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Perylene diimide cysteine derivatives self-assembled onto (111) gold surface: Evidence of ordered aggregation

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ABSTRACT

Perylene diimide derivatives containing pendant cysteine residues are subjected to a strong self-assembly onto [1 1 1] Au films due to the presence of thiol functionality. The preparation of two different Au surfaces easies the understanding of both surface packing and morphology of the aggregated ordered films, by means of the combination of X-ray photoelectron spectroscopy, atomic force microscopy, and grazing incident wide X-ray scattering - synchrotron radiation - techniques. A proper correlation of the resulting data, together with conformational calculations - using a detailed molecular modelling - allow supplying a coherent scenario.

In particular, isolated ordered pillars upstanding to the substrate plane are detected on native gold surface, while a π-stacked aggregation "unregistered" normally to the film plane is observed when perylene derivatives are grafted onto thermally annealed gold surface.

Such a surface organization is expected to be favourable to the charge mobility, therefore its use in organic field effect transistor is envisioned.

1. Introduction

Modification of metallic material surfaces using self-assembled monolayers (SAM) through deposition/reaction is a well-known way to tune their physical-chemical properties, generally achieved by means of the use of various organic molecules. Specifically gold surface can be properly modified by chemical sorption of appropriate compounds in particular those bearing the reactive thiol (-SH) functional group [1–3].

Such a functionalization proved its utility [4–7] in the preparation of prototypical samples as organic field effect transistor devices (OFET) as well as sensing electrodes.

Progressive successful efforts in the preparation of alkane thiol SAM on Au films were firstly reported, then aromatic molecules bearing thiol residues have been tested [8–10], allowing the electronic quantities, sensible to surface modification, to effectively improve in OFET devices.

On the other hand, periodic density functional theory (DFT) accurate calculations, aiming to clarify the interaction between thiol derivative and Au [111] film together with organic molecule aggregation, can address the choice of material to be chemisorbed onto Au films [11].

In this scenario graphite-like molecules, i.e. with 2D extended π-conjugation, are not extensively represented. In order to bridge this

gap, we conceived the preparation of gold films functionalized with perylene based organic molecules, bearing thiol tails.

A successful attempt of Au coverage with perylene diimide (**PDI**) has already been reported [12], showing that monolayer of **PDI** derivative can be formed onto Au-nanorods through side by side **PDI**-rod π-aggregation, modifying both the electronic and optical properties of the nanocrystals.

PDI derivatives display great versatility as active material in many optoelectronic applications (light emitting diodes, solar cells, OFET etc.) [13–15], because of the extended π-conjugation coupled with HOMO-LUMO suitable values, hence supplying emission properties along with efficient charge transfer.

The limitations due to poor solubility of perylene-based molecules are overcame with proper alkyl or branched alkyl substitution. An appreciable solubility is in fact necessary to allow the solution processability into functional devices or, as in the present study, its reaction with gold surface. Moreover the wide range of substitution of **PDI** tails widens the choice of available molecules [16–21], as recently successfully exploited with the realization of different amino acid functionalized **PDI**s [22] with the aim to prepare active sensors in aqueous media [23,24]. In this respect, a lysinate **PDI** derivative specifically designed to bear π-conjugation backbone and biocompatible tails, was recently reported as a multifunctional material for neural interfacing [25].

One of the aminoacids previously tested by our group [22], cysteine, bears the -SH function suitable for absorption onto gold films, hence was chosen as suitable **PDI** tail. Both mono- and di-substituted imides (**PMI-Cys** and **PDI-Cys** respectively, see Scheme 1) were synthetized starting from perylene dianhydride.

In order to achieve chemisorption of **PDI** derivatives onto [1 1 1] Au layer two differently treated surfaces were tested: high vacuum evaporated films **(AUEV)** and the same Au surface after high temperature annealing **(AUAN)** displaying different morphologies (see atomic force microscopy, AFM, below).

Both **PMI-Cys** and **PDI-Cys** were then adsorbed onto Au surface to form functionalized films, which were characterized with X-ray photoelectron spectroscopy (XPS), AFM, and grazing incident wide angle X-ray scattering (GIWAXS), showing that not only a clear functionalization took place but that some organization of the molecules after proper reaction time was also achieved. The present study intends to provide new insights to the well-established thiol derivatives employment as SAM in OFET devices, [4–7] by exploring the possibility of π-stacking interactions, i.e. a potential improvement of the electrical mobility.

2. Experimental section

2.1. Materials

Perylene-3,4,9,10-tetracarboxylic dianhydride, imidazole, Zn (OAc)$_2$, and L-cysteine were purchased from Aldrich and used as received without further purification.

2.2. Synthesis of PMI-Cys and PDI-Cys

3,4,9,10-Perylene tetracarboxylic acid dianhydride (PDA) (0.5 mmol), L-cysteine (1.05 mmol) and 1 g of imidazole were added into a Schlenk and heated at 120 °C for 4 h, while the colour turned from red to violet. The reaction mixture was filtered to eliminate the unreacted PDA, then was cooled, poured into water, and filtered. The recovered solid precipitate is **PMI-Cys** (15% yield). Then, the filtrate was acidified with 2.0 M HCl and the precipitate was filtered and washed with water several times, then with methanol, dried under vacuum to give the final **PDI-Cys** in 71% yield.

N-(L-Cysteine)-3,4,9,10-perylene tetracarboxylic monoanhydride monoimide (PMI-Cys)

^{1}H NMR (500 MHz, D$_2$O Phosphate buffer 30 mM pH 8.0, ppm): 7.87–7.49 (8H, pery), 6.25 (1H, Cys α), 3.80–3.68 (2H, Cys β)

N,N' -Bis-(L-Cysteine)-3,4,9,10-perylene tetracarboxylic diimide (PDI-Cys)

^{1}H NMR (500 MHz, D$_2$O Phosphate buffer 30 mM pH 8.0, ppm): 7.91–7.54 (8H, pery), 6.32–5.95 (2H, Cys α), 3.90–3.66 (4H, Cys β).

Further details of characterization are reported in Ref. [22].

2.3. Films preparation

Au layer preparation was performed onto either quartz or silica substrates. Au films of variable thickness (20–200 nm) were obtained by evaporation in high vacuum (better than 10^{-6} torr). The thicker ones were subsequently flame annealed at temperatures higher than 800 °C, providing the **AUAN** substrates, while the thinner films were used as evaporated (**AUEV** substrates). All of them were checked by XRD to assess the orientation which resulted to be largely along with [1 1 1].

The Au substrates were introduced in different Becker glasses containing solutions of **PDI-Cys** at a concentration of 0.1 or 1.0 mM or **PMI-Cys** at a concentration of 0.1 mM in degassed dimethylformamide (DMF). The limited solubility of **PMI-Cys** did not allow the preparation of the high concentration sample (1.0 mM) with this material. The Becker glasses were kept into a bigger glass chamber filled with pure nitrogen during the dipping operation and for all the incubation time.

After incubation at room temperature for a time between 2 h and 48 h, the samples were removed from the **PDI** solution, rinsed three times with clean DMF, to eliminate the organic material not grafted to gold and let dry under the fume-hood before being analysed.

2.4. XPS

The analyses were performed by a PHI-5500 – Physical Electronics spectrometer, equipped with a monochromatised source with aluminium anode (Kα = 1486.6 eV), operating at an applied power of 200 W, 5.85 eV pass energy, and 0.05 eV energy-step. XPS spectra were collected at take-off angles of 45° The analysis area is around 0.5 mm^2 and the sampling depth, due to the emerging photoelectrons, is on the average within 10 nm.

During measurements the vacuum level was around 10^{-9} Torr residue pressure. The energy resolution of the spectrometer was measured by full width at half maximum (FWHM) of a standard Ag-foil, it results 0.46 eV for Ag(3d 5/2).

In order to neutralize the surface electrostatic charge of nonconductive samples an electron gun was used and the compensation was dosed until the shape of peaks was not distorted. Furthermore, the charging effect on the analysis was also corrected considering the BE value of C(1s), due to adventitious carbon, at 284.8 (± 0.3) eV.

The BEs were measured at the maximum of the peaks without any baseline subtraction.

The semi-quantitative analysis data were reported as atomic percentage of elements and the normalization was performed without including hydrogen, the resulting data have just a relative meaning between samples.

2.5. AFM

The measurements were performed at 25 °C using a commercial AFM (NTMDT_NTEGRA) in tapping mode with a cantilever NSG10 operating at a typical resonance frequency of 140–390 kHz in air, and under N$_2$ flux in Kelvin probe force microscopy (KPFM) mode with a Pt coated tip NSG10/Pt.

An assay of three areas per sample has been performed. Since no significant morphological difference has been detected among the different areas of each sample, images presented in the corresponding figures can be considered as representative of the whole sample. For image processing the AFM NTMDT software has been used.

2.6. XRD experiments

GIWAXS measurements were performed at the X-ray Diffraction beamline 5.2 at the Synchrotron Radiation Facility Elettra in Trieste (Italy). The X-ray beam emitted by the wiggler source on the Elettra 2 GeV electron storage ring was monochromatized by a Si(111) double crystal monochromator, focused on the sample and collimated by a double set of slits giving a spot size of 0.2 × 0.2 mm. The beam was monochromatised at the energy of 8.86 KeV (λ = 0.14 nm). The samples were oriented by means of a four-circle diffractometer with a motorized goniometric head. The X-ray beam direction was fixed, while the sample holder could be rotated about the different diffractometer axes, in order to reach the sample surface alignment in the horizontal plane containing the X-ray beam by means of laser light reflection. Subsequently it was possible to rotate the sample around an axis perpendicular to this plane or, alternatively, vary the angle between beam and surface (angle of incidence). Bidimensional diffraction patterns were recorded with a 2 M Pilatus silicon pixel X-ray detector (DECTRIS Ltd., Baden, Switzerland), positioned normal to the incident beam, at a variable distance (133 up to 200 mm distance from the sample), to record the diffraction patterns in reflection mode. Sample and detector were kept fixed during the measurements.

The sample inclination to the beam was varied from ω = − 0.05° to