Magnetic atom clustering templated by an extended metal-organic coordination network

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Goal

To nanostructure transition metals using as template the nanocavities from a porous organometallic network.

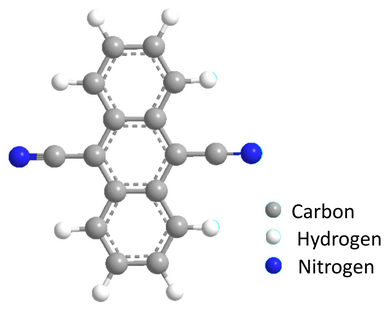
The chosen molecular network is based on 9,10-dicyanoanthracene (DCA) molecules. These self-assemble into an extended monodomain porous arrays when deposited at room temperature in ultra high vacuum conditions on a Cu(111) surface.

The magnetic transition metals evaporated onto the networks are Fe, Co and Mn.

The system has been characterized using STM and LEED.

DCA molecular porous network

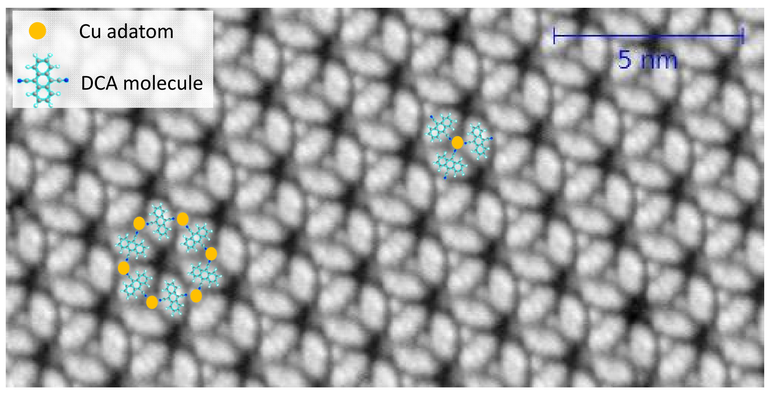
Molecular Precursor: DCA (9,10-dicyanoanthracene)



Consists of an anthracene backbone with two cyano (CN) groups bonded to the central phenyl ring. These generate two dipoles that guide the intermolecular interactions [1,2].

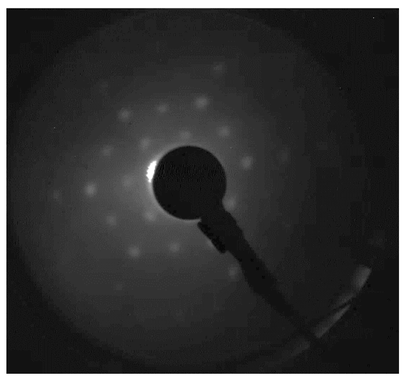
After cleaning the Cu(111) substrate, DCA molecules are evaporated onto the substrate at RT and then post-annealed to 130°C to desorb the molecular excess and form the porous network.

The organo-metallic network is stabilized by Cu adatoms present on the surface that coordinate to three molecules by their cyano groups [1,2].



STM image: I=300pA; V=-1V

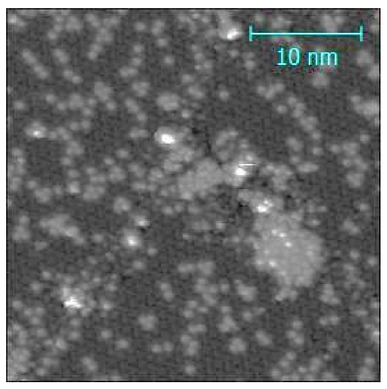
Each pore is surrounded by six DCA molecules, whose anthracene axis point to the centre of a nanocavity. The cyano groups coordinate with Cu adatoms.



LEED image at 22eV

The LEED pattern exhibits extended mono domain (8x8) superstructure.
It is in registry with the Cu(111)

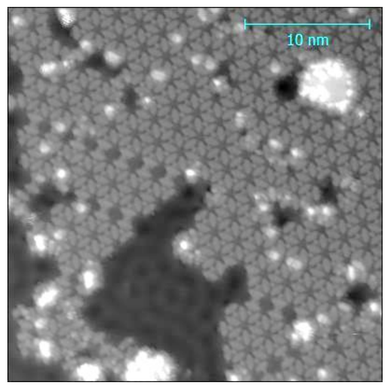
Cobalt + DCA assemblies



STM: I=50pA; V=-200mV

Evaporation of ~0.25 ML Co on molecular network carpet (full surface coverage).

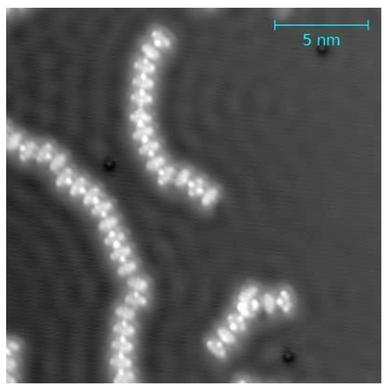
- Co does not nanostructure into dots
- Co compresses the network converting it into a compact one.



STM: I=120pA; V=100mV

Partial surface coverage of DCA network + ~0.25 ML Co .

- Co is not nanostructured
- Network disruption.



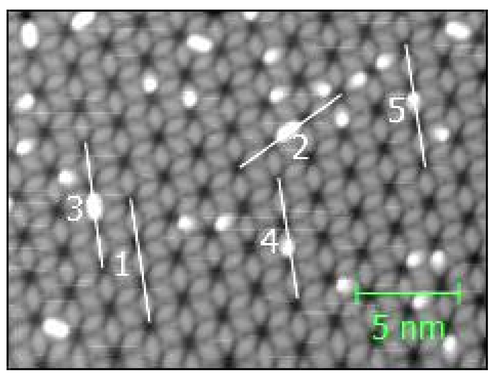
STM: I=120pA; V=-100mV

~0.25 ML Co evaporation + addition of DCA molecules.

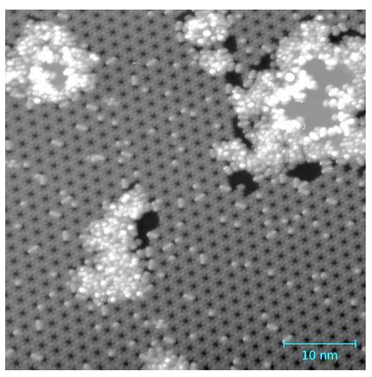
- Chain formation: Co coordinates two cyano groups.
- No network observed with Co presence.

Manganese + DCA assemblies

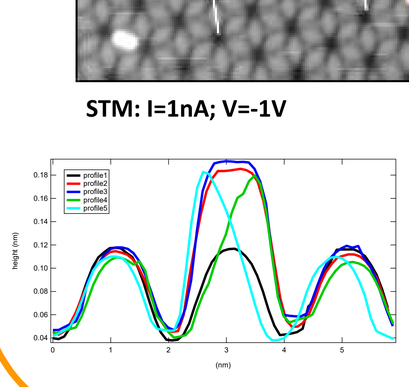
Evaporation of ~0.20 ML of Mn atoms on the porous network.



STM: I=1nA; V=-1V



STM: I=1nA; V=1,5V

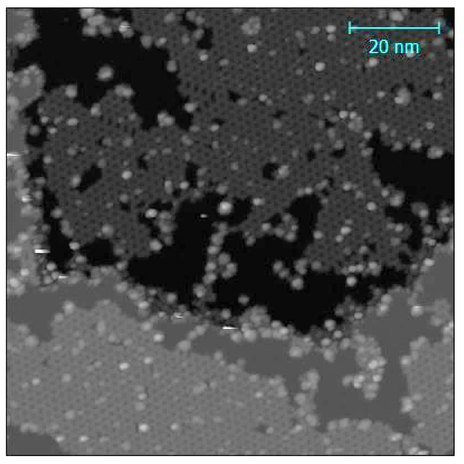


- Mn atoms diffuse underneath the molecules lifting them up.
- They do not stay within the pores.

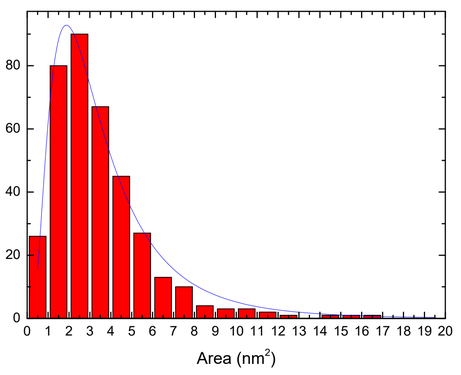
- Mn does not nanostructure into dots.
- Mn atoms nucleate in large and irregular islands pushing DCA molecules to the top.

Iron + DCA assemblies

Evaporation of ~0.15 ML of Fe atoms at room temperature on the DCA network

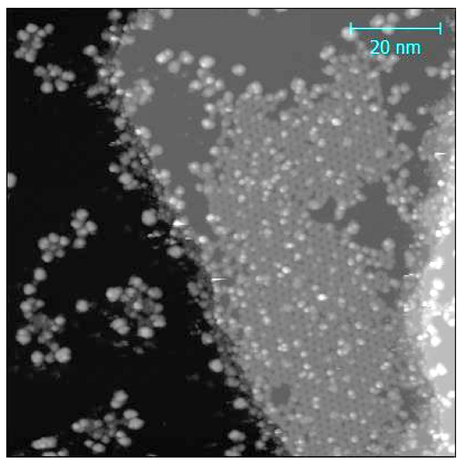


STM: I=100pA; V=1,5V

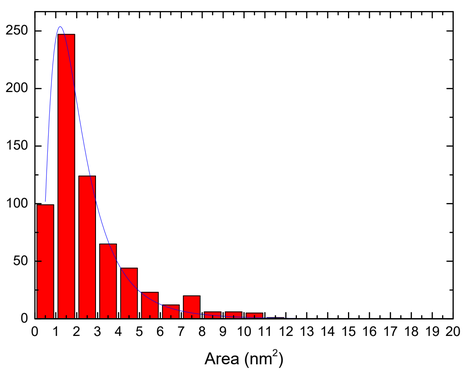


- Observation of Fe nanodots templated by the molecular network
- Fitting the data to a Lognormal function, the average value of the grain projected area is close to 3nm²

Evaporation of ~0.20 ML of Fe atoms at 180 K on the DCA network and post-annealing to room temperature



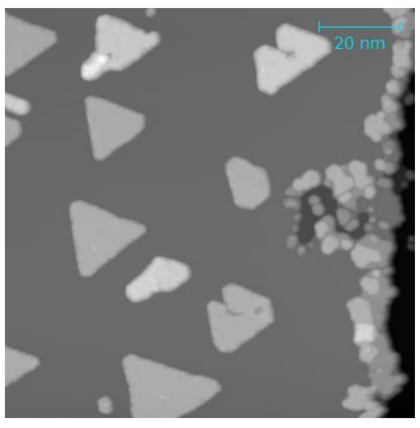
STM: I=40pA; V=1,5V



- Observation of smaller Fe nanodots on the molecular network
- The Lognormal function defines an average size of 1.9nm²

Evaporation of Fe directly on the Cu substrate results in large triangular islands.

- These triangular islands form bilayers, before covering completely the substrate.



STM: I=160pA; V=1,5V

CONCLUSIONS

- We obtained an extended monodomain DCA network on a Cu(111) surface
- Neither Mn nor Co results in defined nanostructures when deposited onto the molecular network.
- Fe is nanostructured into nanodots of 2-3 nm² area after deposition onto the molecular network. We are able to control the grain size by changing the substrate deposition temperature.

Outlook:
X-ray Magnetic Circular Dichroism (XMCD) will be attempted for these systems templated by the DCA molecules. Especial attention will be paid to the Fe nanodots and its dependence with size (deposition temperature).

References

[1] Pawin, G. *et al.* A Surface Coordination Network Based on Substrate-Derived Metal Adatoms with Local Charge Excess *Angew. Chem. Int. Ed.* **47**, 8442 –8445 (2008).

[2] Zhang, J. *et al.* Probing the spatial and momentum distribution of confined surface states in a metal coordination network †. *Chem. Commun.* **50,** 12289–12292 (2014).

Thanks to:
Marten Pianteck and Carlos Martín