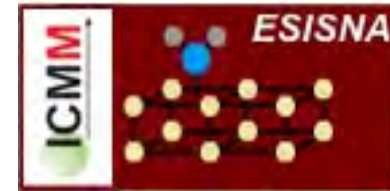
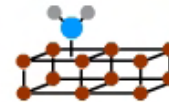


Adsorption, cyclodehydrogenation and graphene formation from molecular precursors on catalytic surfaces



J.A. Martin-Gago, gago@icmm.csic.es

Structure of Nanometric
Systems Group



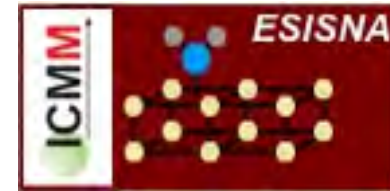
<http://www.icmm.csic.es/esisna/>



On-surface chemistry: Influence of the substrate in de-hydrogenation reactions of PAH (polycyclic aromatic hydrocarbons)



On surface chemistry of cyclic molecules



C₆₀H₃₀- on Pt(111) -> fullerenes

C₆₀H₃₀- on Au(111) -> 2D layers

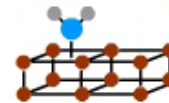
C₆₀H₃₀- on TiO₂(110)-> 2D layers,fulleren-like

Graphene on Pt(111) -> multiphase graphene

Surface science techniques: STM, XPS, synchrotron radiation, DFT...

J.A. Martin-Gago, gago@icmm.csic.es

Structure of Nanometric
Systems Group



<http://www.icmm.csic.es/esisna/>





READIUS.

by

Polymer Vision



Flexible electronics based on organic molecules:

Near-future nanotechnology .
Light, cheap, ecological

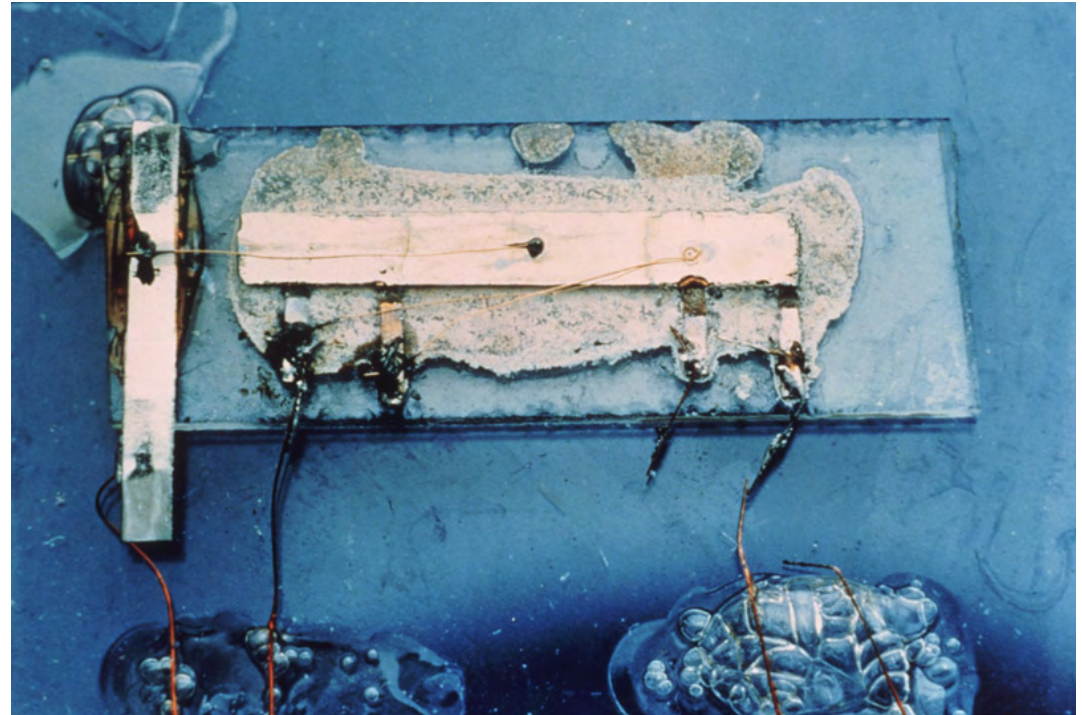


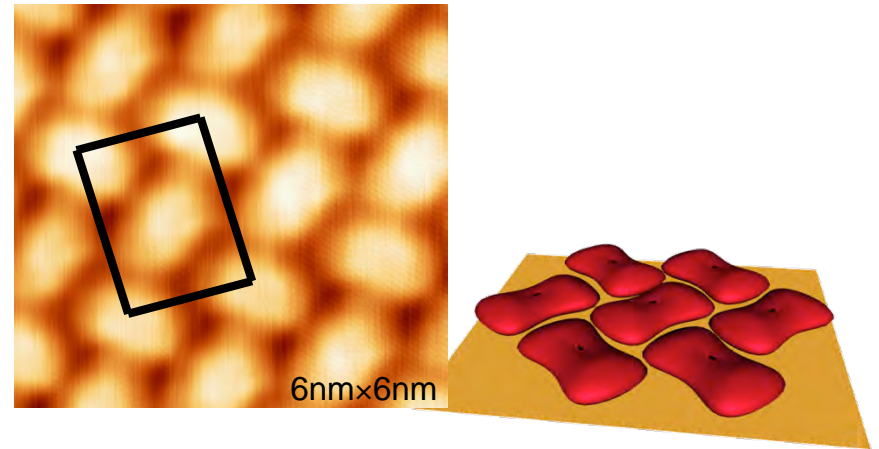
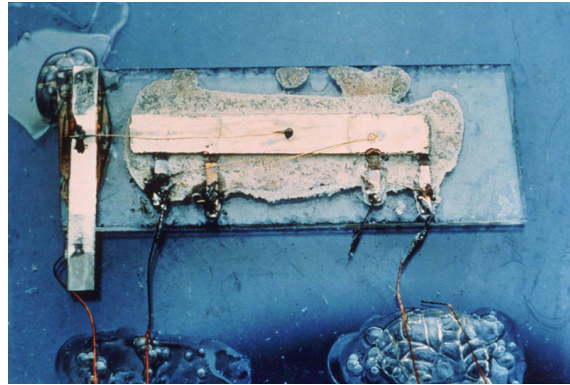
1947: *micro-science*

First transistor:
by Bardeen, Brattain and Shockley



First electronic circuit





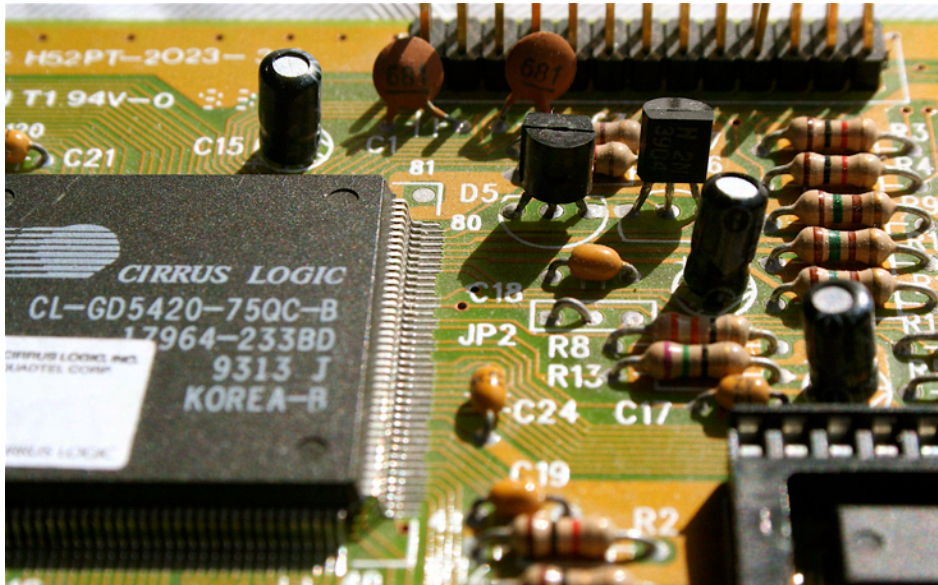
Micro-science

nano-science

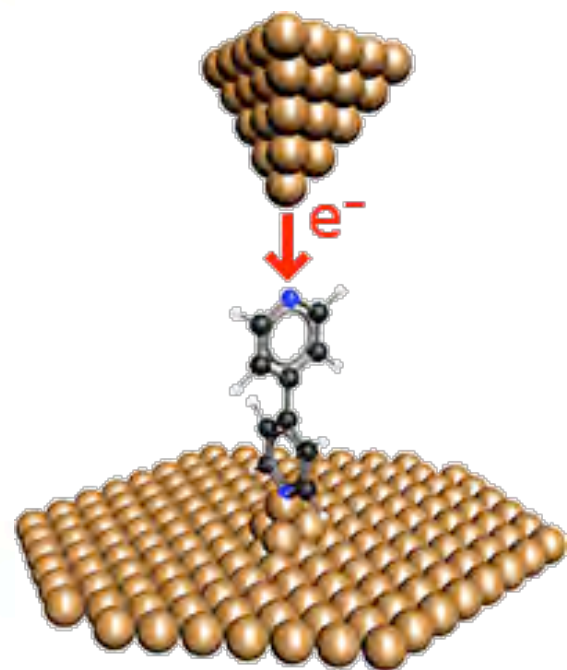
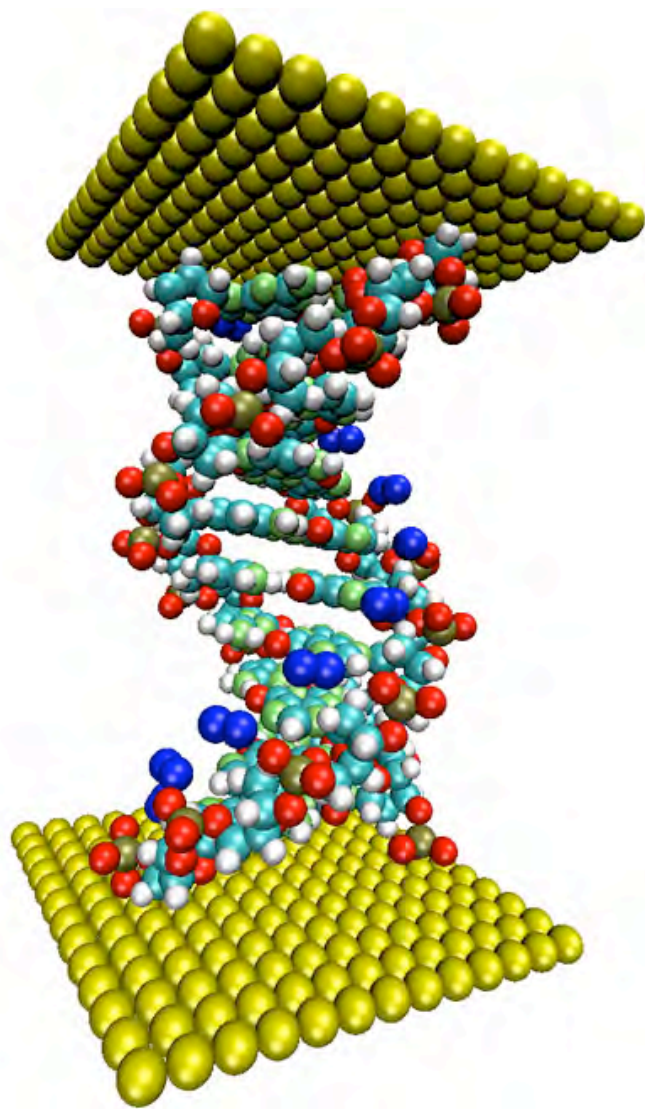
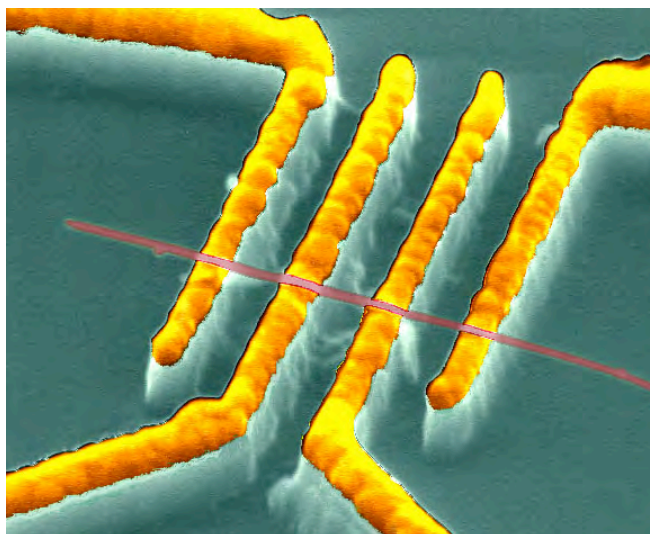


Micro-technology

nano-technology



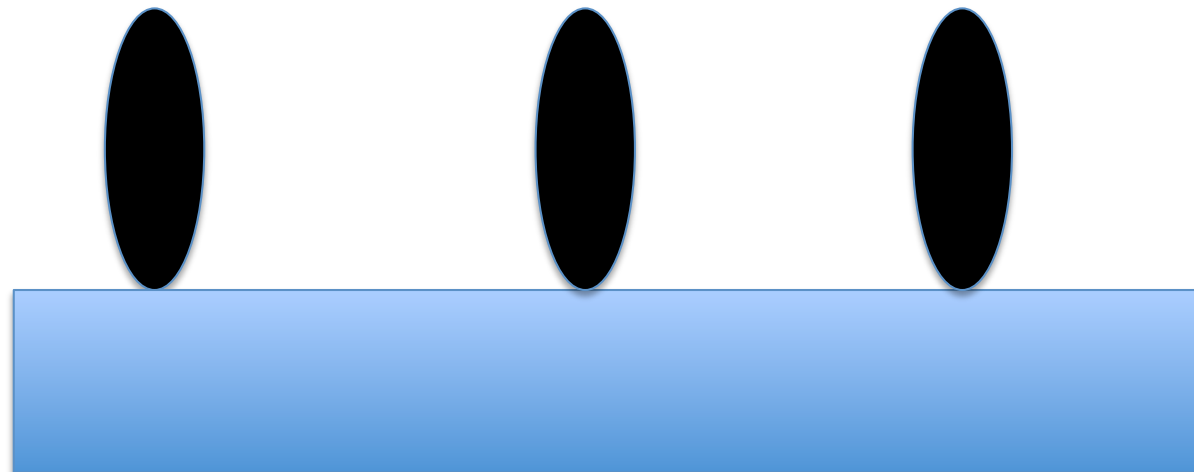
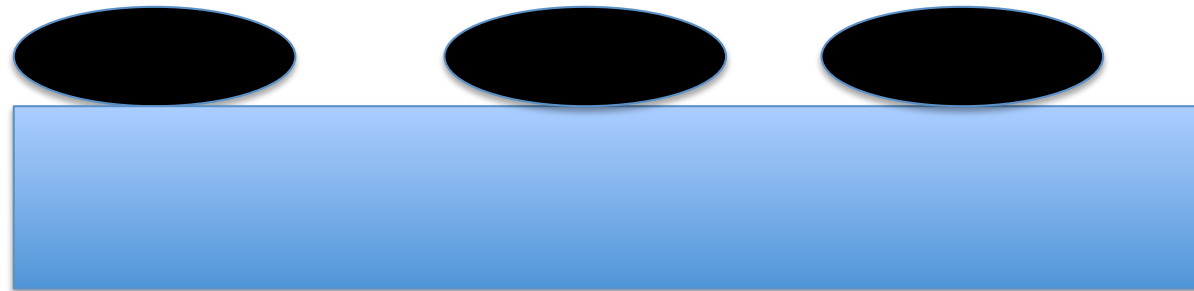
We are doing the science before using molecules for organic devices



Single-molecule electronics: new molecules on-surfaces

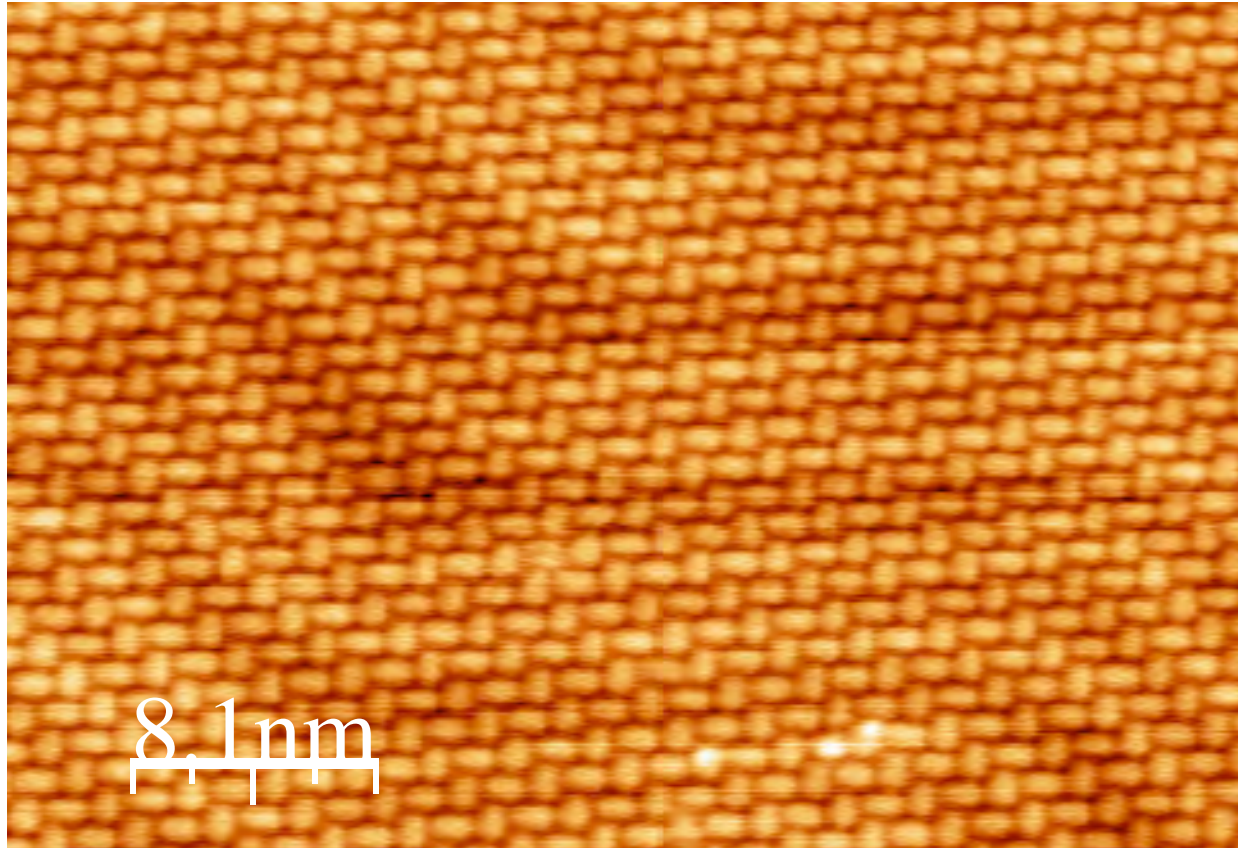
surface science

Structure and electronic properties of molecular layers



PTCDA /Au(111)

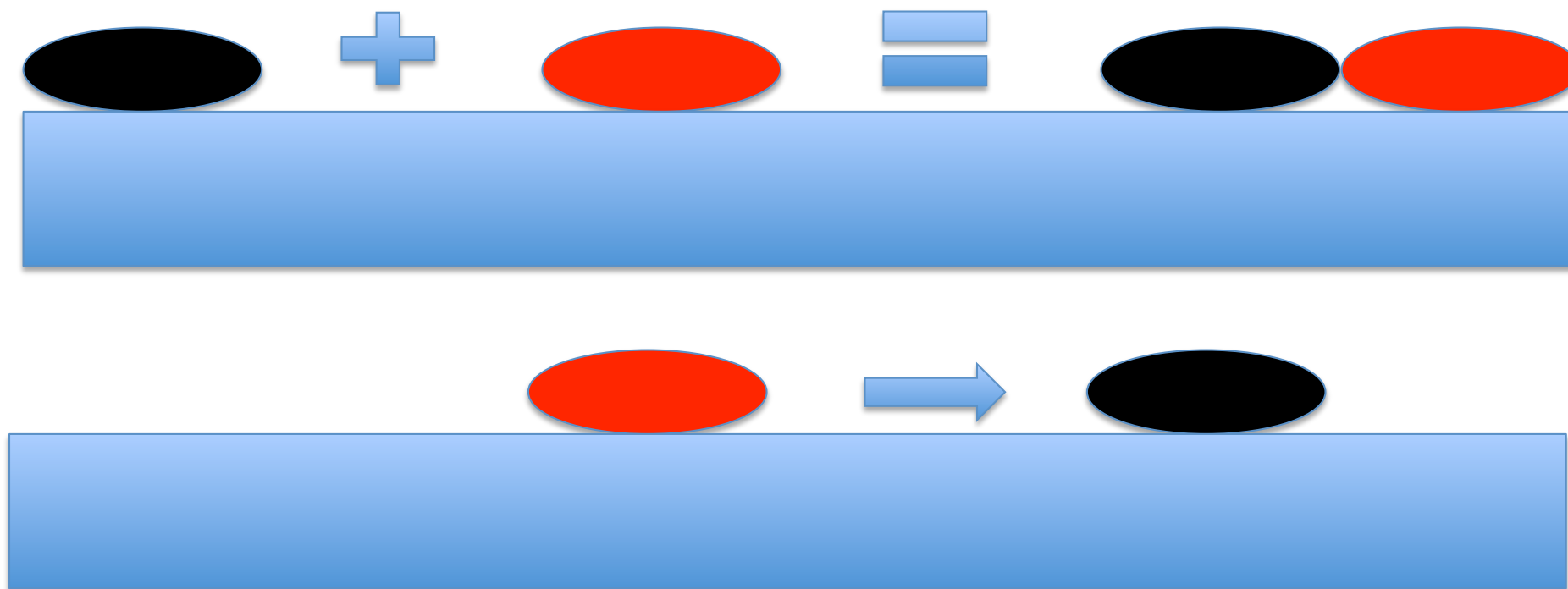
SAMS : very nicely ordered, but...



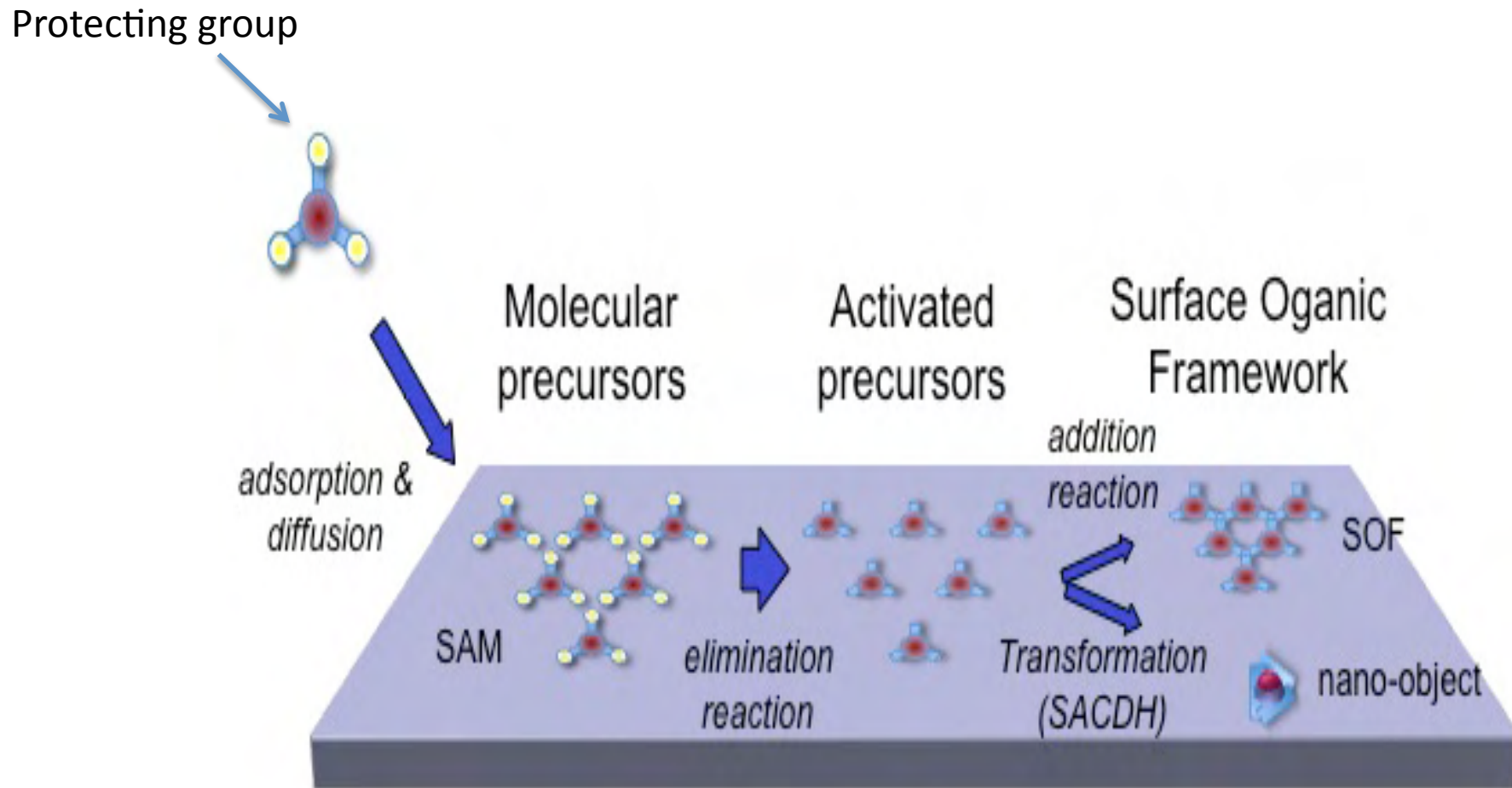
Subjected to time variability and high degradation of the structural properties,
already at room temperature

On-surface synthesis

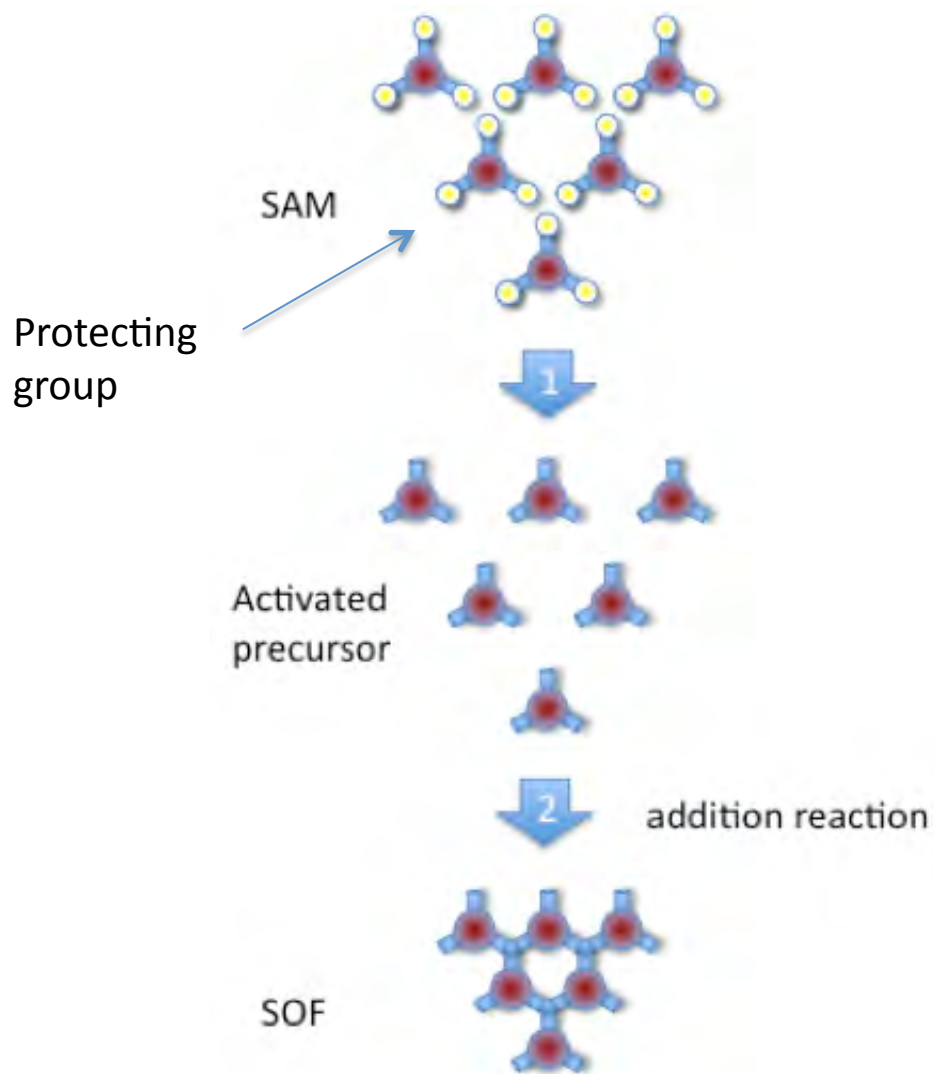
To form directly on the surfaces species that you could not have otherwise



General process



On-surface synthesis: several advantages



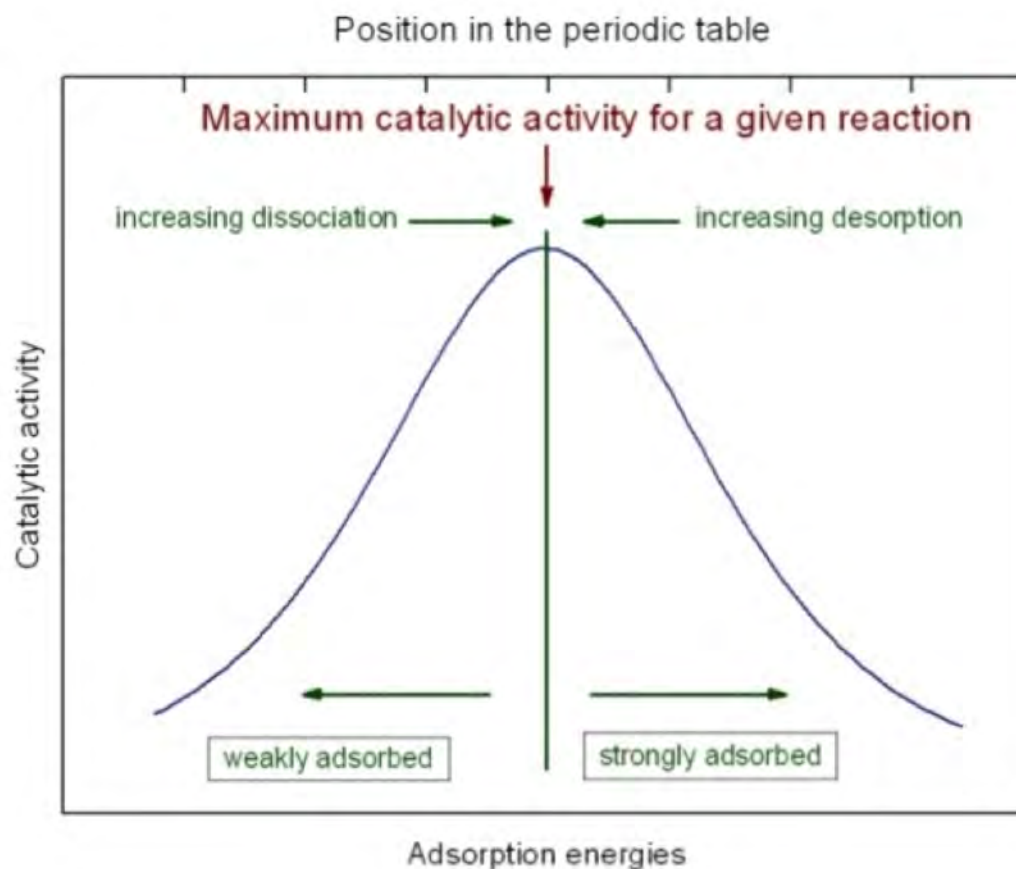
Formation of new species not available by conventional techniques

Stable structures with efficient electron transfer

UHV- compatible: surface science techniques for a controlled growth and characterization, mainly STM

Molecular precursor		Substrate	Activation Temp. (K)	Structure or molecule formed	Mechanism Reaction
2000	Diodobenzene	Cu(111)	STM pulse	Biphenyl molecules	Dehalogenation
2007	HBC	Ru(0001)	770K	Molecular domes	Cyclodehydrogenation
2007	Amine + aldehyde	Au(111)	300K	Imine	Dehydration: $R-NH_2 + O=R' \rightarrow R-N=R + H_2O$
2008	$C_{57}N_3H_{30}$	Pt(111)	700K	Azafullerene $C_{57}N_3$	Cyclodehydrogenation
2007	Br-Porphyrins	Au(111)	590K	Dots, chains and networks	Dehalogenation
2008	TAPP	Cu(111)	520K	Polymeric chains	Tautomerization of pyridine
2008	Porphyrins	Cu(110)	470K	Network	Dehydrogenation $R-CH_3 + CH_3-R \rightarrow R-CH_2-CH_2-R$
2008	[BDBA] _n [BDBA-HHTP] _n	Ag(111)	470K	Organic framework	Dehydration: $-B(-OH)_2 \rightarrow SOF + H_2O$
2009	DBTF	Au(111)	520K	Chains	Dehalogenation
2009	Diodobenzene	Cu(110)	500K	Polymeric lines	Dehalogenation
2009	TBB	Cu(111) Ag(110)	570K	Network	Dehalogenation
2010	DiBr-bianthryl	Au(111)	470K 670K	Graphenenanoribbons	Dehalogenation + dehydrogenation
2011	Polyphenile	Cu(111)	500K	Nanographene	Cyclodehydrogenation

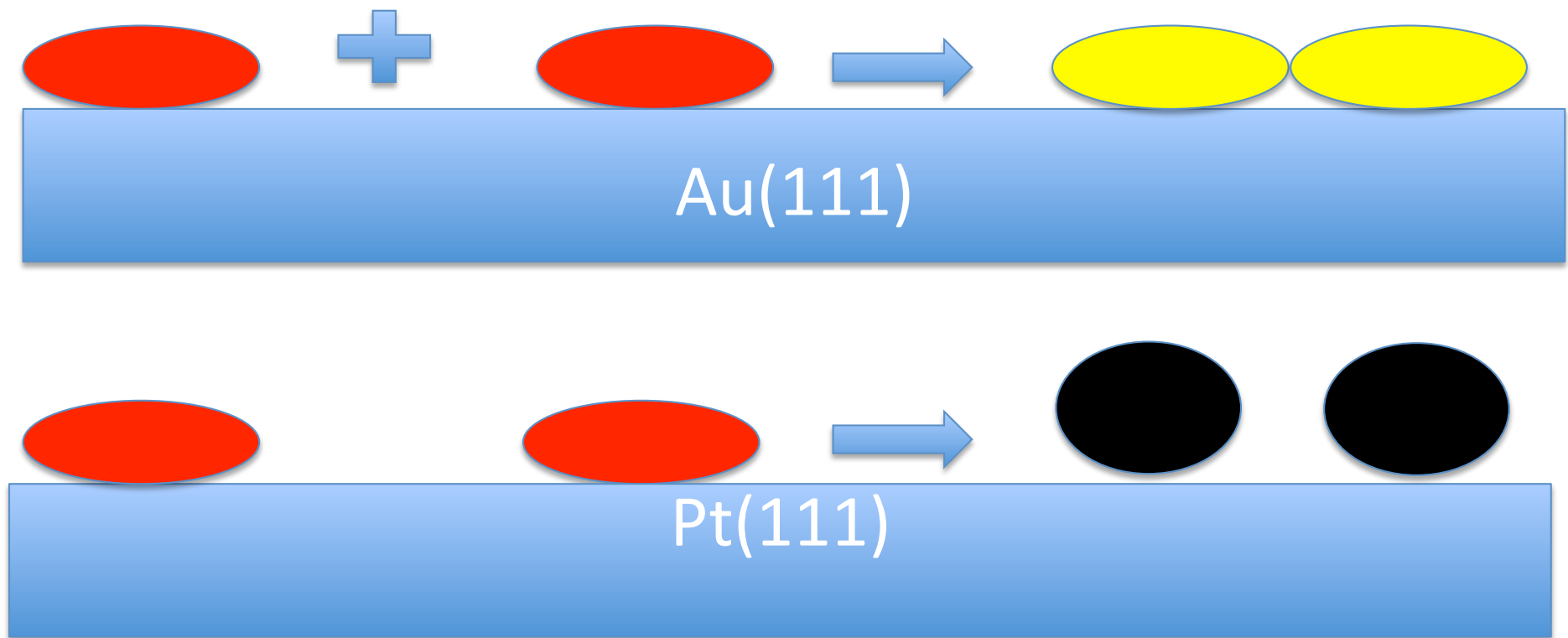
The balance surface-molecule molecule-molecule interaction rules the chemistry



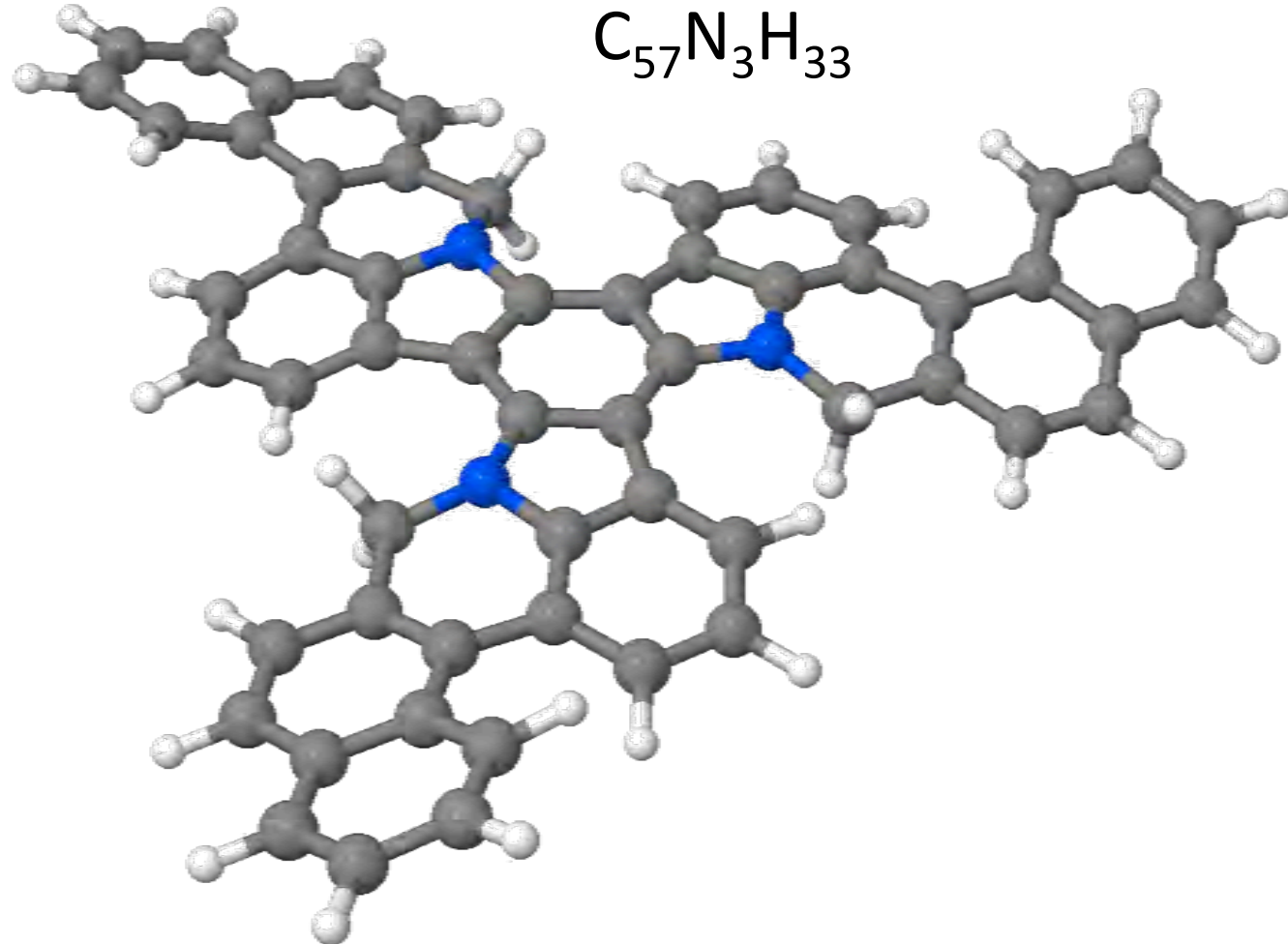
Borrowing ideas from heterogeneous catalysis

On surface synthesis

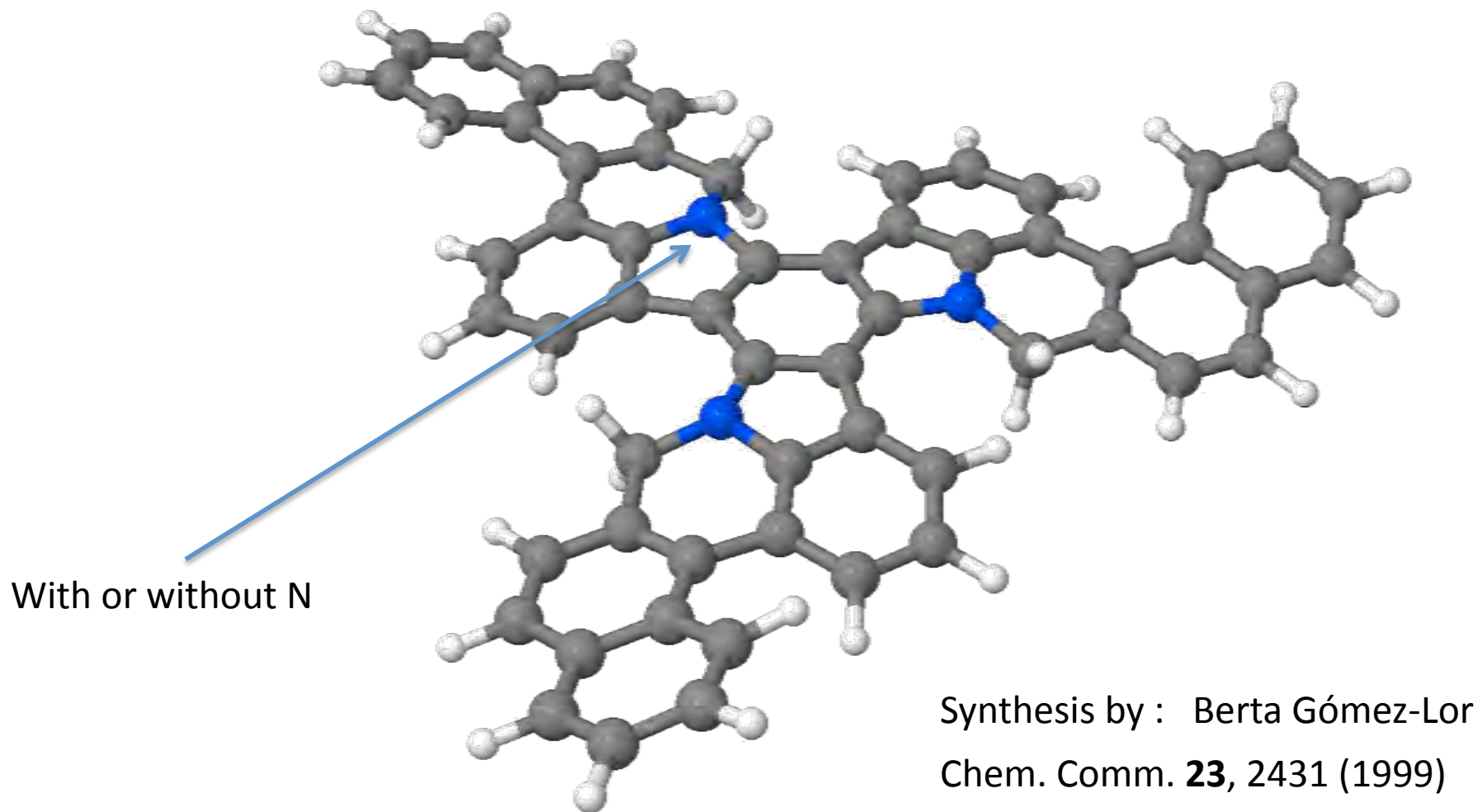
To form directly on the surfaces species that you could not have otherwise



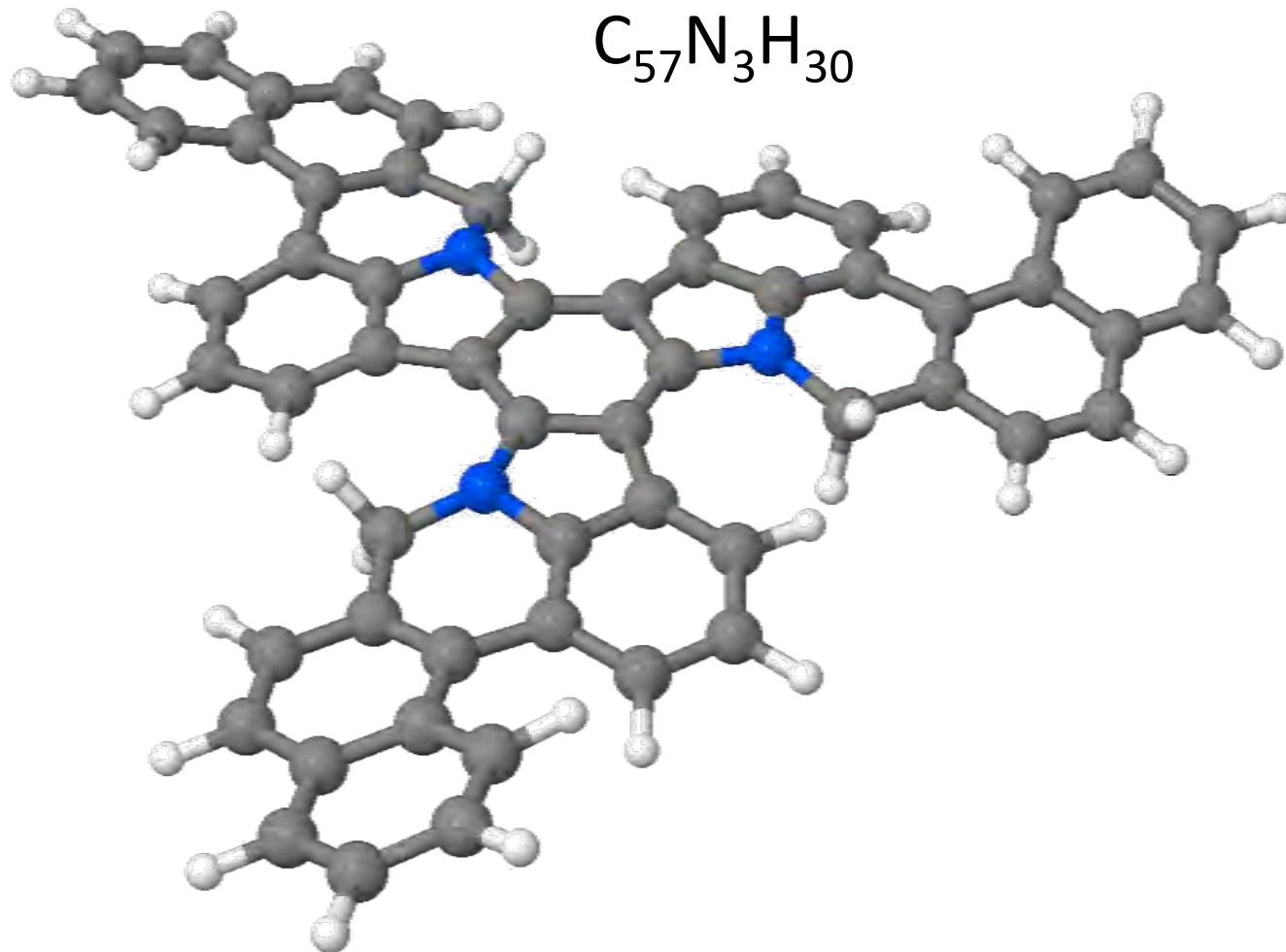
$C_{60}H_{30}$ and $C_{57}N_3H_{33}$:
two kind of Polycyclic aromatic hydrocarbons (PAH)



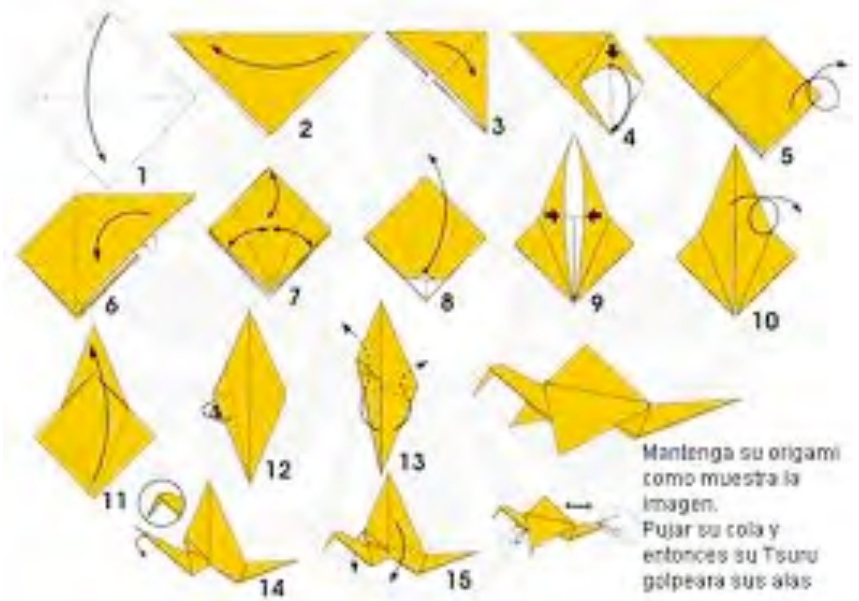
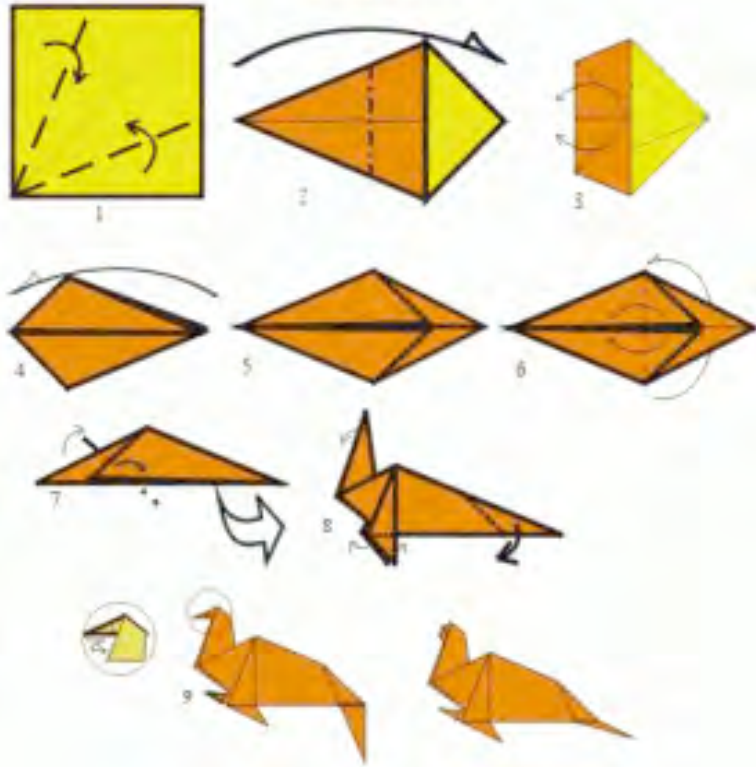
THE PRECURSORS: $C_{57}N_3H_{30}$ AND $C_{60}H_{30}$



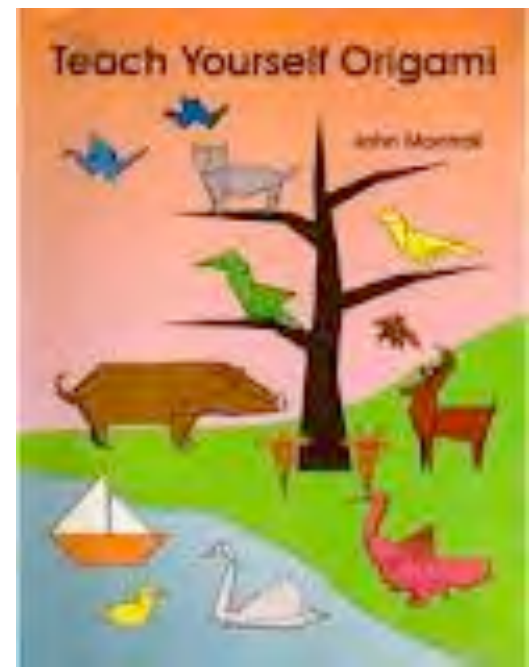
If topologically possible... a PAH could become a fullerene?



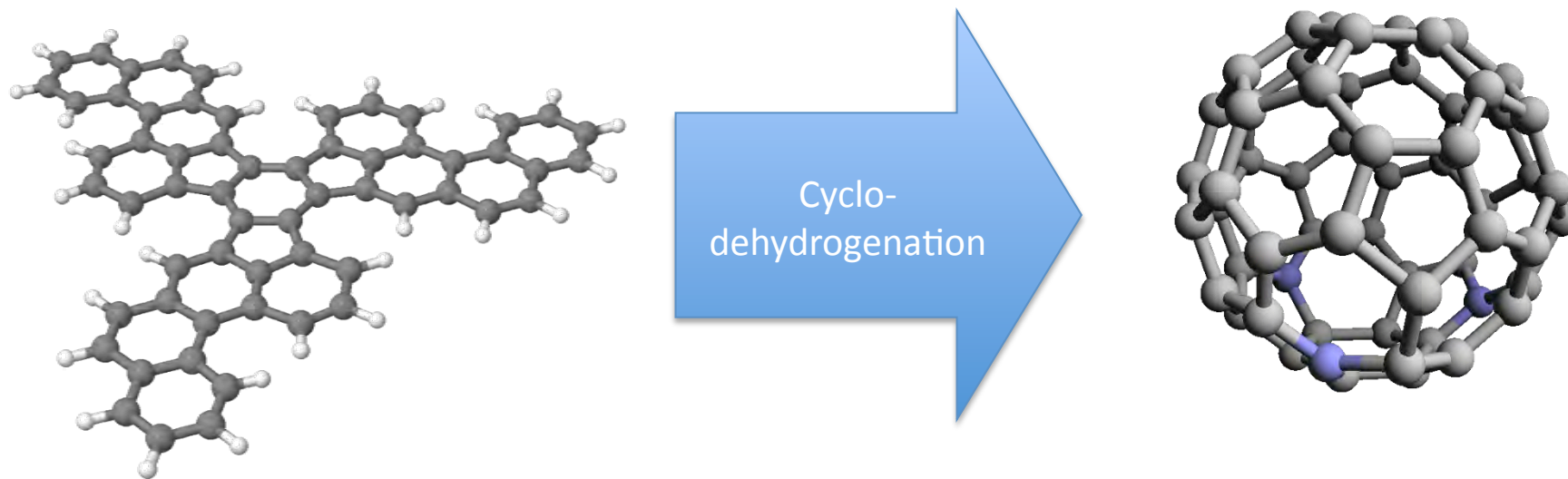
MORSA



Mantenga su origami como muestra la imagen. Pujar su cola y entonces su Tsuru golpeará sus alas



First proposed by Scott, L.T., *et al.* : A rational chemical synthesis of C₆₀.
Science **295**, 1500-1503 (2002).



Proposed from C₆₀H₃₀ to form fullerene

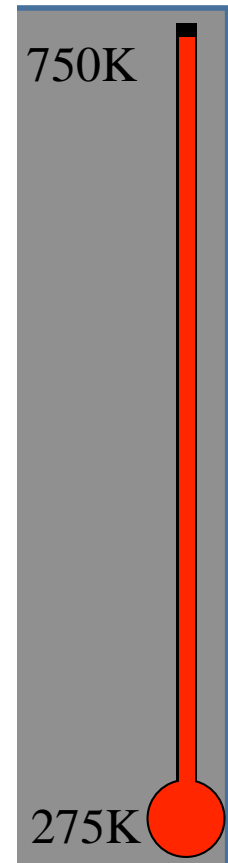
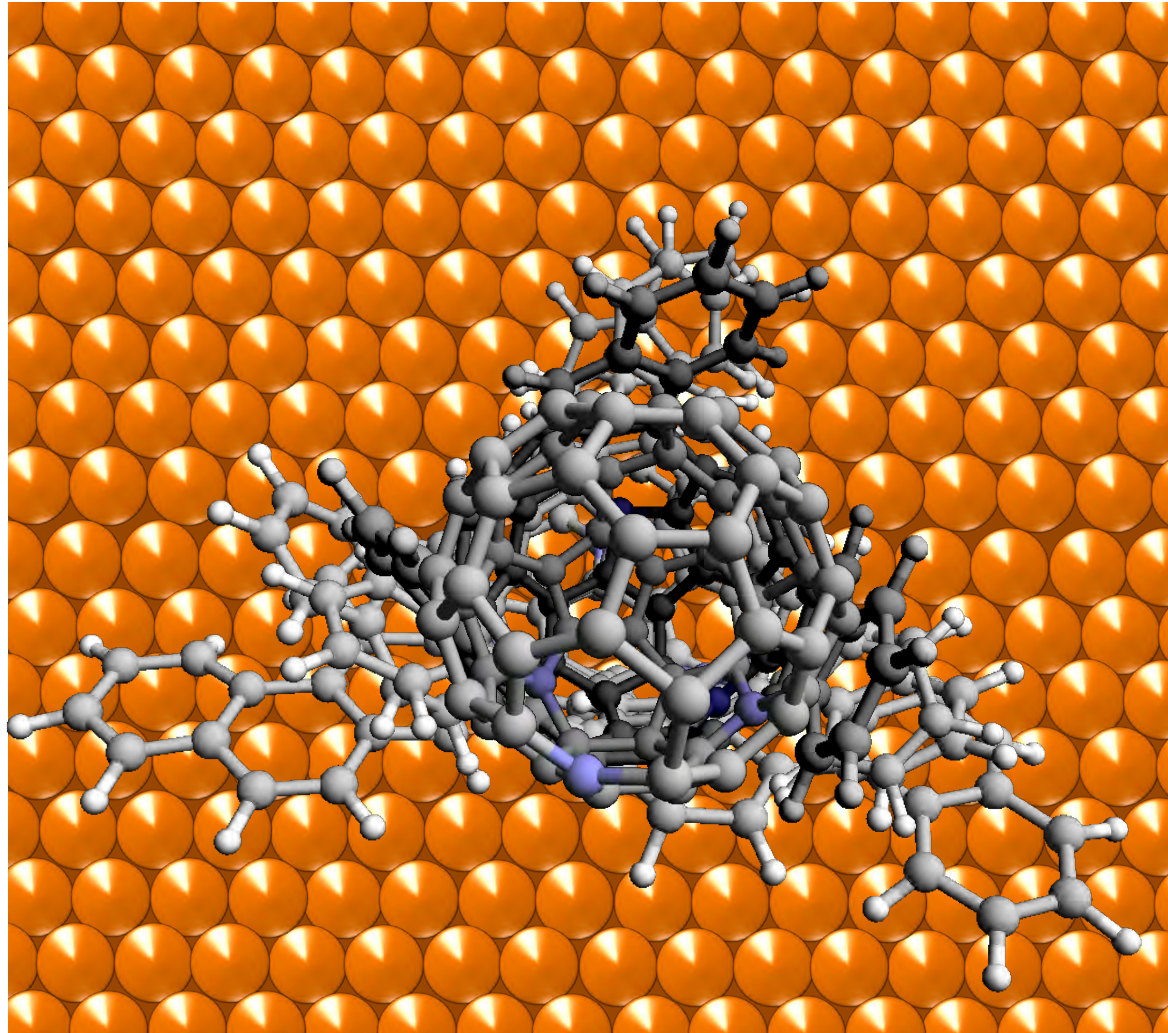
Using high-power laser, Mass analysis detection

Extremely low efficiency (1%), 11 steps

Question is: do you re-make all bonds what this huge energy supply?

ORIGAMI AT THE NANOSCALE

- Surface Catalysed process

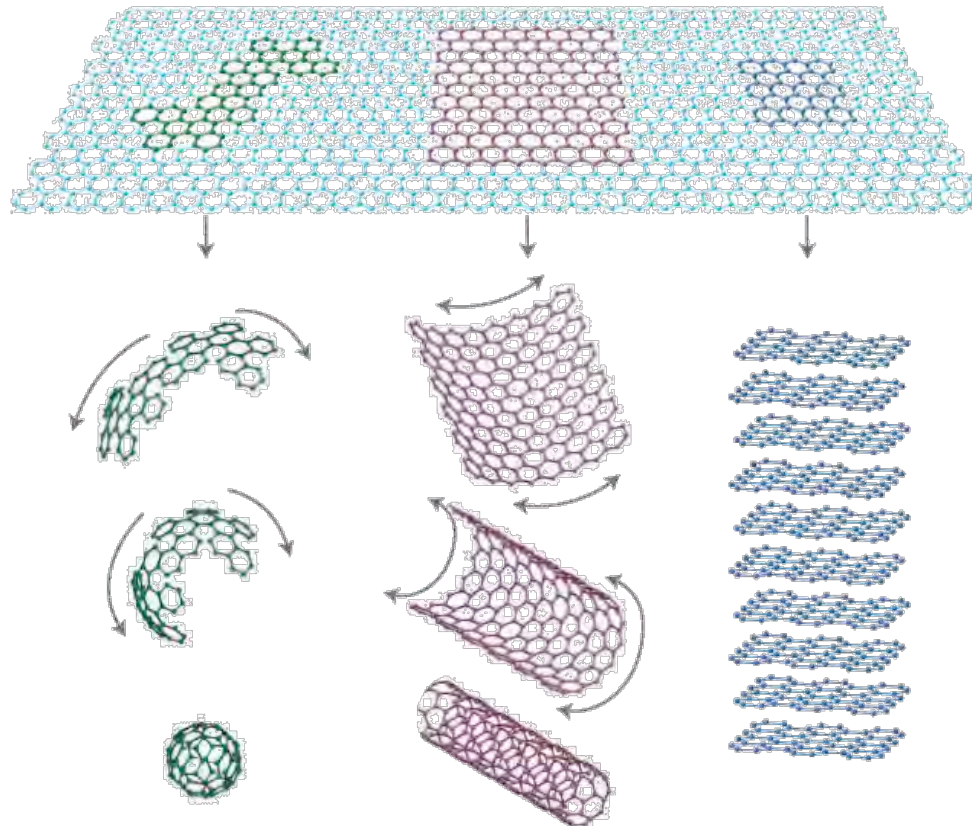


The rise of graphene

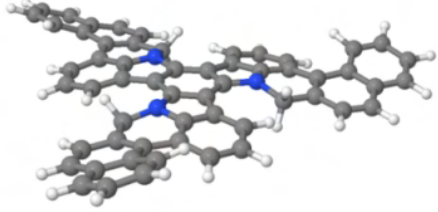
A. K. GEIM AND K. S. NOVOSELOV

Manchester Centre for Mesoscience and Nanotechnology, University of Manchester, Oxford Road, Manchester M13 9PL, UK

Graphene is a rapidly rising star on the horizon of materials science and condensed-matter physics. This strictly two-dimensional material exhibits exceptionally high crystal and electronic quality, and, despite its short history, has already revealed a cornucopia of new physics and potential applications, which are briefly discussed here. Whereas one can be certain of the realness of applications only when commercial products appear, graphene no longer requires any further proof of its importance

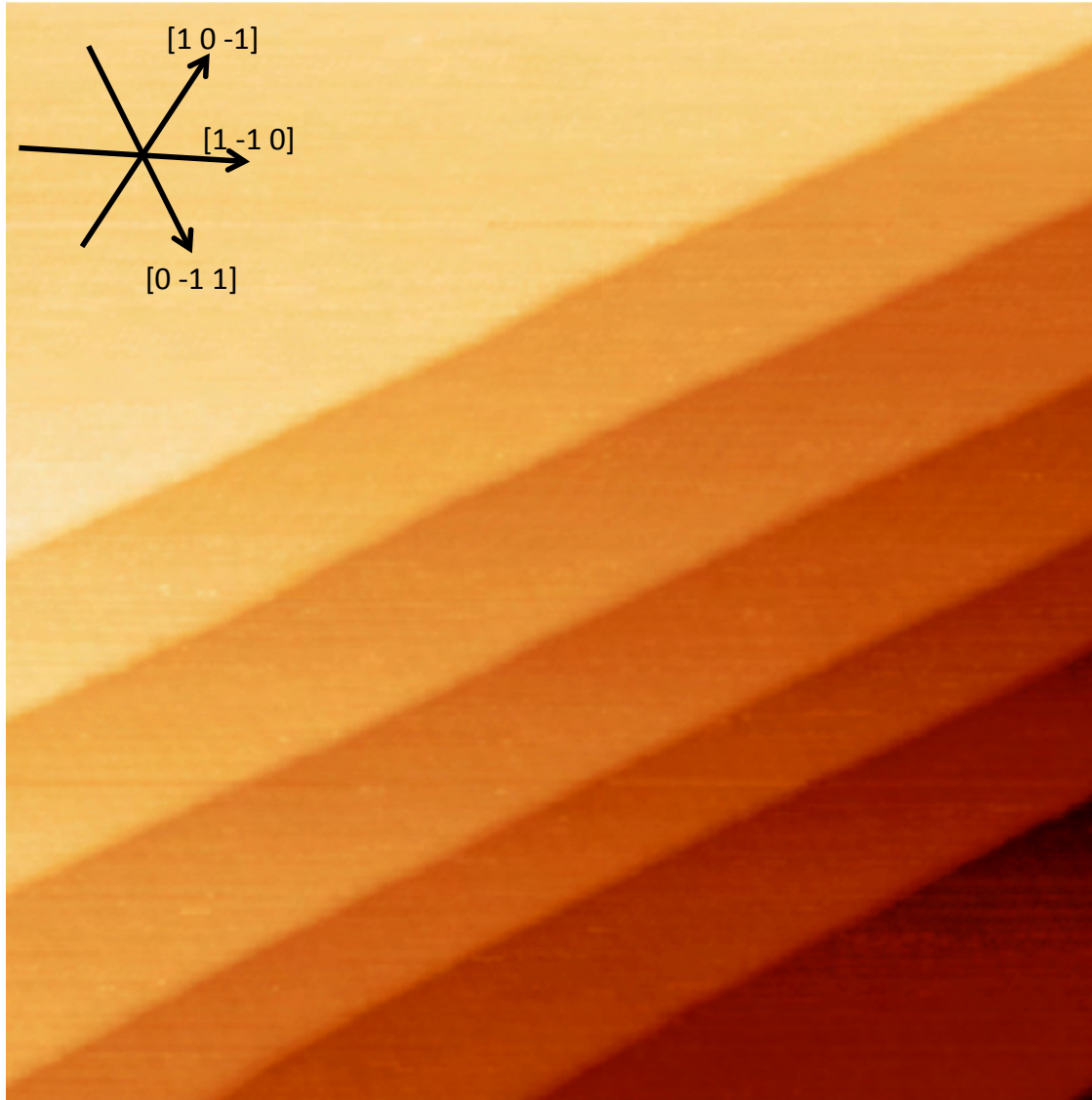


1935: Landau and Peierls argued that strictly 2D crystals were thermodynamically unstable and could not exist -> large thermal fluctuations -> folding mechanism



In-vacuum evaporation of PAH

Clean Pt(111) at RT



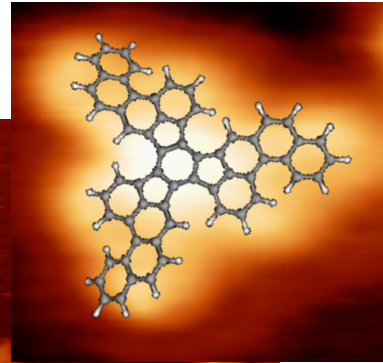
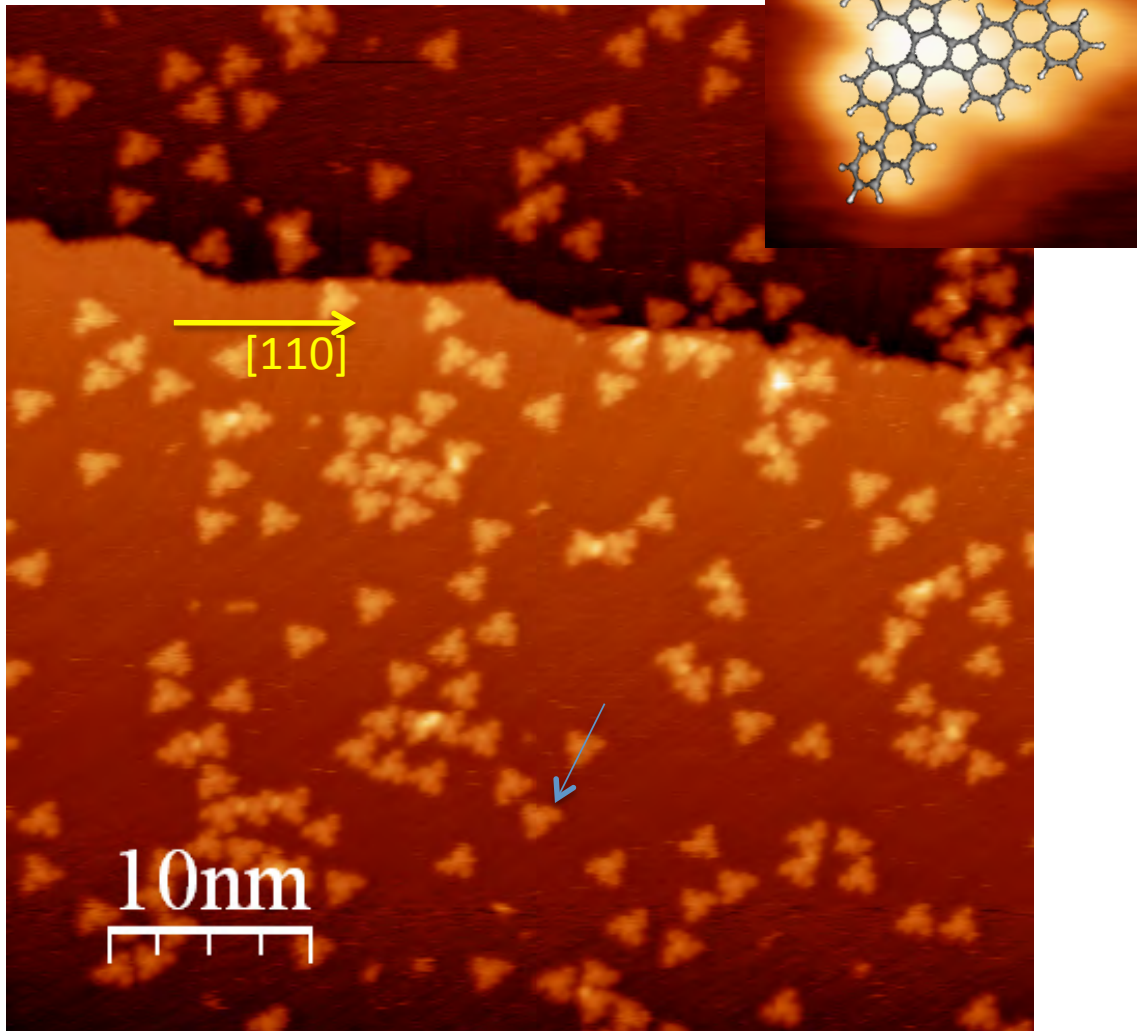
(50 x 50) nm²

Constant current image

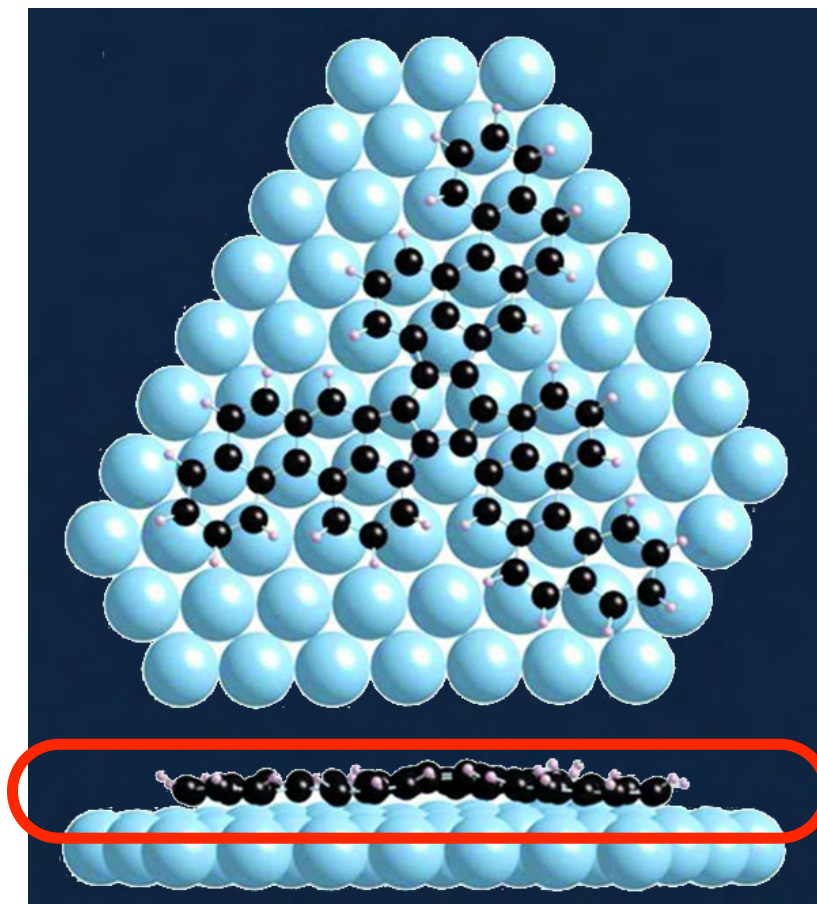
$I = 0.2$ nA

$V = 1000$ mV

Randomly adsorbed C₆₀H₃₀ molecules



More stable adsorption position



$\text{C}_{60}\text{H}_{30}$ is flattened upon adsorption

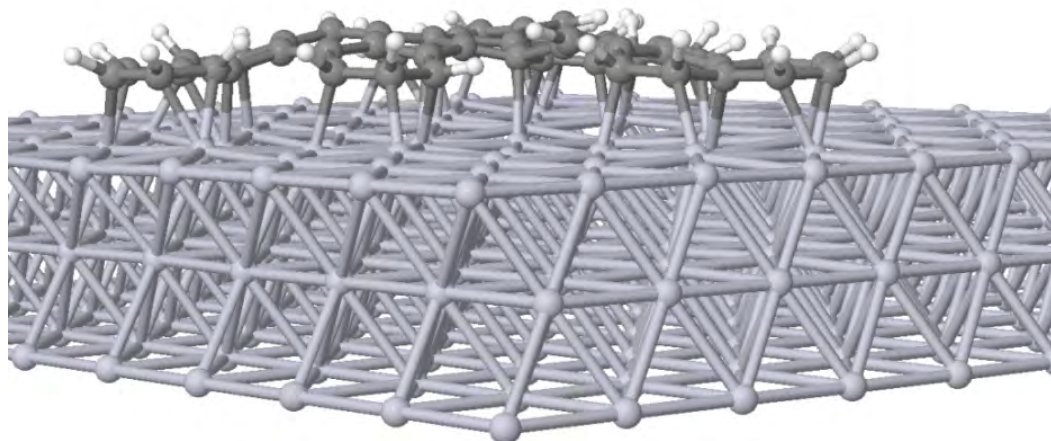
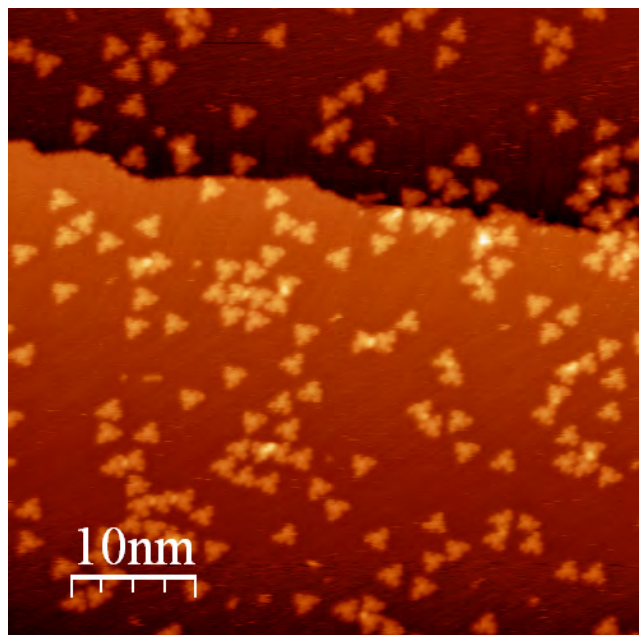
Dr. Rubén Pérez
Giulio Biddau
(UAM)

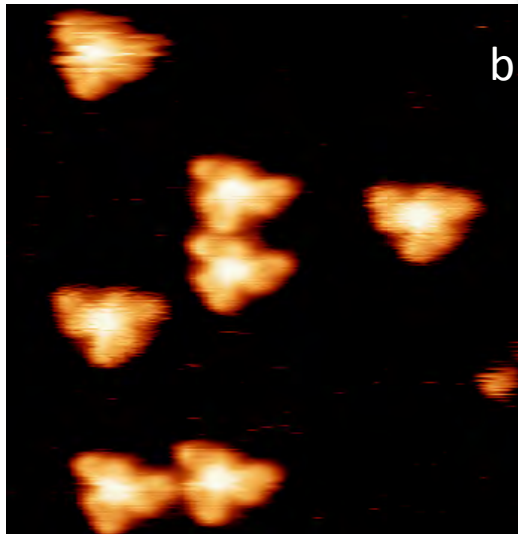
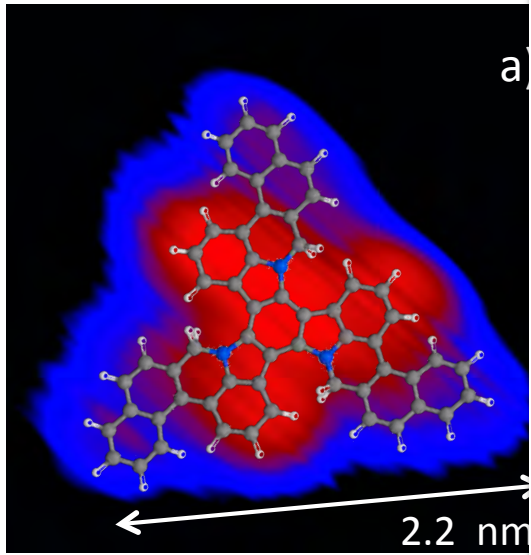
Adsorption may be described in terms of the constituent benzene subunits.

ENANTIOMERIC SURFACE SEPARATION

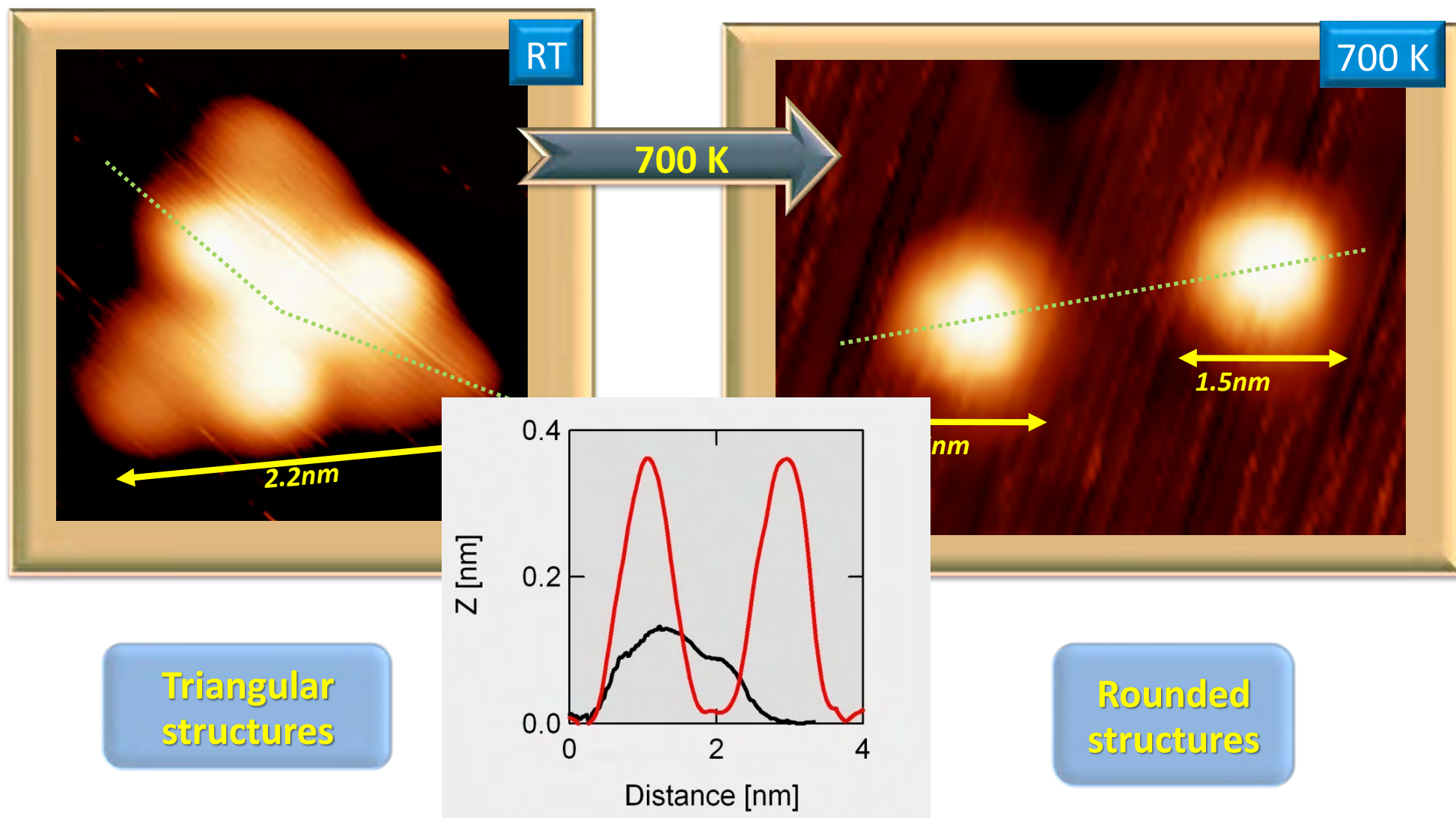
Preferential adsorption site

No surface molecular diffusion:
strong surface-molecule bonding
just reorientation





Cyclodehydrogenation



Triangular structures

Rounded structures

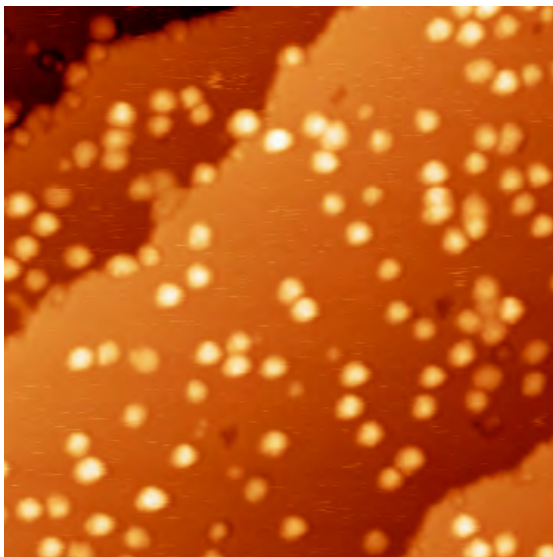
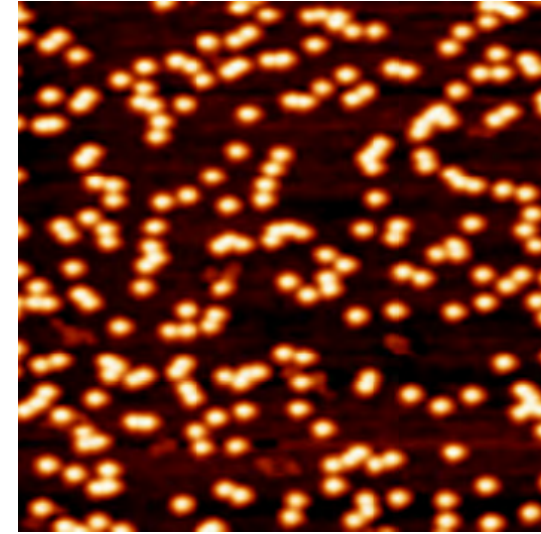
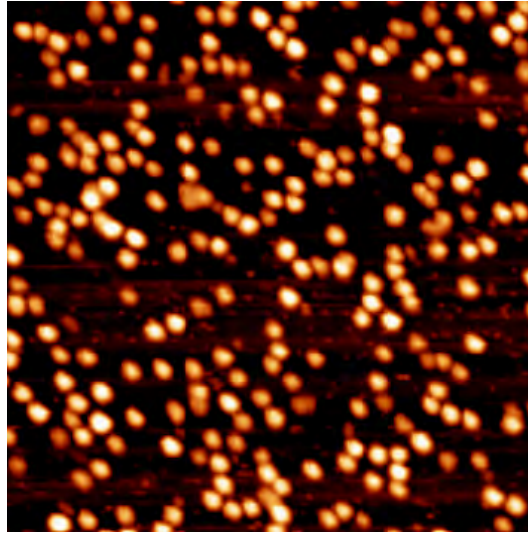
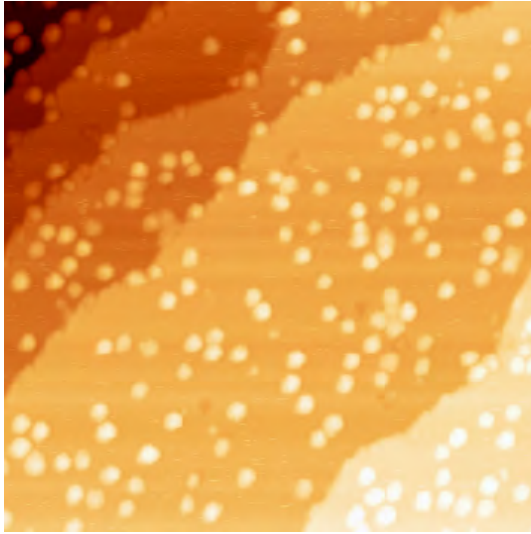
Low corrugation of C60: compatible with results of C60/Pd(110), Pt(111),Pt(110)

Strong interaction with the surface: Pt removal. *Felici et al. Nature materials 4, 688 (2005)*

Synthetized C_{60} / Pt(111) from dehydrogenation of $C_{60}H_{30}$

Commercial C_{60} / Pt(111)

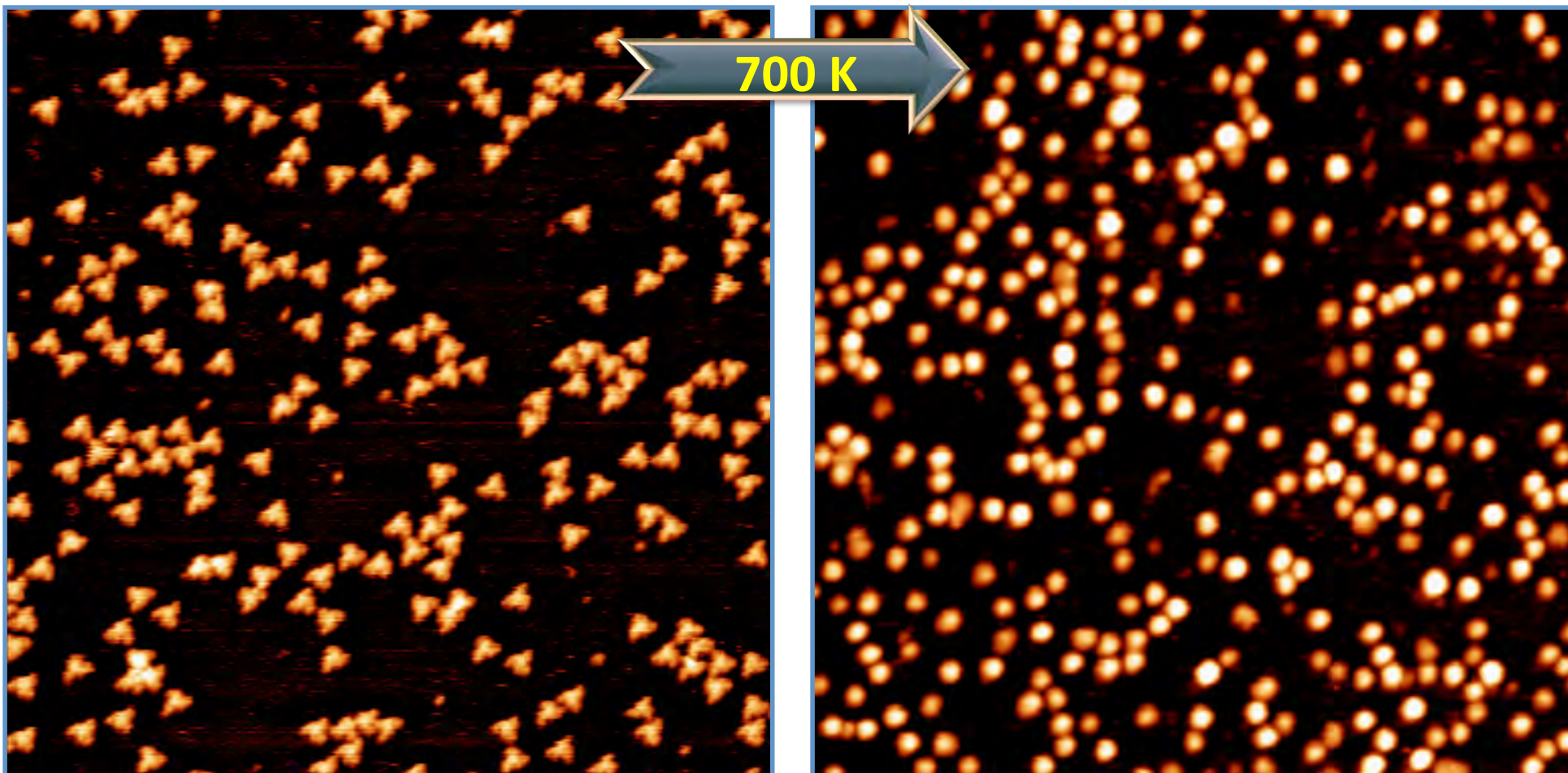
(40.0nm x 40.0nm)



100% efficiency!!!

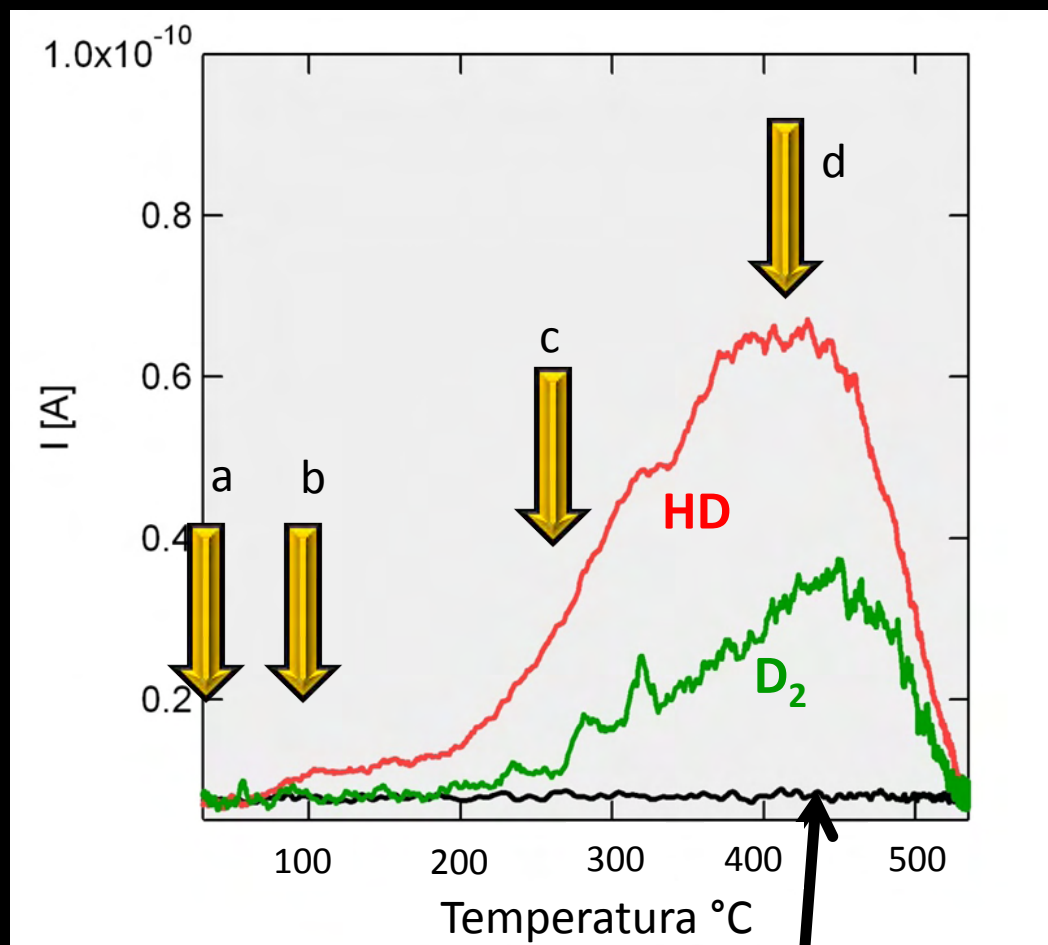
$C_{57}N_3$ synthesized for the first time

Cyclodehydrogenation

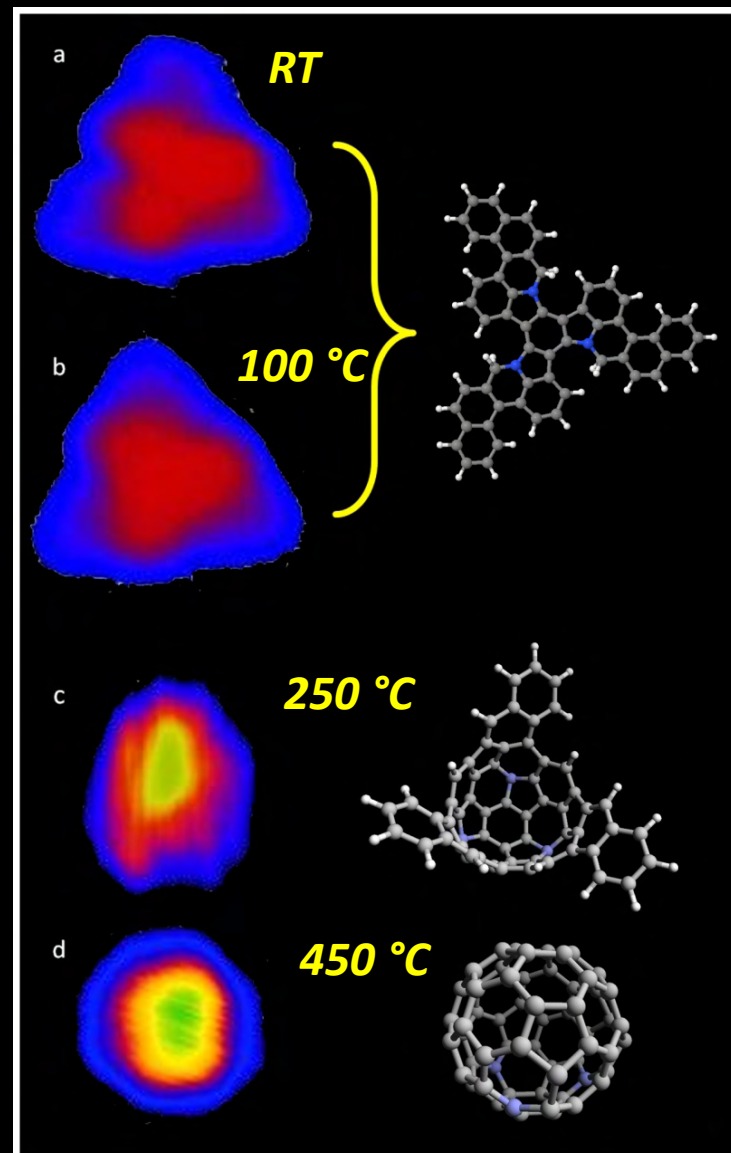


High efficiency

TPD

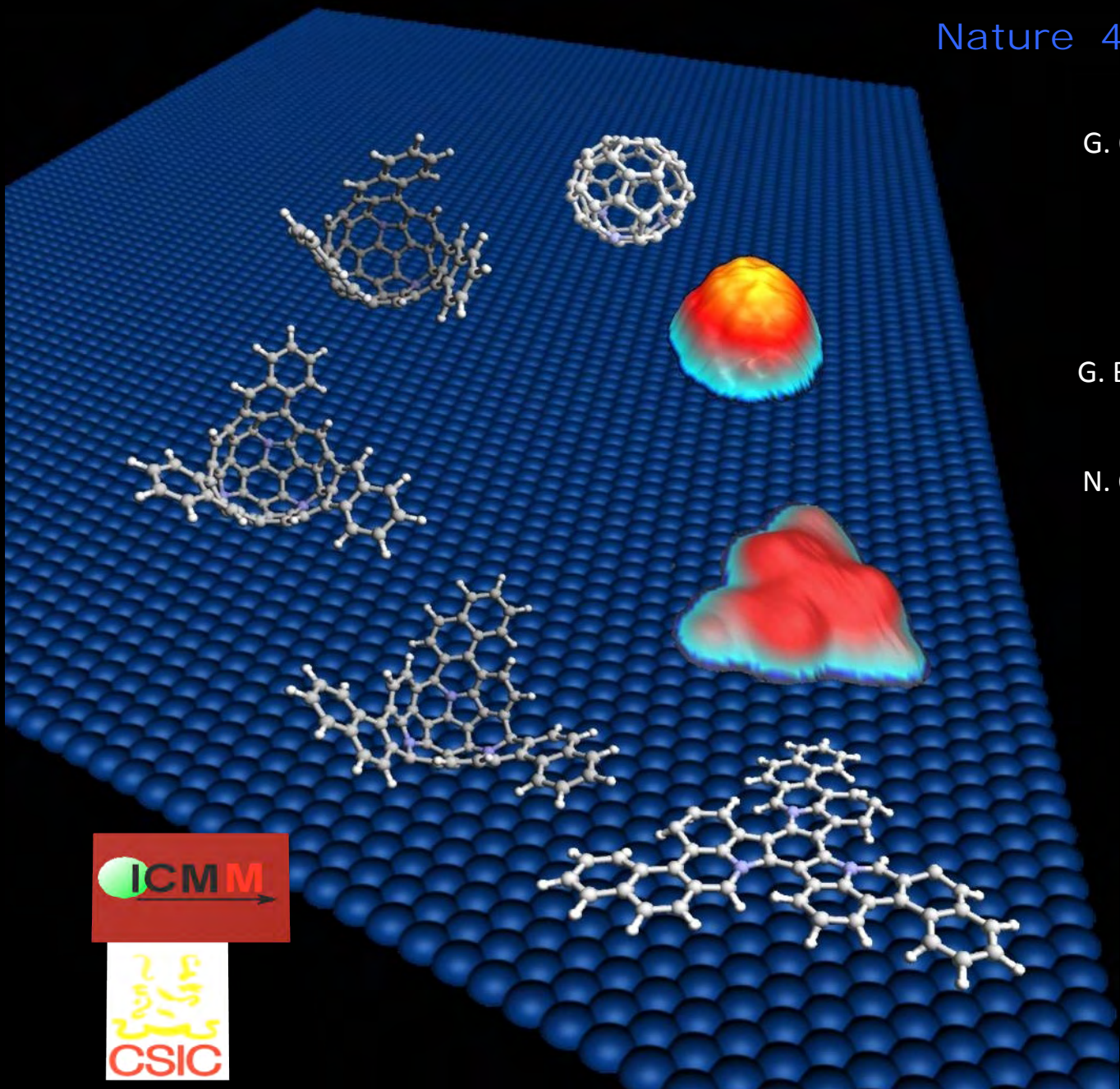


Without molecules



Fullerenes from aromatic precursors by surface catalysed cyclodehydrogenation

Nature 454, 865 (2008)

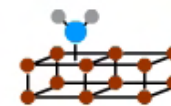


G. Otero, C. Sánchez-Sánchez, L. Alvarez, R. Caillard, C. Rogero, M. F. López, F. J. Palomares, J. Méndez,
José A. Martín-Gago
(ICMM-CSIC, CAB)

G. Biddau, M. A. Basanta, J. Ortega, R. Pérez
(UAM)

N. Cabello, A. M. Echavarren, B. Gómez-Lor
(ICIQ, ICMM)

Structure of Nanometric
Systems Group

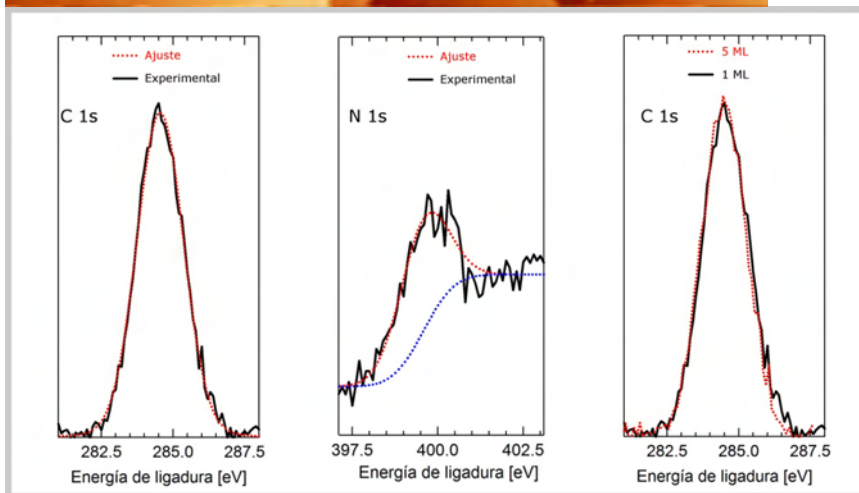
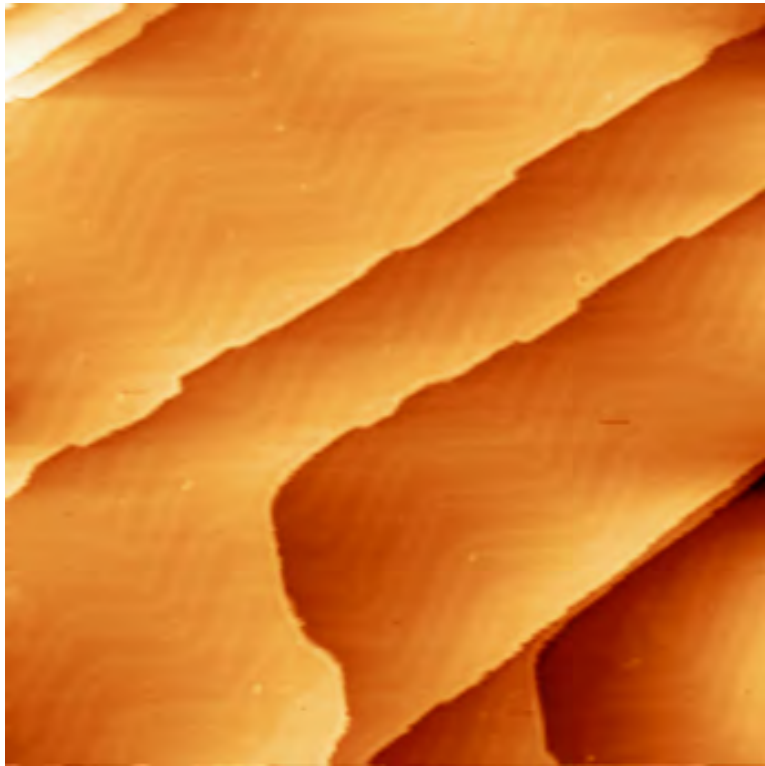


<http://www.icmm.csic.es/esisna/>



Substrate Influence

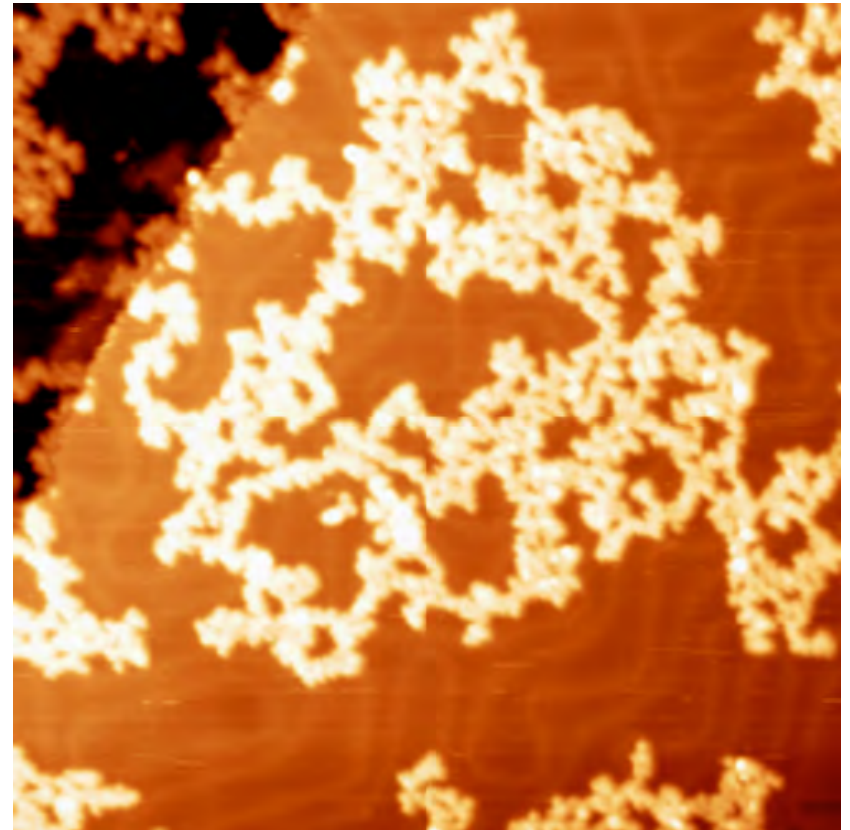
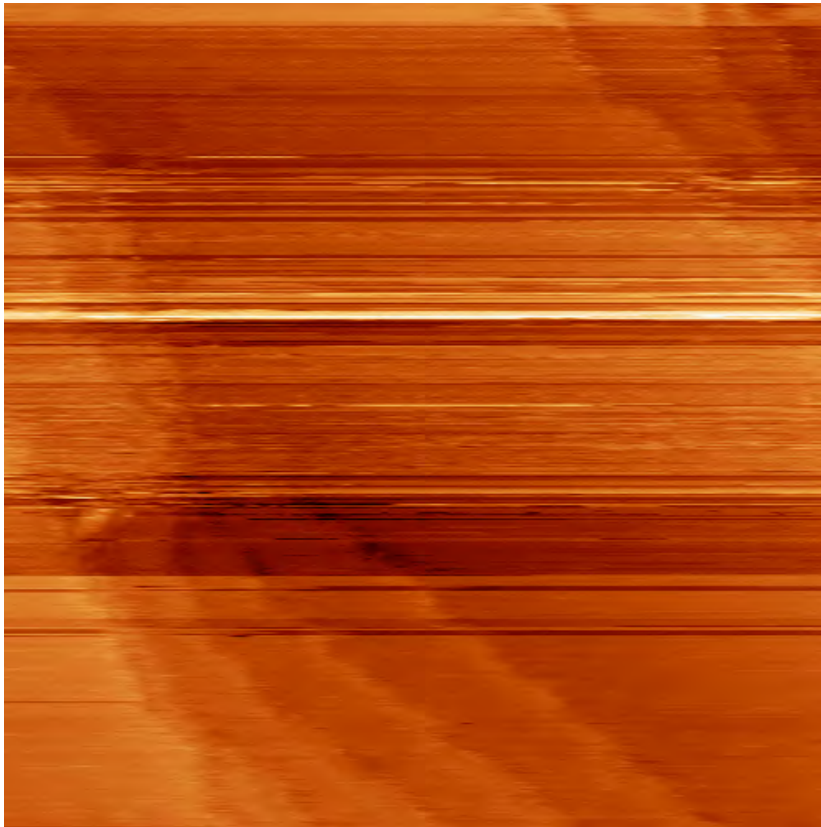
Au(111) at RT



Molecules diffuse on the surface at RT
Very low molecule-substrate interaction

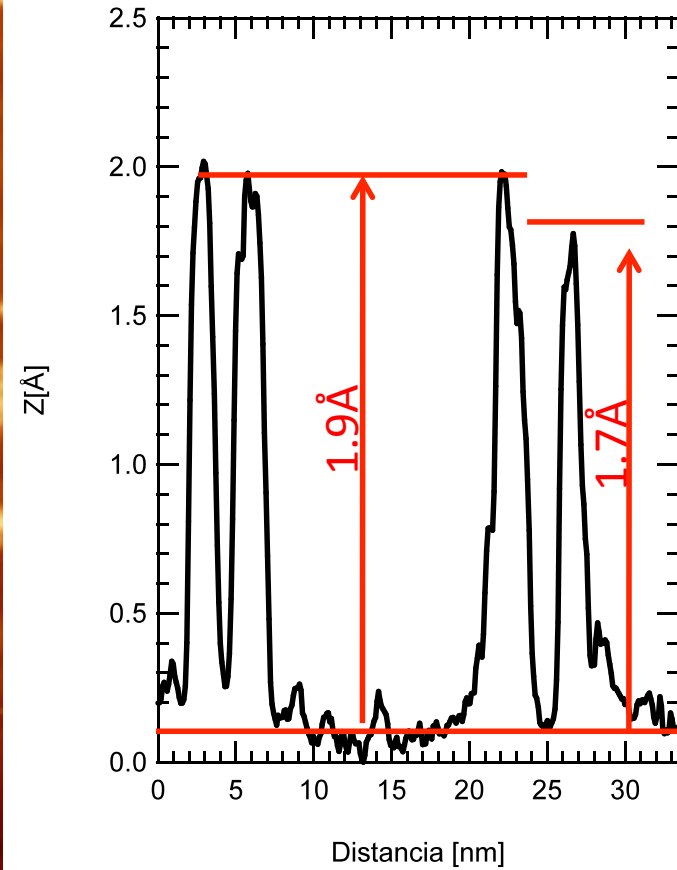
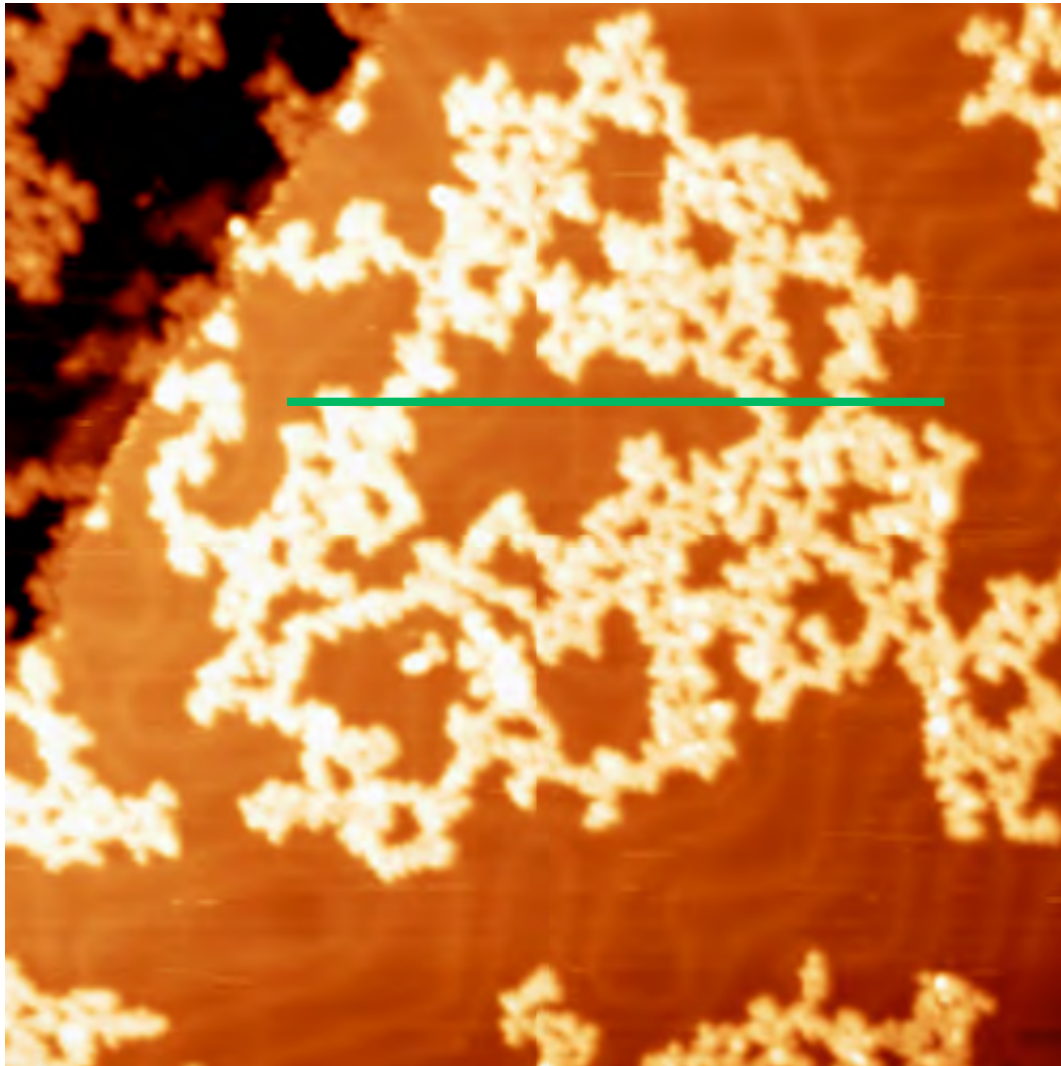
C57H33N3/Au(111) after 200°C

C57H33N3/Au(111) after 330°C



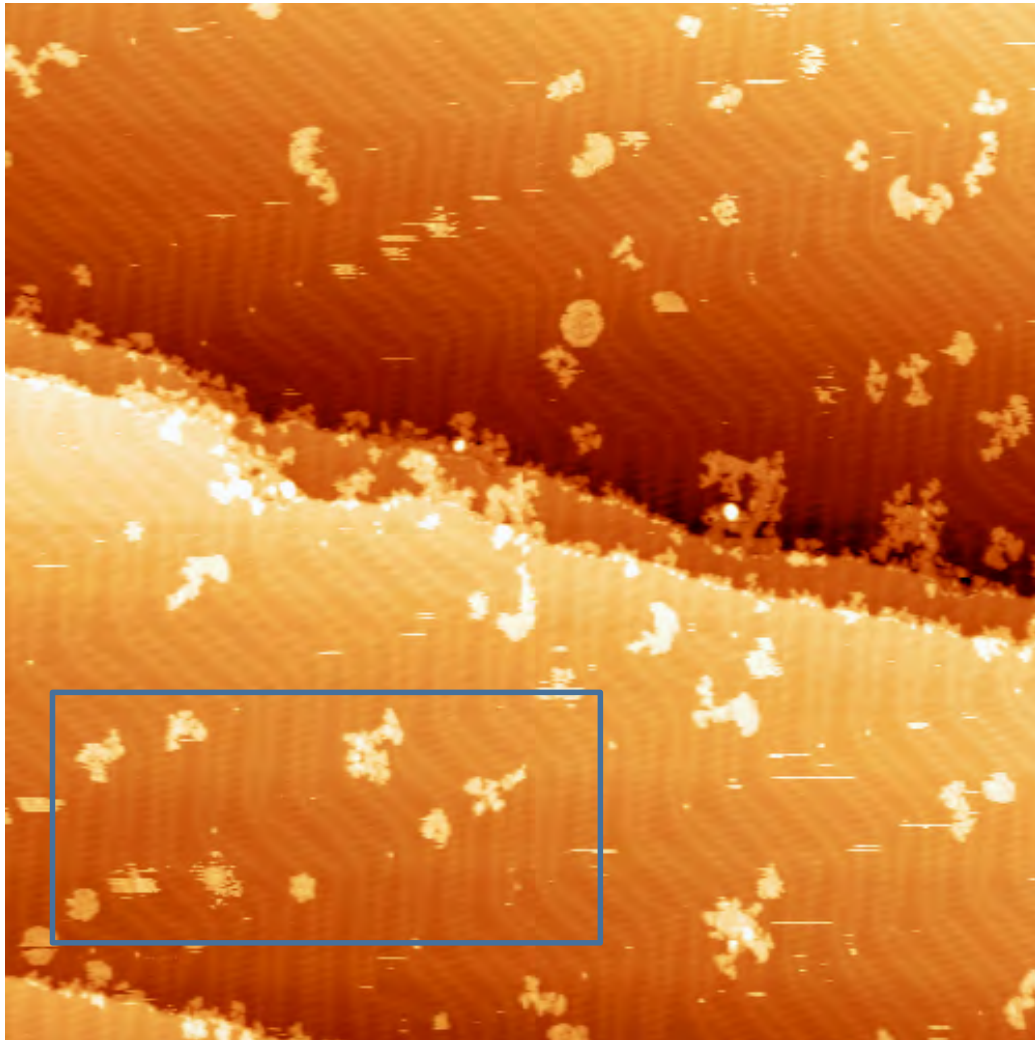
(50.0nm x 50.0nm)
I=0.05nA, V=1000mV

C57H33N3/Au(111) after 330°C

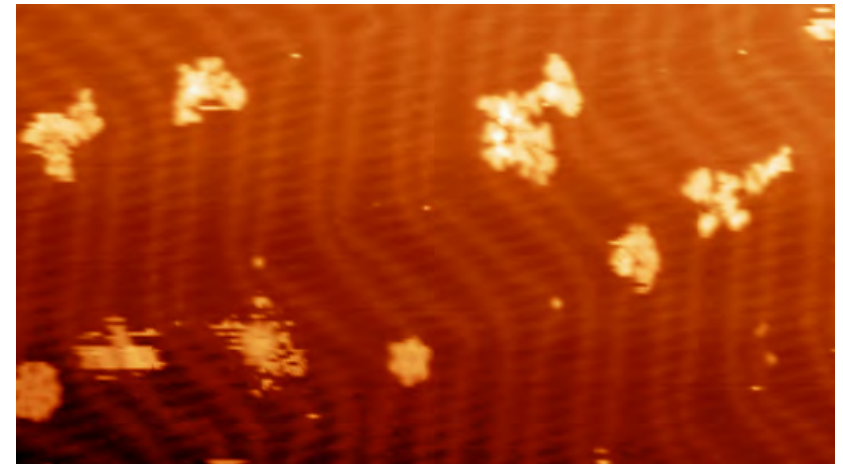


C57H33N3_Au111_110810_2003.f.top
(50.0nm x 50.0nm)
I=0.1nA, V=1000mV

C57H33N3/Au(111) at 270°C – Low coverage



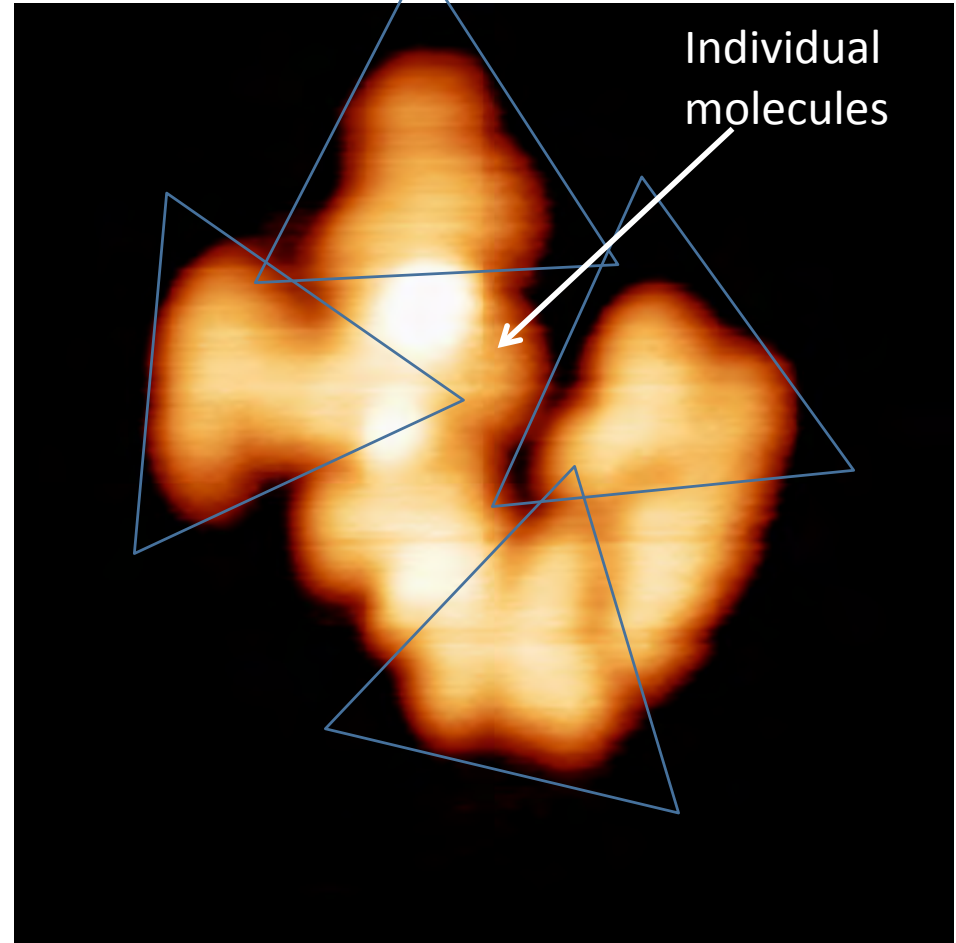
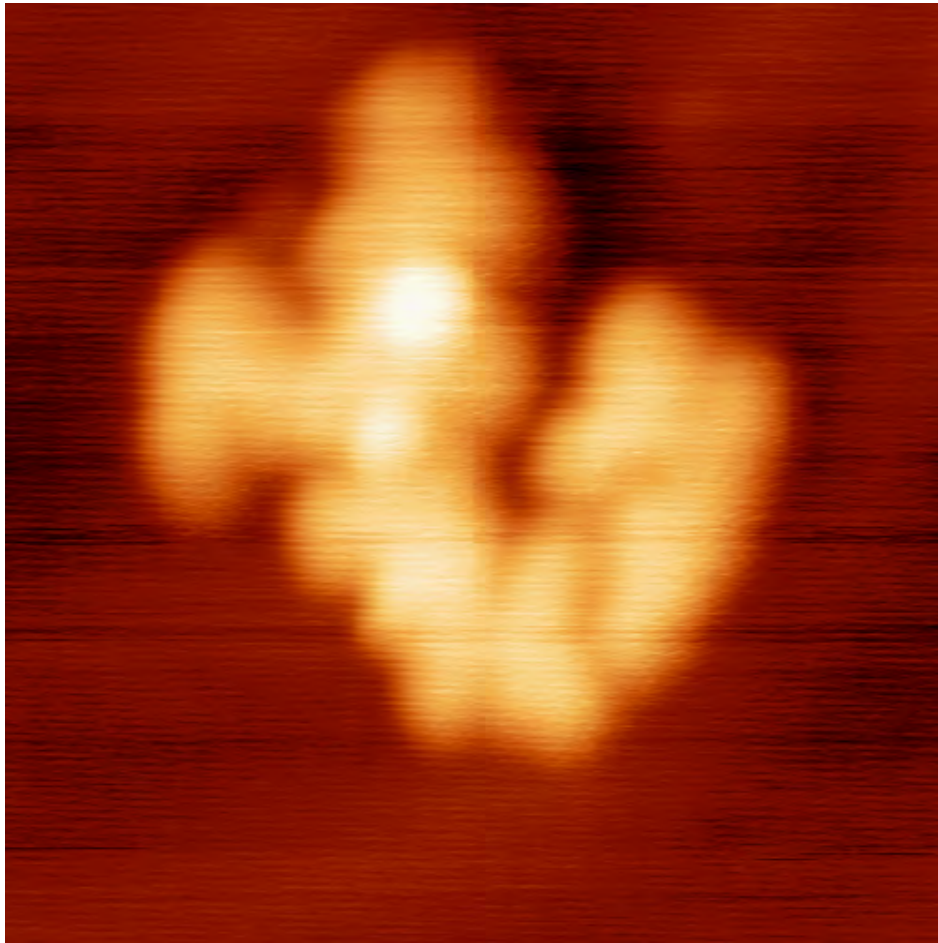
(100.0nm x 100.0nm)
I=0.2nA, V=-1500mV



Clustered at step and
reconstruction edges.

Weakly bound

C57H33N3/Au(111) at 270°C – Low coverage



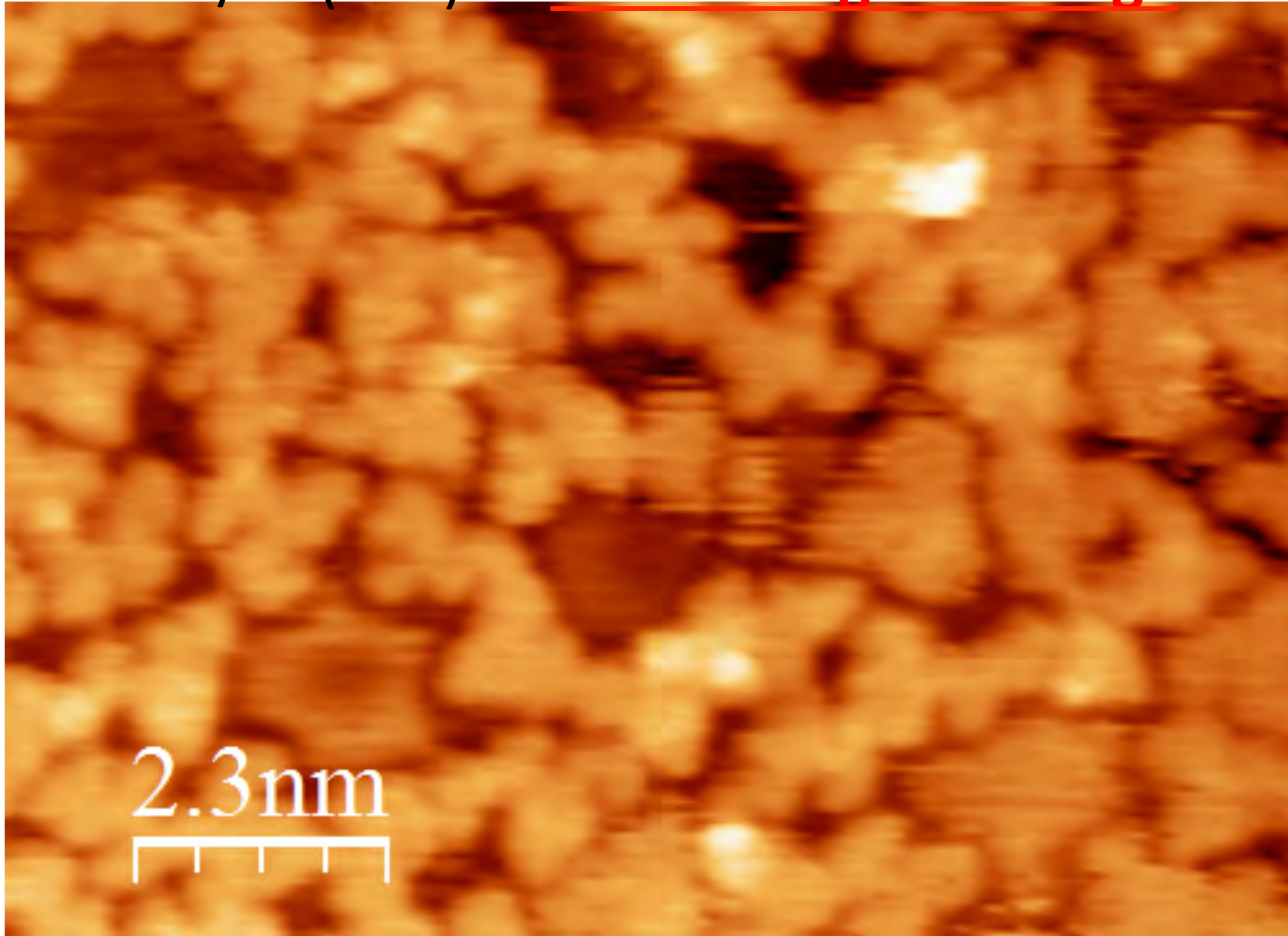
C57H33N3_Au111_110809_1034.f.top
(7.0nm x 7.0nm)
I=0.35nA, V=-930mV

C57H33N3/Au(111) at 270°C – Low coverage



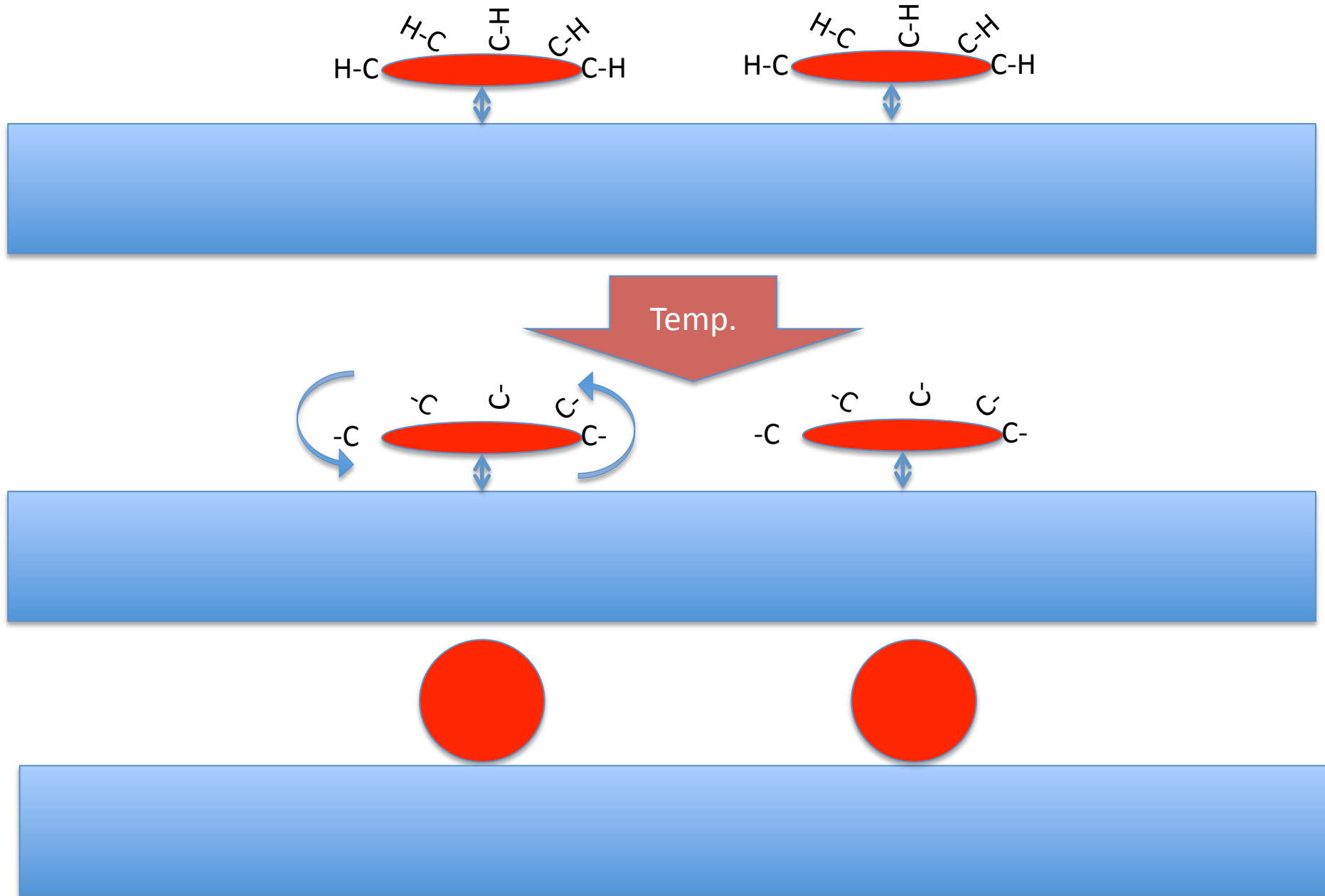
C57H33N3_Au111_110809_1072.f.top
(27.9nm x 16.7nm)
I=0.23nA, V=-1500mV

C₅₇H₃₃N₃/Au(111) at 270°C – High coverage

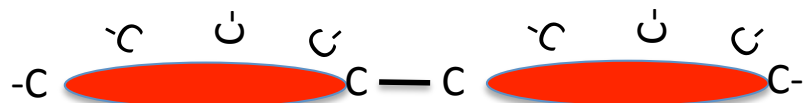


Carbonaceous layer N-doped

On a reactive surface, efficient in dehydrogenation

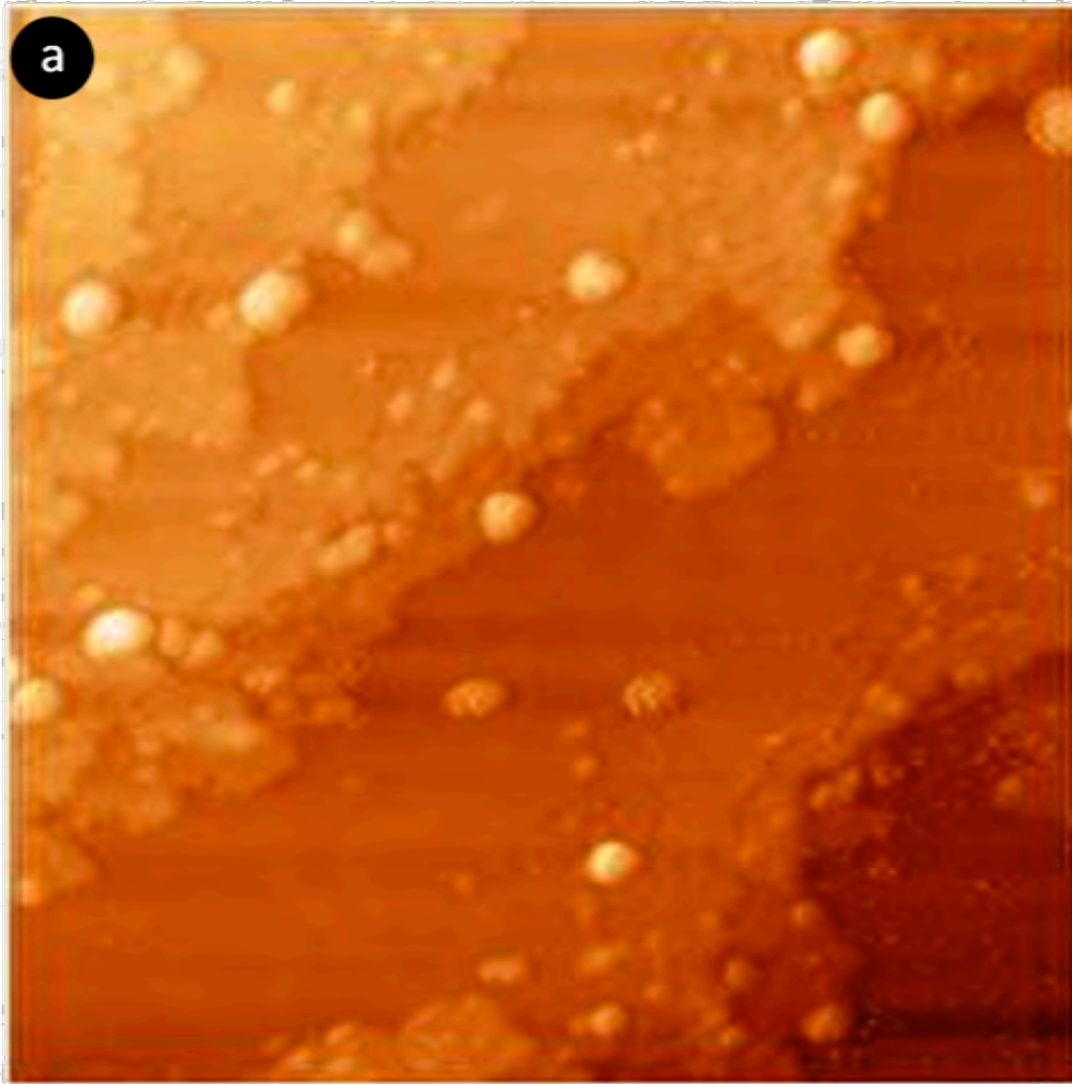


On a weakly interacting surface

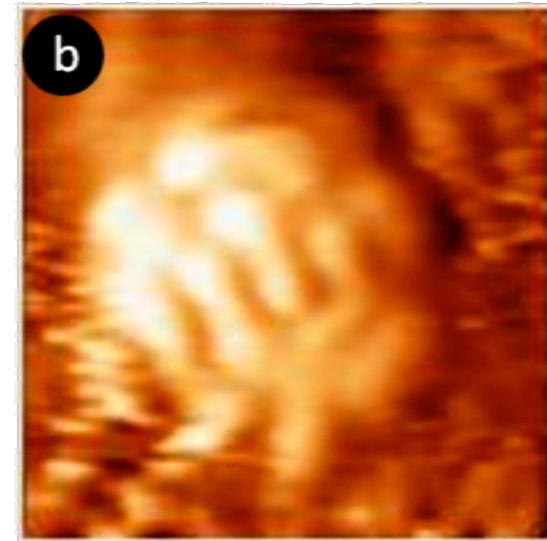


Substrate Influence

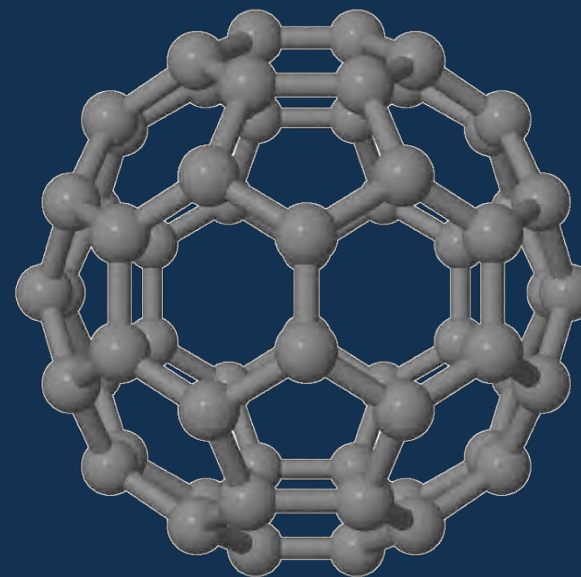
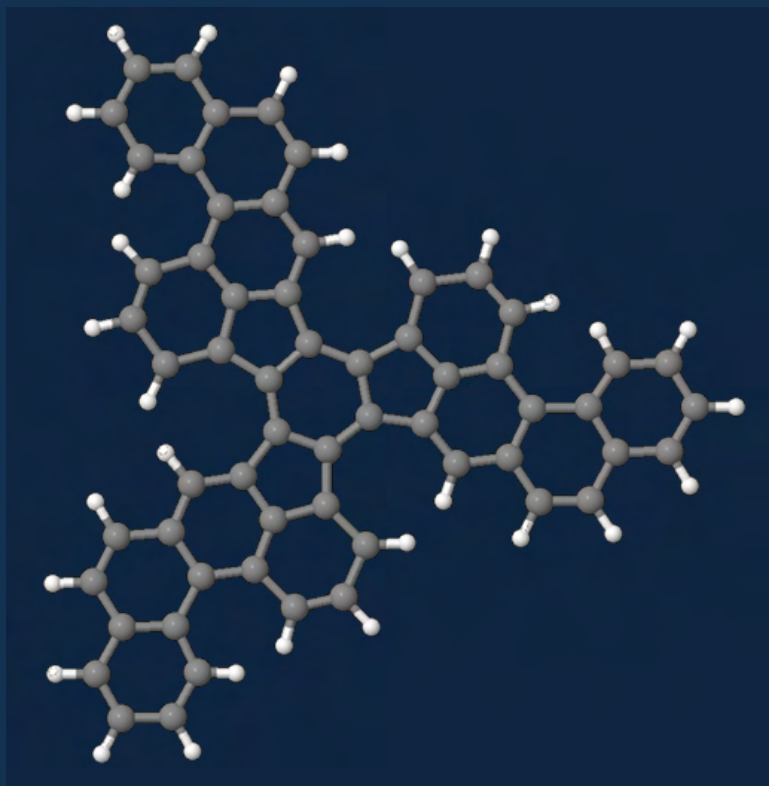
Au(111)
650 °C



Some rounded
structures looking like
fullerenes



Very low
efficiency
< 1%



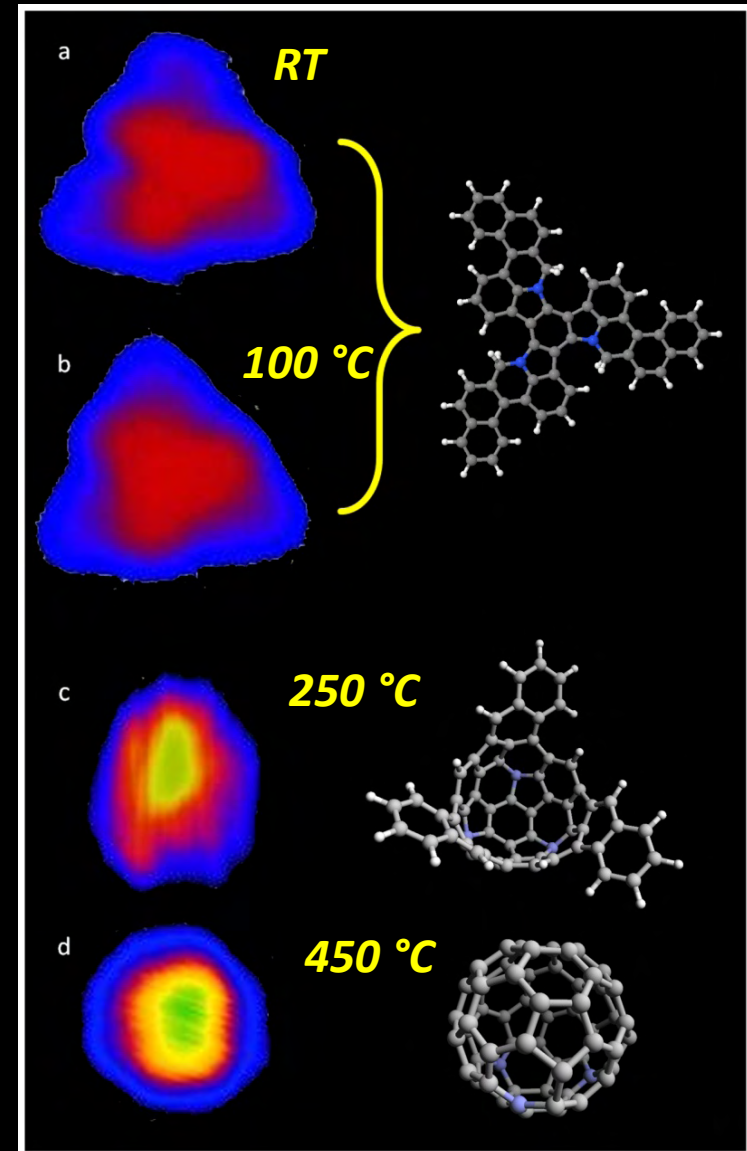
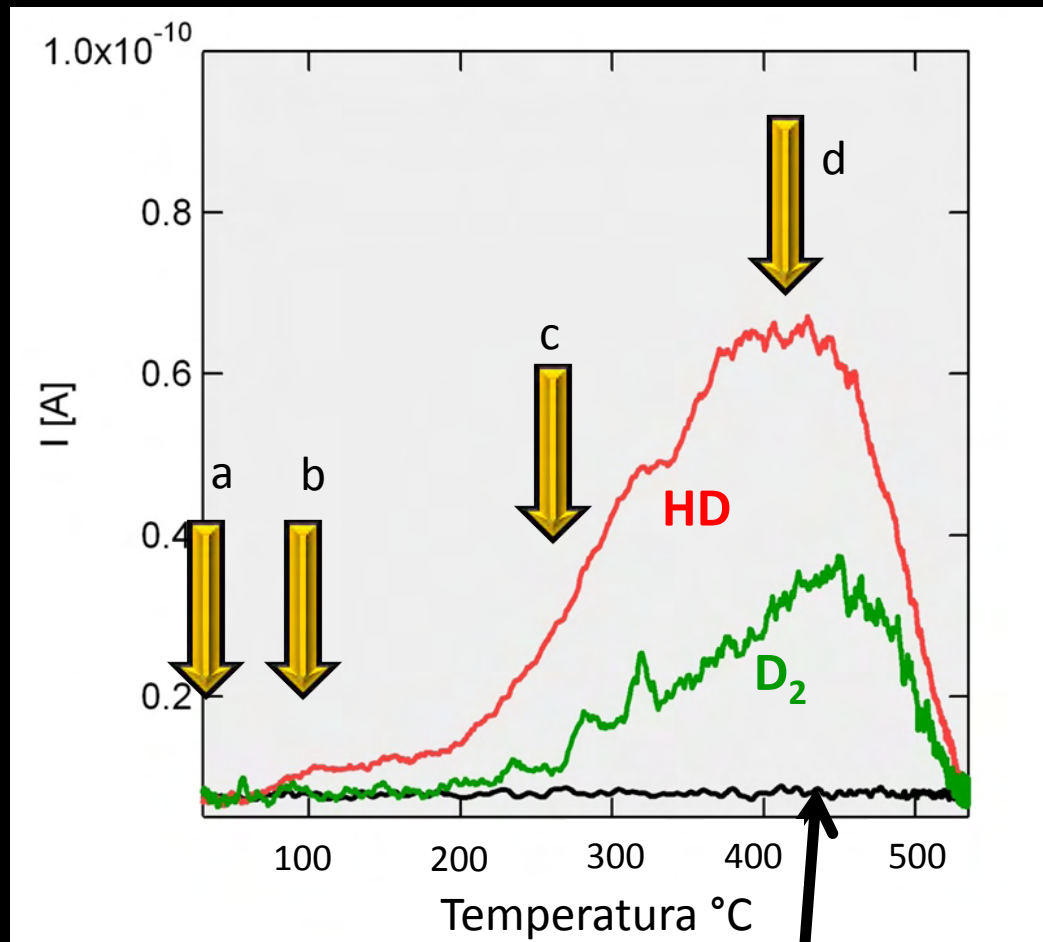
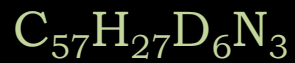
Interaction

	Temperature	efficiency
From vapor	> 1200 °C	0.1 – 1 %
Au(111)	650 °C	< 1 %
Cu(111)	550 °C	< 1 %
Pt(111)	450 °C	~ 100 %

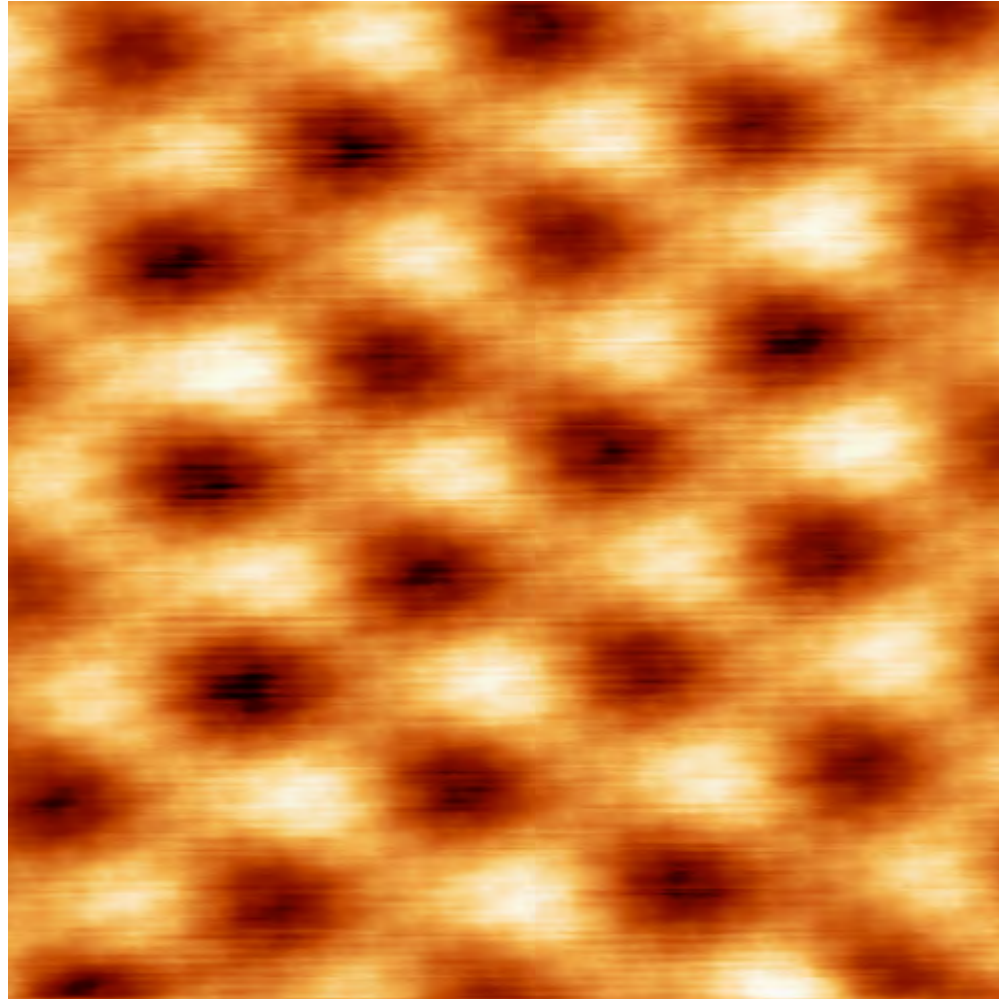


Pt is efficient in
dehydrogenating the surface

What beyond cyclodehydrogenation?

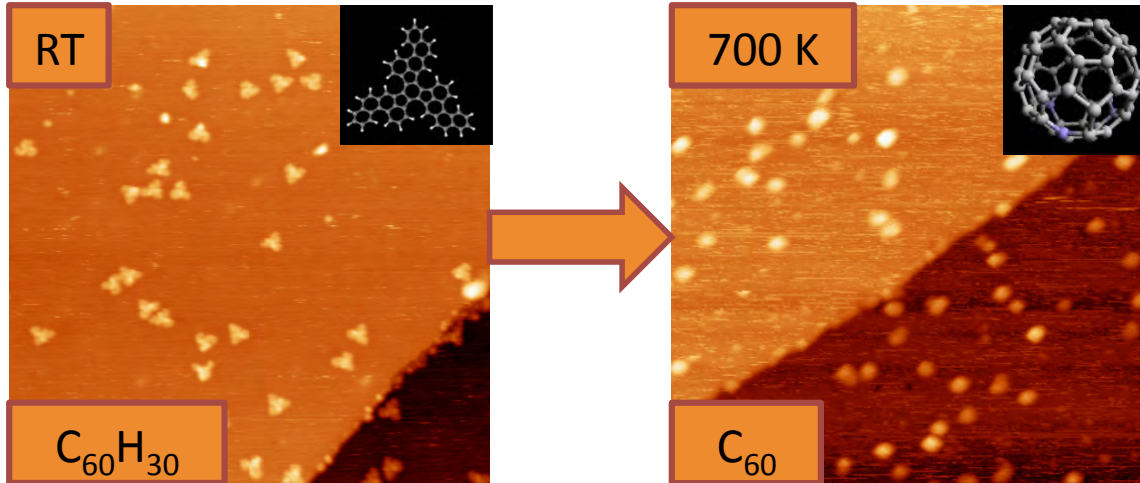


Graphene

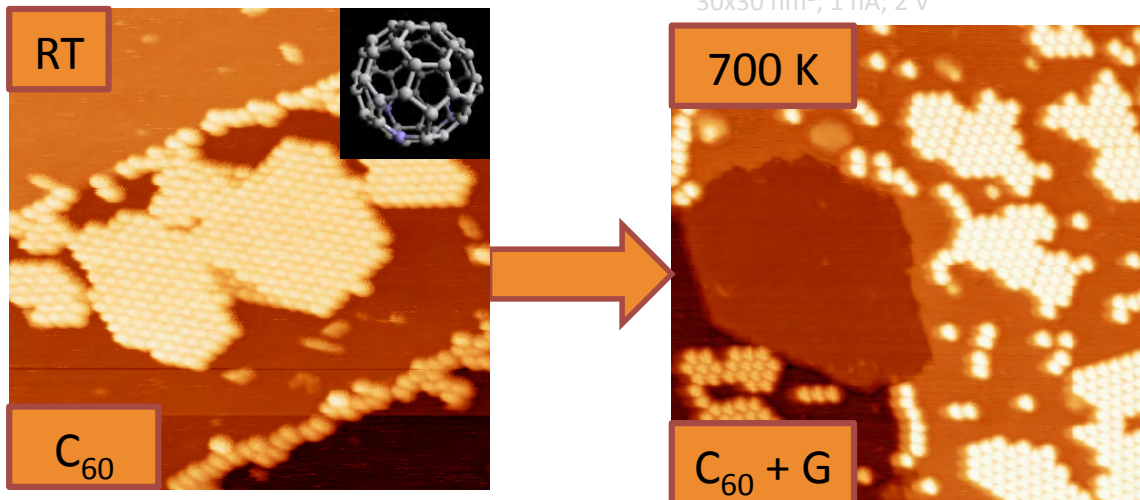


LARGE PAH AS PRECURSORS: MULTI-DOMAIN G/Pt(111)

Otero et al., *Nature*, **454** (2008)

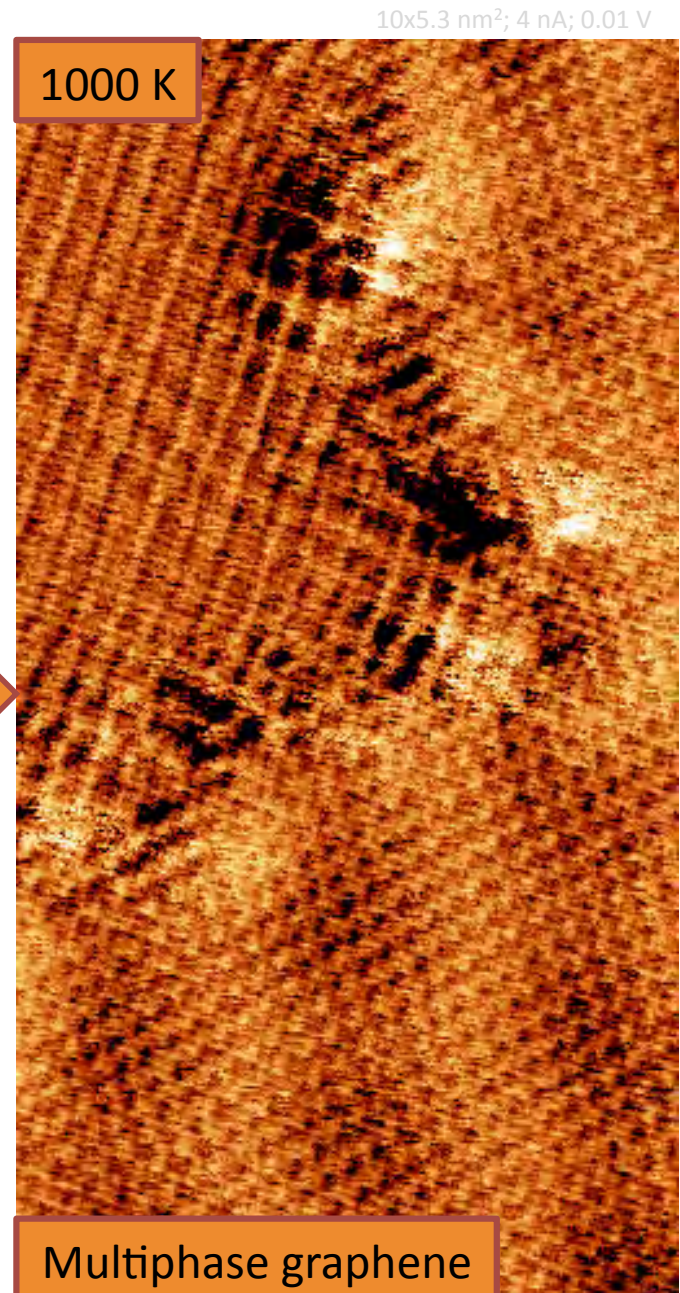


30x30 nm²; 1 nA; 2 V



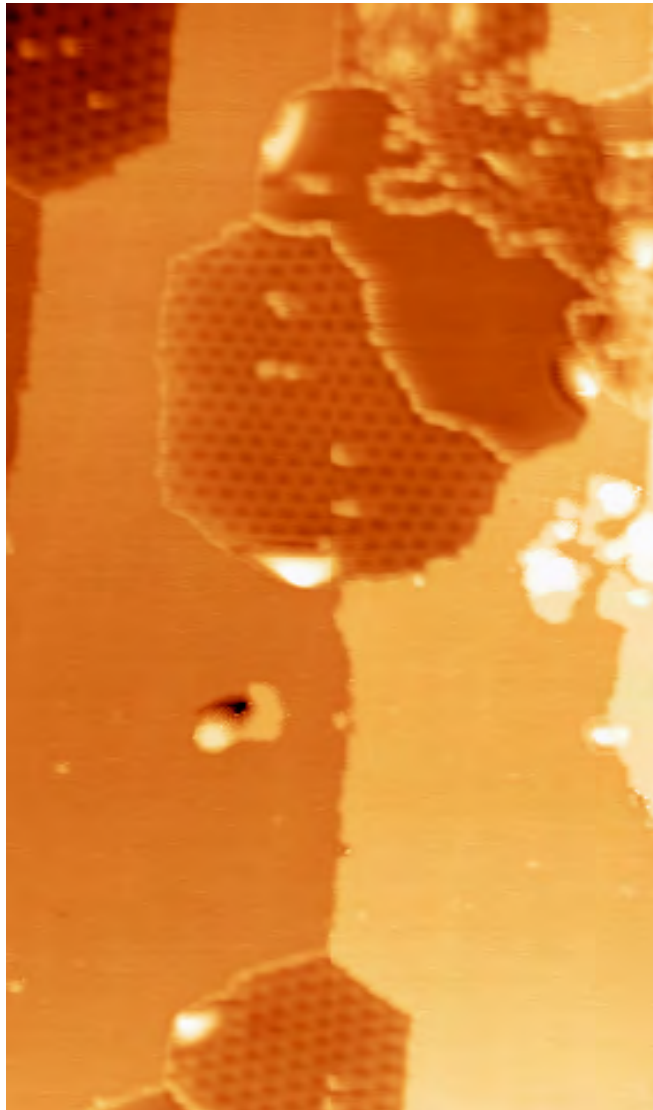
30x30 nm²; 1 nA; 2 V

Otero et al., *Phys. Rev. Lett*, **105** (2010)

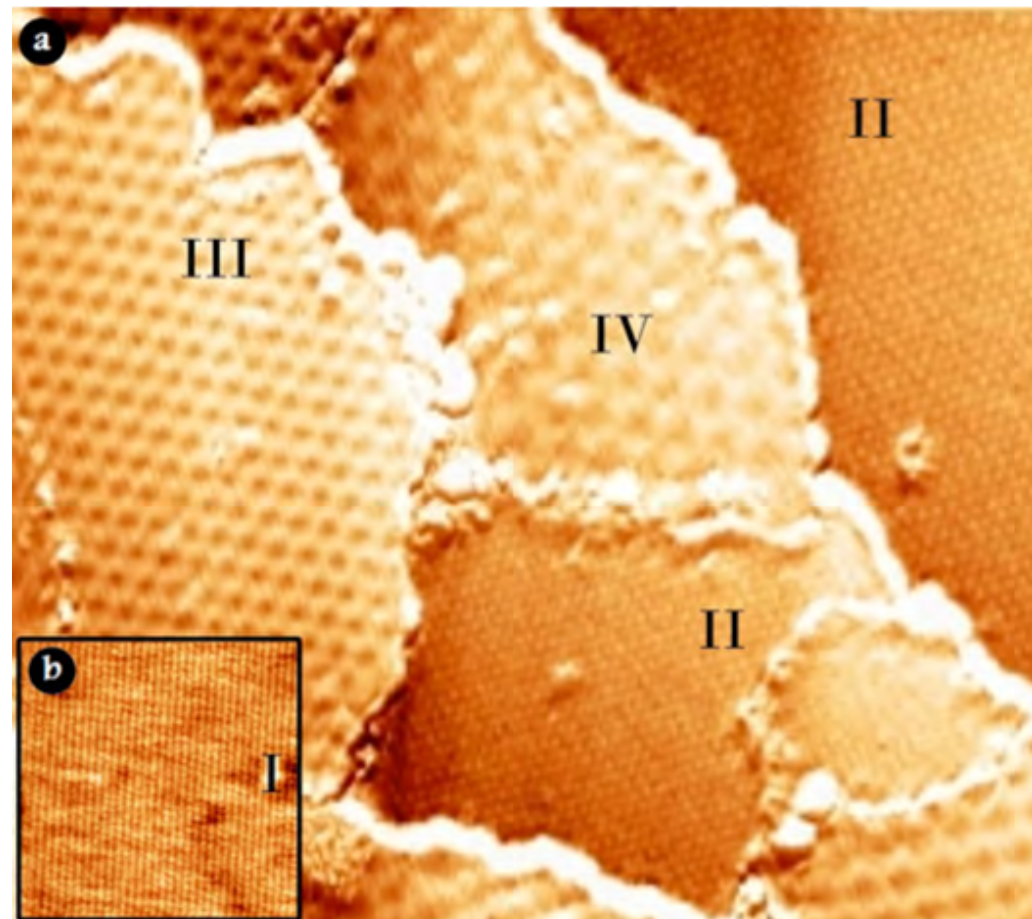


LARGE MOLECULES AS PRECURSORS: MULTI DOMAIN G/Pt(111)

Multiphase and Low than 1 ML coverage:
Graphene Laboratory
we can observe and compare



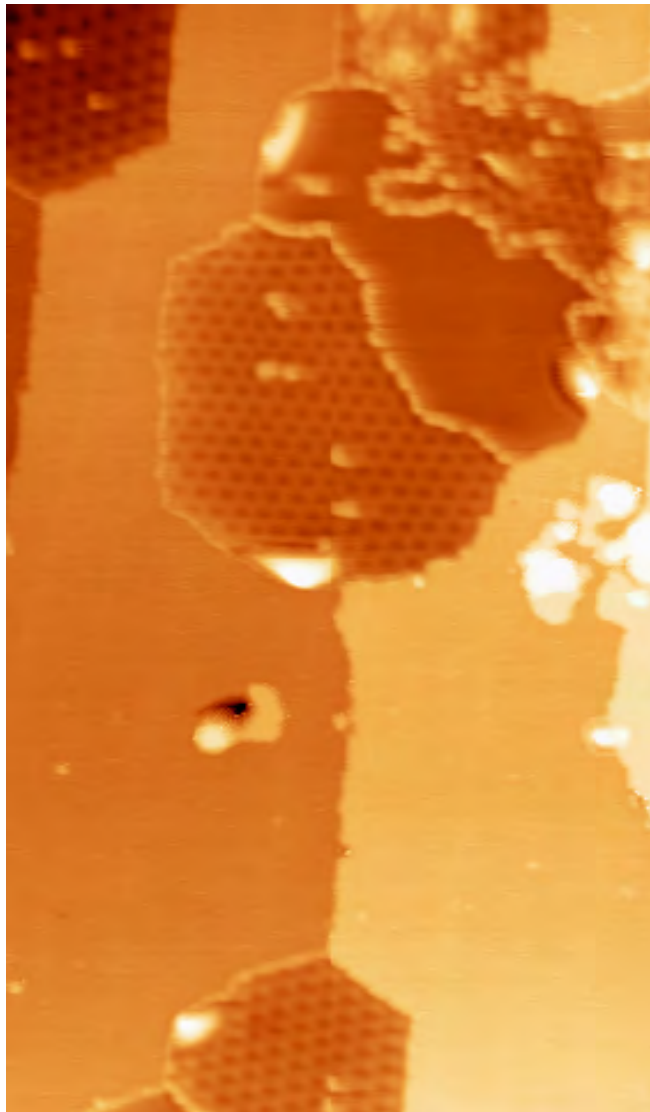
90x35 nm²; 0.2 nA; 0.4 V



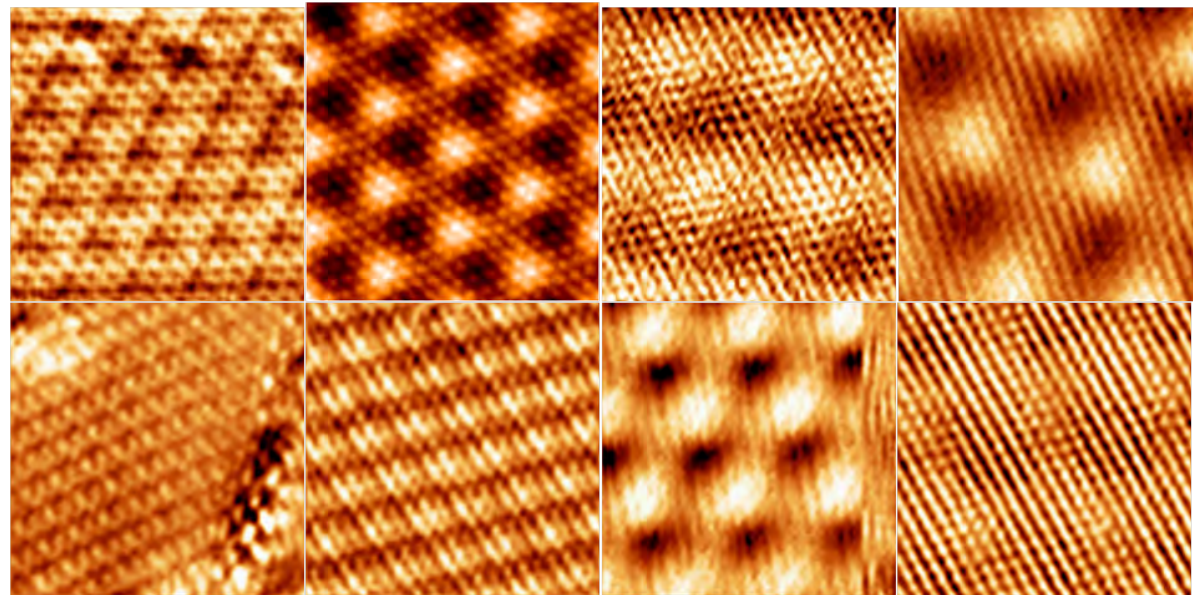
50x50 nm²; 1 nA; 0.2 V

MULTI DOMAIN G/Pt(111)

Use of low temperatures and large PAH



90x35 nm²; 0.2 nA; 0.4 V



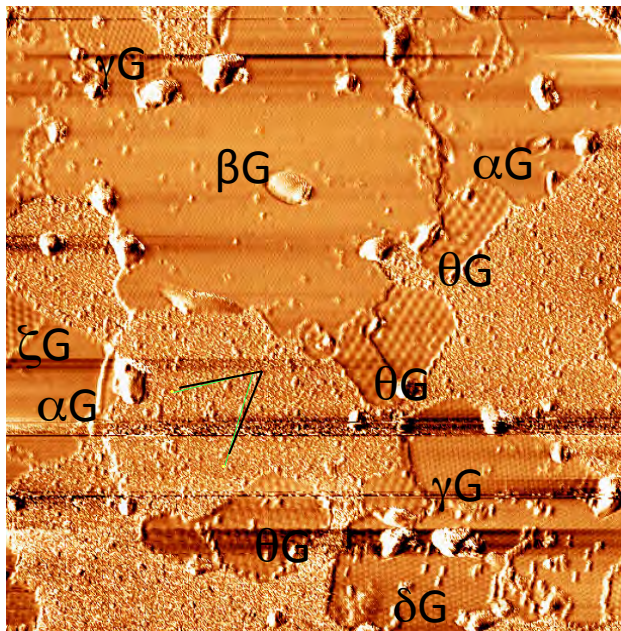
4x4 nm²; 2-4 nA; 0.01-0.1 V

How many moiré superstructures can be accommodated on a single-crystal metal surface?

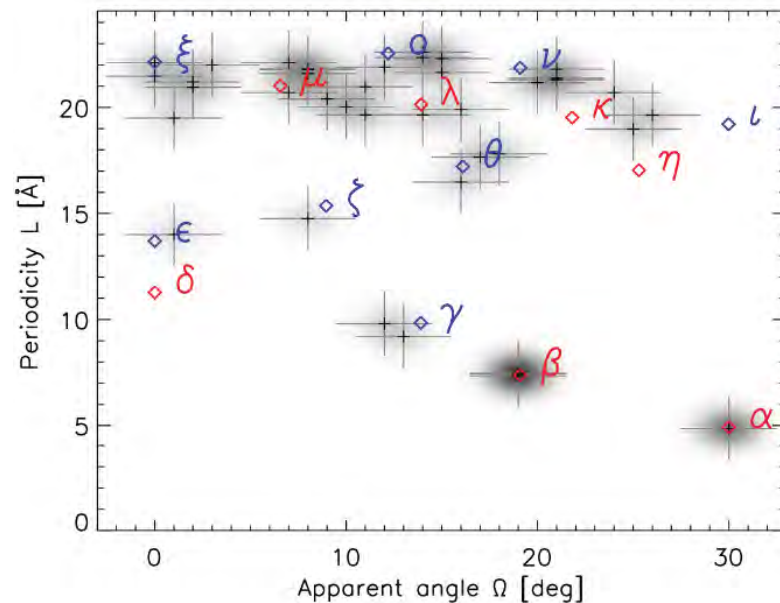
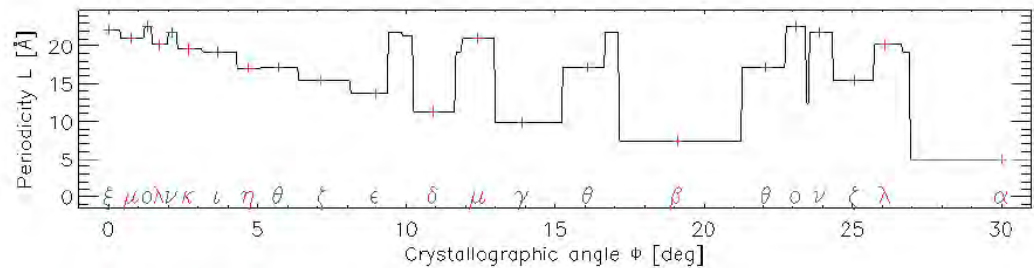
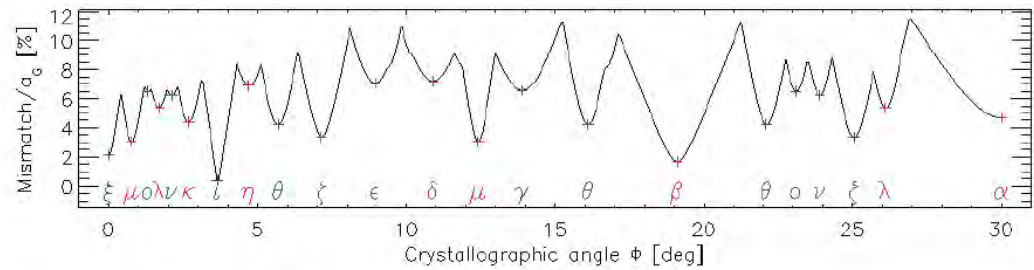
As much as minimize the strain

$$|\Delta_{i,j}^{n,m}| = |\vec{a}_{Pt_{n,m}} - \vec{a}_{gr_{i,j}}(\Phi)|$$

22 Moiré Superstructures for Pt(111)

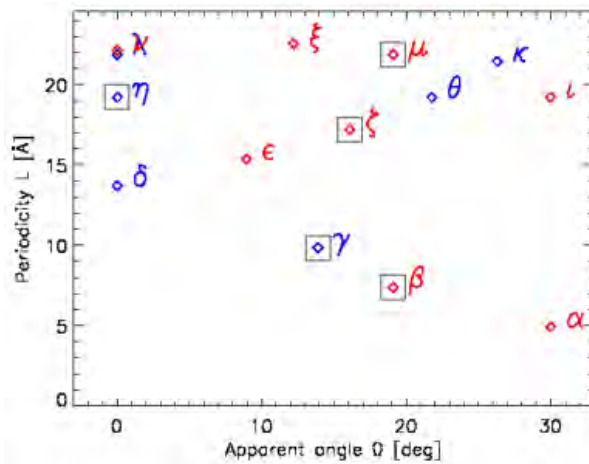


Only 19 Moirés are discernable.



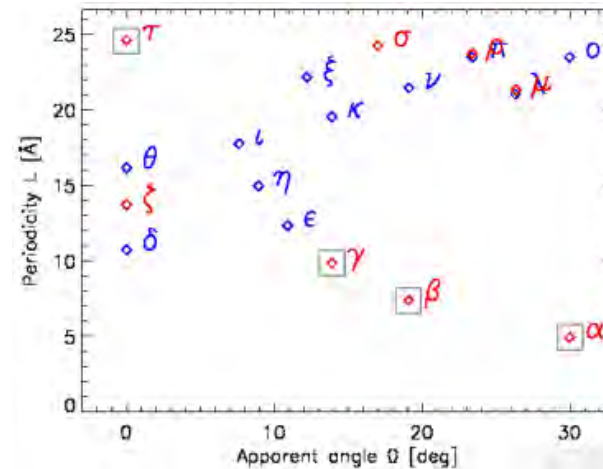
MODEL ON OTHER TRANSITION METALS

Merino et al., ACS Nano 5 (2011)



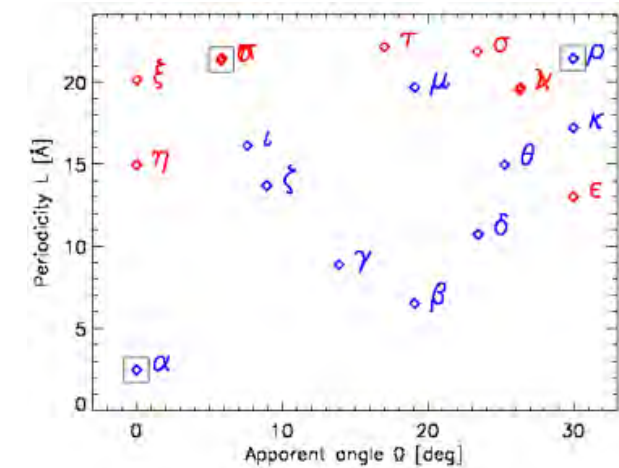
G/Pd(111)

The model predicts **14** superstructures;
5/6 reported reconstructions are predicted by the model



G/Ir(111)

The model predicts **18** superstructures;
4/4 reported reconstructions are predicted by the model

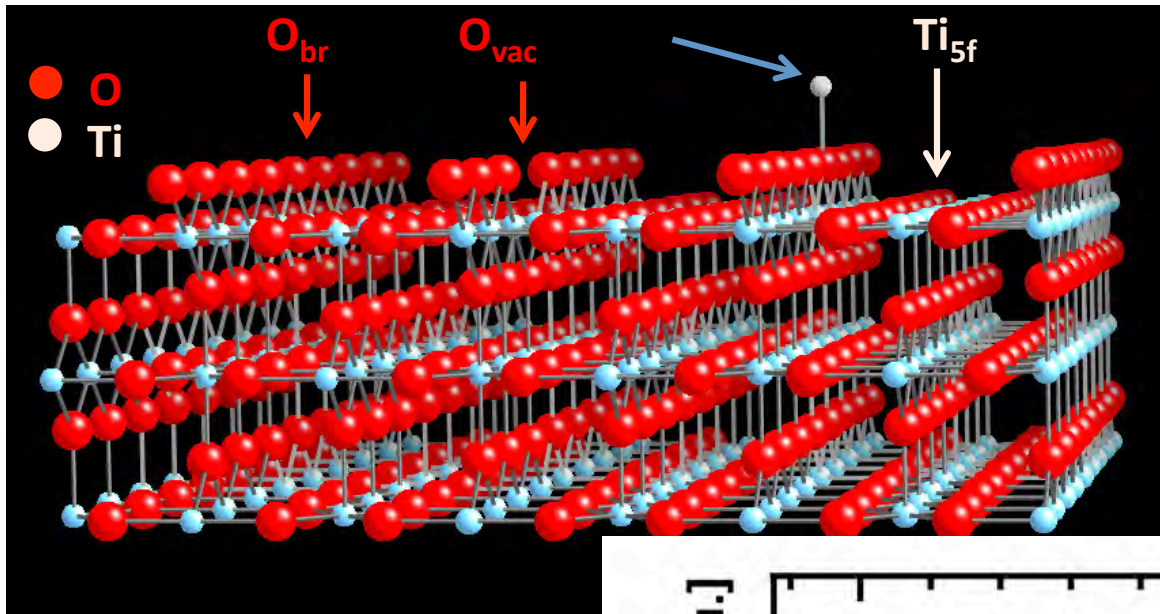


G/Ni(111)

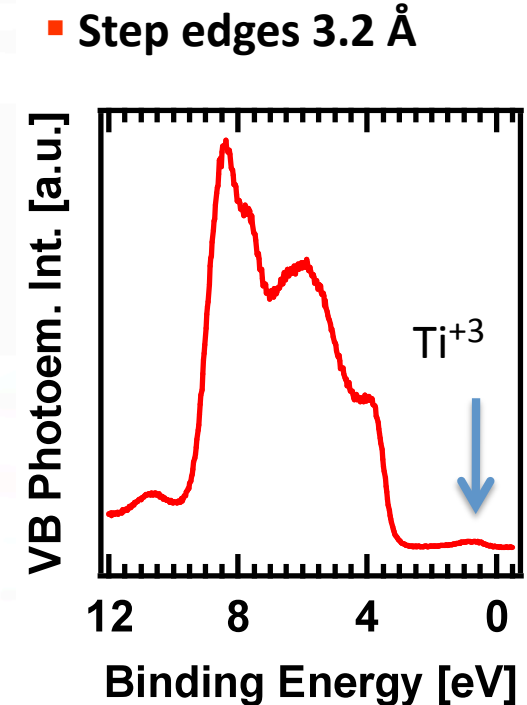
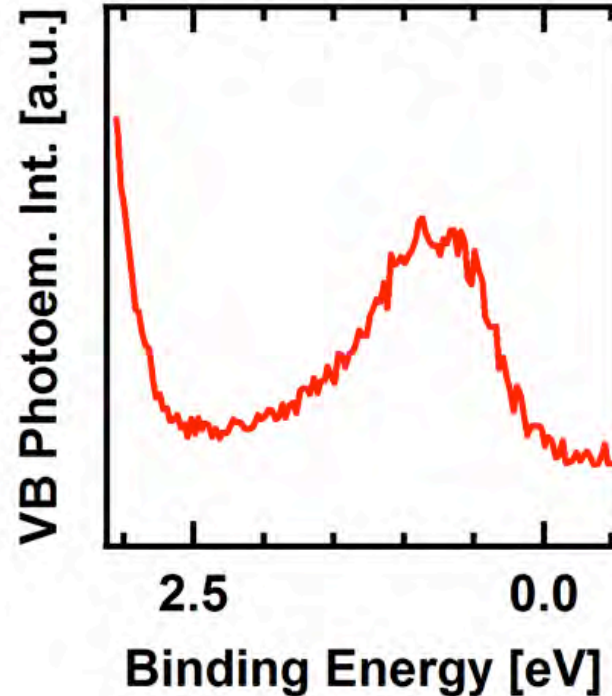
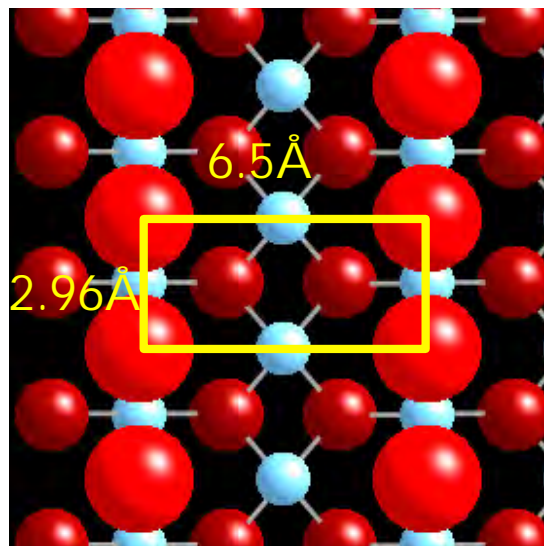
The model predicts **22** superstructures;
3/3 reported reconstructions are predicted by the model

Are other surfaces than transition metals good for dehydrogenation reactions?

The rutile $\text{TiO}_2(110)$ (1x1) surface



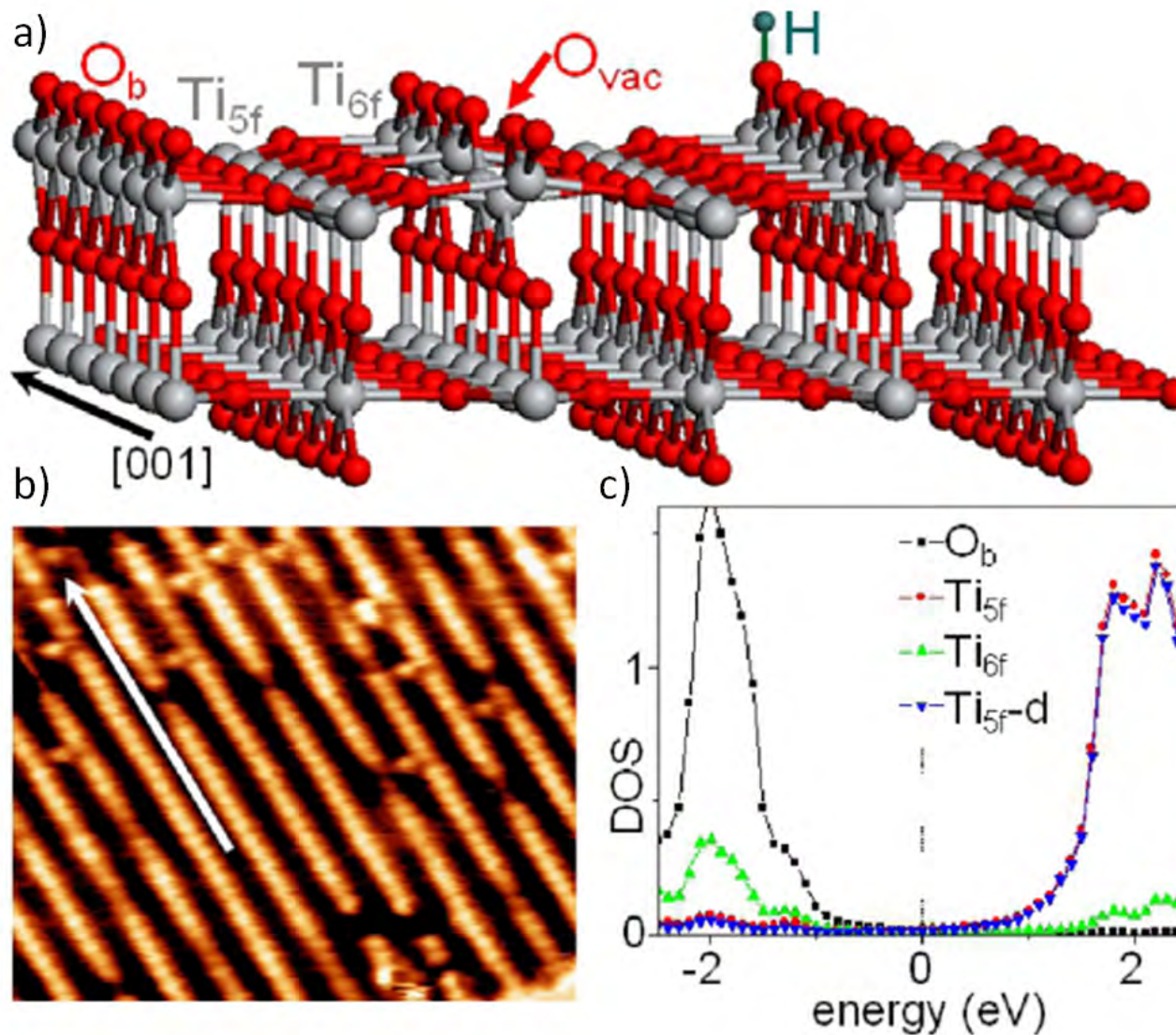
- Bulk-like structure
- Stable at low temperature ($T < 900 \text{ K}$)
- Low reduction (low density of defects)
- Two main defects: O_{vac} & OH



- Step edges 3.2 Å

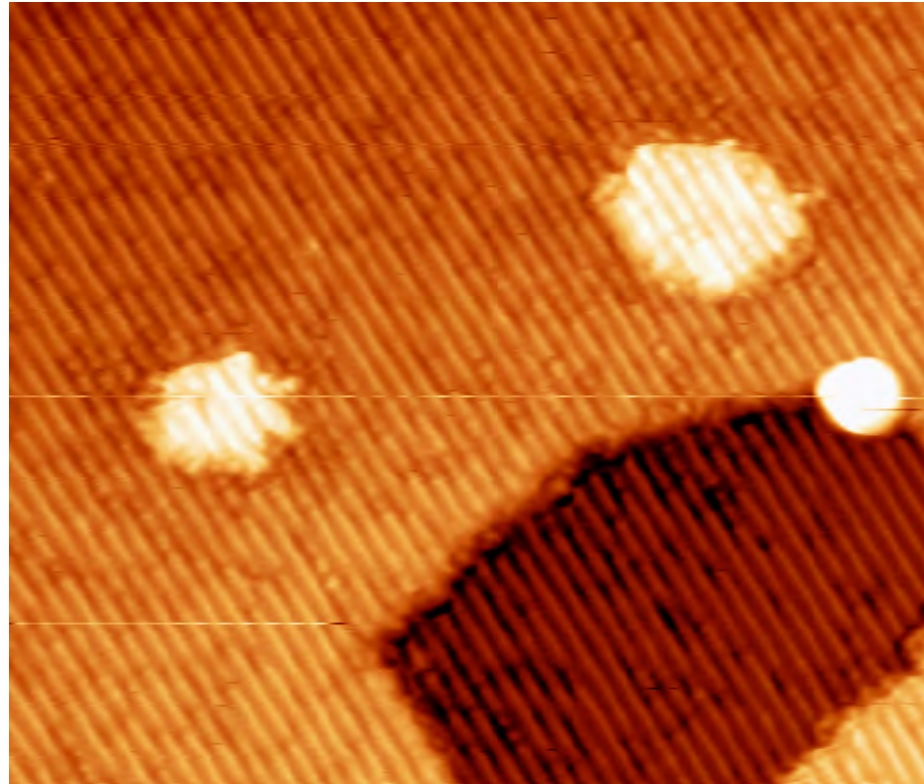
Accepted appearance of the (1x1) surface

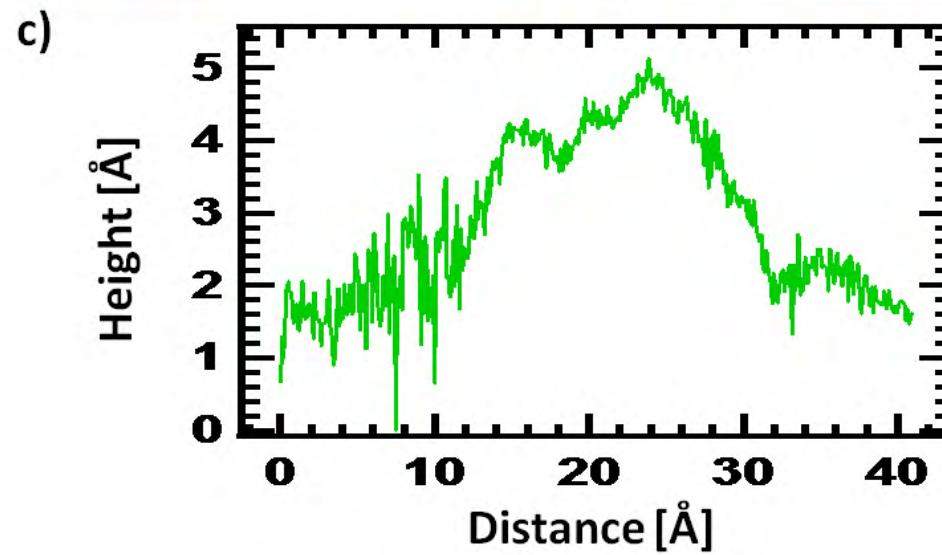
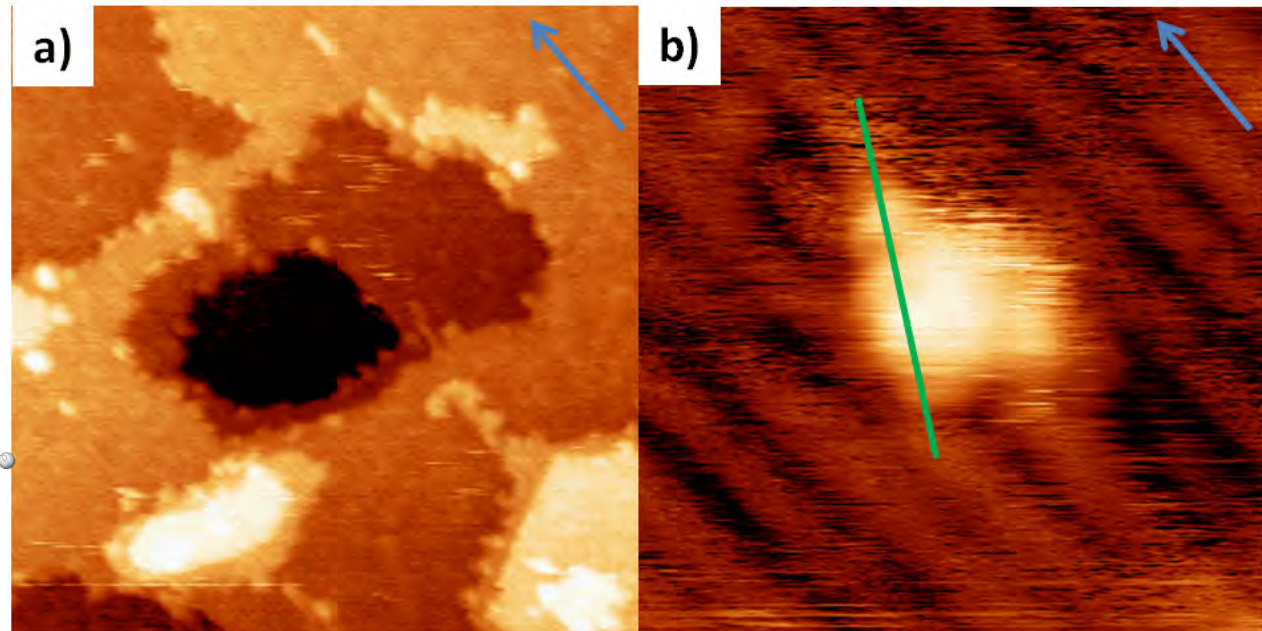
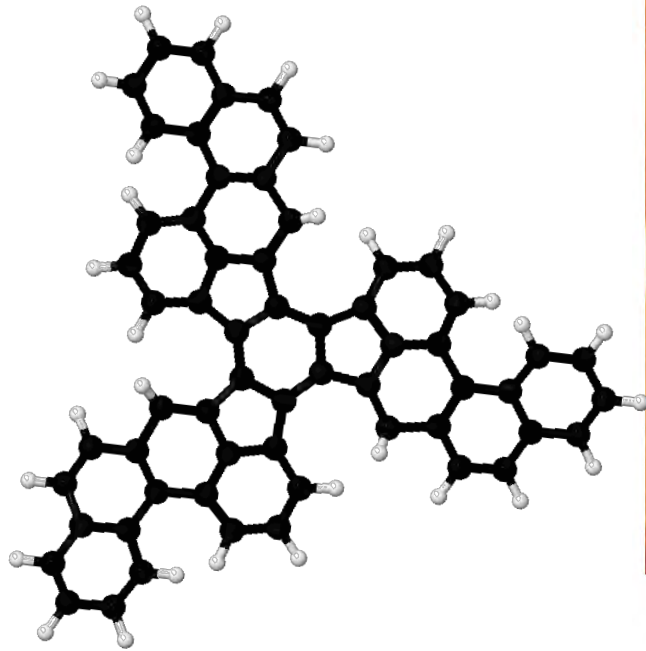
$R_p = 0.29$, Lindsay et al., PRL 94, 6102 (2005)



80 Å x 67 Å
 $I = 0.17 \text{ nA}$, $V = 1.5 \text{ V}$

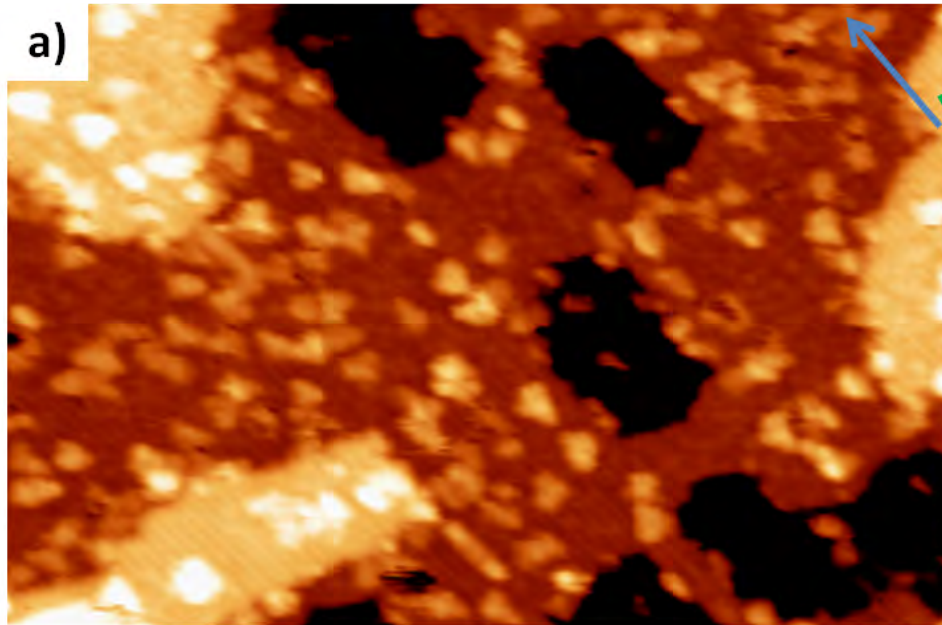
TiO₂ WITH RT_STM... A Difficult substrate....





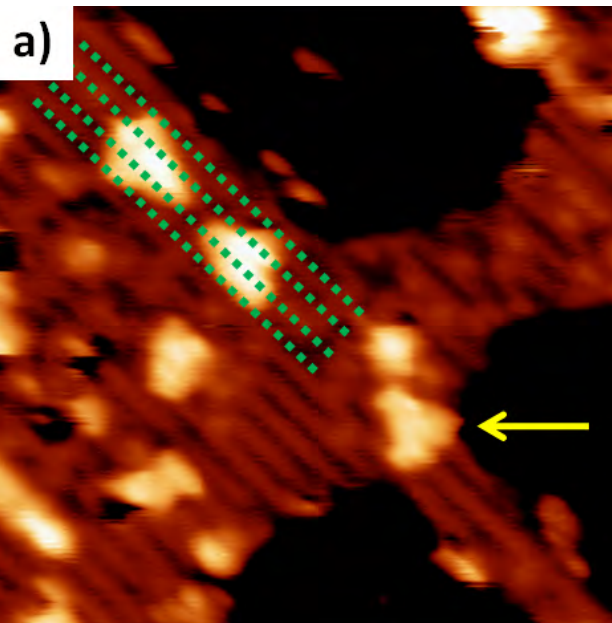
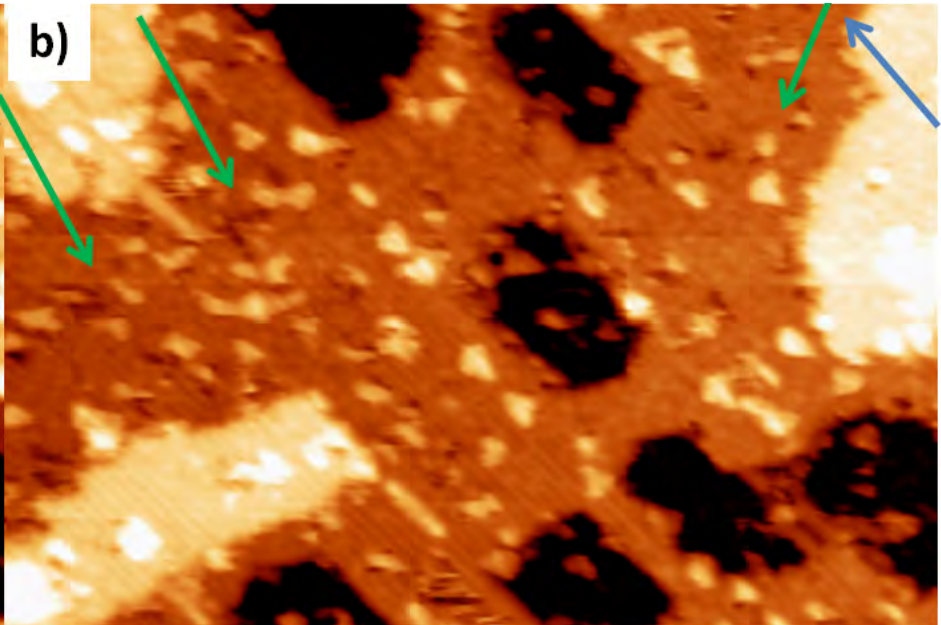
50.0nm x 33.0nm

I=0.2nA V=1.6V

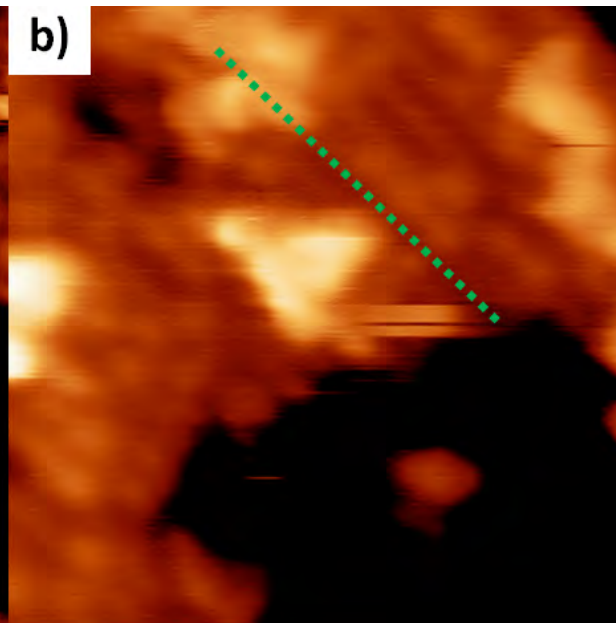


50.0nm x 33.0nm

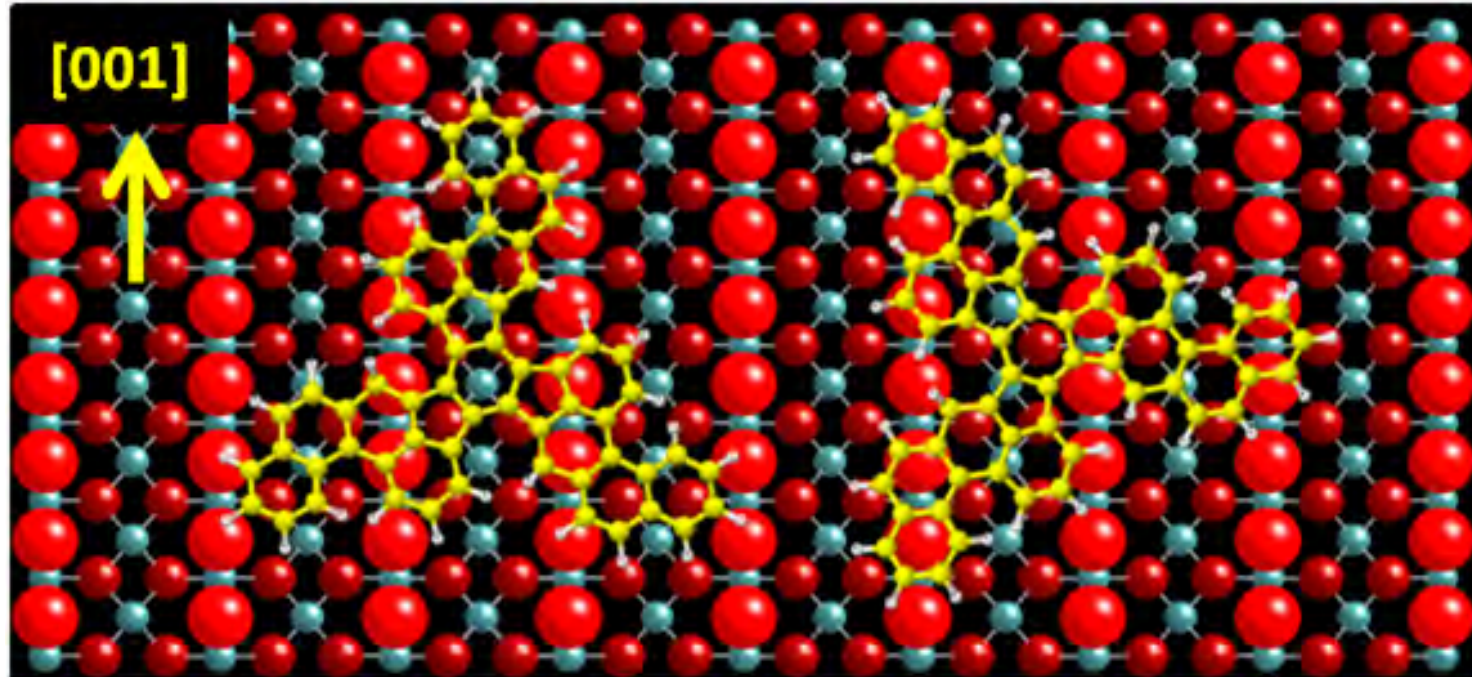
I=0.15nA V=1.45V

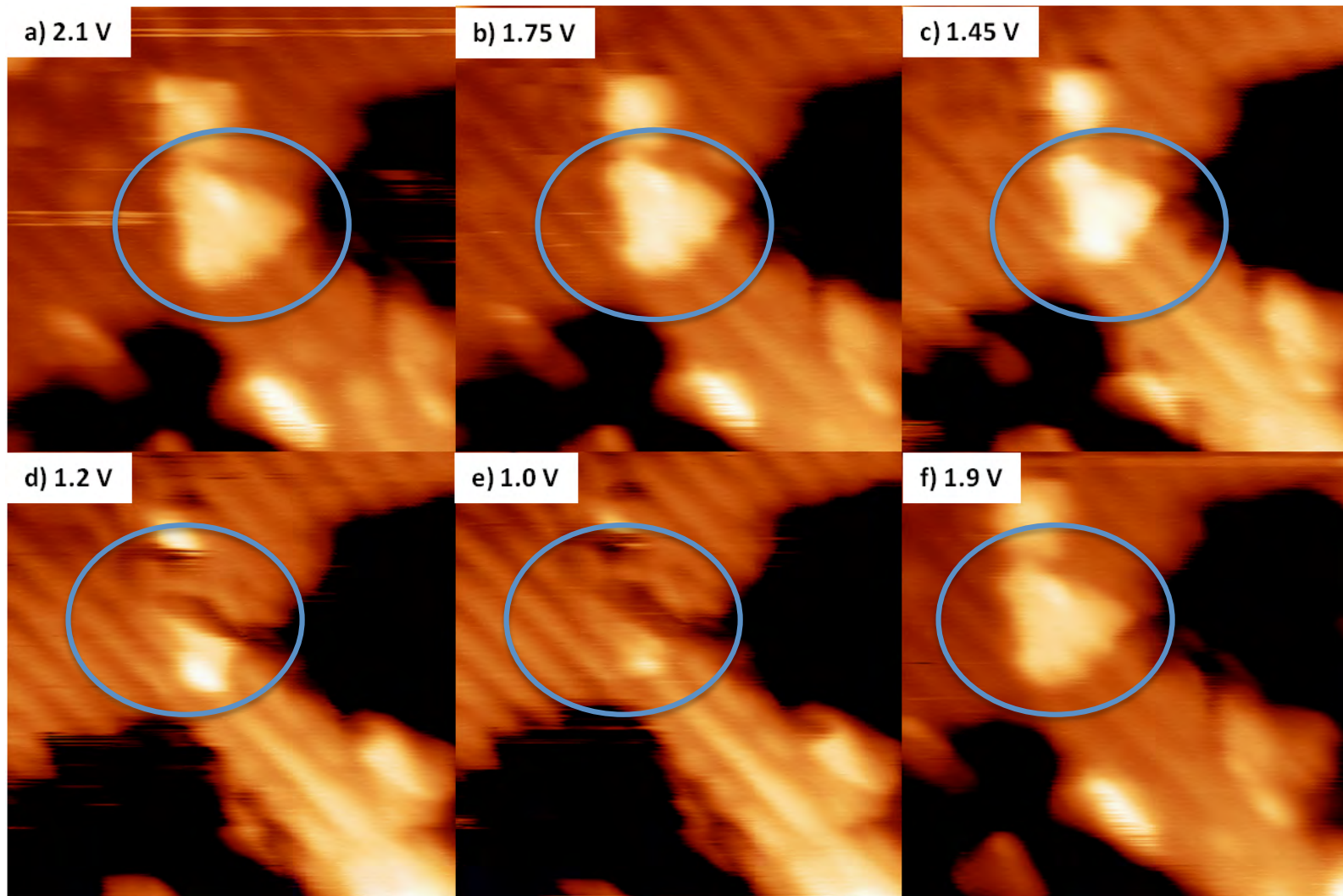


15.0nm x 15.0nm
I=0.15nA V=1.8V



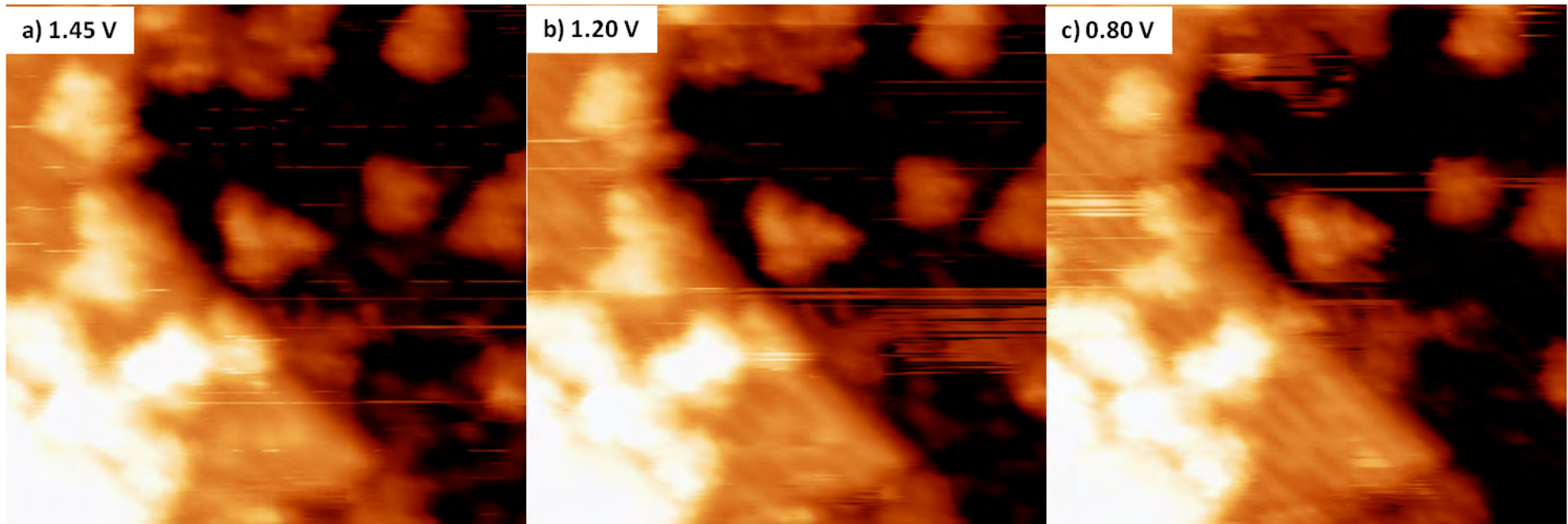
10.0nm x 10.0nm
I=0.2nA V=1.45V





8.0nm x 8.0nm

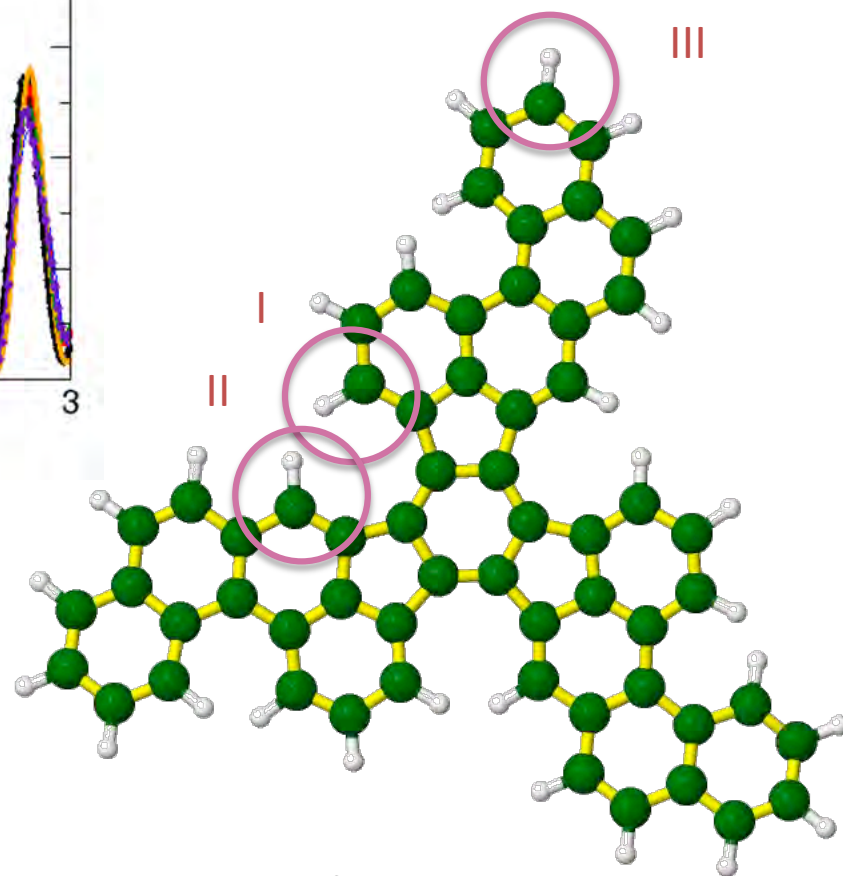
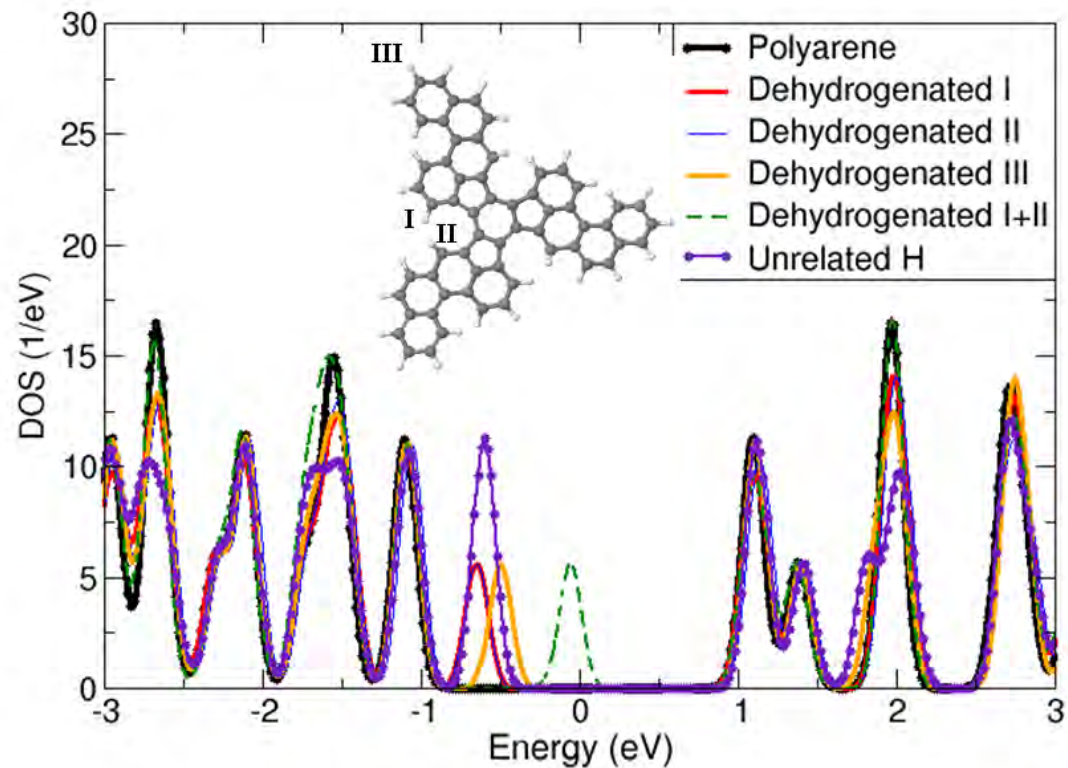
$I=0.15$ nA



15.0nm x 15.0nm

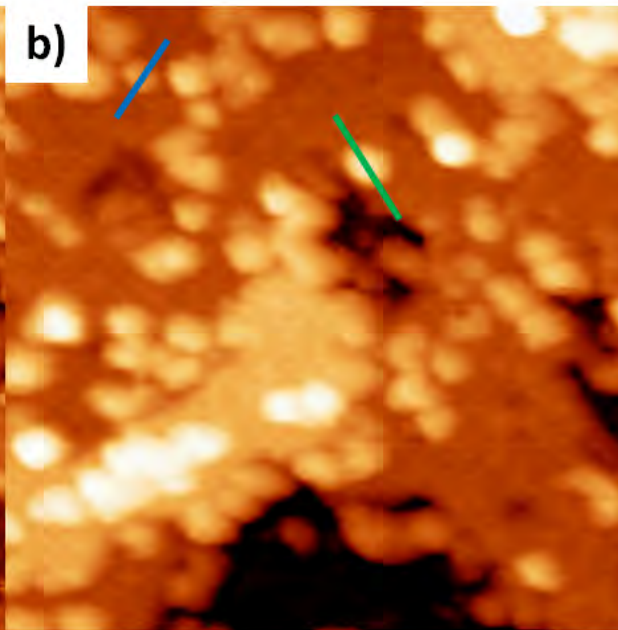
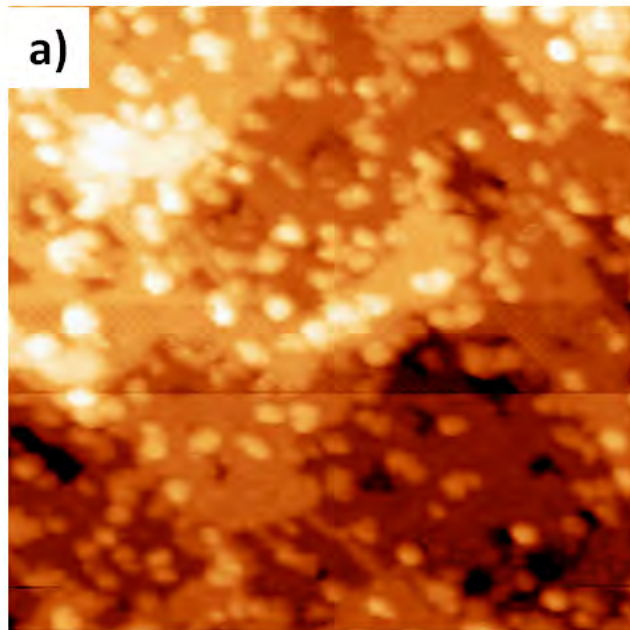
$I=0.15$ nA

Free Molecule total DOS calculations

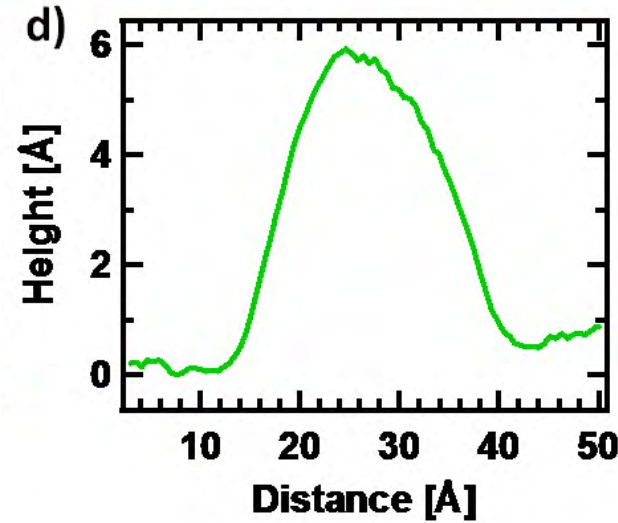
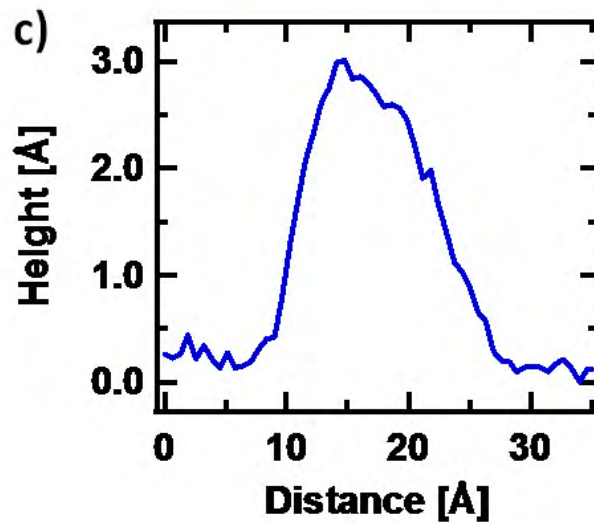


TiO₂ can promote surface de-hydrogenation reactions on surfaces

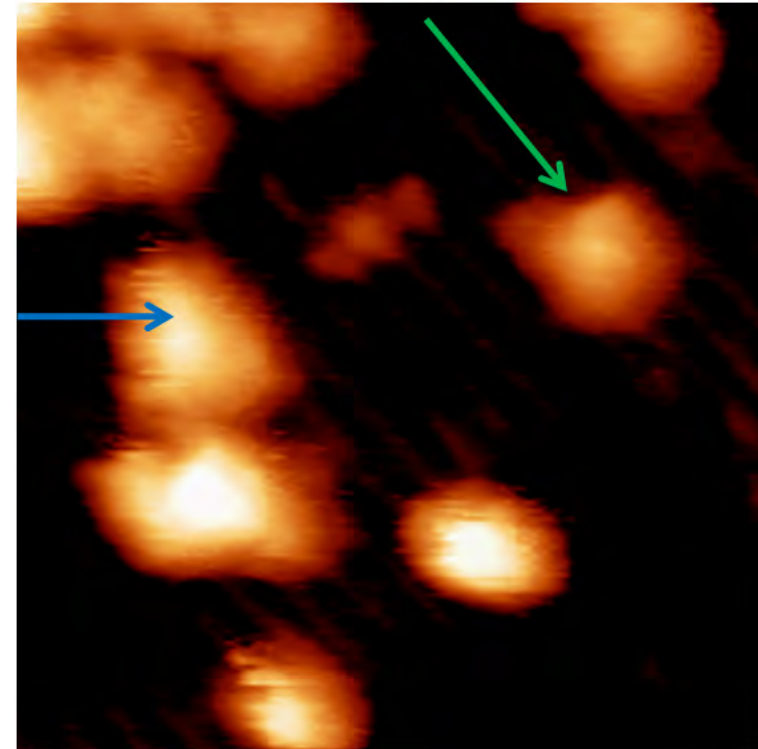
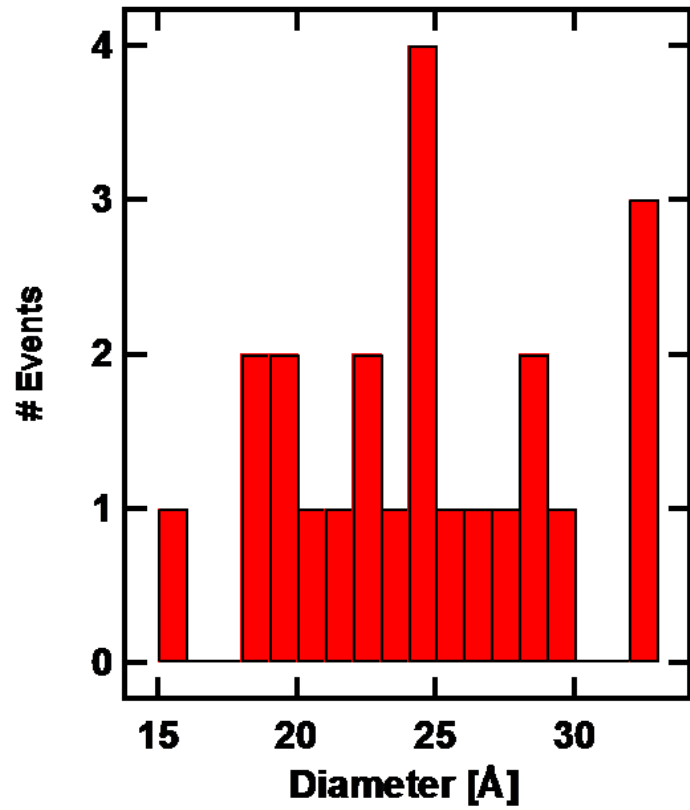
50.0nm x 50.0nm
 $I=0.11$ nA $V=1.9$ V



30.0nm x 30.0nm
 $I=0.11$ nA $V=1.9$ V



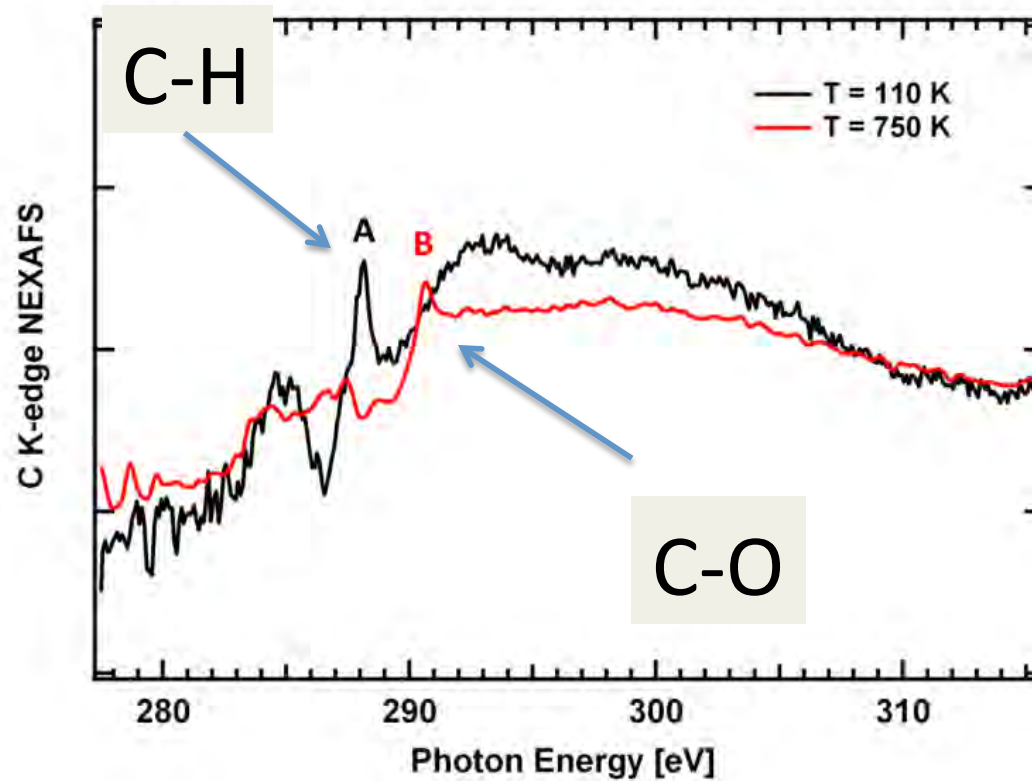
FORMATION OF FULLERENE-LIKE STRUCTURES



11.0nm x 11.0nm

I=0.11nA V=1.9V

NEXAFS indicate a dehydrogenation reaction



CONCLUSIONS

***On-surface chemistry is new field for surface science and nanotechnology that could lead to new kind of polymeric networks or molecular objects**

***The interaction of PAH with the single-crystal is critical for defining the final product of the reaction.**

**Fullerenes or polymers, extended graphene or multidomain can be obtained from the same molecular precursor
EVEN IN WEAKLY BOUND SYSTEMS.**

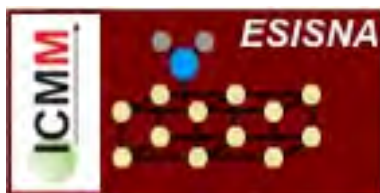
Thank You!



Ruben Pérez
G. Bidau

SPM-TH group
UAM

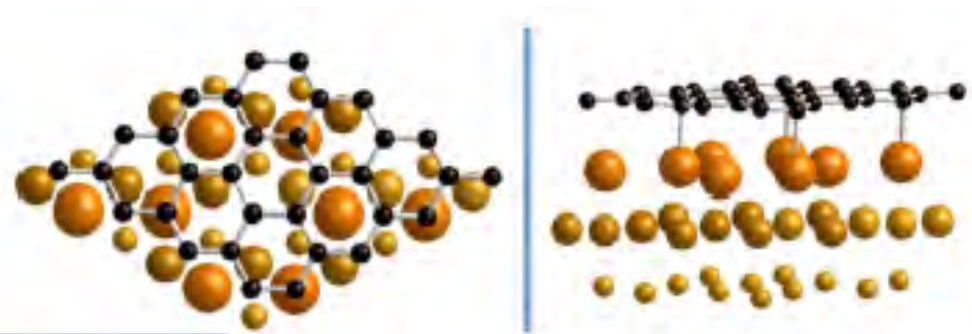
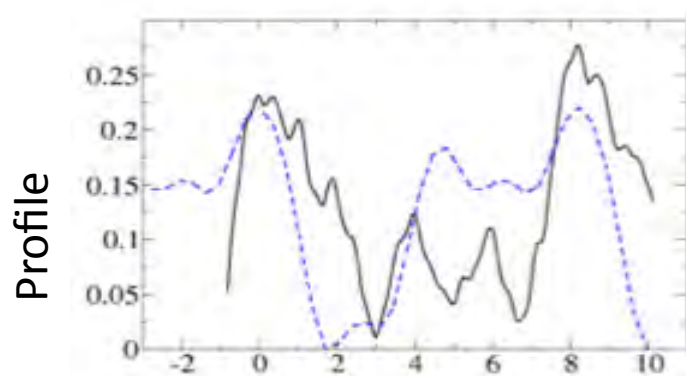
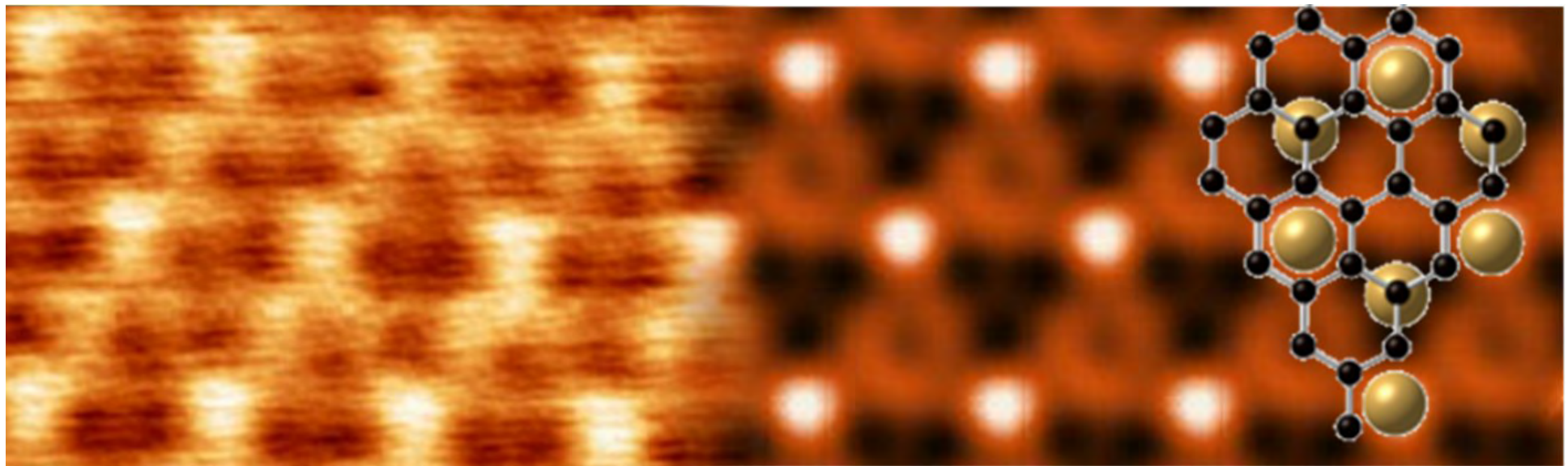
- Dr. C.F.J. Flipse and K. Van de Ruit from TUE
- Dr. S. Gardonio and Dr. S. Lizzit from Synchrotrone Trieste
- Dr. M. Blanco-Rey from University of Cambridge



α G/Pt(111)DFT: vacancy model

STM Simulations:

G. Otero *et al.* PRL, 2010, 105, 216102.



G. Otero *et al.* PRL, 2010, 105, 216102.