

# **Macroscopic Anisotropy in Thiol Capped Au NPs embedded in polyethylene oriented films.**

Here we study the possibility of inducing macroscopic anisotropy in a system containing spherical thiol capped Au NPs, which are embedded in a polymeric matrix that can be stretched up to 20 times the initial length in one direction. The different mechanical properties of the Au and S atoms cause the break of some bonds at the NP surface when the polymer is stretched. The magnetic and optical properties dependent on these bonds are also dependent on the drawing direction. This opens the possibility of inducing a macroscopic anisotropy in systems containing spherical NPs.

## **1. Introduction.**

Anisotropy is defined as a spatial dependence of the physical properties of a system. The anisotropy arise naturally in non-spherical nanostructures as nanowires, nanotubes or nanorods. For these nanosystems, the properties depend on the size due to size and surface effects. Thus different sizes for different spatial direction led to a different response arising anisotropy in these systems. Nowadays it is possible to develop non-spherical nanostructures by top-down lithography process and bottom-up methods as colloidal chemistry . However the observation of macroscopic anisotropy requires the orientation of macroscopic quantities of these nanostructures: In a system of system of randomly oriented nanostructures, the average over the all possible orientations, arise a macroscopic isotropic behavior. The size of patterned surface achievable by litography scarecely achive the millimeter size. For nanostructures obtained by chemical methods, that can not be ordered individually, self-assembly can provide a partial solution, but the size of these assembly is usually limited to some microns.

Therefore, the development of nanostructured materials exhibiting macroscopic anisotropy

An alternative approach to achieve these materials is the induction of anisotropy in spherical nanostructures by applying uniaxial macroscopic forces. The permanent modification induced by the external forces will induce anisotropy in the nanostructures. If the forces are applied to nanostructure immobilised in a solid matrix the induced anisotropy will be .....

The method can be particularly useful in complex nanostructures with different elements

In previous works it has been demonstrated that thiol capped Au NPs present a ferromagnetic-like behavior, despite the diamagnetic behavior of gold and thiol chains [1]. This surprising behavior has been confirmed by X ray Magnetic Circular Dichroism (XMCD) an element sensitive technique that allows to discard the presence of magnetic impurities as the origin of the magnetic characteristics [2,3]. The ferromagnetic-like behavior is preserved when the NPs are dispersed in a polyethylene matrix [4]. The origin of the magnetic response is located in an outer shell of the NPs and is due to the Au-S bonds. The optical behavior through the surface plasmon resonance (SPR) band is also strongly dependent of those bonds [5].

When the NPs are embedded in a polymeric matrix it is possible to manipulate easily the macroscopic sample containing the Au NPs. As optical and magnetic properties are dependent on the Au-S bonds, modifications in the macroscopic sample affecting these bonds could alter the behavior of the whole system. Since the mechanical properties of the Au and S atoms are different, slight modifications of the environment may significantly alter the bonds and therefore the magnetic and optical properties of the system.

The dependence of the optical absorption and the magnetic behavior as a function of the drawing direction of the polymeric matrix is analyzed, in order to study if it is possible to induce an optical and magnetic anisotropy in macroscopic samples due to modifications in the Au-S bonds. Structural characterization with EXAFS measurements is presented in order to try to understand and to explain the anisotropy.

## 2. Experimental details.

**Para los italianos.** Dodecanethiol-capped Au NPs were prepared as described in the literature following a bottom-up approach [6,7]. Briefly, polymeric Au nanocomposites (Au NPs-PE film) were prepared by casting a solution of 4 wt. % of Au NPs and ultra high molecular weight polyethylene (UHMWPE, Stamylan UH210, supplied by DSM, The Netherlands) in p-xylene at 125°C, and recovering the film after solvent evaporation at room temperature.

### Describe TEM characterization.

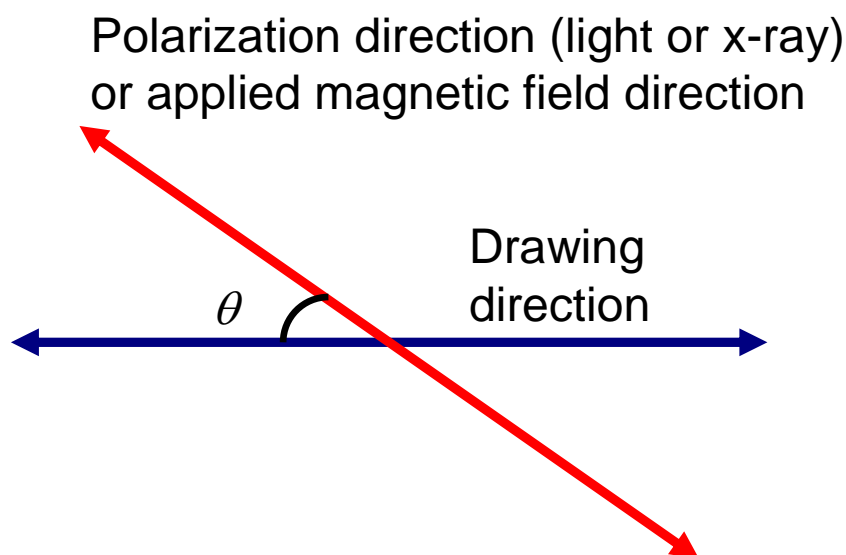
In order to study the surface plasmon resonance (SPR), we measured the UV/Vis optical absorption of the NPs. SPR is the most remarkable optical property of metallic NPs [8] strongly correlated to particle size and changes in the electronic structure of the NPs induced by thiol capping.

Magnetic characterization has been carried out with a Superconducting Quantum Interference Device (SQUID) magnetometer. The diamagnetic contribution from the sample holder has been previously measured and removed from the final data. As we are dealing with

small magnetic signals, all possible sources of experimental errors have been taken into account [9].

The x-ray measurements were carried out at beamline SpLine (BM25) at ESRF and at 4-ID-D beamline of the Advanced Photon Source at Argonne National Laboratory [10]. The data were recorded in transmission mode at the  $L_3$  edge of Au (electric dipole transition  $2p \rightarrow 5d$ ). The EXAFS analysis has been performed with the programs Athena and Artemis of the *IFEFFIT* package [11].

In order to study if the samples present any type of anisotropy, we have performed different characterization (optical, magnetic and structural) as function of the different orientations with respect to the drawing direction. We take  $\theta$  as the angle between the drawing direction of the film and the polarization of light (for optical absorption measurements), the magnetic field (for magnetic characterization) or the x-ray beam polarization (for EXAFS measurements), figure 1.



**Figure 1.** Scheme of the angle between the drawing direction and the polarization or the magnetic field.

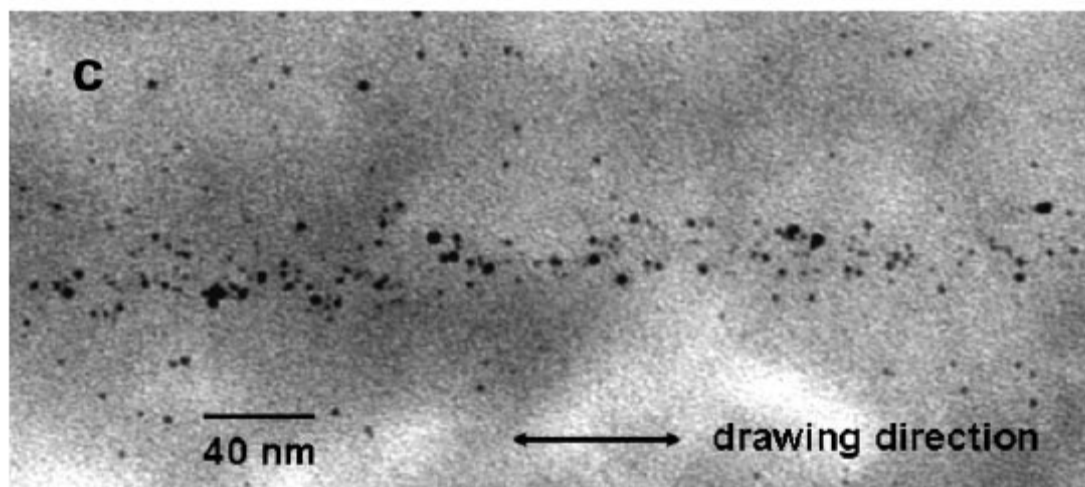
### 3. Results and discussion.

#### 3.1. TEM characterization.

Para los italianos For TEM characterization, we get your paper from Materials Chemistry.

After the stretching, the NPs result oriented along the drawing direction distribution and assumed an anisotropic. NPs size and size distribution were substantially unchanged in the

process of thermomechanical elongation, thus suggesting aggregation phenomena to be negligible.



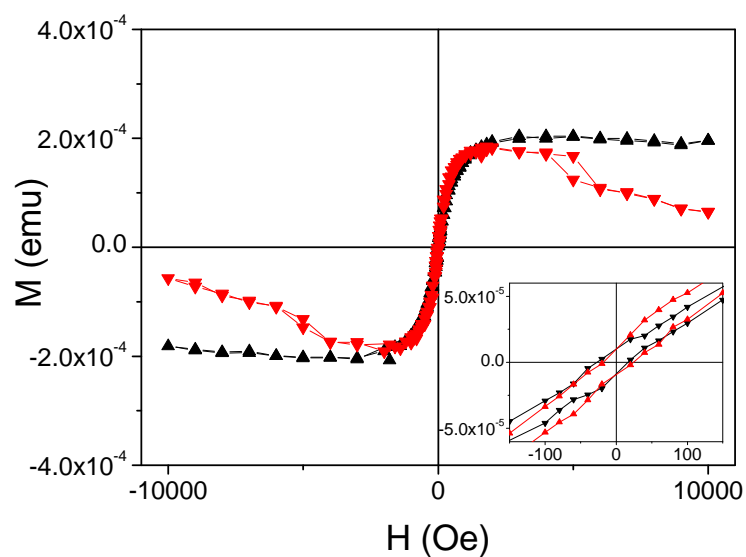
**Figure 2.** Bright-field transmission electron micrograph of the oriented film, (draw ratio  $\sim 20$ ).

### 3.2 Magnetic properties.

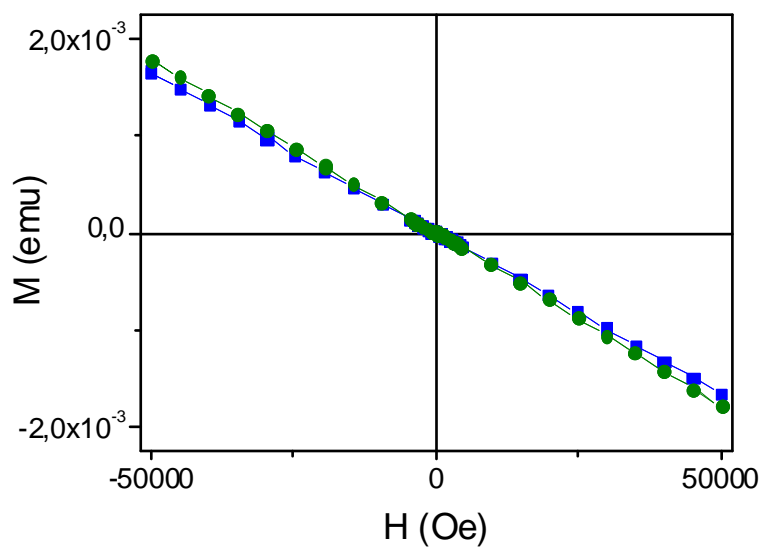
The magnetic characterization at 300 K, figure 3, confirms the ferromagnetic-like behavior of thiol-capped Au NPs, with hysteresis up to room temperature. This surprising magnetic response has been previously reported, and arises from the bonds between Au atoms located at the NP surface and S atoms at the end of the thiol chain [4].

When a magnetic field is applied to the same sample, parallel ( $0^\circ$ ) and perpendicular ( $90^\circ$ ) to the drawing direction, we obtain different results. The value of the magnetic saturation is slightly smaller when the field is applied at  $0^\circ$ . In addition, a diamagnetic component is visible.

In order to confirm that the differences in the magnetic behavior come from Au NPs and not from the polyethylene matrix, we have measured a piece of the stretched polymer applying again the field in both directions, perpendicular and parallel to drawing direction. The sample has been measured at 300 K and with magnetic fields up to 5 T. It is possible to observe that there is a small difference in the diamagnetic behavior, indicating a small anisotropy in the polymer, but not enough to account for the differences observed in the sample containing thiol-capped Au NPs. So we can conclude that the differences in the magnetic behavior arise from the NPs and their interactions with the stretched polymer, producing a macroscopic anisotropy.



**Figure 3.** Magnetization curves of the sample at 300 K with the field applied at  $0^\circ$  (red down triangles  $\blacktriangledown$ ) and at  $90^\circ$  (black up triangles  $\blacktriangle$ ) after subtracting the diamagnetic matrix component.



**Figure 4.** Diamagnetic contribution of the stretched polymer with the field applied at  $0^\circ$  (green circles  $\bullet$ ) and at  $90^\circ$  (blue squares  $\blacksquare$ ).

### 3.3. Optical characterization.

In a previous paper [6], Pucci *et al* demonstrated that terthiophene-coated gold NPs in polyethylene oriented films show big differences in the optical absorption when the angle between the polarization of light and the drawing direction of the film is changed. This

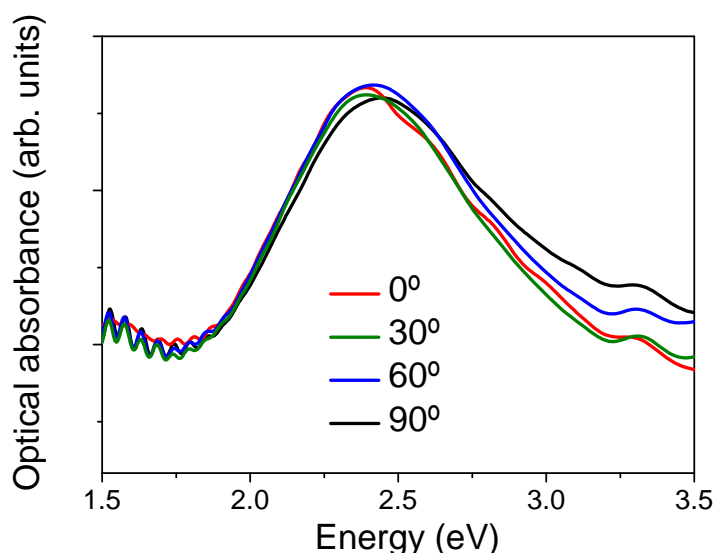
anisotropic absorption, which is due to organic molecules, indicates a sensitivity of the adsorbed chromophores to mechanical orientation.

Now we study if it is possible to induce anisotropy in the optical absorption of thiol capped gold NPs, where the absorption is only due to Au NPs and their interactions with S atoms bonded at the NP surface.

The optical absorption spectra have been measured as a function of the angle between the polarization of light and the drawing direction of the film. The angles were  $0^\circ$  (parallel),  $30^\circ$ ,  $60^\circ$  and  $90^\circ$  (perpendicular).

In order to appreciate the small differences in the absorption band, we have made a background linear correction and a normalization of the data. This correction is due to the scattering that comes from the polymer and the interband transitions from gold.

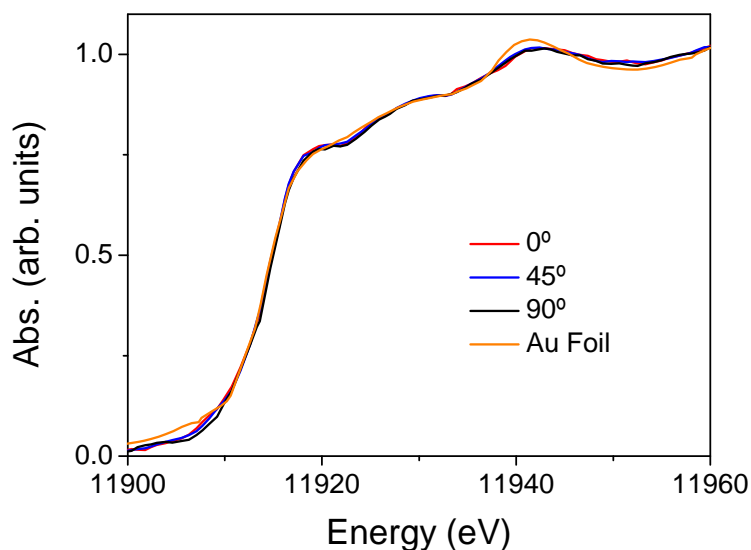
The results, figure 5, show how the width of the absorption band increases when the angle goes from  $0^\circ$  to  $90^\circ$ . We can observe the narrowest band for  $0^\circ$  and the broadest for  $90^\circ$ . The broadening of the absorption band is related to an increase in the surface plasmon attenuation. The SPR is strongly dependent on the size of the particles and interactions between the NPs and capping molecules [12]. In this case, we are measuring the same sample, so the differences in the absorption band can not be ascribed to these parameters. They should be due to an interaction between the polymeric matrix and Au NPs. This interaction is dependent on the drawing direction, which produces a macroscopic anisotropy in the optical properties.



**Figure 5.** Optical absorption spectra as a function of the angle between the polarization of light and the drawing direction of the film, after a lineal correction.

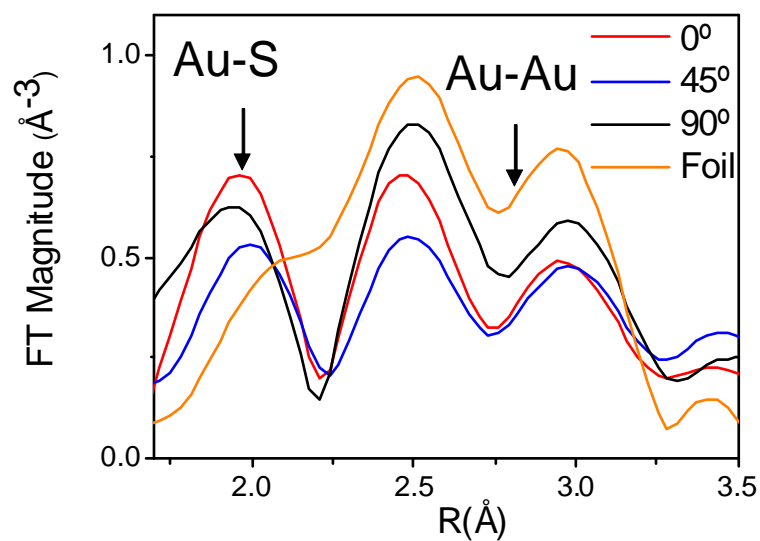
### 3.4. XANES and EXAFS analysis.

XAS spectra at the L3 edge of Au (electric dipole transition  $2p \rightarrow 5d$ ) from the sample and a reference Au metal foil are presented in figure 6 (XANES region, background subtracted, edge step normalized). The measurements have been done varying the angle between the x-ray beam polarization and the drawing direction of the polymer. The differences between the Au foil and Au NPs confirm the charge transfer from Au to S when thiols are attached to the nanoparticle in agreement with previous results [1,13].

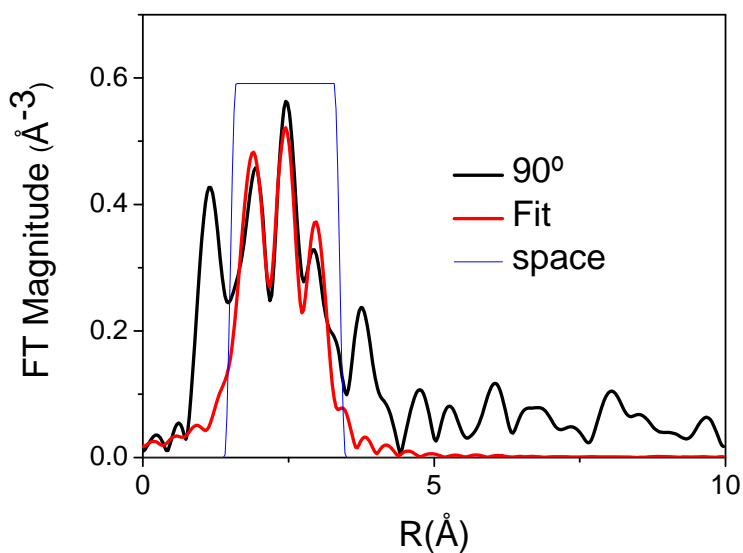


**Figure 6.** XANES spectra of the Au L3 edge for the Au NPs film and Au foil

The EXAFS data were fit in real space on Fourier transformed data, according to the model described in the literature [14]. Figure 7 show  $k^2$  weighted EXAFS in  $r$  space. The parameters used for the Fourier transform (FT) in the real space were  $k = 3-12 \text{ \AA}^{-1}$ ,  $R = 1.5-3.38 \text{ \AA}$ ,  $k^2$  weighting. The scattering paths used in the fit were Au-S single scattering and Au-Au first neighbor. Figure 8 shows the FT magnitude of the EXAFS data (black line) and full multiple-scattering-path fit (red line) following the model of Frenkel et al. [1515], for one of the measurements. The most relevant fitting parameters, i. e. coordination number of neighbors and bond lengths, are presented in table 1.



**Figure 7.** Modulus of the FT of EXAFS oscillations



**Figure 8.** EXAFS data (black line) and theoretical fit (red line) for Au NPs. Angle of 90° between the drawing direction and x-ray polarization.

Table 1. EXAFS fitting results

Fitting Parameter	Au NPs 0°	Au NPs 45°	Au NPs 90°	Au Foil
$N_{SS1}$ (Au-Au)	$4.22 \pm 2.3$	$4.35 \pm 2.05$	$5.64 \pm 1.99$	$10.9 \pm 0.9$
$R_{SS1}$ (Au-Au), Å	2.83	2.86	2.86	2.88
$N_{SS1}$ (Au-S)	$0.83 \pm 0.62$	$0.91 \pm 0.63$	$0.99 \pm 0.51$	-
$R_{SS1}$ (Au-Au), Å	2.34	2.35	2.32	-



The interatomic distance between Au atoms, first nearest neighbor distance show a small contraction from the bulk values. The distance between Au-Au atoms is approximately 2.8 Å, while the distance Au-S is 2.35 Å. These results agree with those observed for other authors [15,16,].

In figure 7 the contributions of the Au–Au or Au–S interactions to EXAFS are indicated by arrows. These contributions are different for different angles. The relative contribution of Au-S bonds in the Au L3 edge changes when the angle between the drawing direction and the polarization of the x-ray increases. For the Au foil only the signal corresponding to Au-Au bonds is present, with intensity larger than the case of NPs.

When the x-ray beam polarization is perpendicular (90°) to the drawing direction, a larger number of Au-S bonds are observed. When the angle goes to 0° (parallel orientation), the contribution coming from Au-S interactions and the number of bonds decreases. It seems that there is anisotropy in the number of Au-S bonds, because of the polymer stretching. However, the results for the number of Au-Au neighbors are not well understood, because the number should be independent of the drawing direction. The sensitivity of the XAS measurements to the organic bonds has been observed in Au films covered with organic molecules [17]. For these self assembled monolayers, the EXAFS signal in the carbon K edge is dependent on the angle between the beam and the surface. This dependence is related to the orientation of the organic chains.

The result agrees with the optical absorption measurements and the magnetic characterization. EXAFS shown the larger number of Au-S Bonds is observed when the incidence is at 90°. SPR band is modified by these Bonds. In this way, a larger number of Au-S bonds, will produce an extra damping in the plasmon resonance and as a result a broader absorption band. This is the behavior observed in figure 5. The same argument could used to explain the results for the magnetic characterization: a smaller number of Au-S bonds along the drawing direction (0°) produce a smaller magnetic signal when a magnetic field is applied in such orientation and hence, a larger diamagnetic signal is observed. This signal comes from the inner Au atoms and those surface Au Atoms not bonded to S atoms. However, when the magnetic field is applied perpendicular to drawing direction (90°), the number of Au-S bonds is larger. Since these bonds are responsible for the ferromagnetic-like behavior, the diamagnetic component is smaller, not visible in  $M$ . vs.  $H$  measurements and the value of the magnetic saturation is larger, figure 3. The smaller number of Au-S bonds along the drawing direction could be due to the mechanical stretch, which break some bonds along this direction while the bonds in the perpendicular direction remain unaffected.

#### **4. Conclusions.**

The optical and magnetic anisotropy observed in a system containing thiol capped Au NPs embedded in a polymeric matrix have been studied. The origins of this behavior are the modifications in the Au-S bonds. These modifications are due to the stretching procedure of the polymeric matrix, which affect to the Au-S bonds located at the NP surface. Since the optical and magnetic properties are dependent on these bonds, the slight modifications caused by the stretching opens the possibility of inducing a macroscopic anisotropy in systems that contain spherical NPs.

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