ on Ag(111) evaporated at a substrate temperature of T = 45 °C.

3. XSW measurements on monolayers of PEN, PQ and PT on Ag(111)

After several sputtering and annealing cycles the Ag(111) crystal used in the experiment showed a suitable reflectivity curve (FWHM 1.2 – 1.4 eV in back-reflection geometry). The variation of the photo electron yield Y_p around the Bragg peak at E_{Bragg}=2.63 keV was measured to derive the coherent positions P_H and coherent fractions f_H , see Fig. 3. The corresponding parameters for PEN, PQ and PT on Ag(111) collected in Tab. 1 were used to calculate the average bonding distances d_H of the three molecules.

The XSW data show that compared to PEN and PQ the interaction of PT with the Ag(111) substrate is surprisingly strong (chemisorption). This finding is in agreement with photoelectron spectra that were taken in our home laboratory [1]. Furthermore, we found a significant distortion of the planar PT molecule on the surface. Similar to PTCDA on Ag(111) [2,3] the C=O bonds of the molecule are bent towards the metal surface.

A manuscript with these results for PEN, PQ, and PT on Ag(111) is in preparation. - We wish to thank our local contact for the excellent support on ID32.

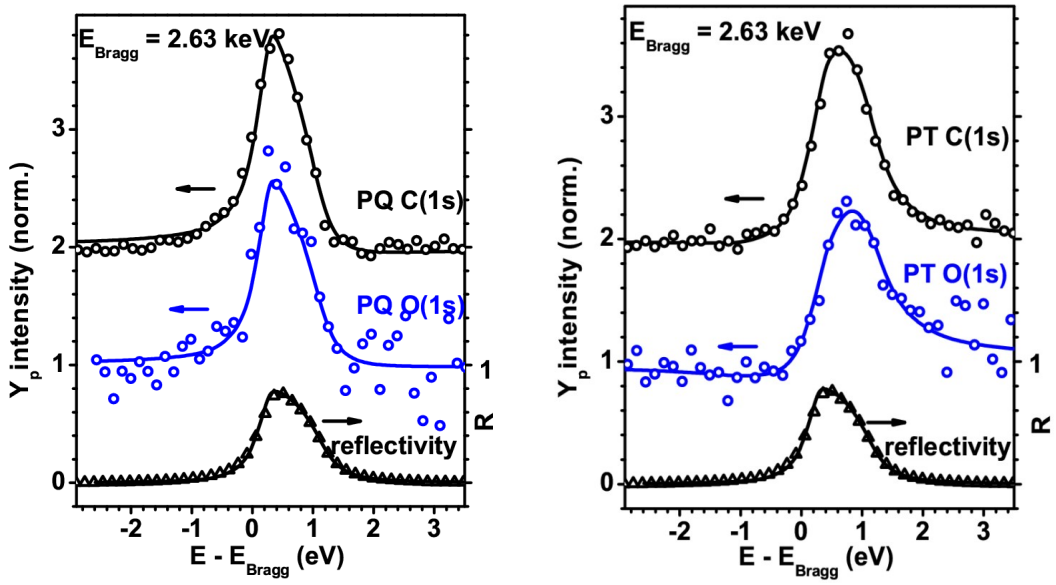

Figure 3: X-ray standing wave scans obtained on PQ and PT on Ag(111). The open circles and triangles represent the photo electron yield and the reflectivity data, respectively. The different shapes of these curves reveal the relatively small bonding distance of PT on Ag(111)..

	PEN	**PQ**		**PT**	
	C1s	**C1s**	**O1s**	**C1s**	**O1s**
$\mathbf{f_H}$	≈0.17	0.26	0.13	0.29	0.36
$\mathbf{P_H}$	≈0.31	0.41	0.41	0.14	0.03
$\mathbf{d_H}$	≈3.09 Å	3.32 Å	3.32 Å	2.69 Å	2.43 Å

Table 1: Summary of X-ray standing wave results for PEN, PQ, and PT on Ag(111)

4. References

[1] S. Duhm, A. Gerlach, G. Heimel, B. Bröker, T. Hosokai, T.-L. Lee, J. Pflaum, S. Kera, N. Ueno, F. Schreiber, and N. Koch. DPG conference Dresden 2009, *DS 23.2.*

[2] A. Hauschild, K. Karki, B.C.C. Cowie, M. Rohlfing, F.S. Tautz, M. Sokolowski, *Phys. Rev. Lett.* **94** (2005) 036106.

[3] A. Gerlach, S. Sellner, F. Schreiber, N. Koch, and J. Zegenhagen, *Phys. Rev. B* **75** (2007) 045401.