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Synthesis of supramolecular nanoarchitectures based on carbonitrile functional groups

Shanmugasibi K. Mathialagan, Sofia O. Parreiras, Cristina Martín-Fuentes, Daniel Moreno, José I. Urgel, Beatriz Muñiz-Cano, Koen Lauwaet, Manuel Valvidares, Miguel A. Valbuena, Pierluigi Gargiani, José I. Martínez, Nazario Martín, Julio Camarero, José M. Gallego, Rodolfo Miranda and David Écija

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GOBIERNO DE ESPAÑA
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AGENCIA ESTATAL DE INVESTIGACIÓN

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Comunidad de Madrid

Introduction

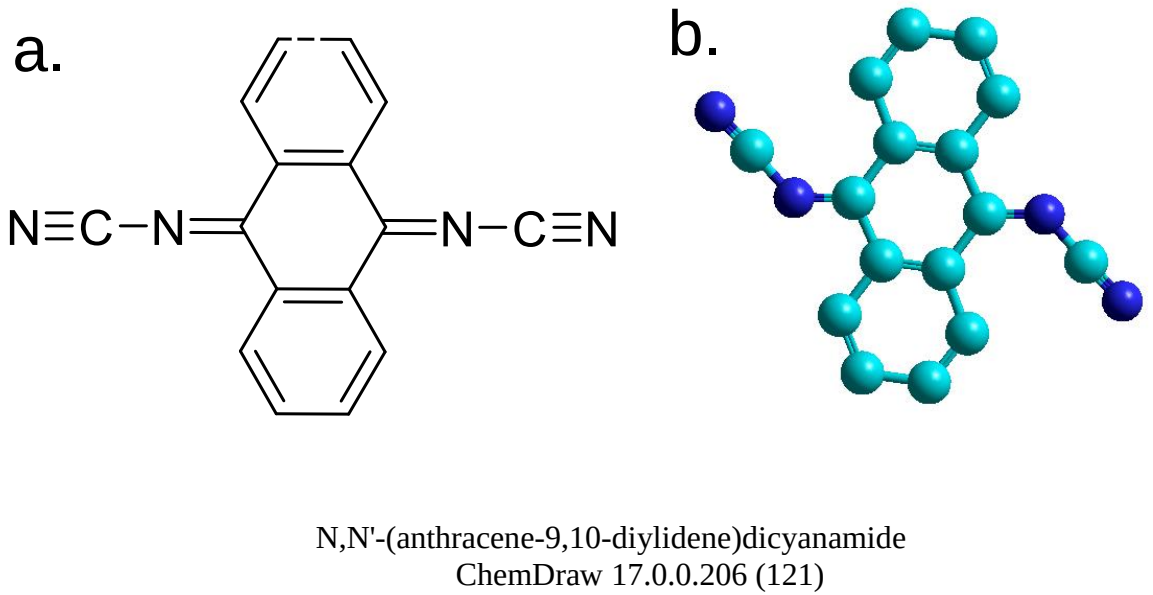
Metal organic frameworks

- Technology is rapidly progressing towards miniaturization of electronic circuits.
- As most electronic devices rely on magnetic storage, nano-magnetism carries a significant importance in the electronic industry.
- Low dimensional metal organic frameworks show great potential as new spintronic devices for information processing and storage.
- They possess a vast reservoir of properties including exotic quantum phenomenon which can be manipulated, making them promising building blocks for next-generation information devices.

Introduction

- In this work, we have experimentally investigated metal-organic networks consisting DCAAQ (N,N'-(anthracene-9,10-diylidene) dicyanamide) molecules coordinated with Co atoms on Au(111).

- We have synthesized the network and inspected its structure, electronic properties with Scanning tunneling microscopy (STM) and experiments related to magnetic properties were performed at ALBA Synchrotron.

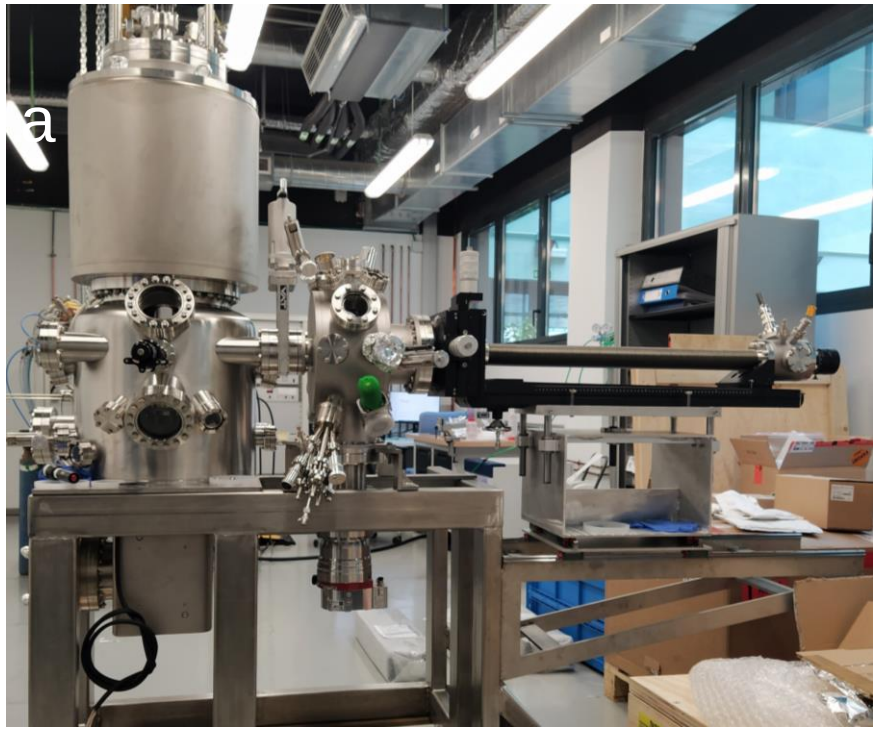


N,N'-(anthracene-9,10-diylidene)dicyanamide
ChemDraw 17.0.0.206 (121)

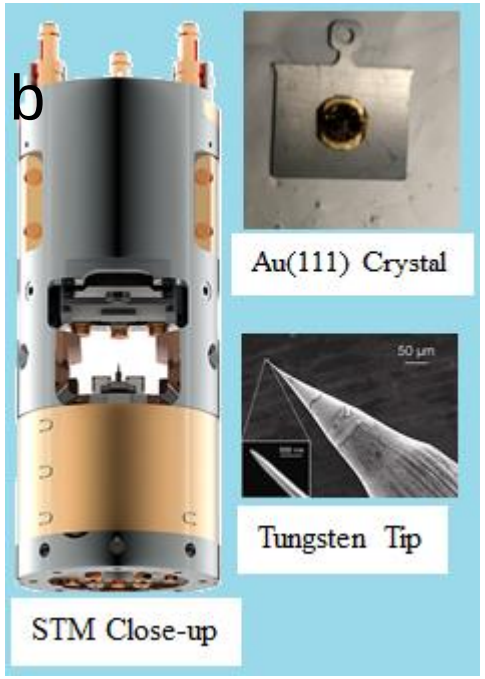
Figure 1. Molecular structure (a) Chemical structure of N,N'-(anthracene-9,10-diylidene)dicyanamide molecule (b) Ball & stick model.

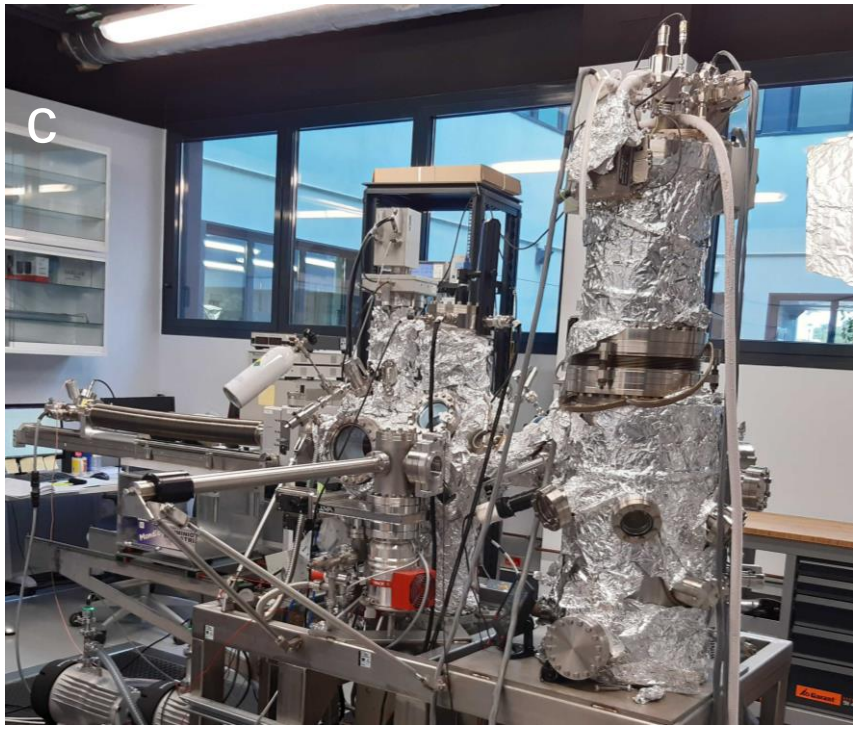
Experimental set-up

STM - IMDEA,Madrid.



Polar STM- IMDEA Nanociencia, Madrid





(Non-contact AFM) STM- IMDEA Nanociencia, Madrid

Figure 2. STM setup (a) Polar STM set-up at IMDEA Nanociencia, Madrid (b) Parts of the Polar STM: STM head, Au(111) crystal, Tungsten tip (c) (Non-contact AFM) STM- IMDEA Nanociencia, Madrid.

- Topography and Electronic properties measurements were performed with the STMs in IMDEA Nanociencia, Madrid.
- The samples were measured at Helium temperature in a UHV environment with a base pressure of the order of $1x10^{-10}$ mbar.

Experimental set-up

BOREAS-ALBA

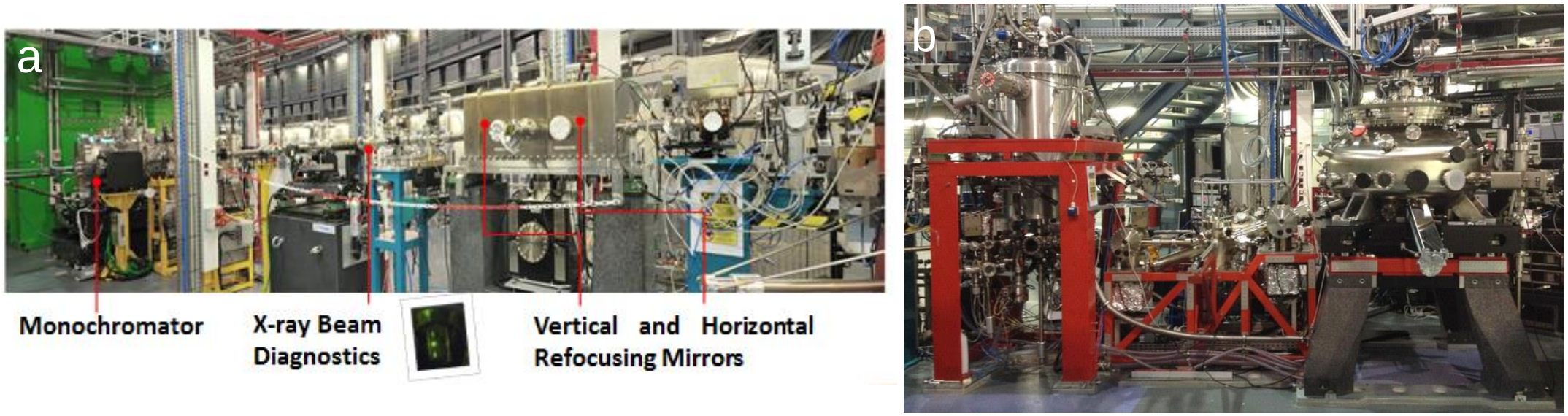


Figure 3. Boreas beam line setup (a) BOREAS Beam line – ALBA, Barcelona. (b) X-ray Absorption Spectroscopy and magnetic circular dichroism endstation (Hector)

- X-ray absorption spectroscopy (XAS), Soft X-ray (magnetic) circular and linear dichroism (XMCD/XLD) measurements were performed in BOREAS beamline.

- The samples were measured in a UHV environment with a base pressure of the order of $<1x10^{-10}$ mbar.

Results

Molecular Self-Assembly

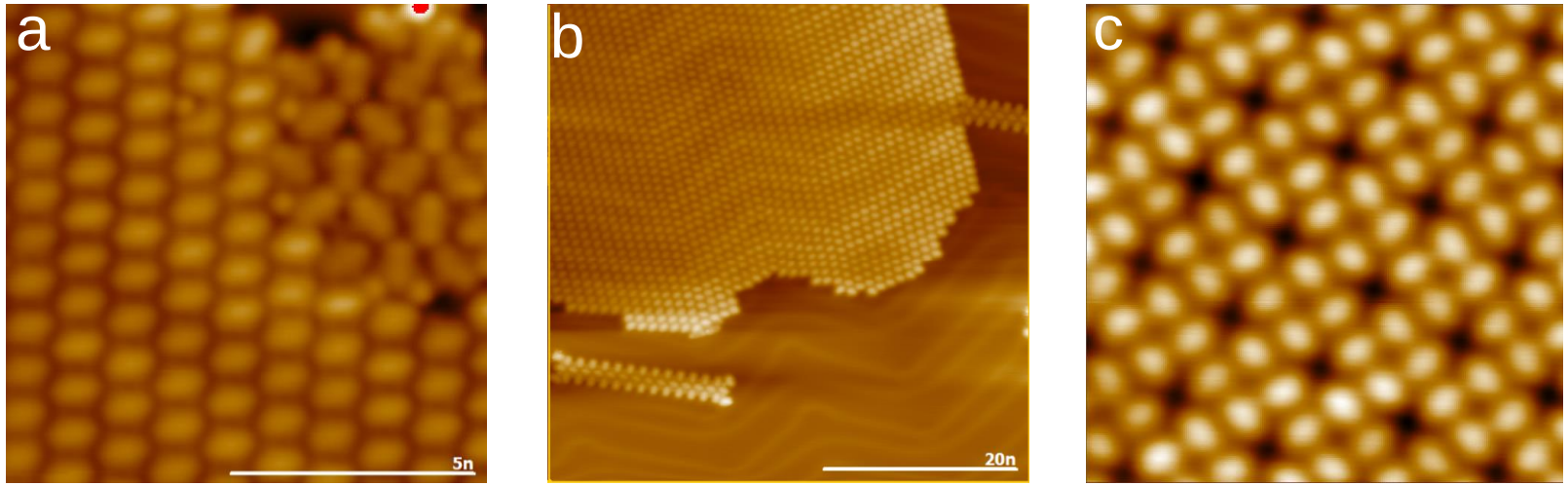


Figure 5. Molecular Self-Assembly (a) 10 x 10 nm image showing hexagonal and triangular assemblies (b) 50 x 50nm long-range image showing) 10 x 10 nm image showing chain-like assembly (c) 4nm x 4nm image showing square assembly.

- The sample was prepared by sublimating the molecules at 130 ℃ molecules on Au(111) substrate.
- We observe four different types of self-assembly Hexagonal (main phase), Chain, triangular and square.

Results

Coordinated network: 2-Fold phase

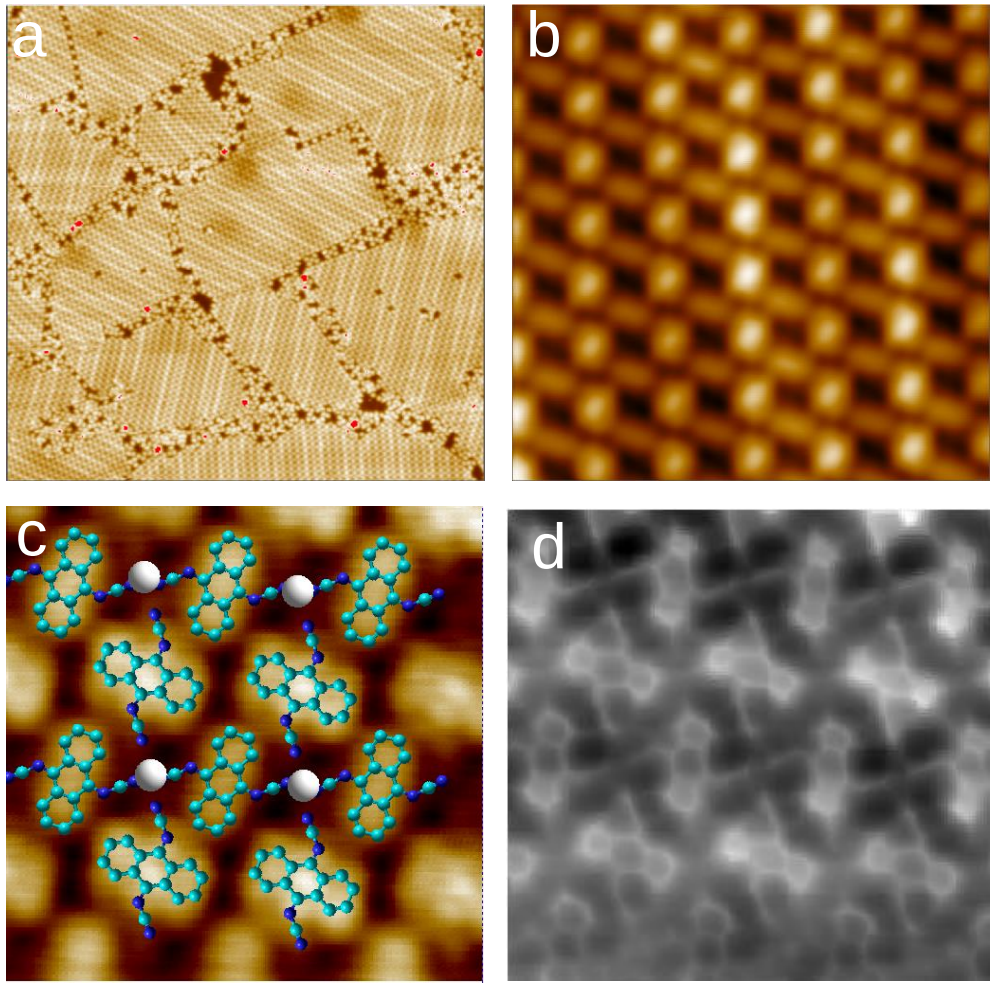


Figure 6: Metal-Organic framework long range, short range images (a) N,N'-(anthracene-9,10-diylidene) dicyanamide and Cobalt on Au(111) surface 100 x 100 nm image. (b) 10 x 10nm image (c)3.5nm x 3.5nm image with super-imposed model (d) Non-contact AFM image 4.4nm x 4.4nm

- The sample was prepared by depositing molecules and metal on an Au(111) and annealing at 140°C
- We obtain an interesting network of coordinated stripes consisting of 1D stripes formed with two-fold coordinated molecules and mononuclear Co centres
- Co-CN distances are distinct in transversal direction and in longitudinal direction.

Results

DFT Calculations: 2-fold phase

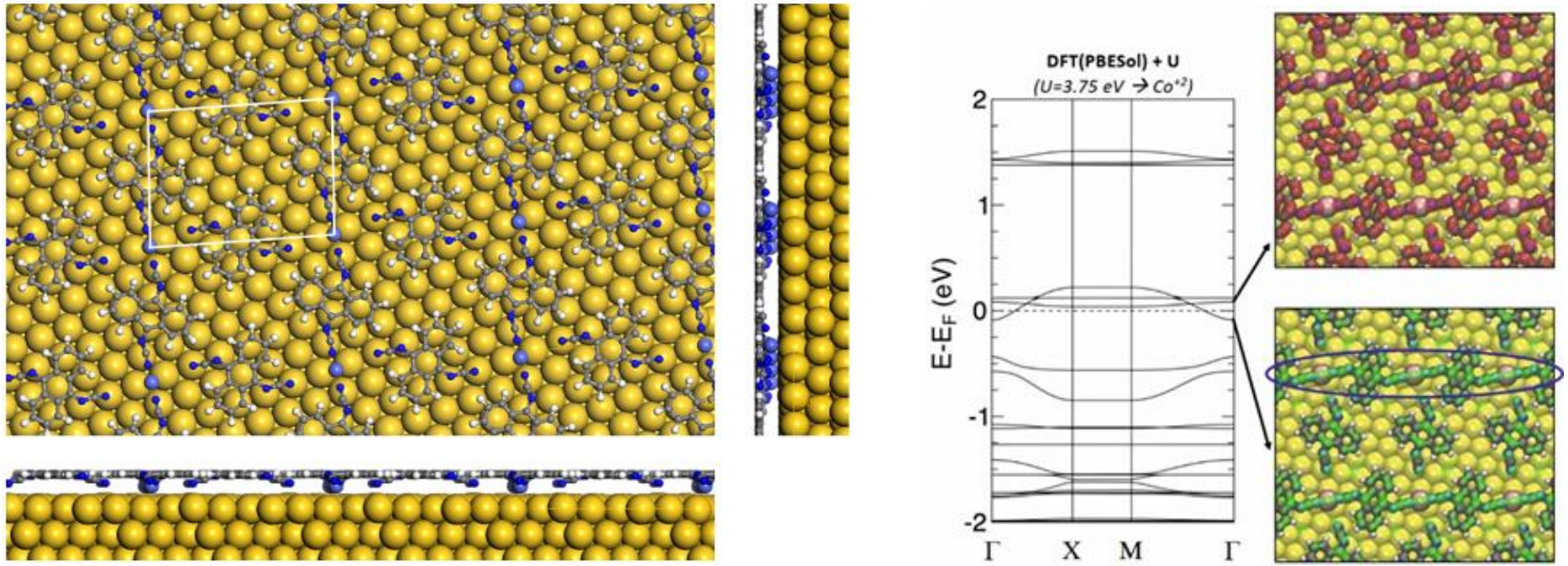


Figure 7. DFT calculation of the Metal-Organic framework (a) Top and side view of the metal-organic system (b) Computed DFT+U band structure (U = 3.7 eV for Co+2).

- Co-CN distances are (1.8 Å) in transversal direction and (4.27 Å) in longitudinal direction.

- DFT calculations predict metallicity along the 1D chain.

Result- Electronic properties

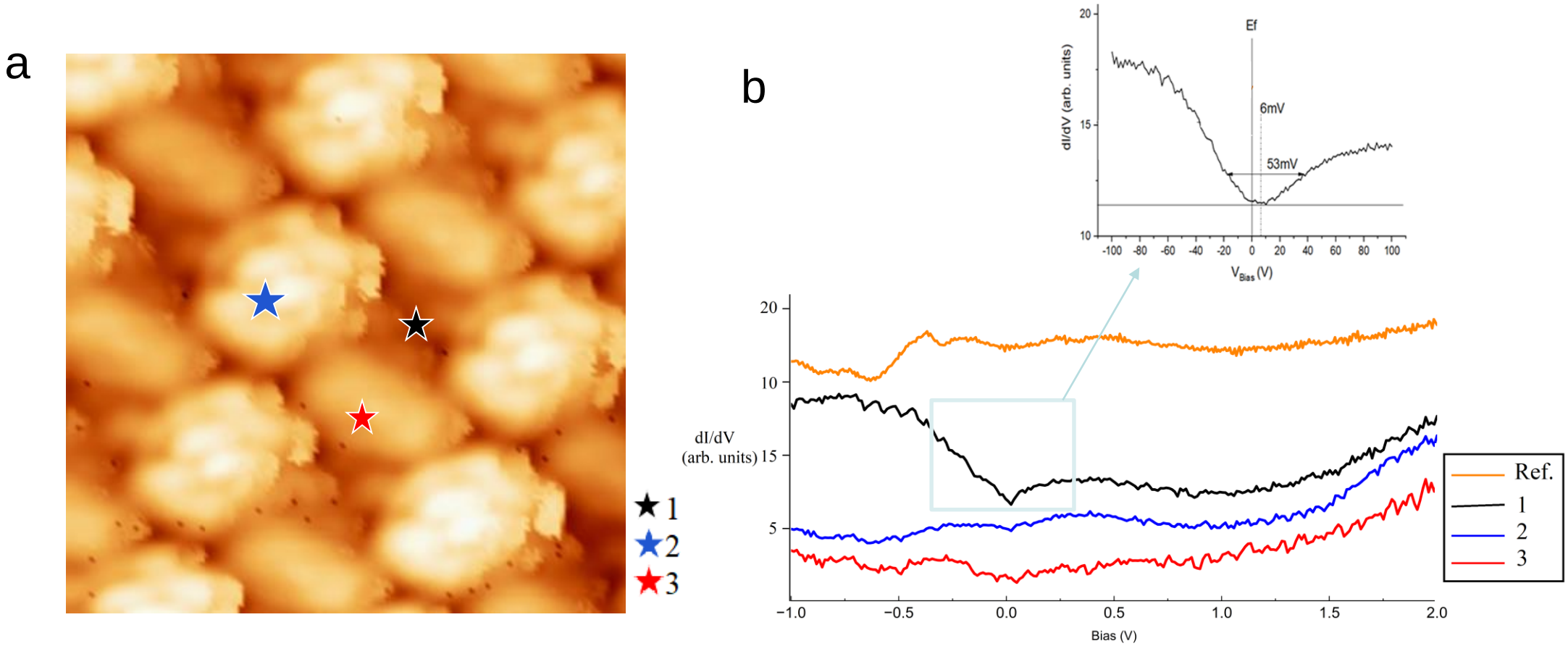


Figure 8. Electronic properties long range(a) STM image of the network 3.5x3.5nm image showing spectroscopy locations. (b) Scanning Tunneling Spectroscopy (STS) in range -1V to +2V at different points of the network. Inset graph shows a short range STS of the cobalt centre.

- STS reveals no fingerprints, but a profound dip at Fermi, probably of Kondo origin.

Results - Electronic properties

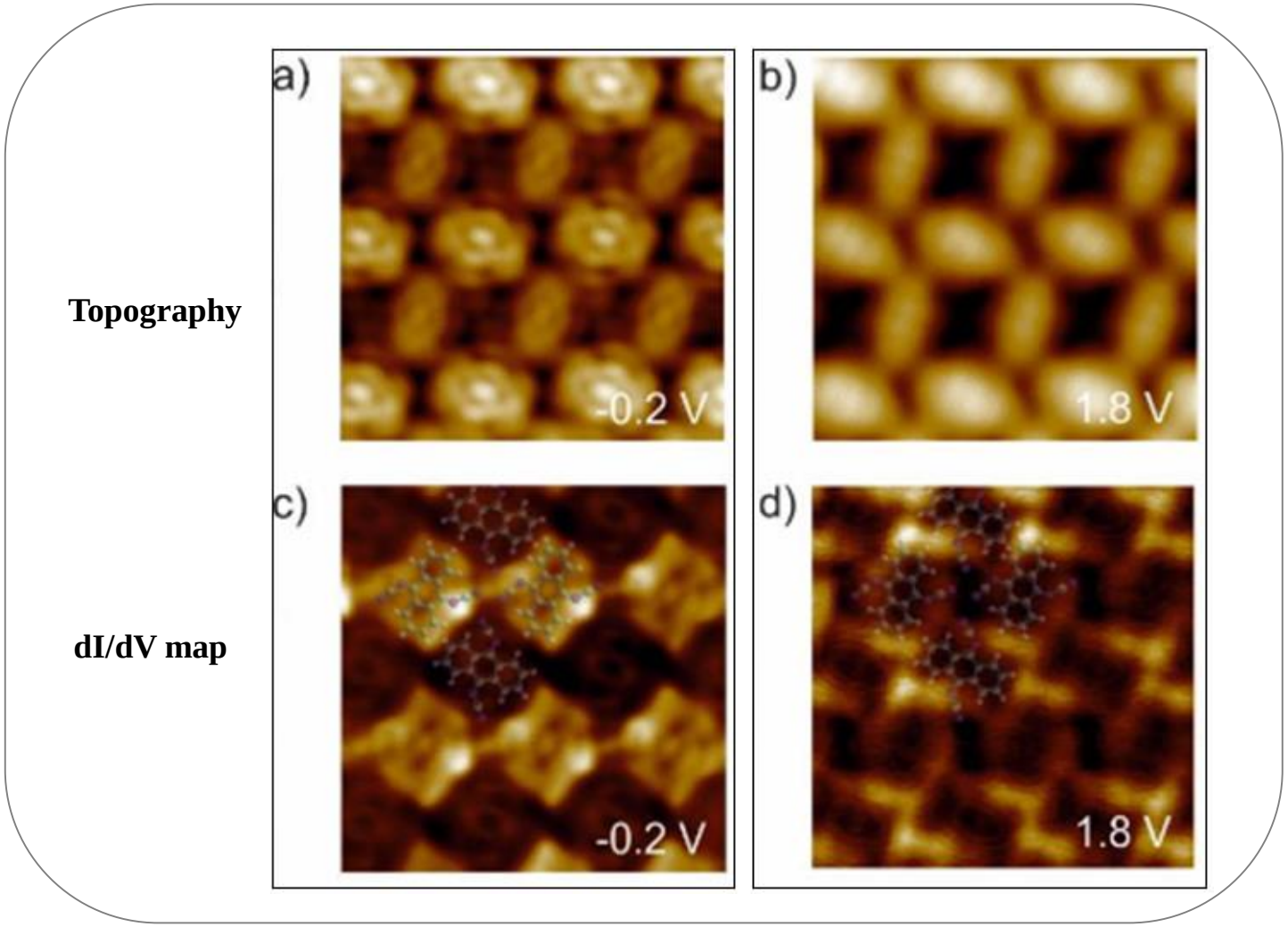


Figure 9. dI/dV maps and constant height images (a,b) STM topography. 3.5 x 3.5nm images (c) dI/dV map corresponding to image (a) obtained at voltage -200mV images (d) dI/dV map corresponding to image (b) obtained at voltage 1.8V (f) Constant current image 5nmx5nm (g) Constant height image 5nmx5nm.

- The bandgap is not clear by STS but dI/dV mapping shows two different electronic states at -0.2V and 1.8V. Bandgap (if any) lower than 0.4eV

Result - Magnetic properties

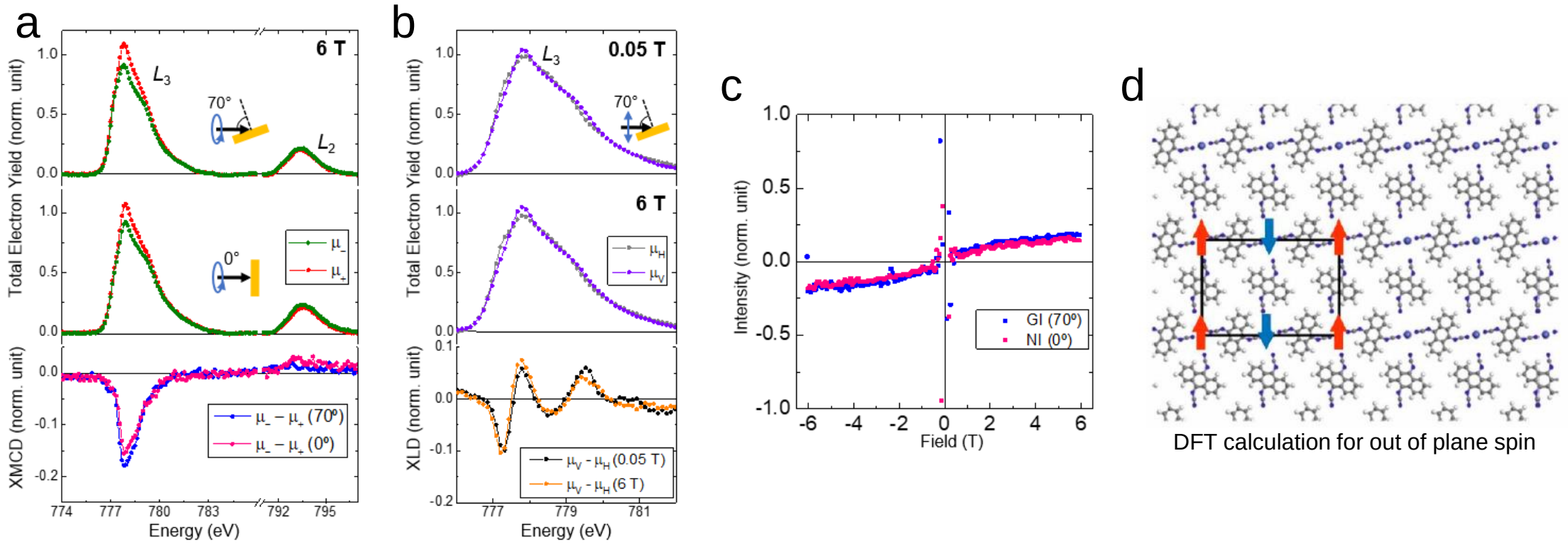
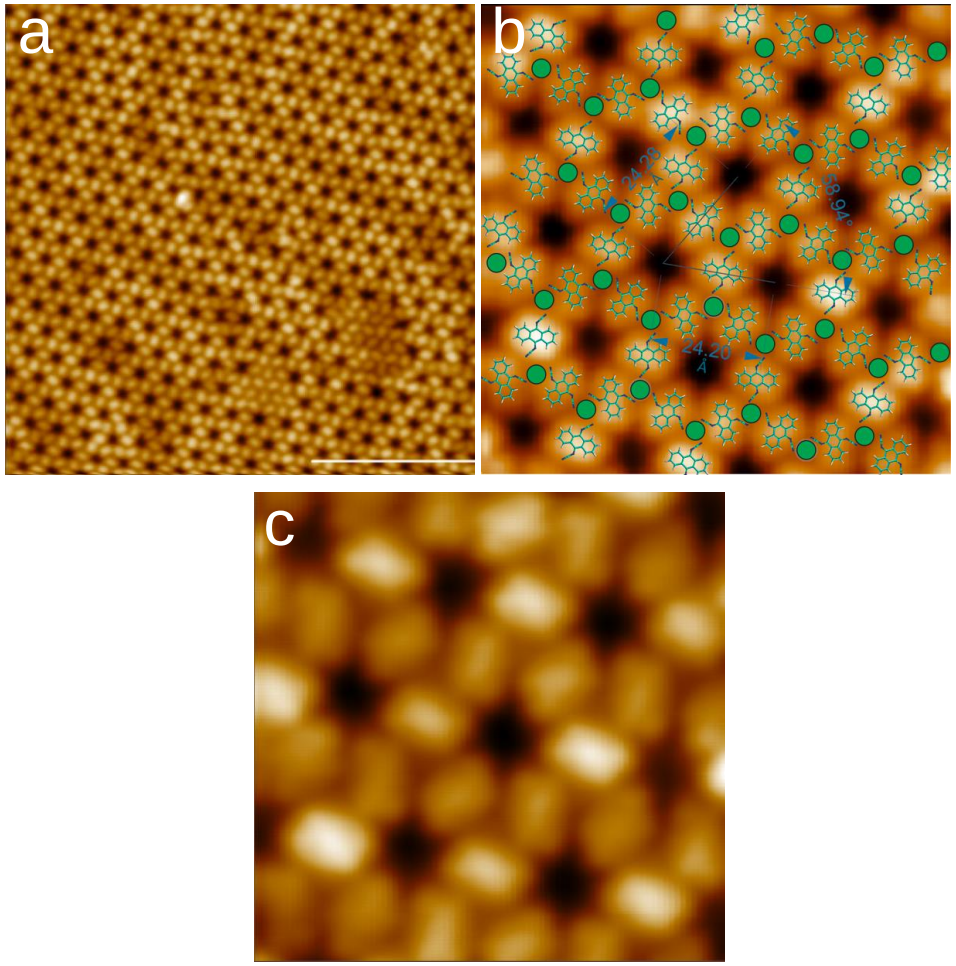


Figure 10. Magnetic properties (a) XAS spectra with positive (μ_+, red) and negative (μ_-, green) circularly polarized light and XMCD (($\mu_- - \mu_+$)) taken at Co $L_{2,3}$-edges at grazing (70°, blue) and normal (0°, pink) incidences (B = 6 T, T = 2 K). (b) XAS spectra acquired with vertical (μ_V, purple) and horizontal (μ_H, grey) linearly polarized light and XNLD ($\mu_V - \mu_H$) taken at Co L_3-edge at grazing (70°) incidence for fields of 0.05 T (black) and 6 T (orange) (T = 2 K). (c) Magnetization curves constructed by measuring the XMCD intensity at the highest peak of Co L3-edge at grazing (70°, blue) and normal (0°, pink) incidences (T = 2 K).(d) DFT calculation for out of plane spin.

- The XMCD spectra have a low intensity and are almost isotropic and XLD spectra features a very low charge anisotropy, with around 10% of dichroism.
- Magnetization curves present a behavior compatible with paramagnetic or antiferromagnetic, with low intensity and no remanence.

Results

Coordinated network: 3 fold phase



- The sample was prepared by depositing molecules and metal on an Au(111) and annealing at 140°C
- We obtain a symmetric network consisting of three-fold coordinated molecules and mononuclear Co centres.
- DFT calculations in progress

Figure 11. Metal-Organic framework long range, short range images (a) N,N'-(anthracene-9,10-diylidene) dicyanamide and Cobalt on Au(111) surface 40 x 40 nm image. (b) 3.5 x 3.5nm image (c)10nm x 10nm image with super-imposed model.

Result- Electronic properties

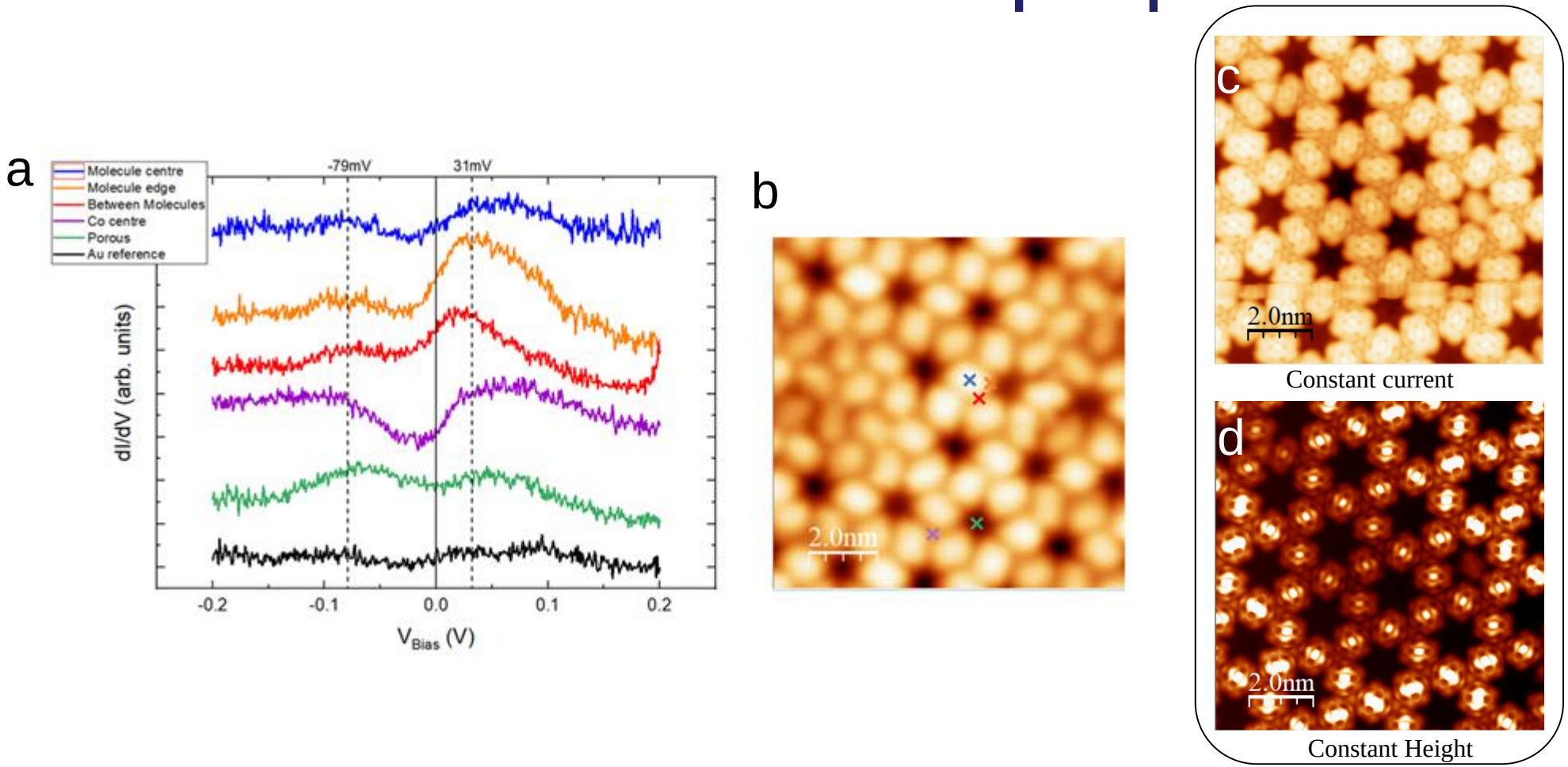


Figure 12. Electronic properties short range(a) Scanning Tunneling Spectroscopy (STS) in range -0.2V to +0.2 at different points of the network (b) STM image of the network 3.5x3.5nm image showing spectroscopy locations. (c) Constant current image 5nmx5nm (d) Constant height image 5nmx5nm.

- The spectra on cobalt center features a profound dip at Fermi, probably of Kondo origin.

Conclusions

- Our results shows formation of two networks based on two-fold and three-fold coordinated molecules with mononuclear Co centers.
- STS on the Cobalt atom position in both networks show a wide dip close to Fermi.
- XMCD spectra of two-fold phase Co display a low intensity, absence of saturation and no remanence, which is indicative of paramagnetism or antiferromagnetism.
- Furthermore, density functional theory complemented by a Hubbard model (DFT+U) predict a antiferromagnetic ground-state, that is compatible with our experimental results.

Perspectives

- Both networks will be studied with a Spin ARPES housed in IMDEA nanociencia.
- XMCD for 3-fold network needs to be performed to understand how it varies from the other network.
- DFT calculations on both networks is a work in progress.

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Thank you

Questions!!

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