ESRF	**Experiment title:** Geometry Switching in Large Pi-Conjugated Molecules Studied by XSW	**Experiment number**: SI-977
Beamline: ID32	**Date of experiment**: from: 06 November 2003 **to:** 18 November 2003	**Date of report**: 06/09/04
Shifts: 18	**Local contact(s)**: Bruce Cowie	*Received at ESRF:*

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Report:

The objective of the experiment, i.e. a determination of the adsorption geometry of large pi-conjugated molecules, was successfully accomplished. We studied the perfluorinated copper-phthalocyanines (F_{16}CuPc) on Cu(111), see Figure 1. From the XSW measurements we derive a lying down configuration of the molecules and, importantly, that F_{16}CuPc bends significantly upon adsorption on the surface. The coherent positions P_H for fluorine and carbon differ beyond the experimental uncertainties: While the inner carbon rings are located at d_H=2.61 Å above the copper substrate, the outer fluorine atoms are found 0.27 Å further away from the surface, see table 1 for details.

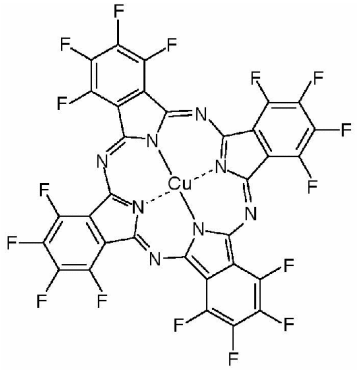

***Figure 1**: F_{16}CuPc molecule*

Our analysis is based on the generalized XSW equation

$$Y_{XSW} = 1 + S_R R + 2C\sqrt{R}|S_I| f_h \cos(\nu - 2\pi P_H + \psi)$$

that takes the non-dipolar contributions to the photoelectron yield into account. Based on the results for the parameter S_R, obtained in a previous experiment (SI-750), we were able to analyze the coherent signal from a monolayer of F_{16}CuPc for all elements with high precision, see Figure 2.

This non-planar adsorption geometry is a very surprising and potentially important result for the understanding of molecular adsorption on surfaces.

	C(1s)	N(1s)	F(1s)
f_{eff}	0.69(4)	0.41(4)	0.42(3)
P_{eff}	0.260(5)	0.308(8)	0.395(9)
f_H	0.50(1)	0.30(1)	0.31(1)
P_H	0.251(5)	0.297(8)	0.381(9)
d_H	2.61 Å	2.70 Å	2.88 Å

***Table 1**: XSW result for $F_{16}CuPc$ on Cu(111)*

From a fundamental point of view this substrate induced effect is very interesting as it allows to study the interaction of organic molecules with the surface atoms on an atomic level. Together with theoretical studies on the adsorption behaviour our XSW results will enhance the understanding of large molecules on surfaces.

We are currently preparing a publication of these new findings including a detailed analysis of the non-dipole contributions to the photoelectron yield, see Figure 2.

We wish to acknowledge the excellent support by our local contact, as always on ID32.

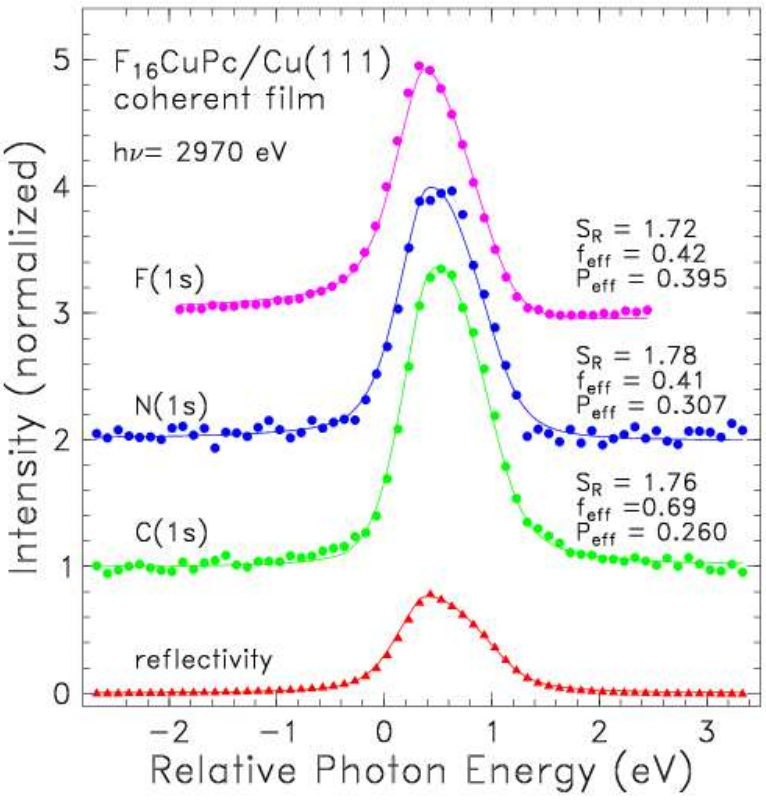

***Figure 2:** X-ray standing wave scans on a submonolayer of $F_{16}CuPc$ on Cu(111). The different coherent positions of fluorine and carbon can be related to the atomic distances relative to the substrate lattice planes. For clarity the datasets for N(1s) and F(1s) are plotted with an offset.*

References

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