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Names and affiliations of applicants (* indicates experimentalists):

Dimas G. de Oteyza[a,b], Elizabeth Goiri*[,c], Afaf El-Sayed*[,d], Manfred Matena*[,c], Jorge Lobo-Checa*[,e]

a Centro de Física de Materiales CSIC/UPV-EHU, San Sebastián, Spain
b Department of Physics, University of California, Berkeley, U.S.A.
c Donostia International Physics Center, San Sebastián, Spain
d Universidad del País Vasco, Dpto. Física Aplicada I, San Sebastián, Spain
e Centre d'Investigació en Nanociència i Nanotecnologia CIN2, Barcelona, Spain

Report:

Introduction

The study of organic layers is of great of interest due to their applications in organic-based nanodevices such as light-emitting diodes, transistors and solar cells [1]. For the latter in particular, the synthesis of nanostructured donor-acceptor molecular mixtures is important for further development in the field. Interfaces play a key role in these devices, where the donor-acceptor interface determines the charge separation, while the metal-organic interface defines the charge carrier extraction. Donor-acceptor mixtures [2-4] maximize the organic-organic interface, while their two-dimensional assembly on metallic surfaces represents a model system of the metal-organic interface.

Copper Phthalocyanine (CuPc, donor) and Perfluoropentacene (PFP, acceptor) are organic semiconductors well known for their successful integration into optoelectronic devices [5, 6] (see Fig. 1). In this study, monolayers of CuPc and PFP are deposited on metallic substrates Ag(111) and Cu(111) separately as well as together. The molecules then spontaneously arrange into an ordered layer (Fig. 2). This so called self-assembly is the result of the interplay of all the different interactions in the system: interactions of the molecules with the substrate, and intermolecular interactions among themselves. The balance between these will determine the structure of the molecular overlayer.

The codeposition of CuPc and PFP leads to the formations of an ordered binary network (Fig. 2, lower image), presumably through the formation of C-H⋯F-C hydrogen bonds. Our aim is to study the changes induced in the system by these enhanced intermolecular interactions. Previous XPS measurements have revealed significant core-level shifts in PFP's C_{1s} and/or F_{1s} peaks with respect to the single component PFP

layer. Now, XSW measurements are able to show changes in the height of the molecules above the substrates, which may perhaps be related these core-level shifts [3].

Sample Preparation

In order to prepare the mixed phase, approximately 0.5ML of CuPc was deposited on our substrate, followed by another 0.5ML of PFP. A quarz crystal microbalance was used to calibrate the evaporation. XPS peak intensities of N_{1s} and F_{1s} were used to identify the amounts of CuPc and PFP respectively. 1ML of CuPc can be easily obtained by multilayer desorption and its N_{1s} intensity used as a reference. Then, the intensity ratio between CuPc's N_{1s} and PFP's F_{1s} peaks can be used to check that the desired molecular ratio (1CuPc:1PFP) has been obtained throughout the sample.

Beam Damage

From previous experience with fluorinated molecules such as PFP we were aware that beam damage might pose a problem. The effects of beam damage can be seen in both molecules as shifts of the core level peaks to lower binding energy, but most notably in PFP's F1s core-level. The effect of irradiation was therefore evaluated and the exposure time reduced to minimum by taking only one measurement at any single point on the sample and using a reduced measurement time. It was found that exposure to the radiation noticeably reduces the coherent fraction with time, but only slightly alters the coherent position.

XSW Results

Initially, it was expected that the enhanced interactions between the molecules would lead to their aligning in a same plane, in order to facilitate the interaction of their surrounding hydrogen (CuPc) and fluorine (PFP) atoms. Instead of doing so, our results indicate that, upon mixing, the main changes as compared to the single layers (again) occur in the PFP molecule: the fluorine atoms lift up, positioning themselves substantially above the CuPc plane.

This curious effect is observed on both Cu(111) and Ag(111), being larger in the former case.

Fig. 3 compares our results for the heights of the mixed molecules with those of the single component layers, and table 1 shows coherent fractions (CF), coherent positions (CP) and height above the substrate d of each atomic species. The change in height compared to the single component layers Δ is also given, based on previous XSW studies of monolayers of CuPc and PFP on Cu(111) and Ag(111) [7, 8, 9].

The buckling of the PFP molecule seen in Fig. 3 should be taken with care, since the coherent fractions for the CC_{PFP} carbon atoms are quite low, particularly in the case of Cu(111), however the substantial increase in height of PFF is clear.

Cu(111)	F	N	CF_{PFP}	CC_{PFP}	C_{CuPc}
CF	0.41	0.43	0.48	0.20	0.30
CP	0.69	0.27	0.67	0.39	0.32
d	3.53Å	2.65Å	3.49Å	2.90Å	2.75Å
Δ [7,8]	*+0.45Å*	-0.15Å	*+0.51Å*	+0.08Å	+0.03Å
Ag(111)	**F**	**N**	CF_{PFP}	CC_{PFP}	C_{CuPc}
CF	0.46	0.47	0.58	0.34	0.22
CP	0.53	0.28	0.49	0.39	0.35
d	3.60Å	3.02Å	3.51Å	3.28Å	3.18Å
Δ [7,9]	*+0.44Å*	-0.02Å	*+0.35Å*	+0.12Å	+0.1Å

Table 1: Coherent fractions (CF), coherent positions (CP), distance above the substrate (d) and change with respect to single-component layers (Δ) of 1:1 CuPc-PFP-mixture on Cu(111) and Ag(111). N and C_{CuPc} correspond to CuPc's nitrogen and carbon atoms; F, CF_{PFP}, CC_{PFP} correspond to PFP's fluorine, and carbon (bound to F and C respectively).

Outlook

These interesting XSW results of the mixture will be combined with our STM, XPS and NEXAFS measurements. Additionally, theoretical calculations (Bader analysis, LUMO levels...) will help interpret the meaning of the changes observed with respect to single component layers in terms of charge transfer, elucidating the interactions in this molecule-metal system.
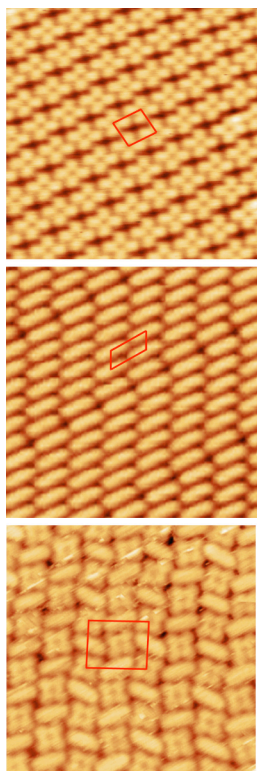
Fig 1. Chemical structure of the molecules used in this study: Copper Phtalocyanine (CuPc, donor) and Perfluoropentacene (PFP, acceptor).

CuPc:

PFP:

Legend: H, C, N, F

CuPc/Cu(111) [7]

CuPc+PFP/Cu(111)

PFP/Cu(111) [8]

CuPc/Ag(111) [7]

CuPc+PFP/Ag(111)

PFP/Ag(111) [9]

Fig 2. STM images of self-assembled mono-layers of CuPc (above), PFP (middle) and a 1:1 mixture of both (below) on an Ag(111) substrate
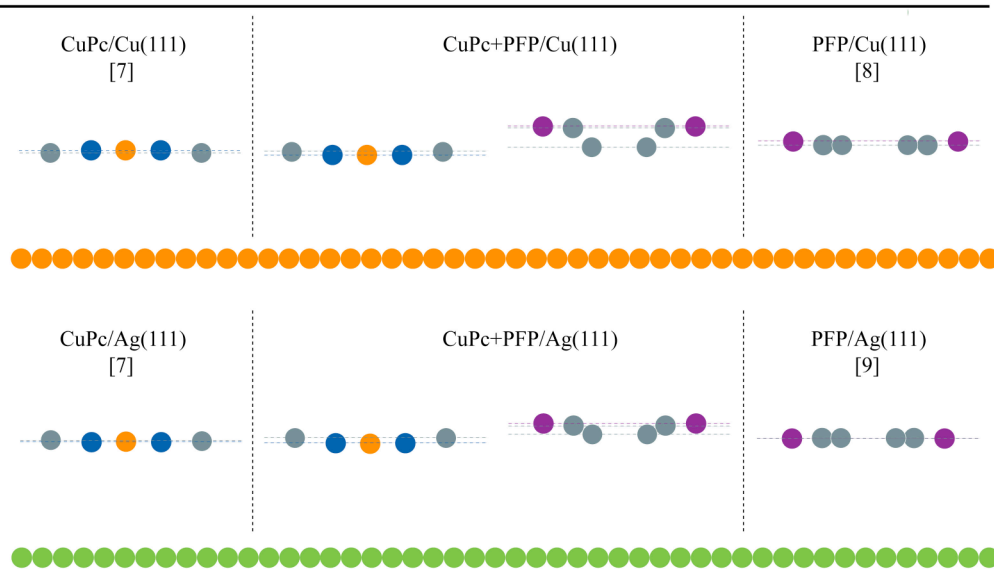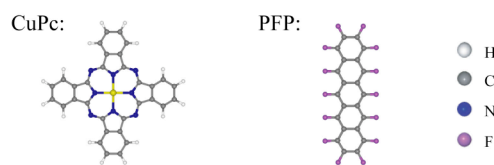
Fig 3. Schematic representation of results for the 1:1 CuPc+PFP mixture on Cu(111) (above) and Ag(111) below, compared with results for single component layers. Legend: Carbon, Nitrogen, Fluorine. (Distance to substrate not to scale)

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