Rectifying behaviour of self assembled porphyrin/fullerene dyads on Au(111)

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Abstract. Here we present an Ultra High Vacuum Scanning Tunnelling Microscopy (UHV-STM) and Scanning Tunnelling Spectroscopy (STS) study of self assembled donor-acceptor conjugate dyads, consisting of fulleropyrrolidines and metallo-porphyrins immobilized on gold. The coverage in the fulleropyrrolidine layers was optimized up to obtain isolated protrusions which we identify with isolated dyads since their lateral dimensions are consistent with the fullerene size. The STS study reveals a diode-like asymmetric behaviour of the dyads, different from the surrounding areas. We investigate also the influence of the tunneling conditions on the rectifying ratio which is found to be dependent on the initial set point conditions and to increase by increasing the tip-sample distance.

1. Introduction
Self-assembled monolayers (SAMs) are a key element of the multidisciplinary bottom-up approach to build complex supramolecular structures from molecular building blocks and have been largely investigated in the past years both from a fundamental and a technological point of view[1]. In this respect, the tunable electrical and optical properties of organic molecules and their ability to self-organize into different nanostructures on surfaces make them ideal for applications in the field of molecular electronics and nanotechnology in general [2].

In particular, metallo-porphyrins are a class of molecules involved in a number of important biological and chemical processes. They play an important role in the catalytic reactions of biological systems and have excellent features as electron-transfer systems and photosynthetic capability to convert light into energy. Therefore, porphyrin films have been employed as gas sensor [3], organic light emitting diode [4], photovoltaic cells [5]. Recently, combined with fullerenes [6] they have been demonstrated to act as donor/acceptor pairs in dyads with important applications in molecular electronics. Based on this, studies [7] have been carried out with the aim of preparing stable metallo-
porphyrin/fullerene monolayers in which metallo-porphyrins and fullerenes are assembled in dyads on surfaces.

To date, scanning tunneling microscopy studies have been carried out in order to investigate the morphological and electronic properties of porphyrins [8,9], fullerenes [10,11] and their mixed films [12,13] at the surfaces. In particular, it has been shown that porphyrin-fullerene pair can act as molecular rectifier[14].

Herein, we present an STM/STS study of self assembled cobalt-porphyrin/fulleropyrrolidine dyads on gold. Both a monolayer and isolated dyads were imaged, while STS analysis revealed a diode-like asymmetric character which depends strongly on the tip-sample distance.

2. Experimental section
We have synthesized the porphyrin Cobalt(II) 5,10,15,20- tetrakis(4-phenyl)–porphyrin (CoTPP), and N-methyl-3,4-fulleropyrrolidine bearing a p-diethoxypyridyl group (PyC2C60), by following standard procedures [15]. 4-Aminothiophenol (4-ATP), 90%, was purchased from Aldrich and used as received. The Au(111) substrate on mica was purchased from Molecular Imaging. All the solvents used were analytical grade. We anchored PyC2C60 to the Au(111) surface via axial ligation to a self-assembled monolayer of CoTPP, by immersing an Au/4-ATP/CoTPP SAM (CoTPP SAM) into a toluene solution of PyC2C60. The CoTPP SAM preparation was described elsewhere [16]. The molecular structures of all the molecules are reported in fig.1.

More in detail, three different type of sample were investigated. Sample A was prepared by immersing the CoTPP SAM in a 10^{-4} M PyC2C60 solution for 24h and rinsed with pure toluene, while sample B was prepared by dipping CoTPP SAM for few seconds in a 10^{-6} M PyC2C60 solution and rinsed with toluene. Sample C was obtained by annealing sample B for ~ 40 minutes at 700K in UHV. All the samples were inserted in UHV environment as soon as possible after preparation.

The STM and STS measurements were carried out in a Omicron VT-STM in UHV condition (10^{-10} mbar) at room temperature, using both W and Pt-Ir tips. The STS spectra showed in this paper are averaged over a set of several I–V curves in a grid over the scanning area.

3. Results and Discussion
Fig 2a) shows an STM image acquired on sample A. In this case we observed an high coverage (more than 1ML) of the surface and the tendency of fullerenes to aggregate. We used the STM image of a native defect of the layer (hole in fig 2a) in order to get information about the apparent SAM thickness, by measuring the height distribution histogram. The histogram, shown in the inset, reveals two peaks resulting from the lower and the higher component of the molecular layer. The difference of (16.0 ± 0.2)Å between the maxima corresponds to the apparent film height which, actually, is a such high value for the PyC2C60 SAM to be the first layer bound to the CoTPP SAM. This is also confirmed by the STS carried out on this sample. I-V curves (not shown here) acquired on different height areas do not reveal any relevant difference between each other.

Fig.1 The molecular structure of a) 4-ATP; b) CoTPP; c) PyC2C60.

The curves are quite symmetric and might be attributed to the physisorbed fulleropyrrolidines. It is
known that, over a wide range of conditions, fullerenes exist in solution in form of aggregates or cluster, and particularly, that the cluster sizes strictly depend on the concentration and the temperature of the solution. As matter of fact, it has been demonstrated that at low enough concentrations, clusters do not form and only isolated fullerenes exist in solution [17]. For this reason we tuned the concentration of fulleropyrrolidine solution and the incubation time.

The image shown in fig.2b is acquired on sample B. The surface seems to be homogeneously covered, even if some small aggregates are visible. After the annealing procedure, the fulleropyrrolidine coverage is so low that the 4-ATP/CoTPP SAM [18] can easily be observed (Fig.2c). The isolated protrusion that can be observed onto the terraces of the functionalised gold are ascribed to the single porphyrin/fulleropyrrolidine dyads. These dyads have an apparent width of about 3nm and a height of 0.4nm. Their lateral dimensions are consistent with the expected one, if a convolution with the finite size of the STM tip is taken into account. The apparent heights in STM are instead smaller [19].

We performed tunneling spectroscopic measurements on these structure in order to study the conductance properties of the dyads. The current-voltage (I-V) collected on the single dyads revealed an asymmetric behaviour with higher current at positive bias voltage. These characteristic curves can be unambiguously and reproducibly distinguished from I-V curves collected on the porphyrin layer beneath. We reported the spectra obtained on different sites of the surface in fig.3a).

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Fig 2 STM image acquired on a) sample A: 2.5V, 50pA, scan area 200nmx200nm; b) sample B 2V, 100pA, scan area 100nmx100nm; c) sample C. Inset in a): height distribution histogram.

Fig 3 STS curves acquired on sample C: a) on different sites of the sample; b) on the single dyad (the current range of the blue curve is larger as indicated in the right Y-axis).
The black curve (■) was collected over a dyad (highest features), while the green (●) and the red curves (▲) are acquired on the surrounding layer. The STS curves show an ohmic or highly conductive behaviour away from the protrusions, which we attributed to the gold substrate and the 4-ATP/CoTPP layer [16], respectively. Over the protrusions the spectroscopy revealed a rectifying behaviour, with a rectifying ratio ($RR = |I(+V)/I(-V)|$) dependent on the initial set point conditions and increased by decreasing the tunneling current (fig. 3b). The corresponding changes, $\Delta z$, in the tip-dyad distance have been estimated from some $I(z)$ measurements to be roughly 0.17nm when the setpoint current ranges from 50pA to 300pA. At higher setpoint current, $I(z)$ curves were less reproducible due to tip instabilities or tip contact with the sample during the measurements. The I-V curves taken at lower tunneling current values show a rectifying character ($RR=12$ at $I_{set}=50pA$, $V_{set}=2V$), while at higher values, the curves are more symmetric ($RR=2$ at $I_{set}=400pA$, $V_{set}=2V$). This could be due to an asymmetric position of the dyad in tunneling gap, so that when the tip is far away from the dyad, the electron are less likely to flow from the molecule to the tip than in other direction. However, a comprehensive explanation of this behaviour has not been elaborated yet.

4. Conclusion
In summary, we report a simple and inexpensive method to produce stable monolayers of donor/acceptor dyads, which could be biomimetic to the natural photoenergy conversion systems. Both self assembled monolayers and isolated porphyrin/fulleropyrrolidine dyads were observed in the STM images. STS results suggested a high rectifying behaviour of the dyad dependent on the tip-molecule distance.

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