ESRF	**Experiment title:** Adsorption Geometry of Fluorinated and Non-Fluorinated Organic Semiconductors	**Experiment number**: SI-1719
Beamline: ID 32	**Date of experiment**: from: 18/06/2008 to:01/07/2008	**Date of report**: 19/12/2008
Shifts: 18	**Local contact(s)**: Dr. Yanyu Mi	*Received at ESRF:*

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Report:

1. Introduction

As outlined in the proposal, the purpose of the experiments at ID32 was to measure bonding distances and conformation of Zn-phthalocyanine(ZnPc; Fig. 1) and perfluorinated Zn-phthalocyanine (F_{16}ZnPc: Fig. 1) on noble metal surfaces. In combination with other complementary techniques the X-ray standing wave (XSW) measurements will establish a fundamental understanding of the two prototypical organic semiconductors in the monolayer regime.

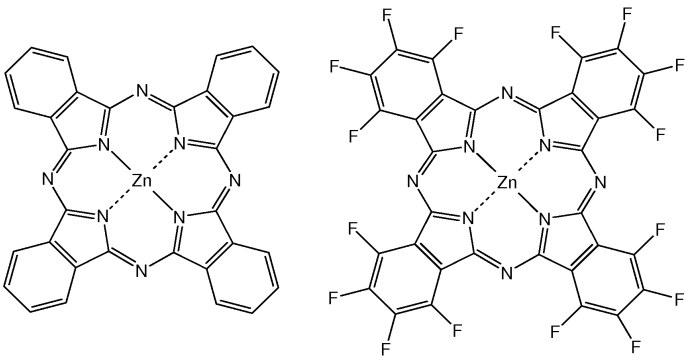

Figure 1: Chemical structure of ZnPc and F_{16}ZnPc.

After setting up the beamline and the UHV chamber for our X-ray standing wave experiments we were able to take high quality XSW data for ZnPc and F_{16}ZnPc on Cu(111). Thanks to preceding arrangements with the beamline staff we had several additional shifts for our experiment. Unfortunately, serious trouble with the cooling system of the primary slits at ID32 consumed nearly all of this time.

Below we give a short summary of results from the beam-time (SI-1719) at ID32.

2. XPS measurements on monolayers of ZnPc and F_{16}ZnPc on Cu(111)

Several films of ZnPc and F_{16}ZnPc with coverages between the sub-monolayer and monolayer were prepared and characterized in detail by XPS and XSW. For ZnPc/Cu(111) we used the carbon C(1s), the nitrogen N(1s), and the Zinc Zn($2p_{3/2}$) core-level signals; for F_{16}ZnPc/Cu(111) we also acquired the relatively strong fluorine F(1s) signal. The XPS spectra from F_{16}ZnPc/Cu(111) shown in Fig. 2. indicate that a fitting procedure similar to Ref. [2] can be used.

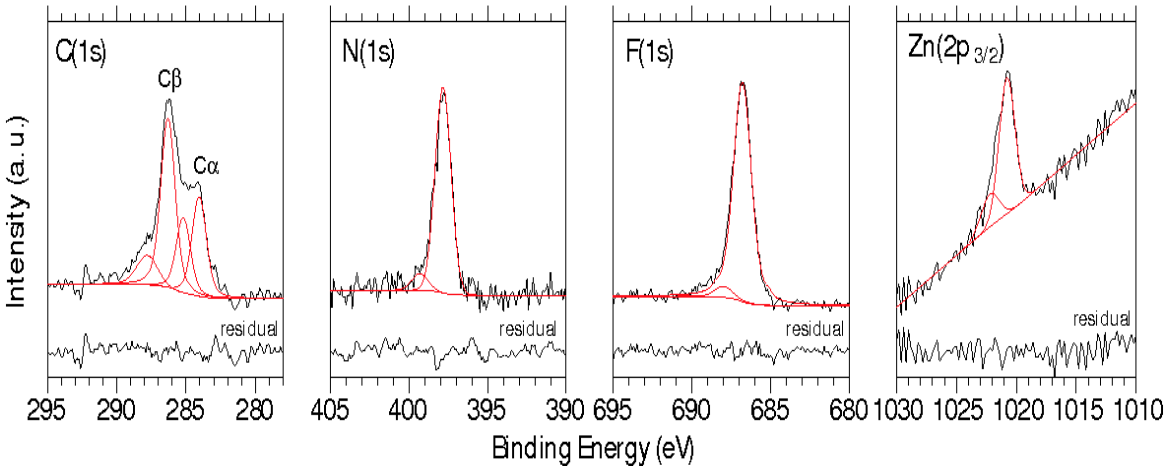

Figure 2: High resolution XPS spectra from a sub-monolayer of F_{16}ZnPc on Cu(111) evaporated at a substrate temperature of T = 45 °C. Note the splitting of the C(1s) (Ca and Cb) for F_{16}ZnPc which corresponds to the different chemical environments of the carbon atoms (C-C and C-N versus C-F bonded) [1].

3. XSW measurements on monolayers of ZnPc and F_{16}ZnPc on Cu(111)

After preparation the Cu(111) single crystal used in the experiment showed a normal incidence rocking width of ~0.90 eV that is close to the intrinsic value. The variation of the photo electron yield Y_p in the X-ray interference field was measured to derive the coherent positions P_{eff} and coherent fractions f_{eff} for the atoms in the ZnPc and F_{16}ZnPc on Cu(111), see Fig. 3.

Currently, we are working on the careful analysis and fitting of the XSW data. Because the low energy boards of the electron analyzer (PHI electronics) had some problems during our beamtime and the high energy boards do not allow to use the constant initial state mode, the processing of the XSW data is more difficult and requires some modifications of our software. Preliminary results indicate that the differences between ZnPc and F_{16}ZnPc are relatively small. The absolute bonding distances d_0 are not very different from the values found for F_{16}CuPc on Cu(111) [1]. However, the slightly different shape of the Zn($2p_{3/2}$) signal in Fig. 3 suggests that the central Zinc atom might be below the phthalocyanine ring, and therefore closer to the Cu(111) substrate.

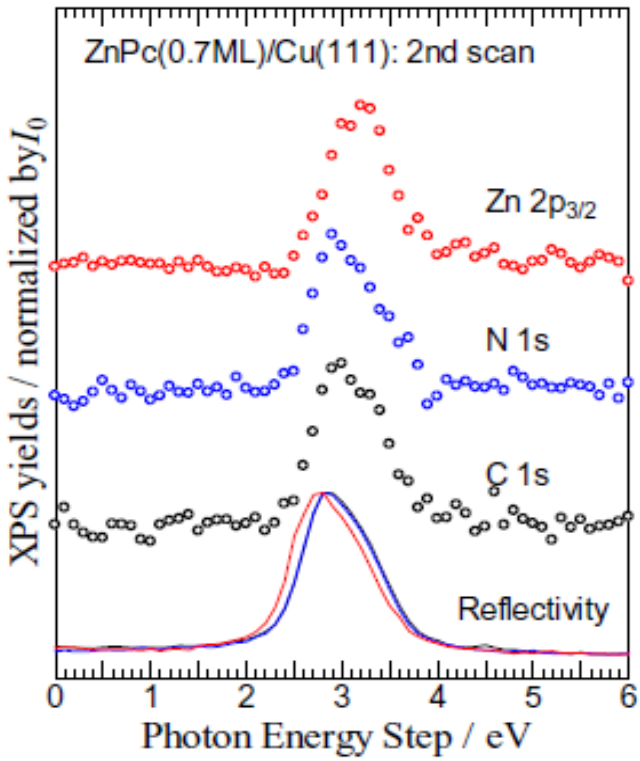

Figure 3: X-ray standing wave scans obtained on ZnPc (0.7 ML) on Cu(111). The circles and solid line represent the photo electron yield and the reflectivity data, respectively. The characteristic shapes of these curves reveal the smaller distance of Zn-Cu atoms than others.

4. Summary

We were able to measure all relevant XPS and XSW data for ZnPc and F_{16}ZnPc on Cu(111). After a careful analysis of the data we expect to find the bonding distances for both molecules which enables us to compare to interaction with the substrate. Possibly, an molecular distortion, with the central Zn atom below the molecular plane of phthalocyanine ring is realized. These findings would be in good agreement with complementary measurements using high-resolution photoemission and scanning tunneling microscopy data.

A manuscript with all results including the XSW data is in preparation. - We wish to thank our local contact for the excellent support on ID32.

5. References

[1] A. Gerlach et al., *Adsorption-induced distortion of F_{16}CuPc on Cu(111) and Ag(111): An X-ray standing wave study,* Phys. Rev. B **71** (2005) 205425.

[2] L. Ottaviano et al., *Copper hexadecafluoro phthalocyanine and naphthalocyanine: The role of shake up excitations in the interpretation and electronic distinction of high-resolution X-ray photoelectron spectroscopy measurements,* J. Electron Spectrosc. Relat. Phenom., **105** (1999) 145.