LT-STM ROME

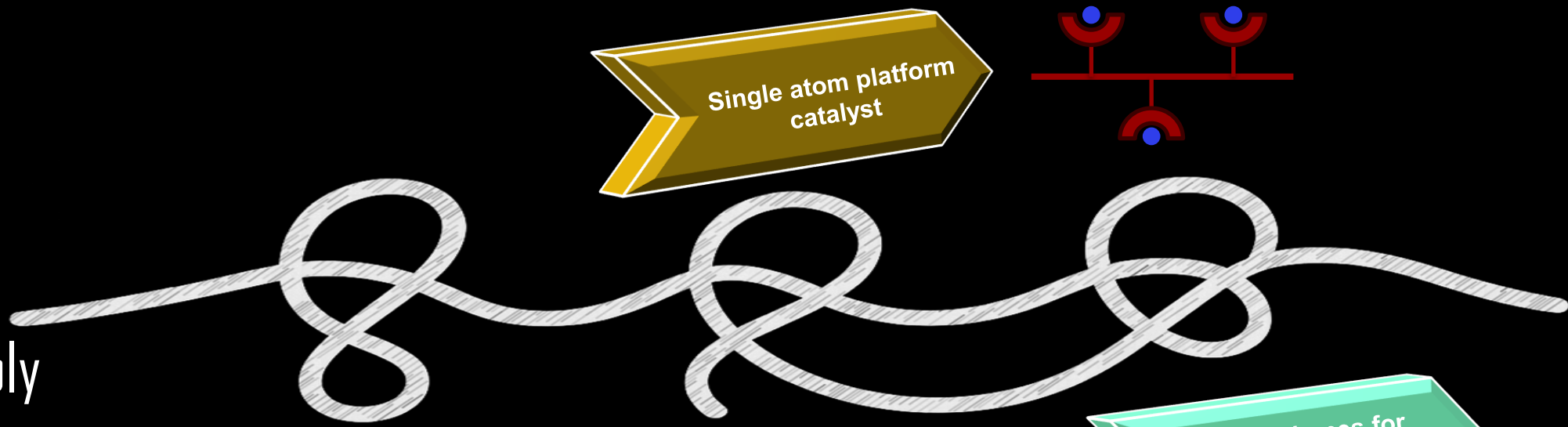
Molecular nanostructures for advanced materials

Antonio Caporale

Physics Department, University of Rome Tor Vergata

Motivation

Molecular Self-Assembly



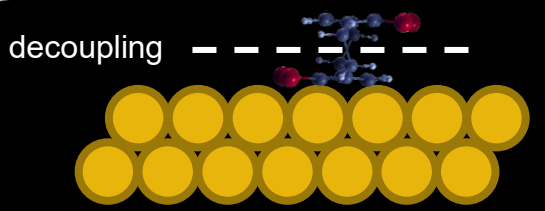
Single atom platform catalyst

Polymeric chains for transport applications

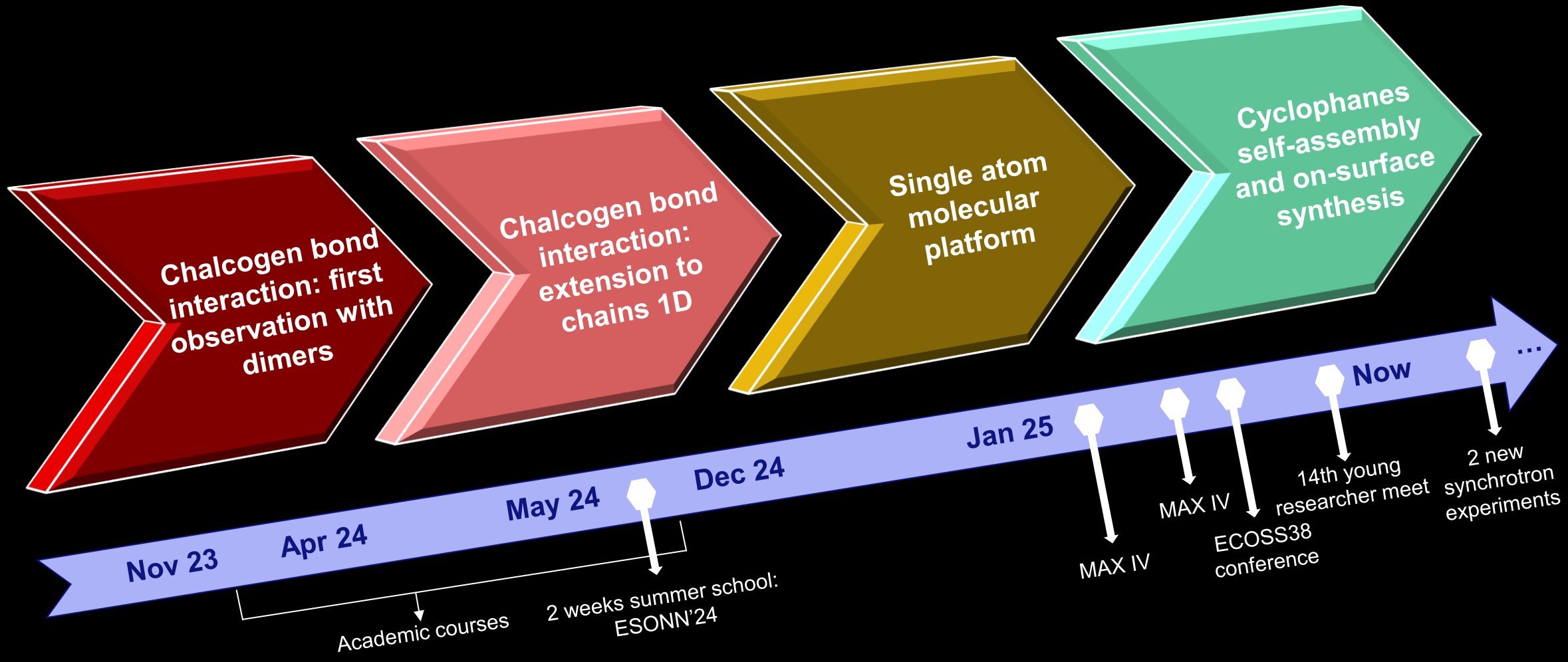
Cyclophanes for substrate decoupling

Chalcogen bonding

(ex. Se···N-C)



Outlook *(main projects)*



Low Temperature Scanning Tunnelling Microscopy (LT-STM)

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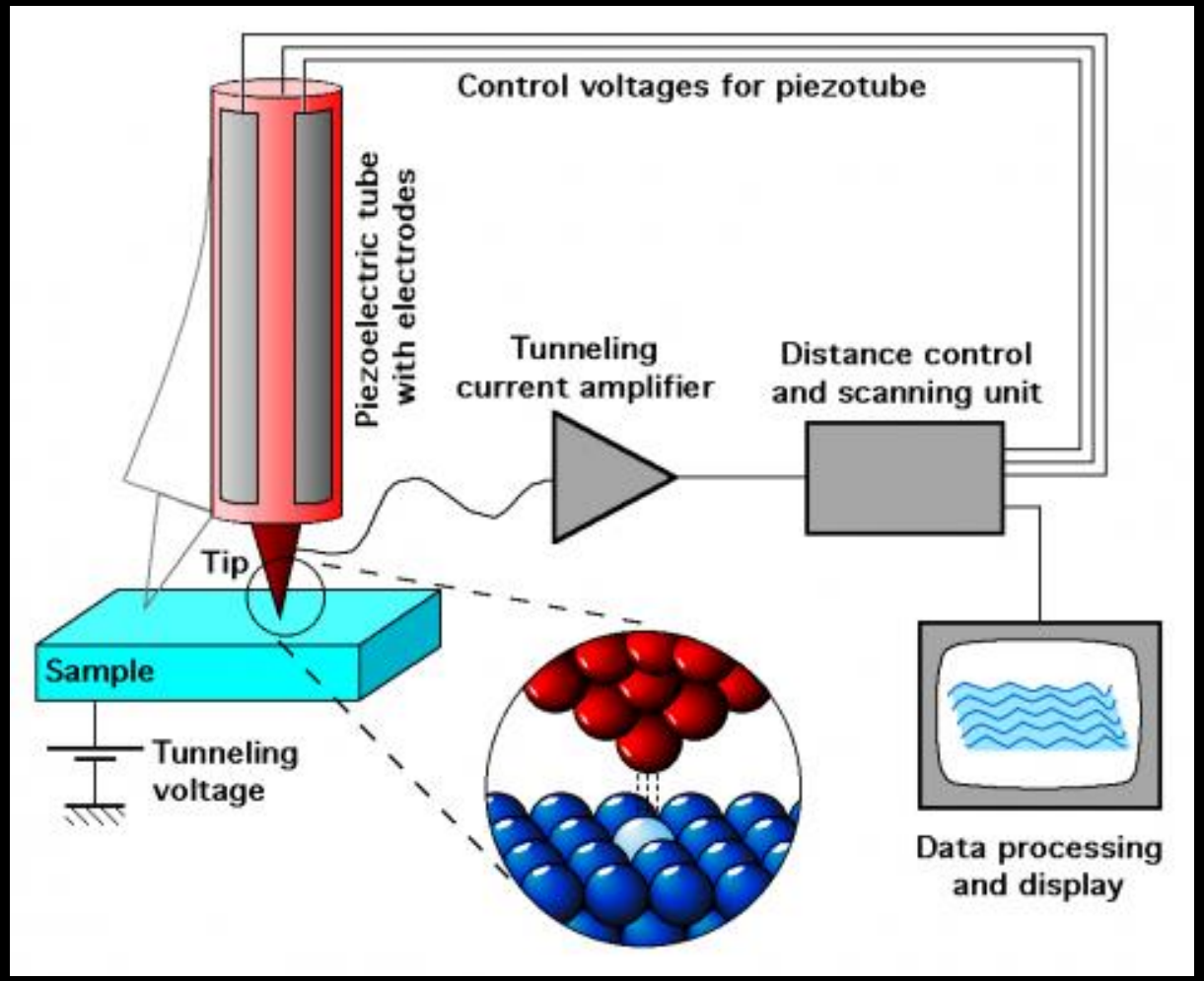

Nobel prize:
Binnig & Rohrer
1986

Working @ 8-10K with a closed helium circuit

$$I_T \propto \int dE\ \rho_s(r_0, E)\rho_p(E - eV)(f(E - eV) - f(E))$$

$I_T^{exp} \propto e^{-2kd}$, d distance between tip and sample

Credits: Wiki

Chalcogen bond (ChB): CGP-Ch molecular structure

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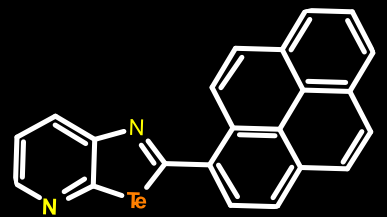
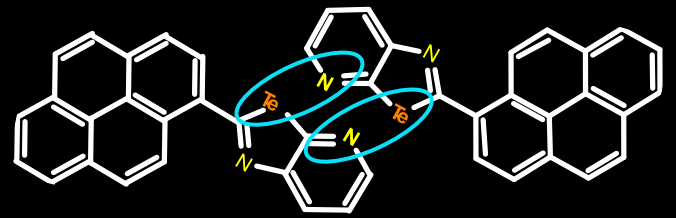
universität wien

Prof. D. Bonifazi and Dr. D. Romito

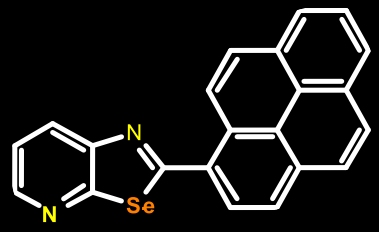


CGP-Te

Chalcogen association



$(CGP\text{-}Te)_2$



CGP-Se

* CGP = chalcogenazolo pyridine; Ch = Te or Se

CGP-Te/Au(111) – STM data

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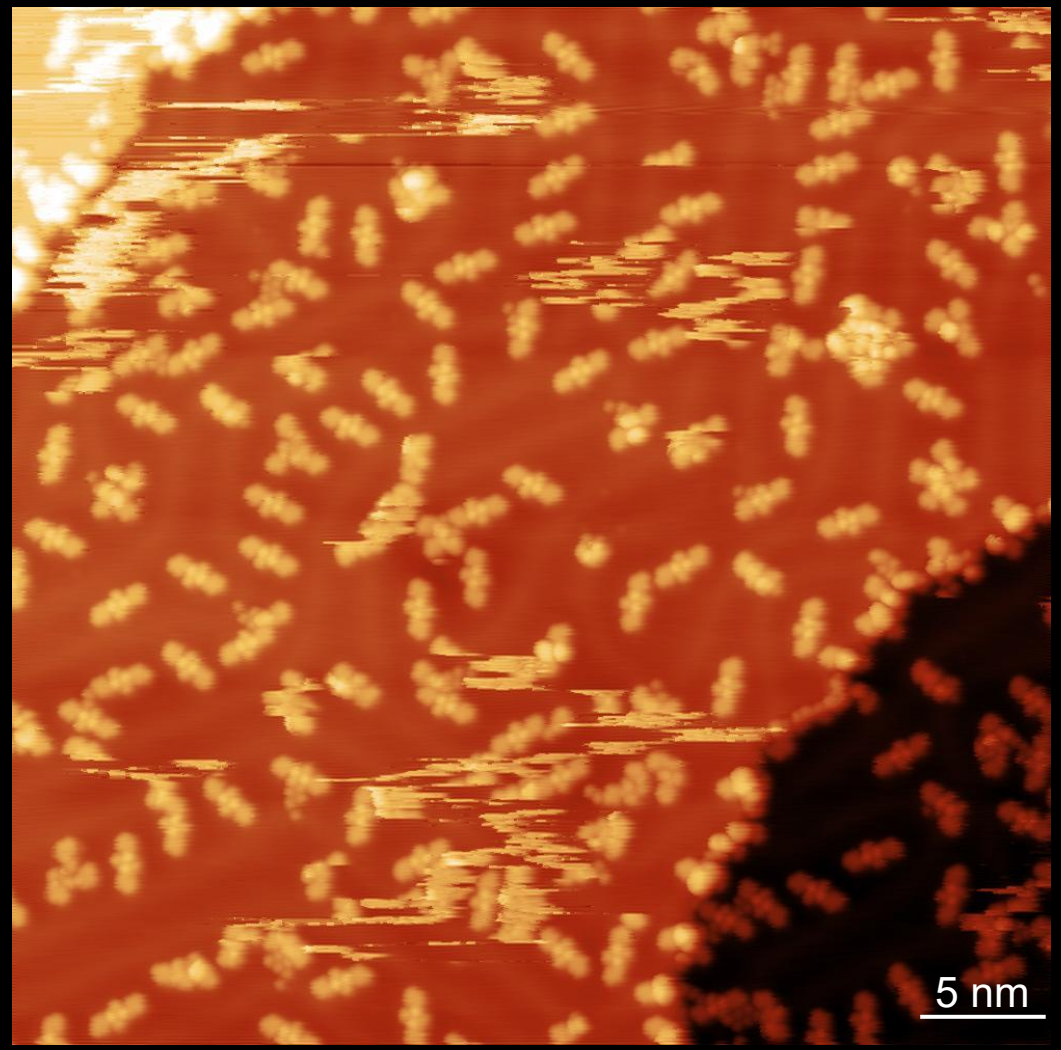
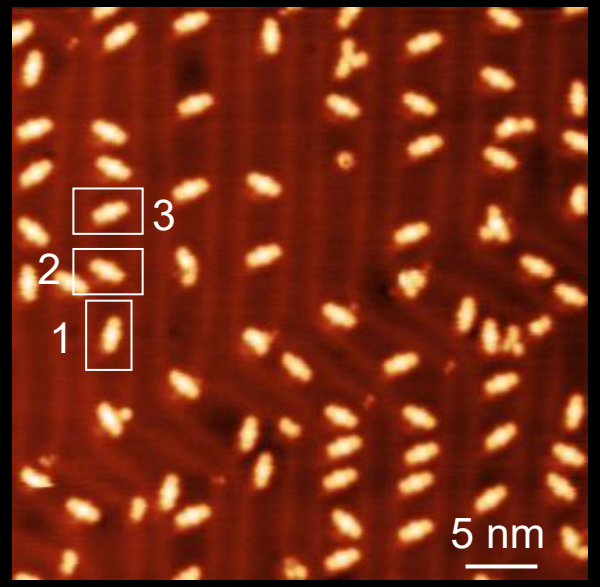
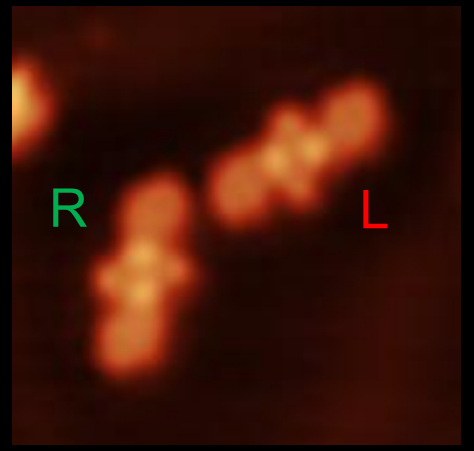
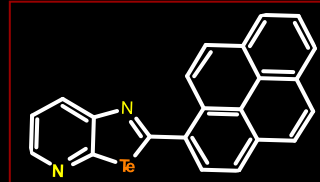


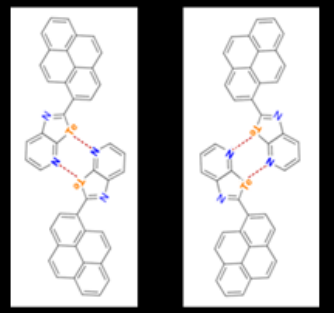


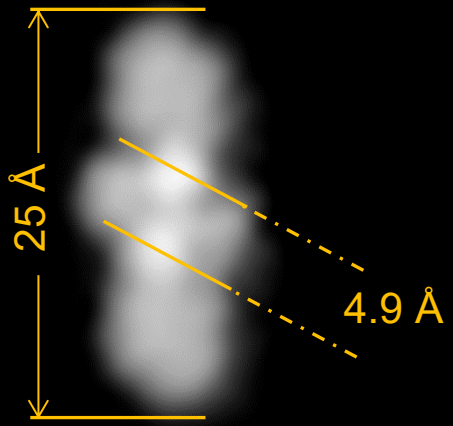


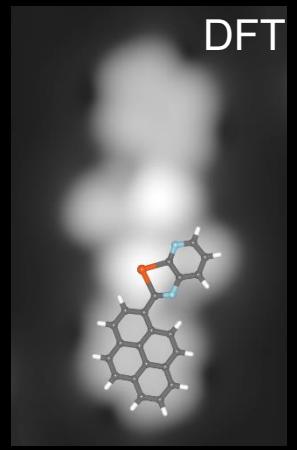


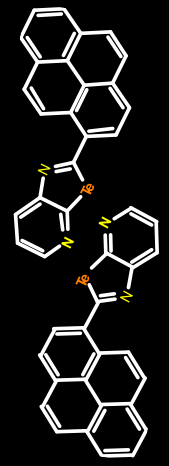
CGP-Te
Deposition: RT
STM: 8.5 - 11 K

L R









Supramolecular dimer

L. Camilli et al. *JACS Au* **4**, 2115 (2024)

Chalcogen bond – BRSTM data and DFT analysis

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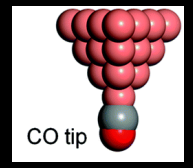
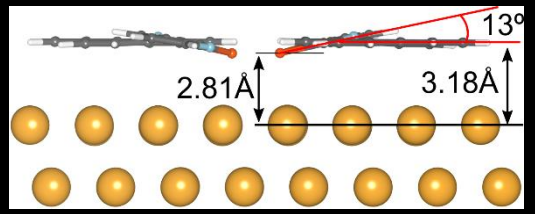
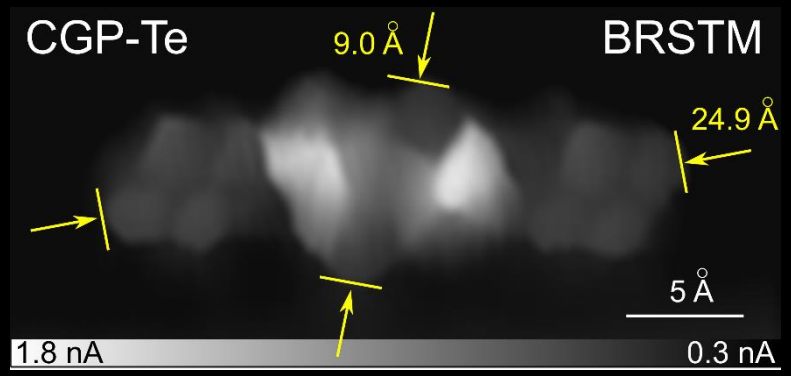
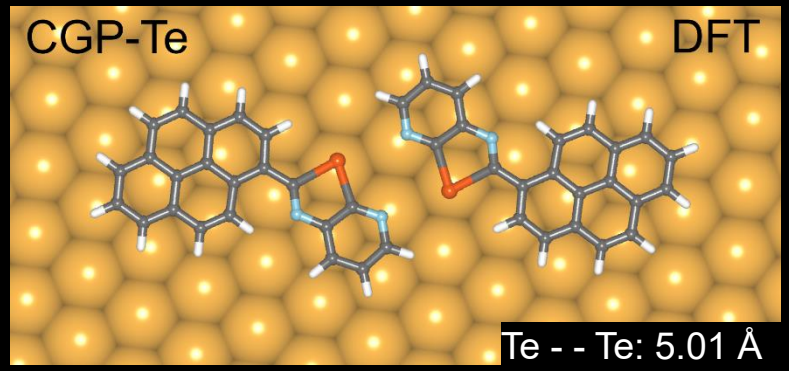
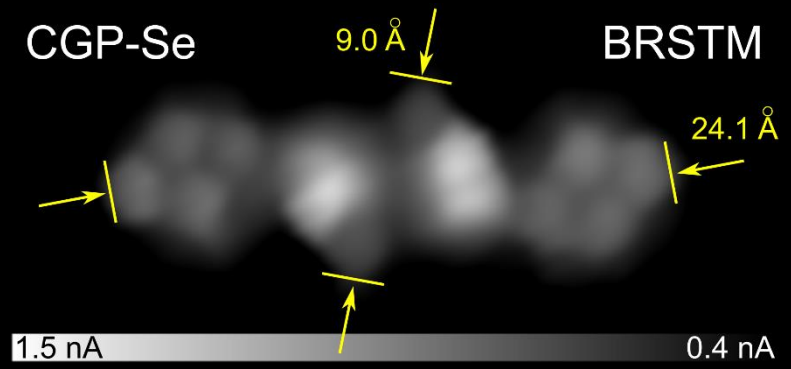


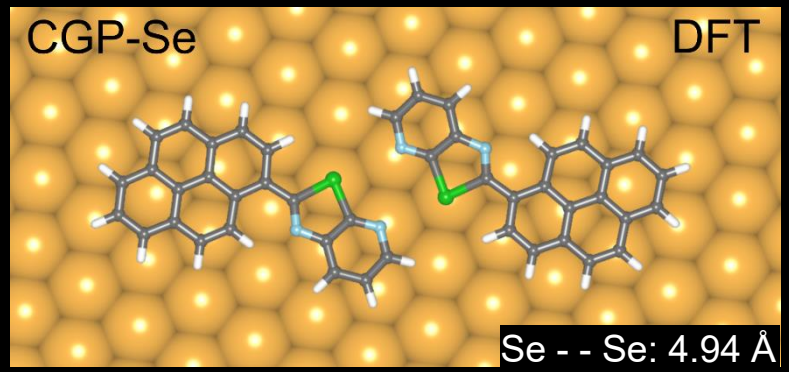
Functionalized tip

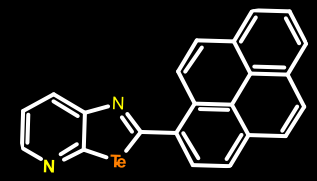




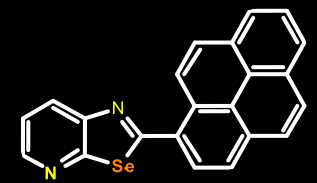








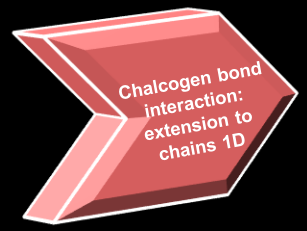
CGP-Te
Deposition: RT
BRSTM: 8.7 K
Constant height
V_t = 5 mV

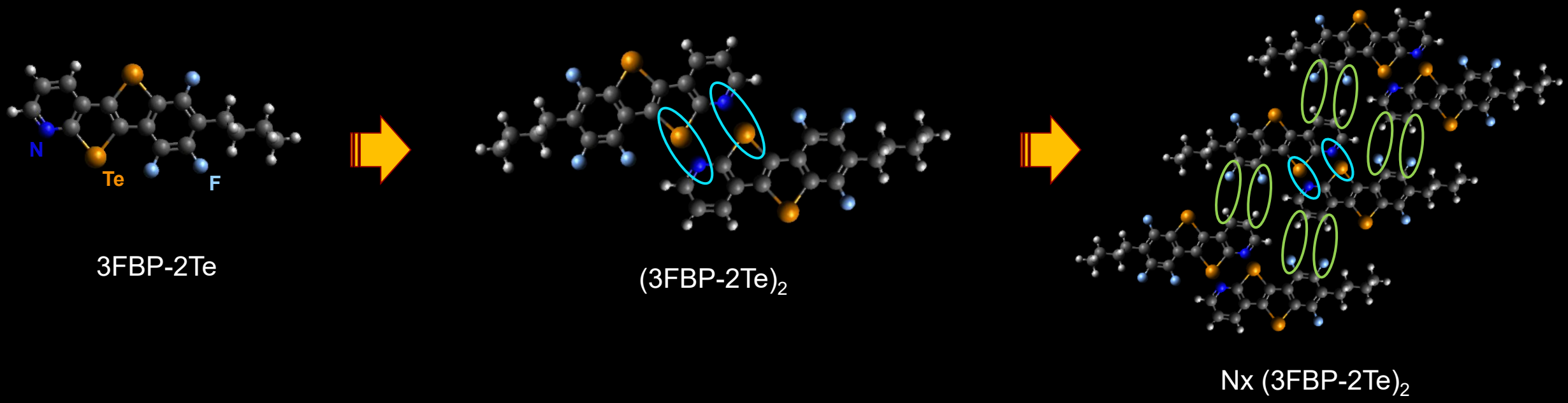


CGP-Se
Deposition: RT
BRSTM: 8.7 K
Constant height
V_t = 5 mV

L. Camilli et al. *JACS Au* **4**, 2115 (2024)

Chalcogen bond (ChB): 3FBP-2Te molecular structure





3FBP-2Te

$(3FBP\text{-}2Te)_2$

Nx $(3FBP\text{-}2Te)_2$

* 3FBP-2Te: 7-butyl-6,8,9-trifluorobenzo[4',5']telluropheno[2',3':4,5]telluropheno[2,3-β]pyridine

Chalcogen bond (ChB): 3FBP-2Te STM data

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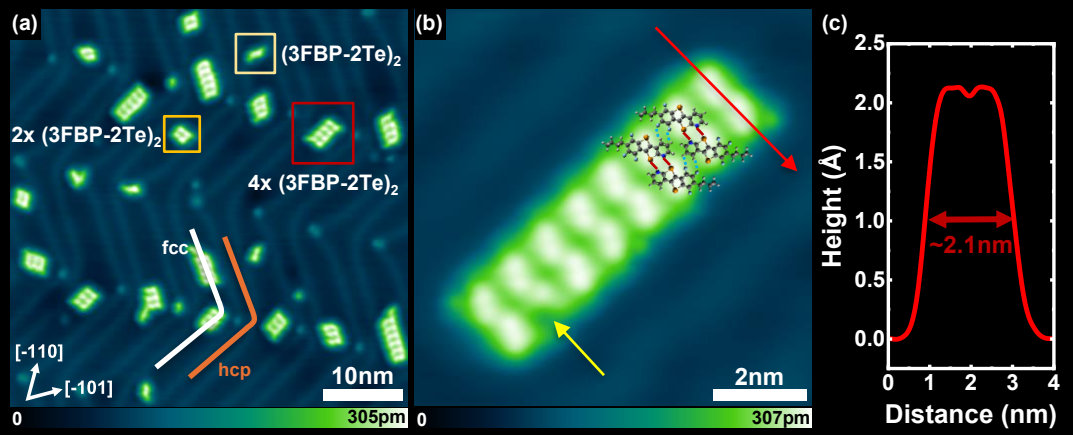

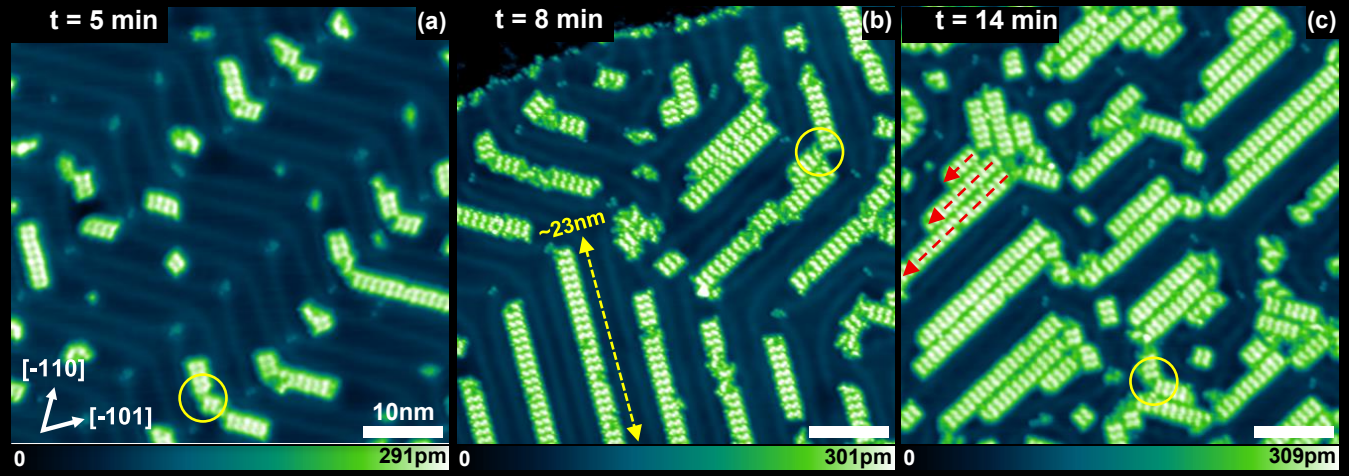

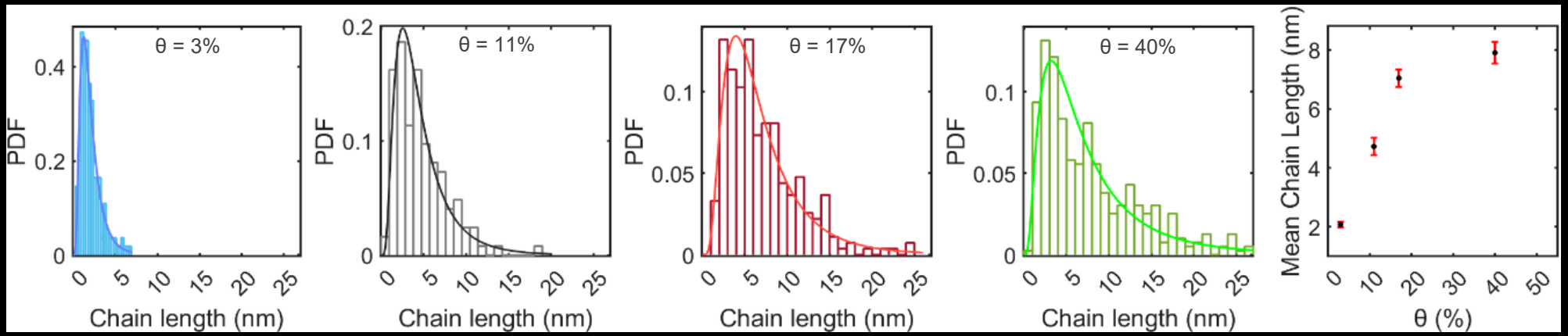

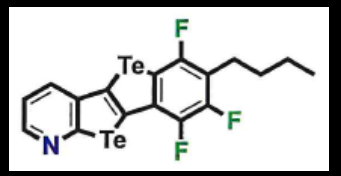

3FBP-2Te
Deposition: RT
STM @ 10K

A. Caporale et al., Manuscript in preparation

Chalcogen bond (ChB): 3FBP-2Te STS data

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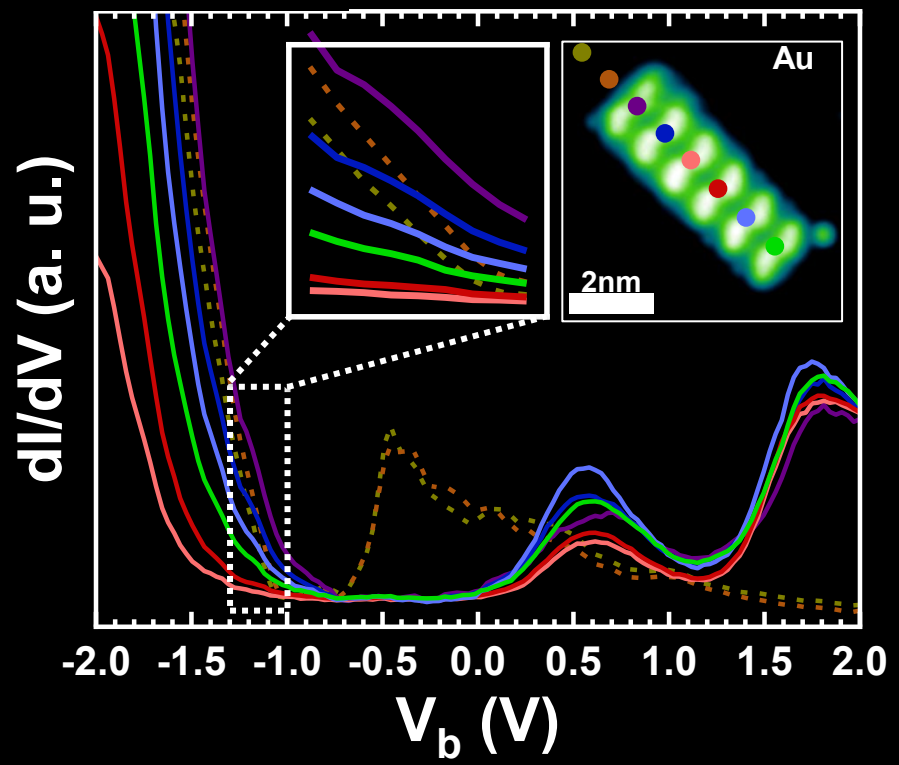

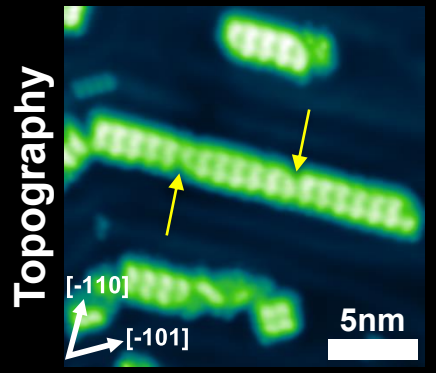

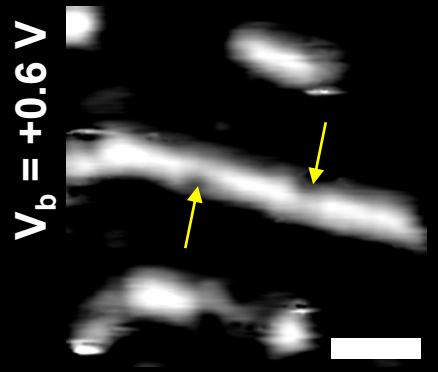

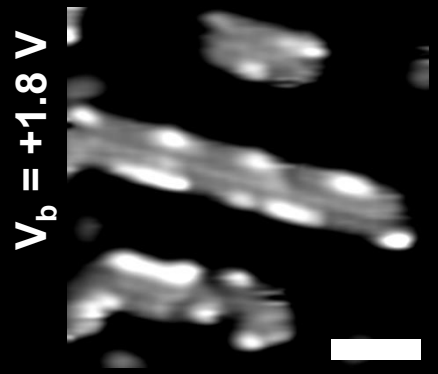

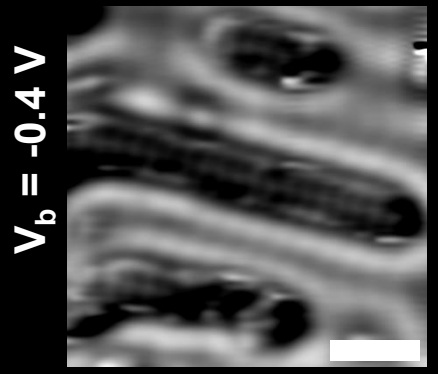

HOMO, LUMO, and LUMO+1 states are centred at -1.2eV, 0.6eV, and 1.8eV, respectively;

Experimental band gap is of about 1.1eV;

dI/dV maps reveal the spatial distribution of the LUMO and LUMO+1 states.

Apparently no electronic differences related to the chains lenght;

A. Caporale et al., Manuscript in preparation

Single atom molecular platform

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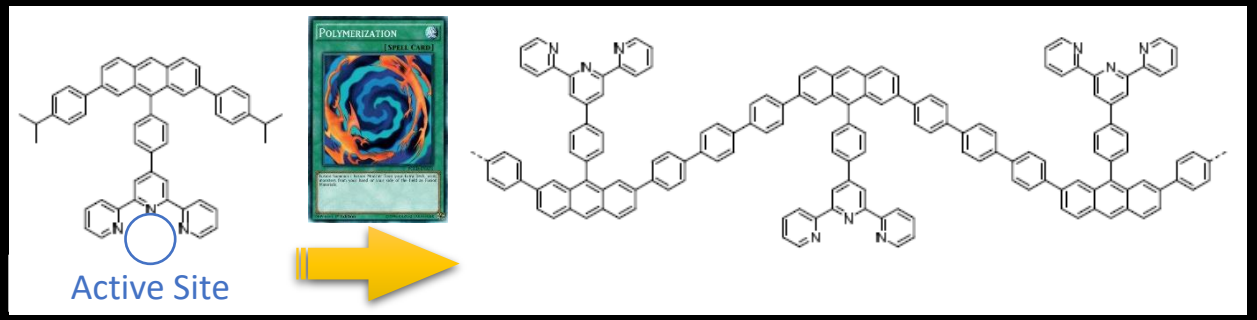
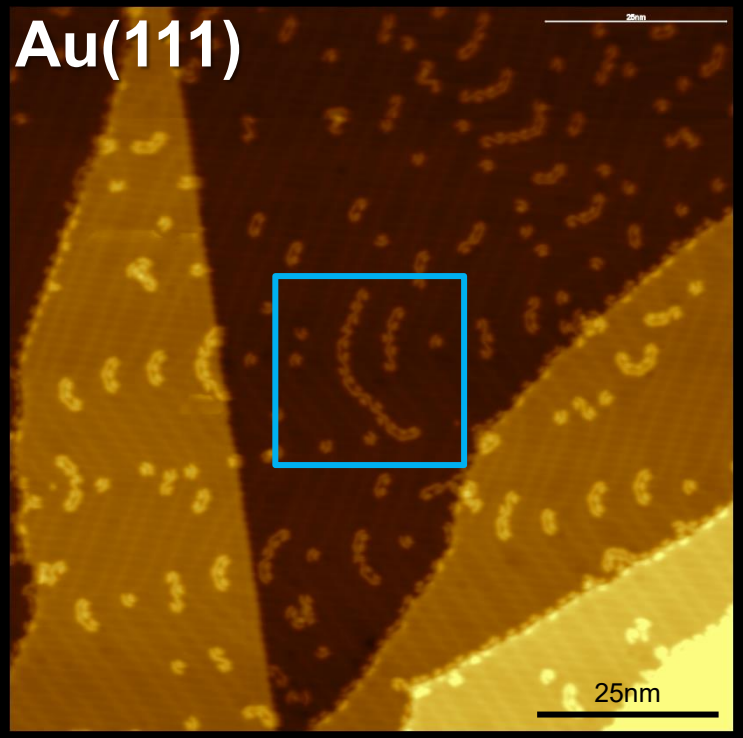
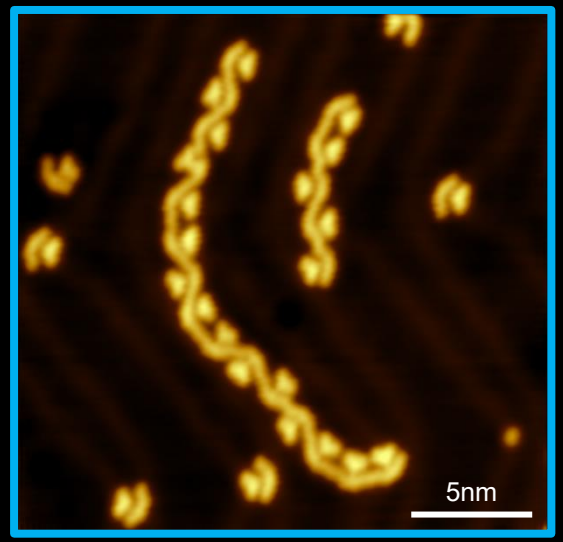
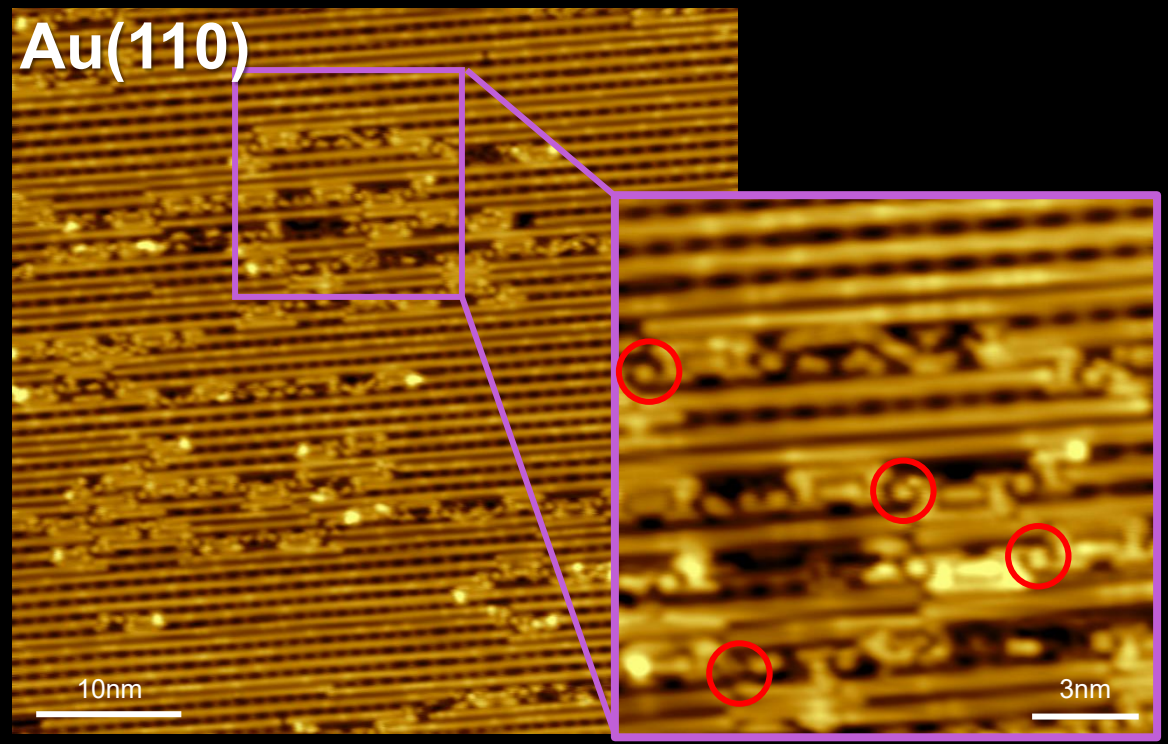
Single atom molecular platform



Deposition with sample hot kept at 580K;
Submonolayer coverage;







Cyclophanes

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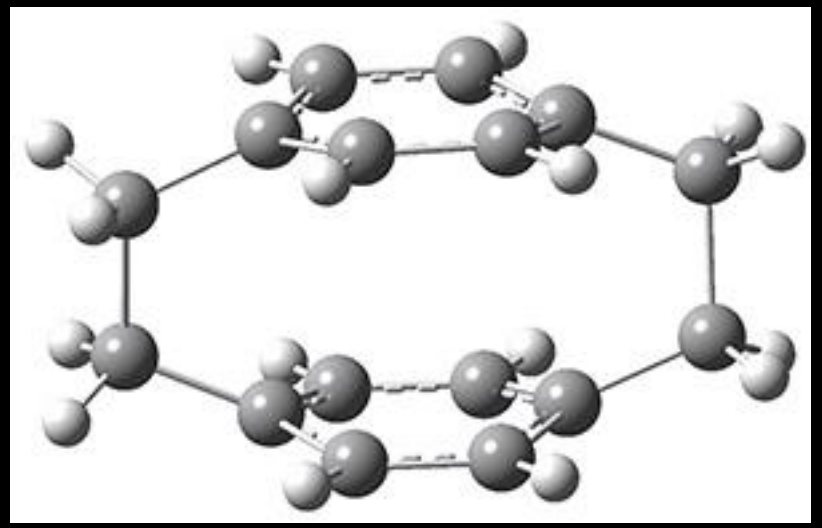
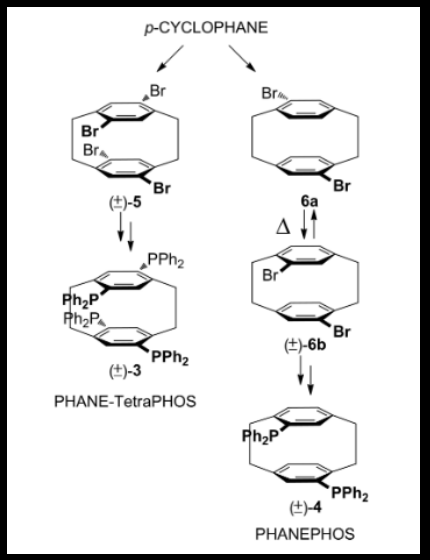
Aromatic compounds bonded by aliphatic bridges

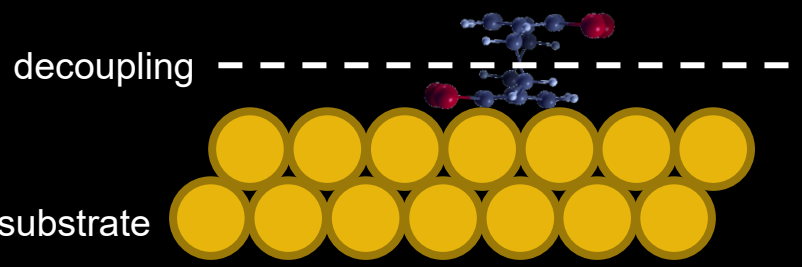


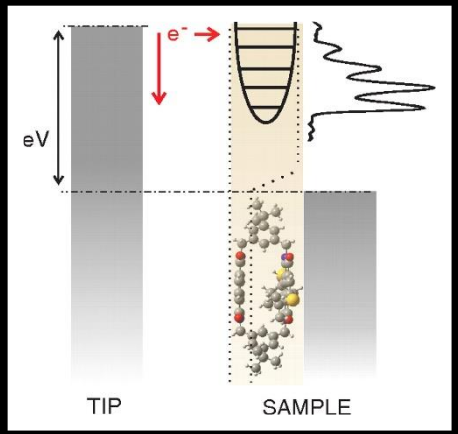


Chiral catalyst: it has been successfully employed in asymmetric catalysis to produce one enantiomer

L. Vaghi et al., *Eur. J. Org. Chem.* 17, 2367-2374 (2021)

guest: metal atoms





Electronic decoupling of the top layer from the metal substrate

F. Matino et al., *PNAS* 108, *961-964* (2010)

bromo[2.2]paracyclophanes (BPCs)

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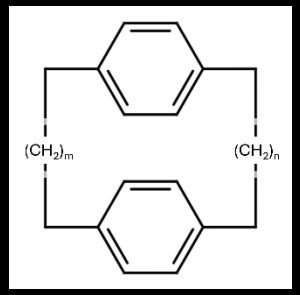
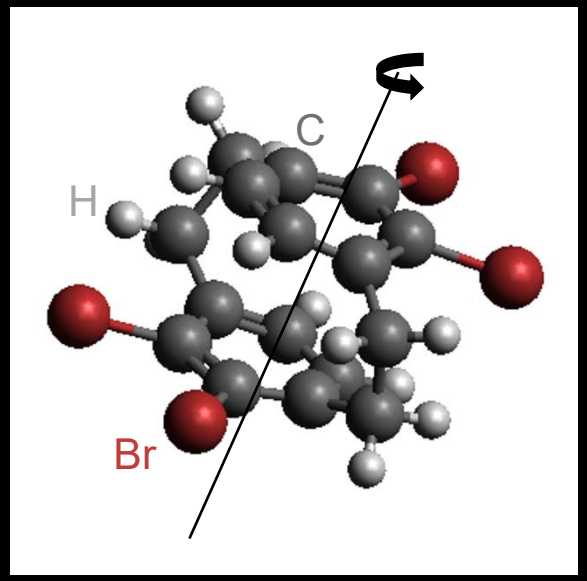


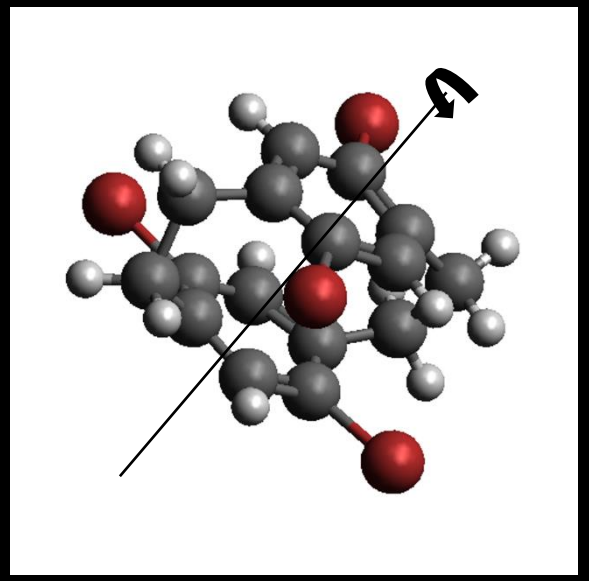
4,5,15,16-tetrabromo[2.2]paracyclophane

(α-TBPC)



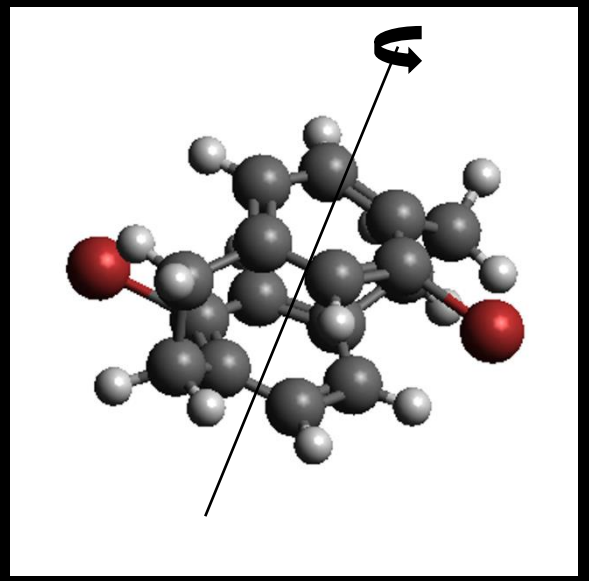
4,7,12,15-tetrabromo[2.2]paracyclophane

(β-TBPC)



4,16-dibromo[2.2]paracyclophane

(DBPC)



The presence of bromine atoms enables on-surface synthesis reactions such as Ullmann coupling

The molecules are provided by the group of Prof. Papagni at the Department of Materials Science, University of Milano Bicocca

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BPCs/Au(111) – STM data

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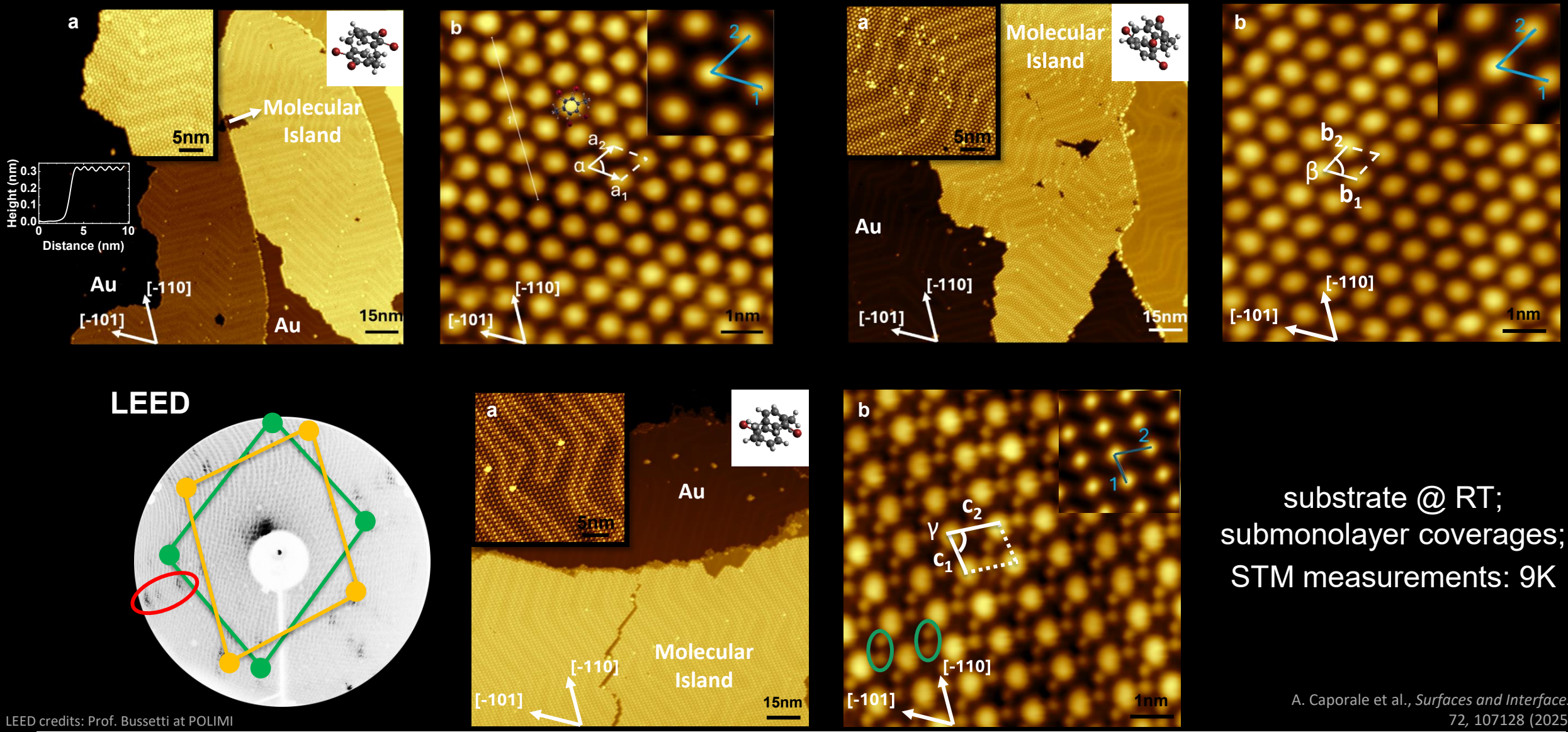


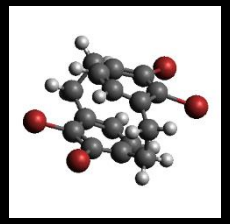
LEED

substrate @ RT;
submonolayer coverages;
STM measurements: 9K

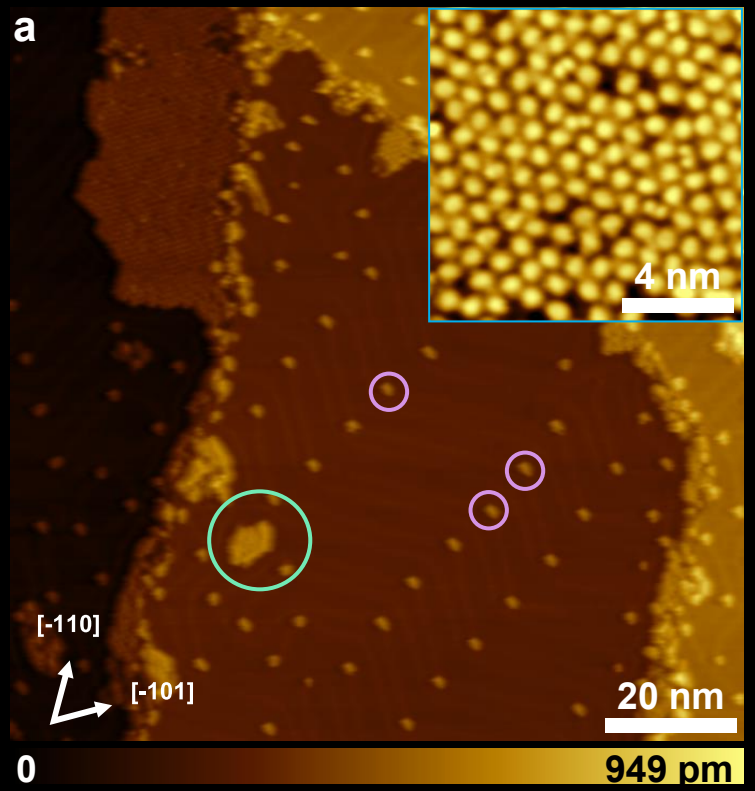
LEED credits: Prof. Bussetti at POLIMI

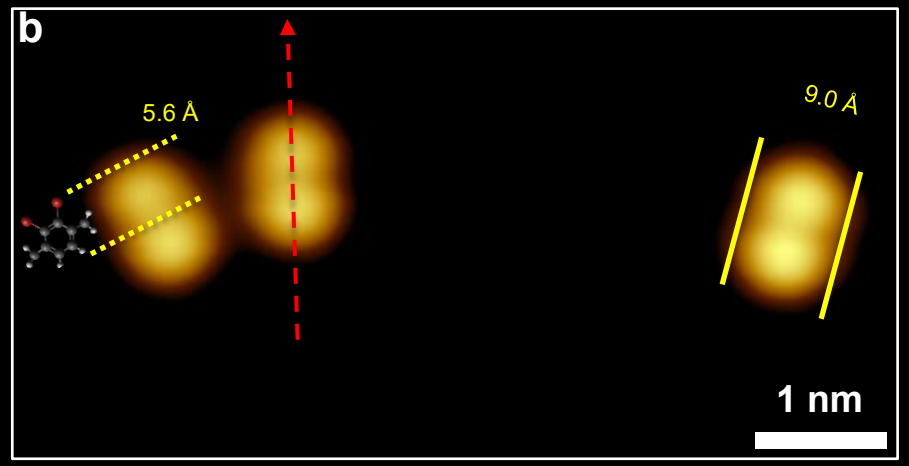
A. Caporale et al., *Surfaces and Interfaces* 72, 107128 (2025)

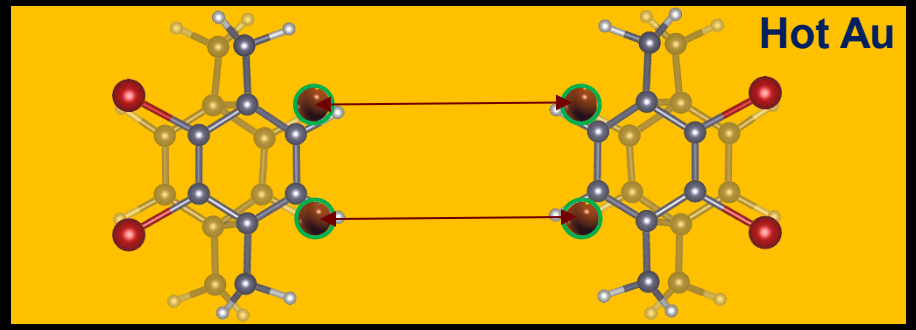
a-TBPC – Thermal treatments

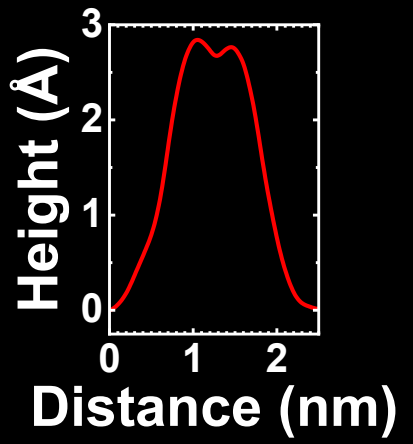


Depositing with the substrate kept at 450 K







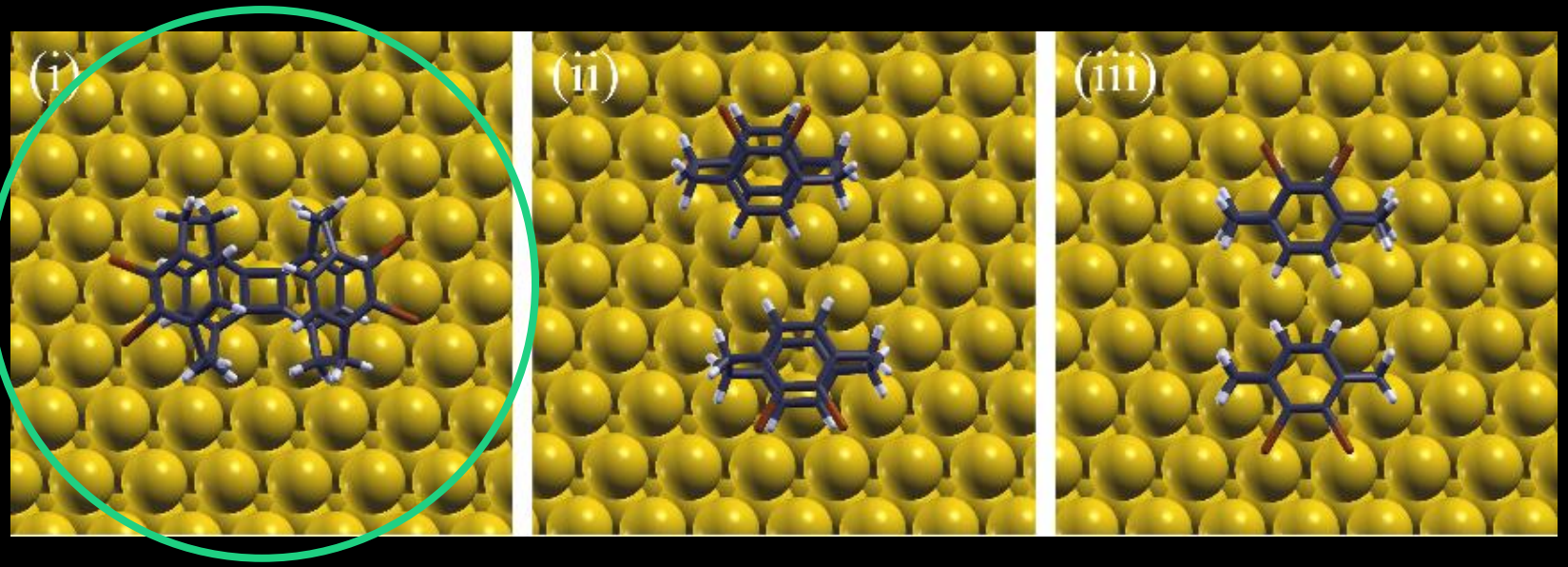


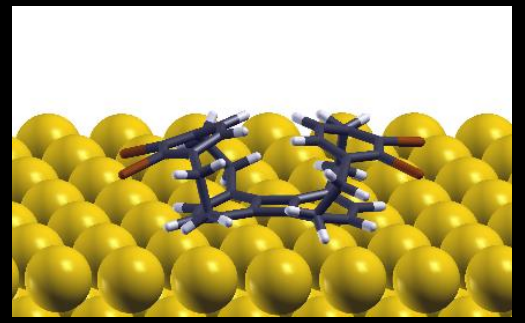
Br dissociation and Ullmann coupling:

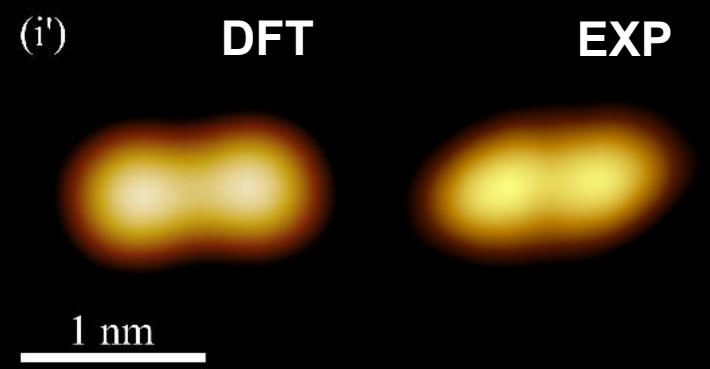
Dimerization!

A. Caporale et al., *Surfaces and Interfaces* 72, 107128 (2025)

Dimer – DFT analysis







(i) unsaturated C atoms in a [2+2] cycloaddition thus forming a four-membered (C4) ring

(ii) replacing the lower 4 Br atoms by an equal number of Au adatoms (Br→ Au exchange)

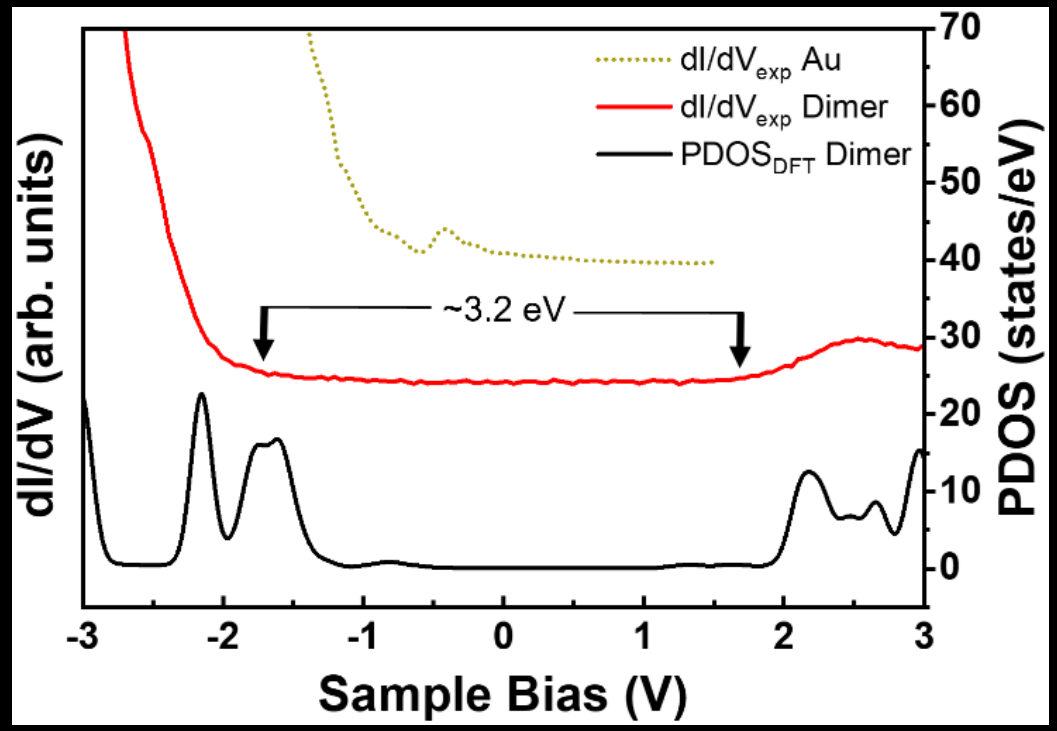
(iii) same as in (ii) but with only two Au adatoms instead of four

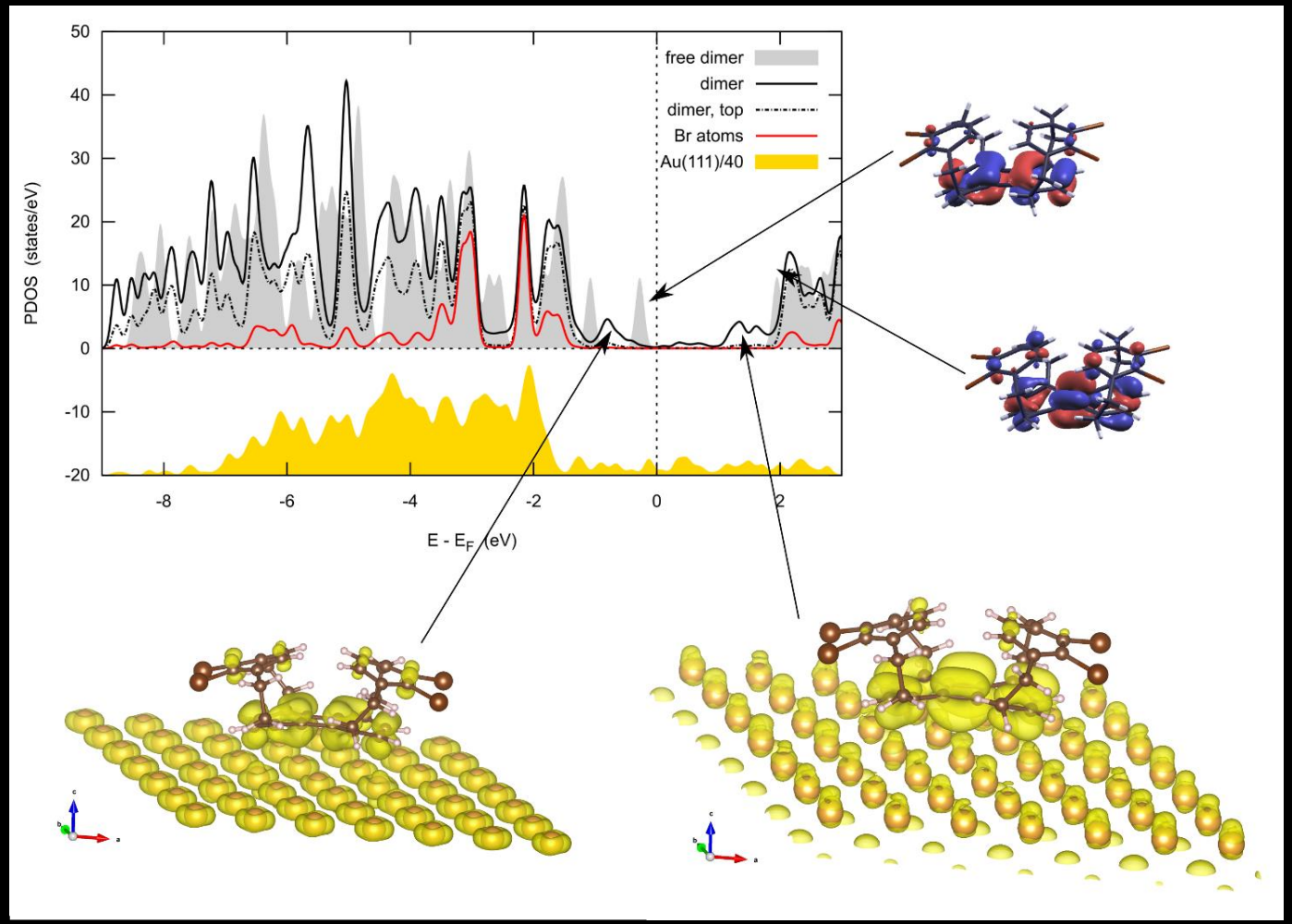
	Formation energy
(i)	**-4.86 eV**
(ii)	-2.22 eV
(iii)	-2.48 eV

DFT credits: Prof. Fratesi at UniMi

A. Caporale et al., *Surfaces and Interfaces* 72, 107128 (2025)

Dimer – STS data





A. Caporale et al., *Surfaces and Interfaces* 72, 107128 (2025)

Open questions/Future perspectives

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- Chalcogen system:
  - Eventually trasnfer the molecular system on an insulator substrate and studying their electronic properties

  - New systems are coming that can form purely chalcogen bond 1D chains and/or 2D ordered networks

- Single atom platform:
  - Designing a molecule that can form straight polymers, indipendent from the substrate (we are collaborating with The Riken Institute of Tokyo)

- Cyclophanes:
  - Synchrotron experiment to understand the adsorption physics of the 4,16dibromo[2.2]paracyclophane

  - Studying all the phases of the three molecules together with STS experiments

  - Depositing magnetic host atoms and studying the properties of the system with an applied magnetic field (part of my next external stay)

Summary

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Planned activities:

Synchrotron experiment in November 2025

Synchrotron experiment in January 2026

External stay of 4 months from Feb. to June 2026

List of publications:

- **A. Caporale** et al., Supramolecular chains by combined hydrogen and chalcogen bond interactions on Au(111); Manuscript in preparation.
- **A. Caporale** et al., *Surfaces and interfaces*, 2025, 72, 107128.
- J. A. Sánchez, **A. Caporale** et al., *Phys. Status Solidi RRL*, 2025, 2500195.
- J. A. Sánchez, **A. Caporale** et al., *J. Phys.: Condens. Matter*, 2025, 37, 185002.
- L. Camilli et al., *JACS Au*, 2024, 4, 2115-2121.
- A. G. Pueyo et al., *Phys. Rev. B*, 2024, 110, 235407.

Activities:

Conference oral presentation

Synchrotron online course

Two weeks PhD Summer School with practical works

Synchrotron experiment

Conference oral presentation

Synchrotron experiment

Conference poster presentation: winner as best poster

A. Caporale – antonio.caporale@uniroma2.it

Thank you

My group: Prof. L. Camilli (supervisor),
Prof. L. Persichetti, G. Anselmi

LT-STM ROME

Prof. A. Papagni
Prof. L. Vaghi
Prof. L. Beverina

Prof. G. Fratesi

Prof. M. Palummo

Dr. J. Aragon Sanchéz

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Dr. C. Hogan
Dr. M. Di Giovannatonio
Dr. O. J. Arrate

Prof. D. Bonifazi and Dr. D. Romito

Ministero dell'Università e della Ricerca
Bando PRIN 2022

3rd October 2025 - 14th Young Researcher Meeting

Best Poster Awards

Backup slides

Noncovalent interactions

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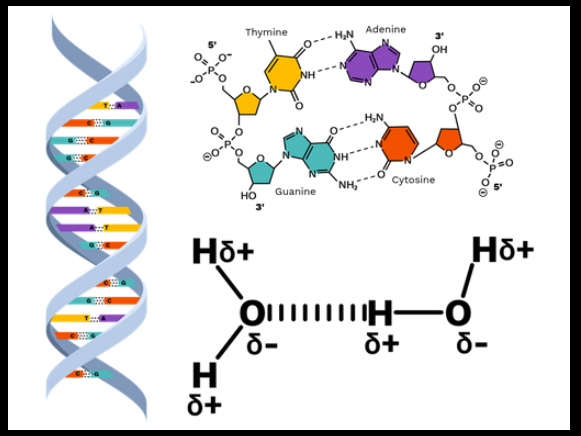
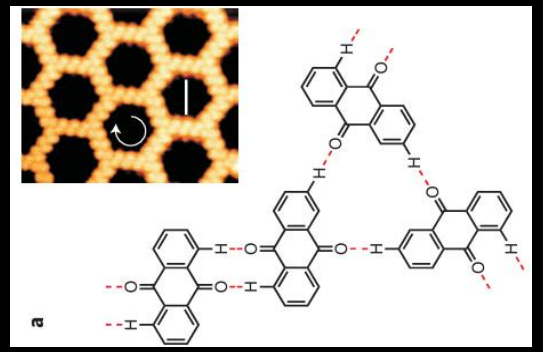
Hydrogen bonding

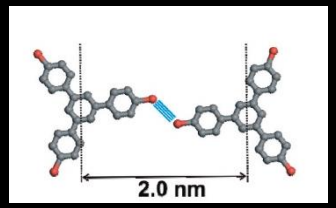


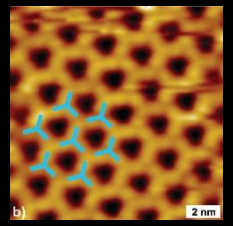


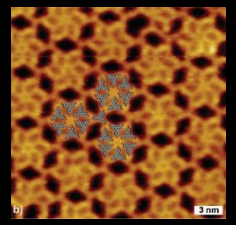
J. A. Theobald et al. *Nature* **424**, 1029 (2003)

Halogen bonding

(ex. C-Cl···O)



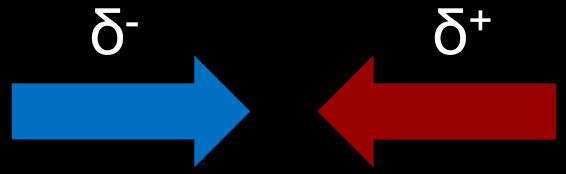




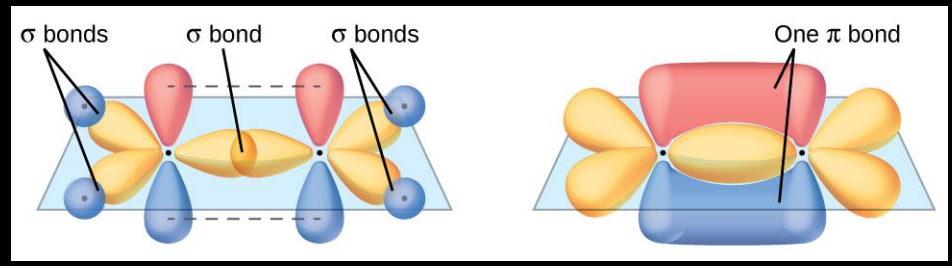
H. Walch et al. *J. Phys. Chem. C* 114, 12604 (2010)

*Chalcogen bonding**

(ex. Se···N-C)

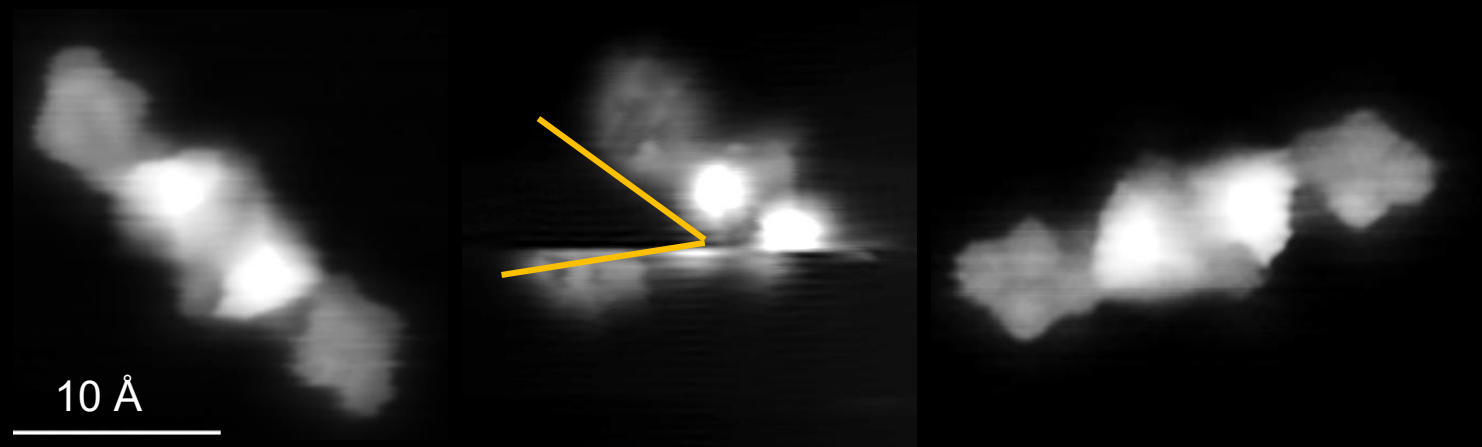


+



* D. J. Pascoe et al. JACS 139, 15160 (2017)

Dimer manipulation



Bond strong enough to resist at an high interaction with the scanning tip

L. Camilli et al. *JACS Au* **4**, 2115 (2024)

Control experiments – STM data

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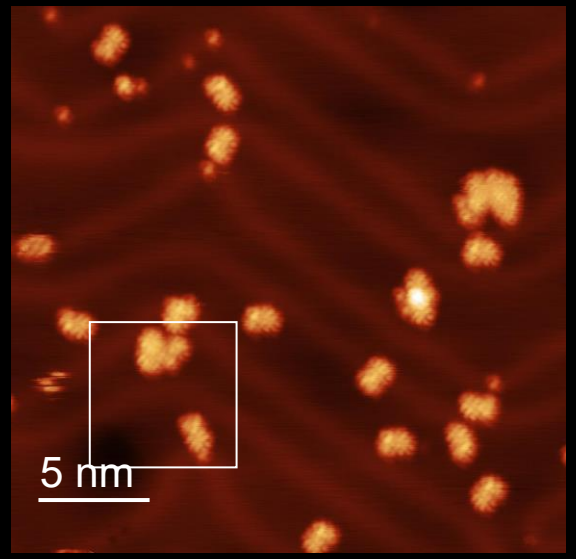
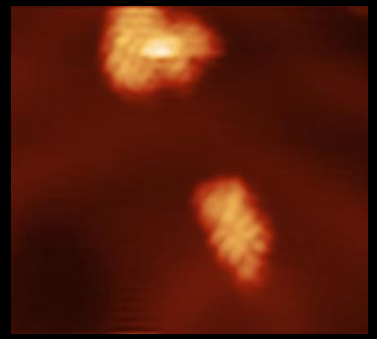
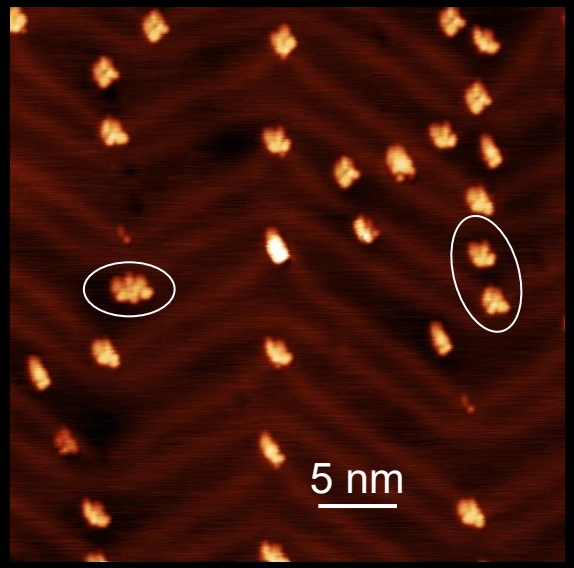
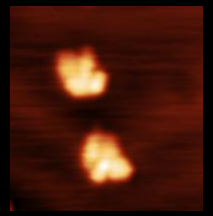
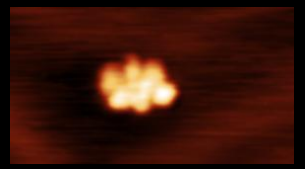
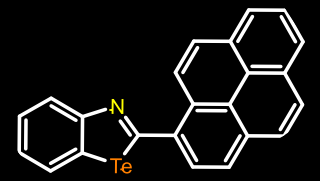




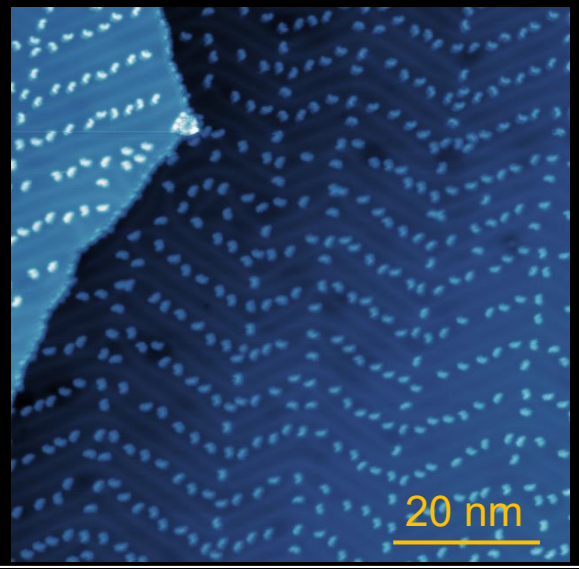


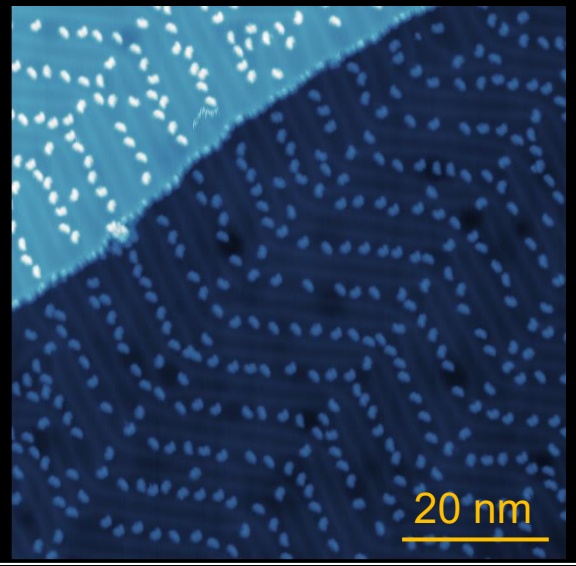


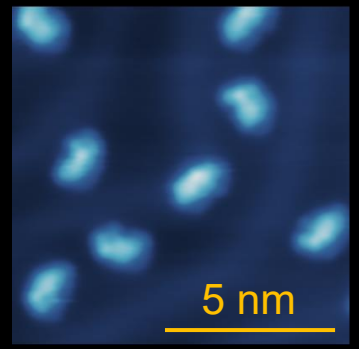


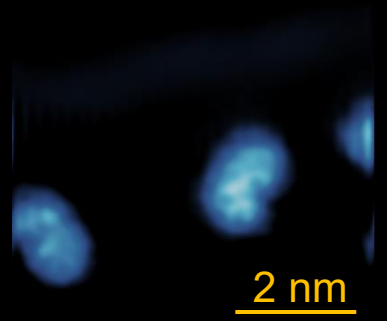


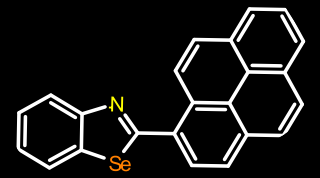
Benzo-Te
Deposition: RT
STM: 11 K







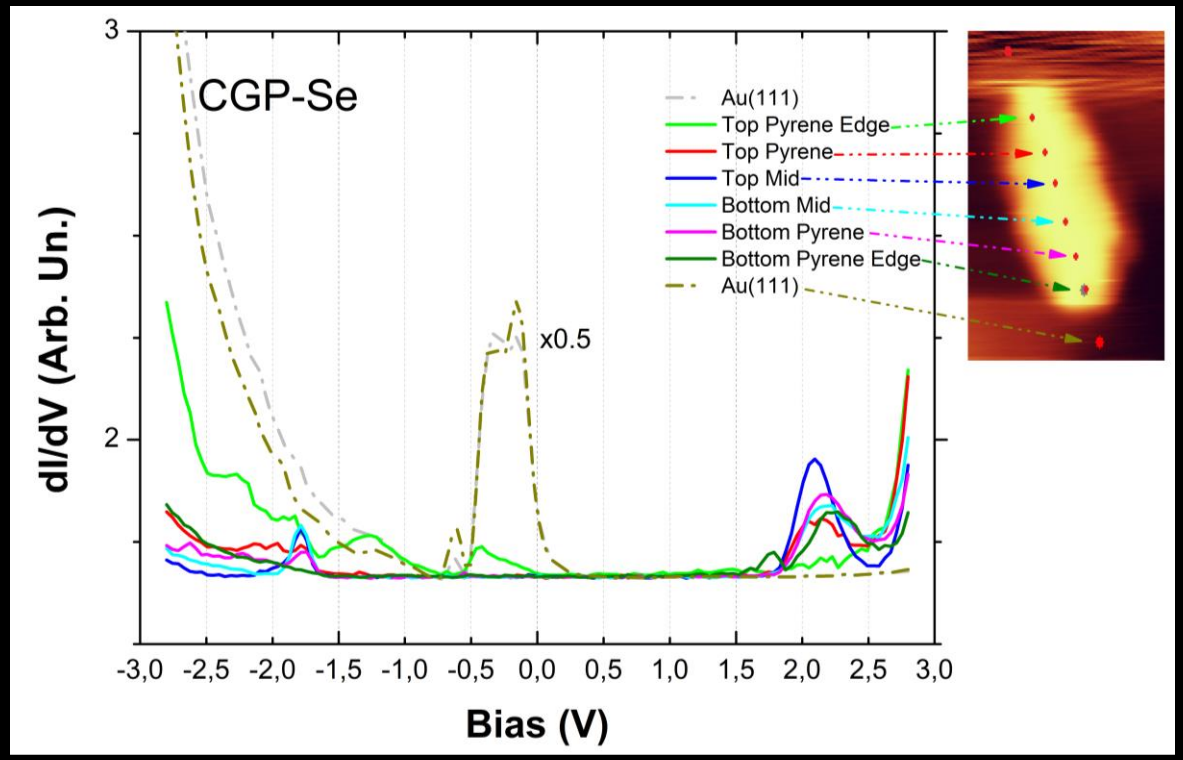


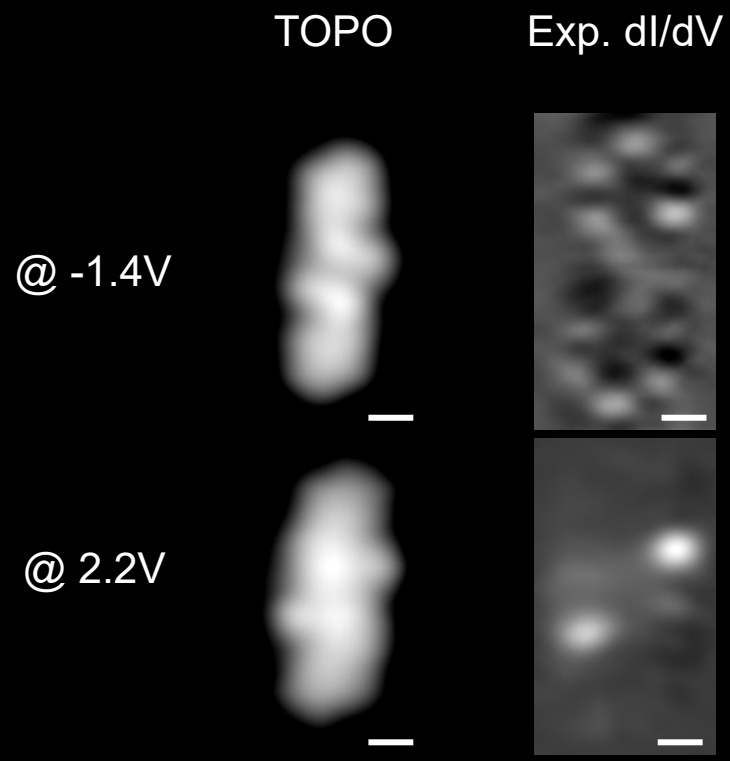


Benzo-Se
Deposition: RT
STM: 9.5 K

L. Camilli et al. *JACS Au* **4**, 2115 (2024)

Preliminary spectroscopy data





Single atom molecular platform

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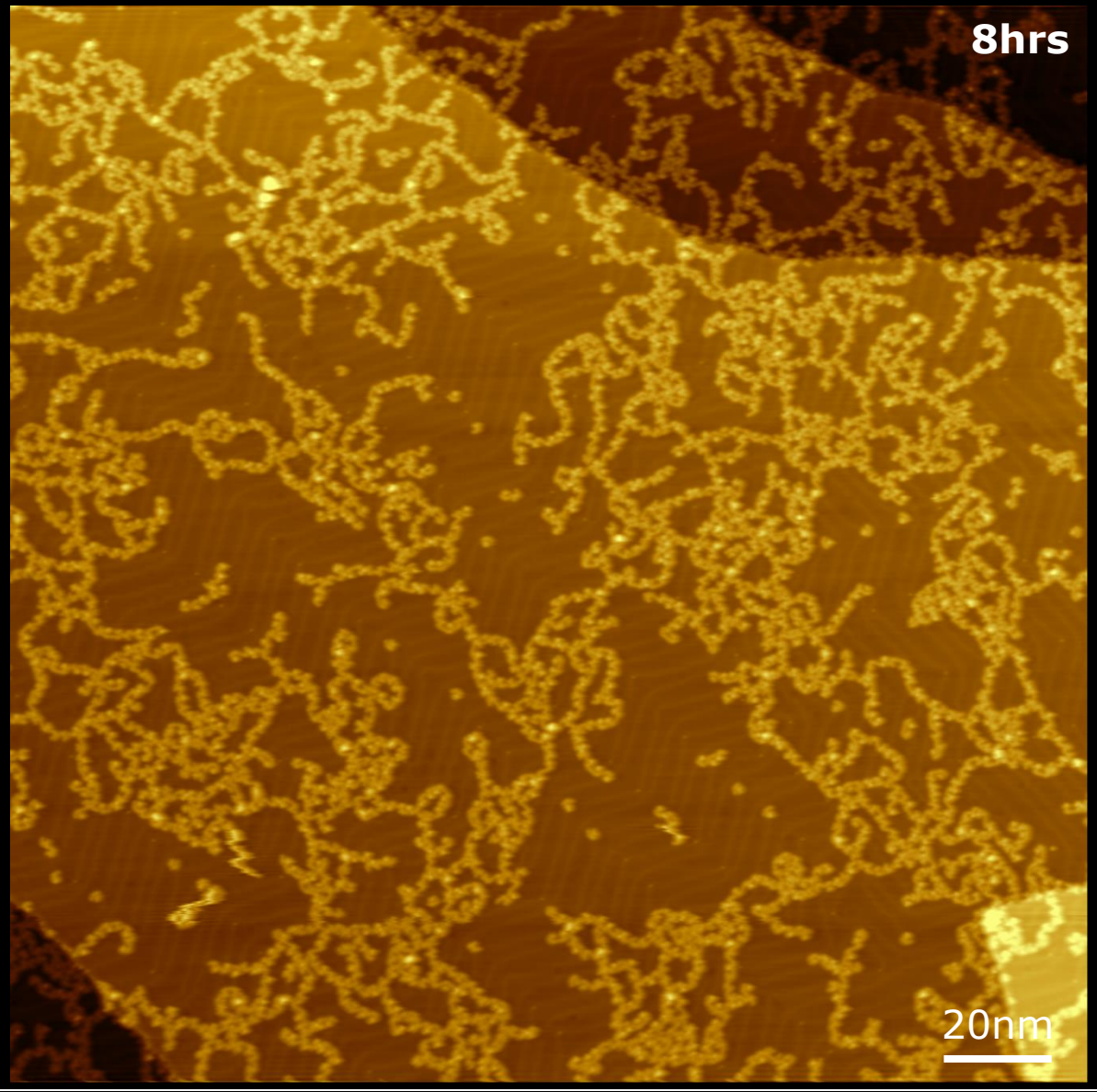

Deposiiton with sample hot kept at 580K with a slow rate;

High coverage;

a-TBPC – DFT analysis

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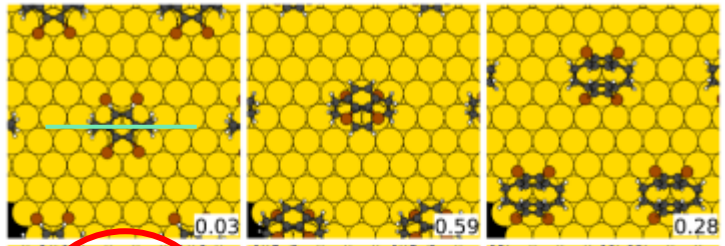
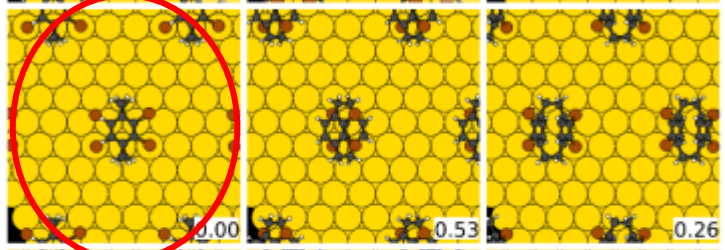
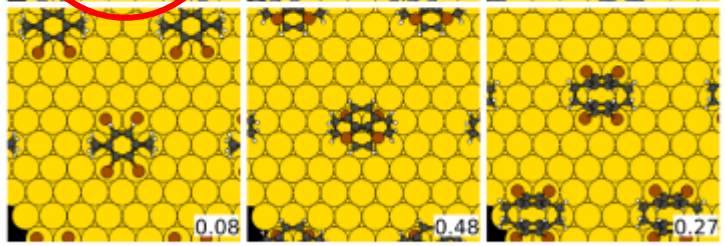
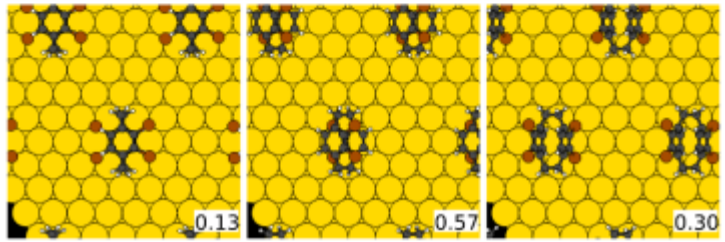
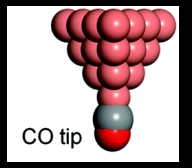
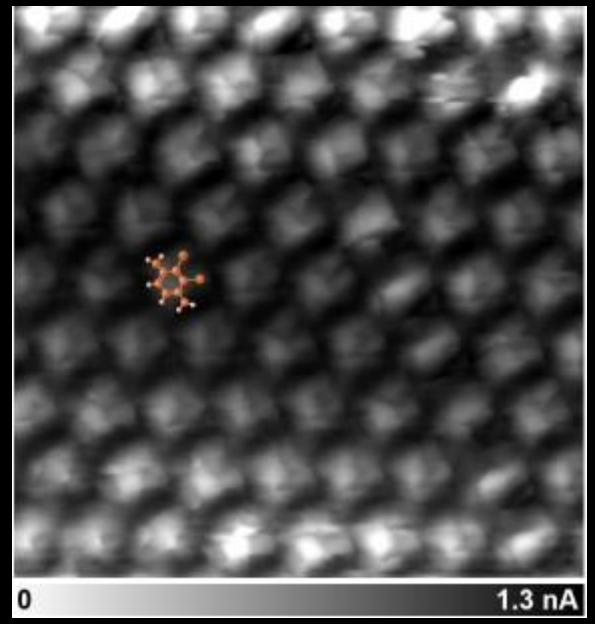
	Flat	45°	90°	Flat	45°	90°
H0				0.03	0.59	0.28
H90*				**0.00** **-1.41 eV**	0.53	0.26
T0				0.08	0.48	0.27
T90				0.13	0.57	0.30
				eV	eV	eV

*Also bridge site (B90) resulted as a possible adsorption site

BR-STM





Molecules lie flat and are oriented in the same direction

A. Caporale et al., *Surfaces and Interfaces* 72, 107128 (2025)

a-TBPC – DFT analysis

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Flat case	E_{ads} (eV)	ΔE_{ads} (eV)
H0°	−1.38	0.03
H90°	−1.41	0.00
B0°	−1.37	0.04
B90°	−1.41	0.00
T0°	−1.33	0.08
T90°	−1.28	0.13

Hollow 90 and Bridge 90 are isoenergetic.

a-TBPC/Au(111) – STS data

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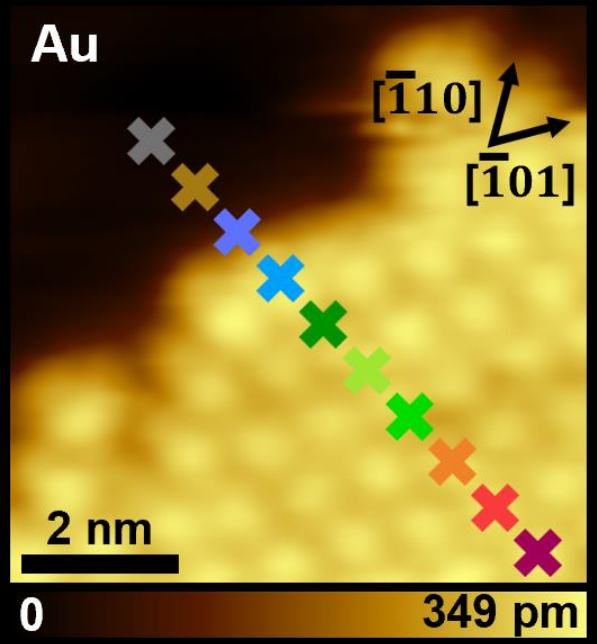
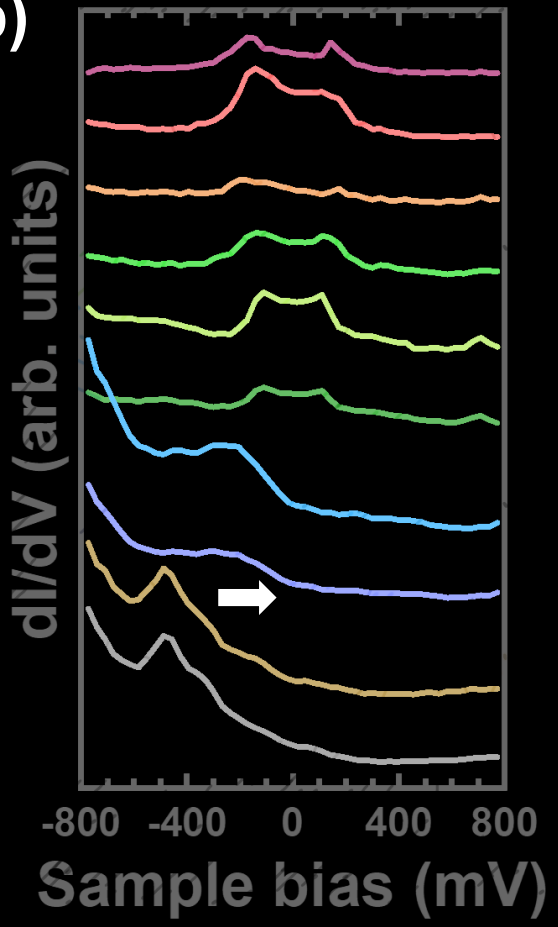
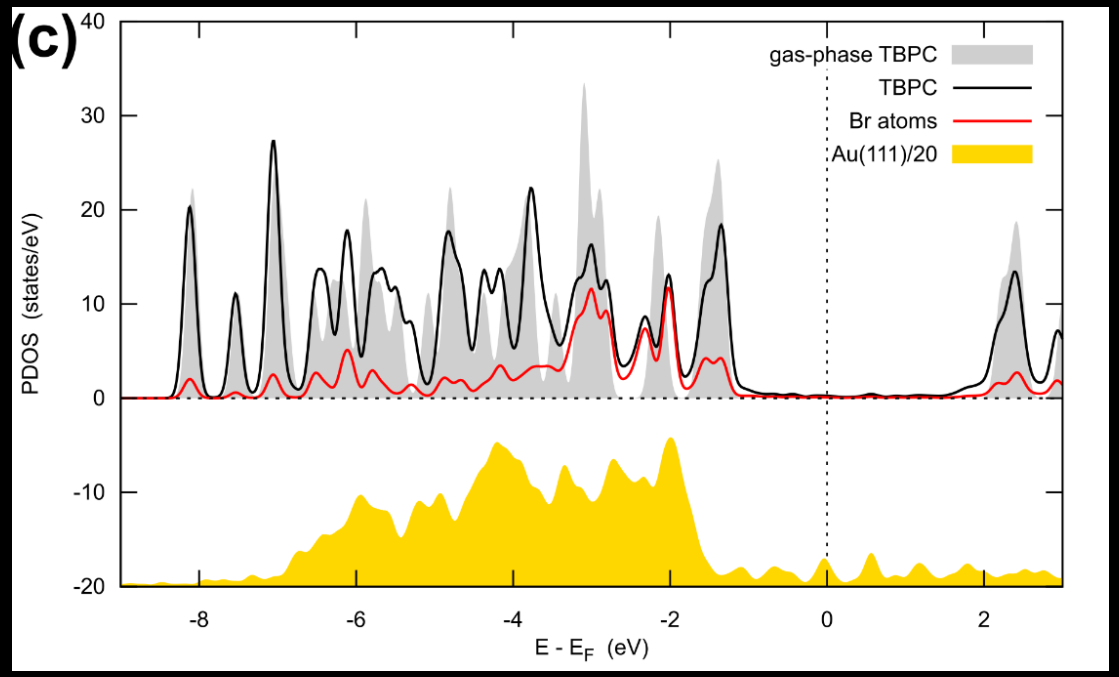
(a)



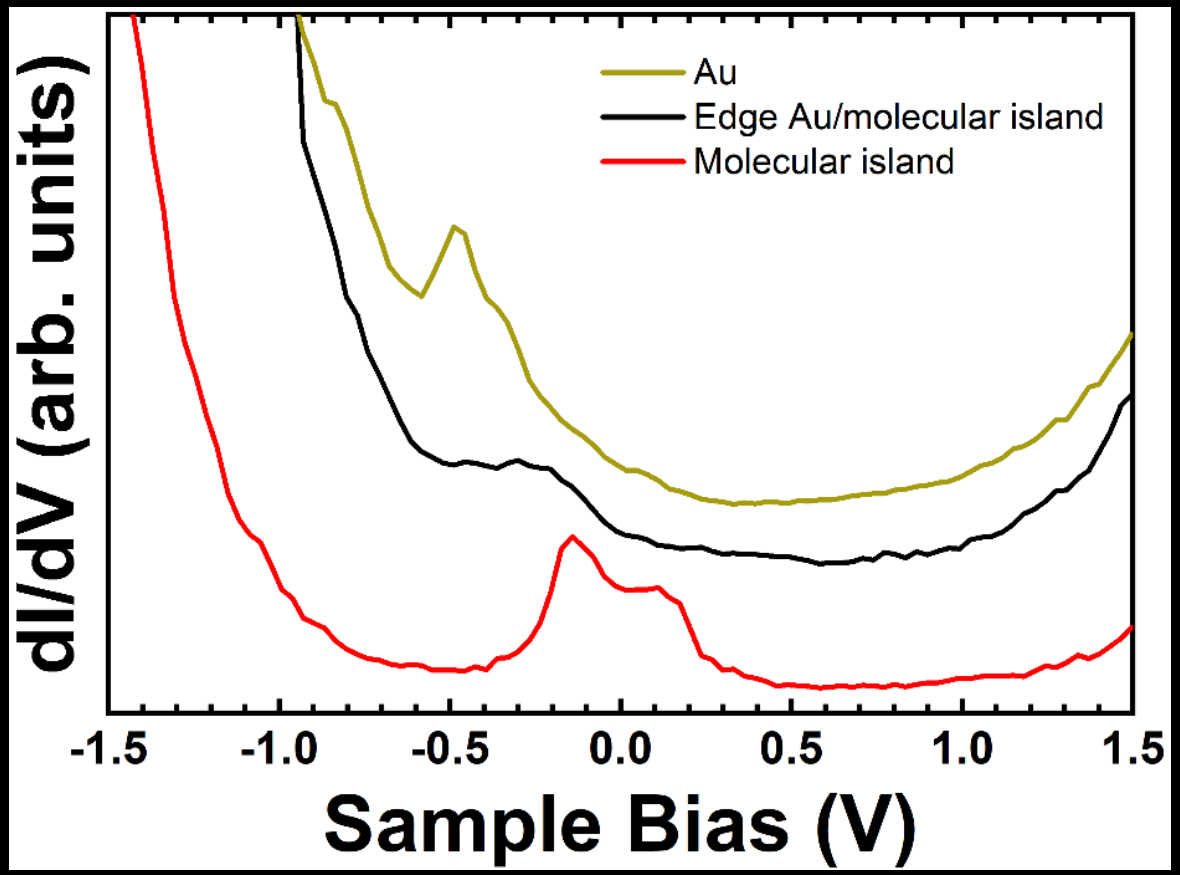
(b)





A. Caporale et al., *Surfaces and Interfaces* 72, 107128 (2025)

a-TBPC – STS data



No molecular states in a larger range

a-TBPC/Au(111) – STM data

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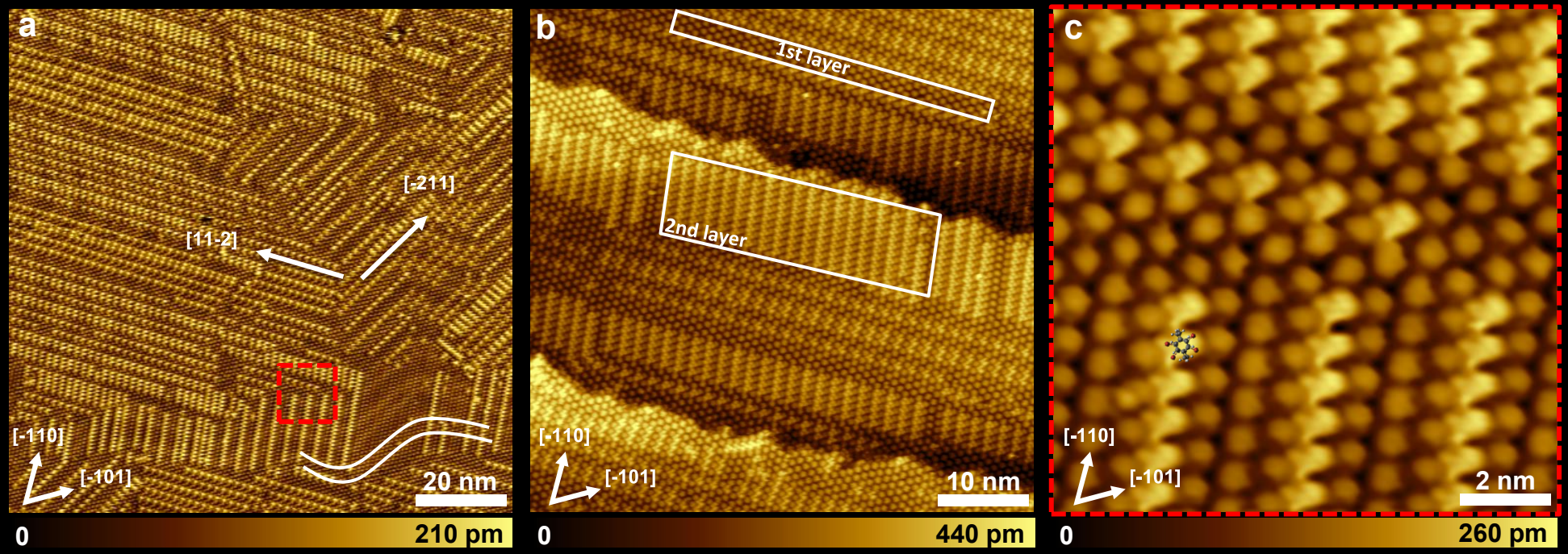
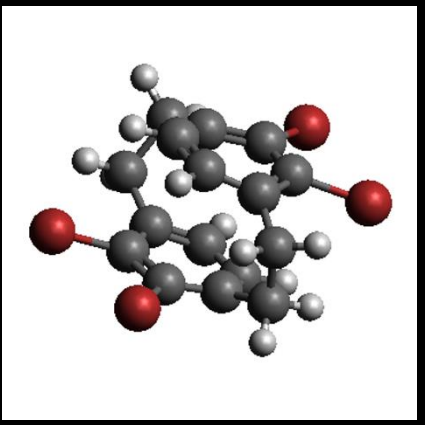
substrate @ RT, coverage > 1 ML

Obtained after long depositions; sample measured after few minutes





2nd layer grows with a row-like symmetry

A. Caporale et al., *Surfaces and Interfaces* 72, 107128 (2025)

a-TBPC – Thermal treatments

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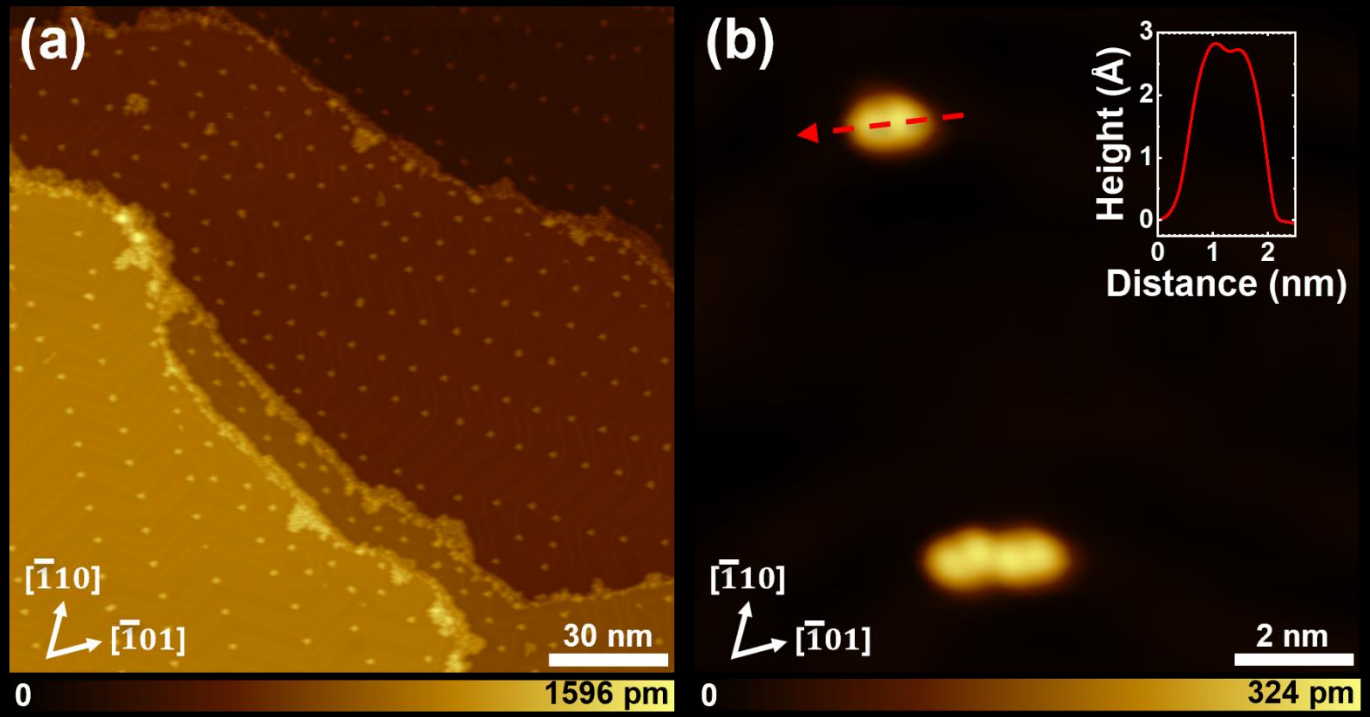
Depositing with the substrate @ RT and then annealed to 450K



Same of hot deposition!

BPCs– Thermal limit

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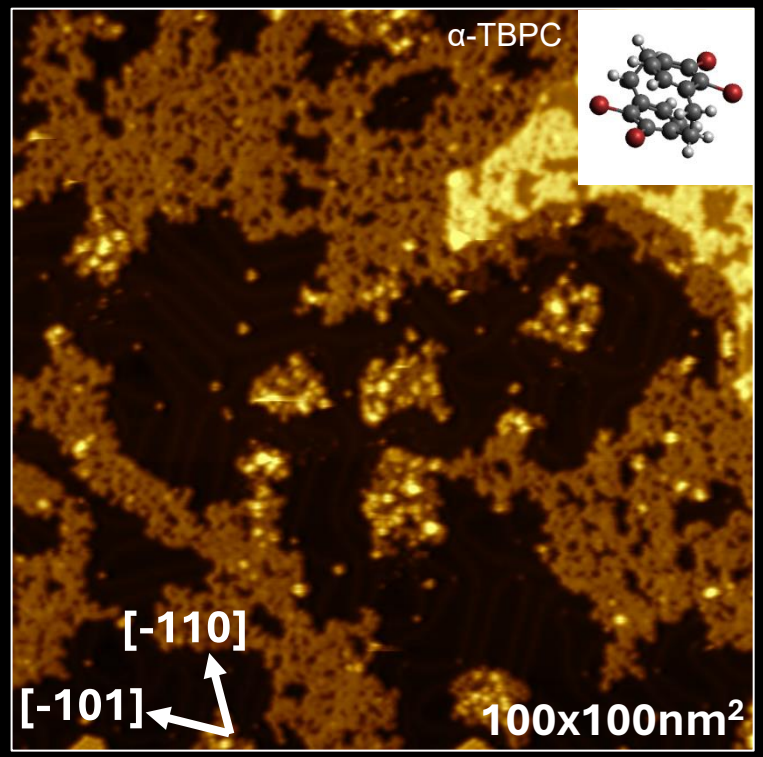
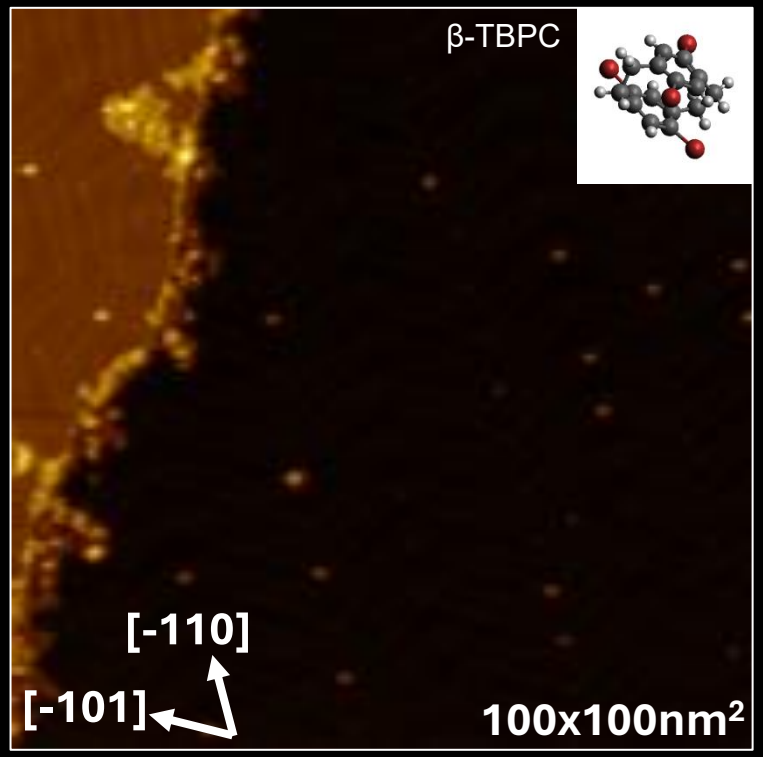
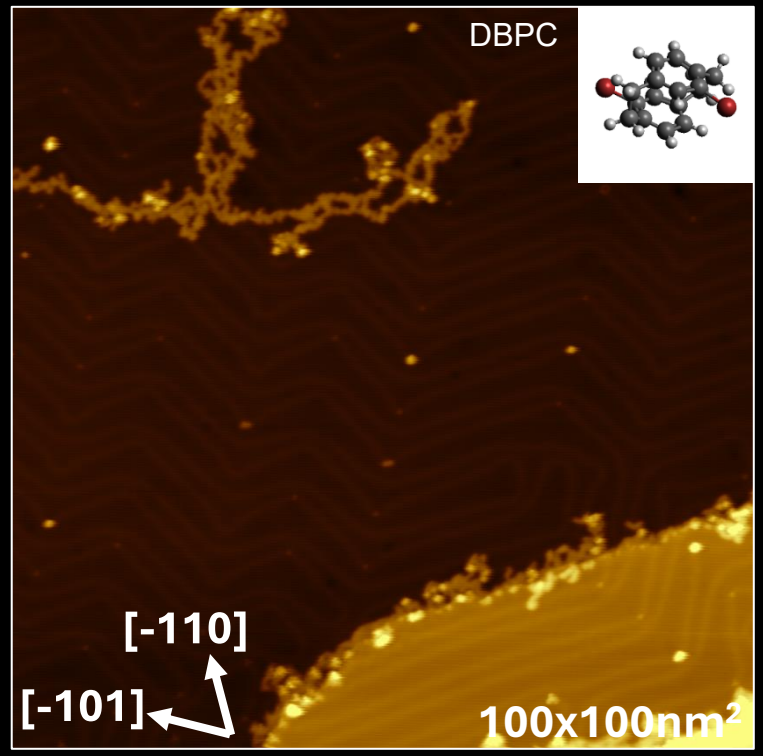
Depositing with the substrate @ RT and then annealed above 500K







Only amorphous things and leftovers.

a-TBPC – Thermal treatments

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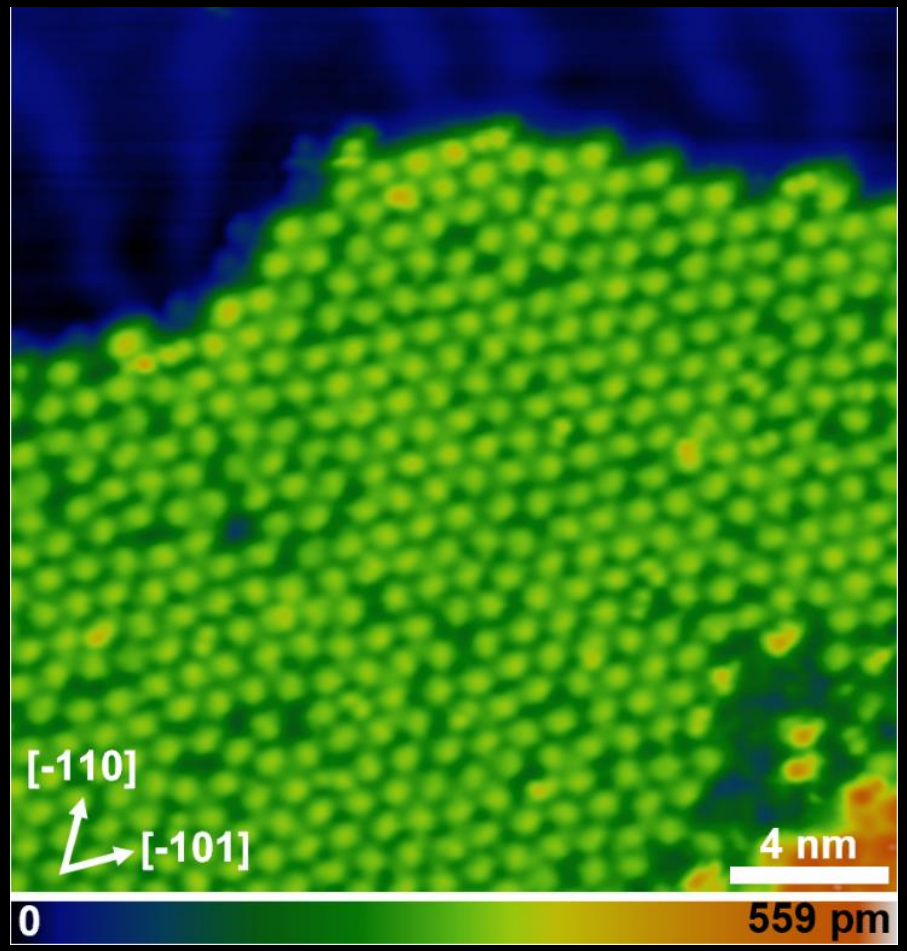
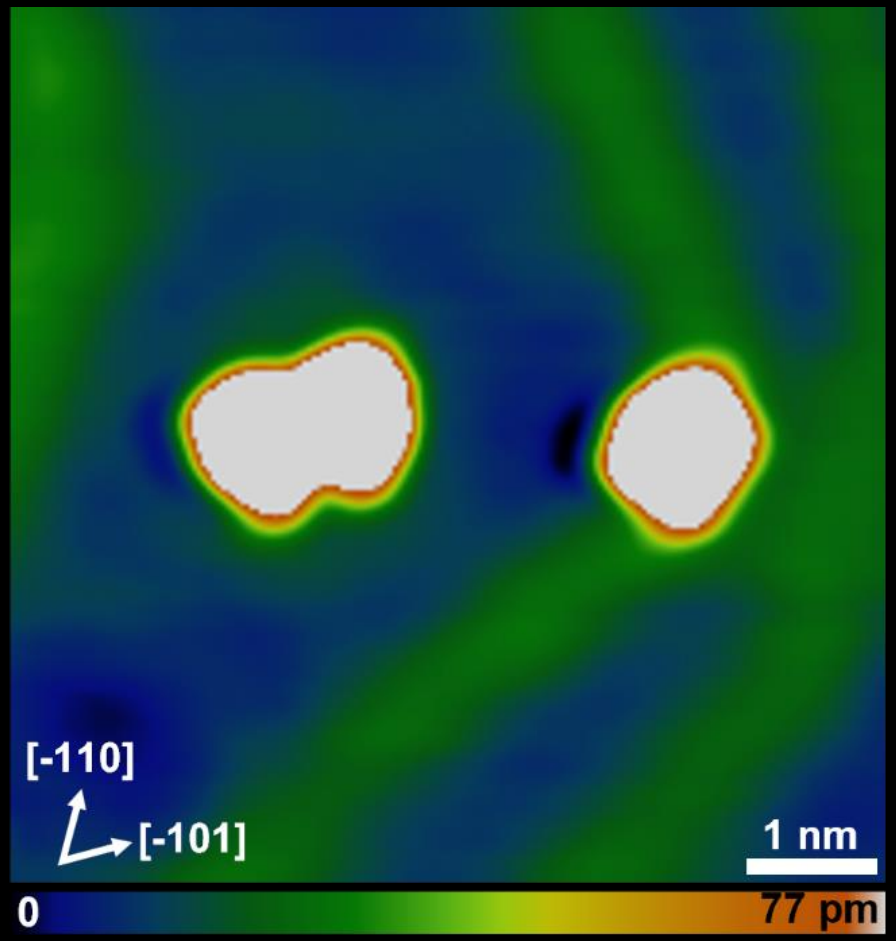


- No herrigbone passing through the island
- Perhaps, monomers deposit over Br islands

Dimers position



BPCs/Au(111) – LEED

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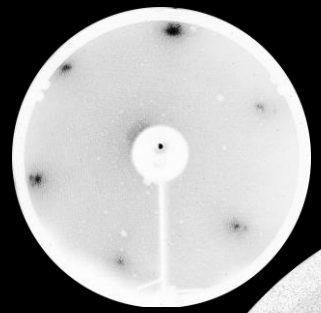
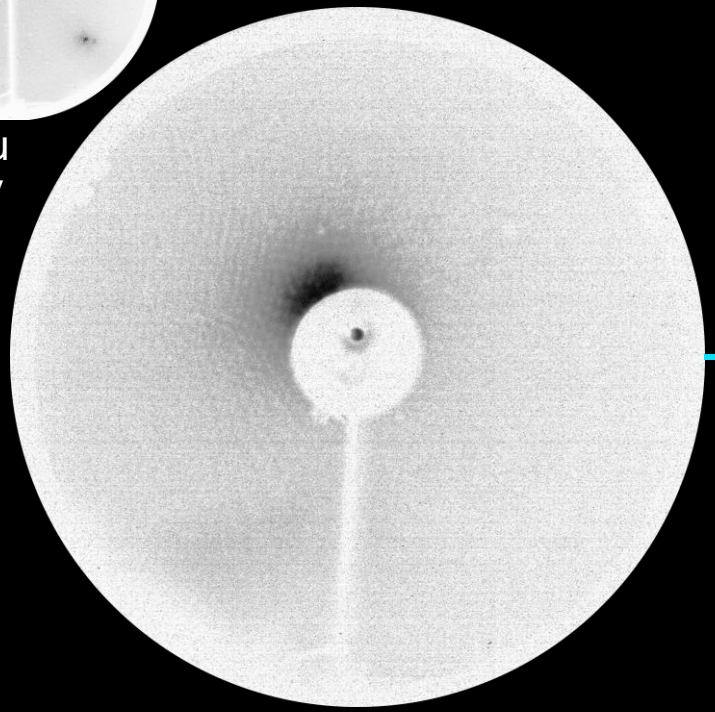
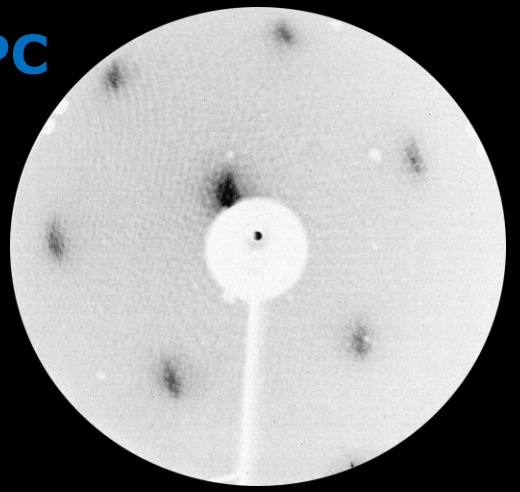


Clean Au
@ 75 eV

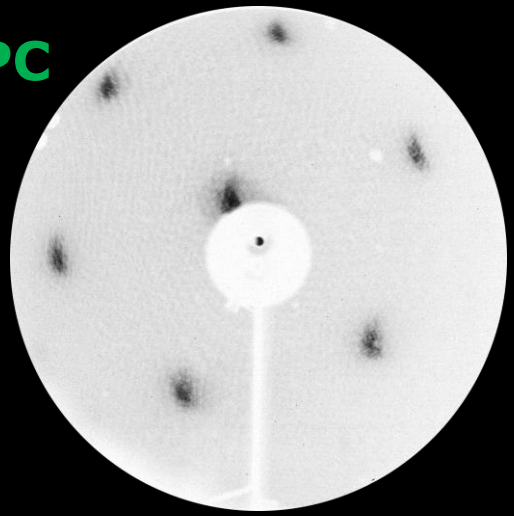


@ 12 eV

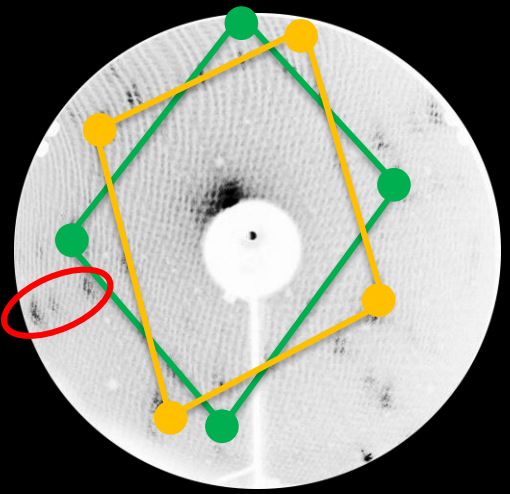
α-TBPC



β-TBPC



DBPC



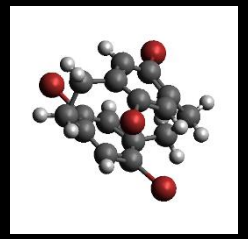
Two different domains
rotated of about 30°

POLITECNICO
MILANO 1863

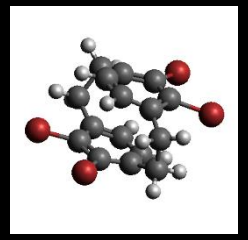
The measurements were performed by the group of Prof. Bussetti
at the Department of Physics, Politecnico di Milano

XPS: ML vs Multilayer

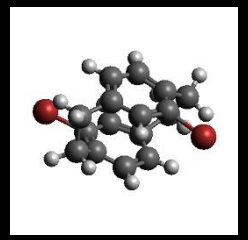
β-TBPC

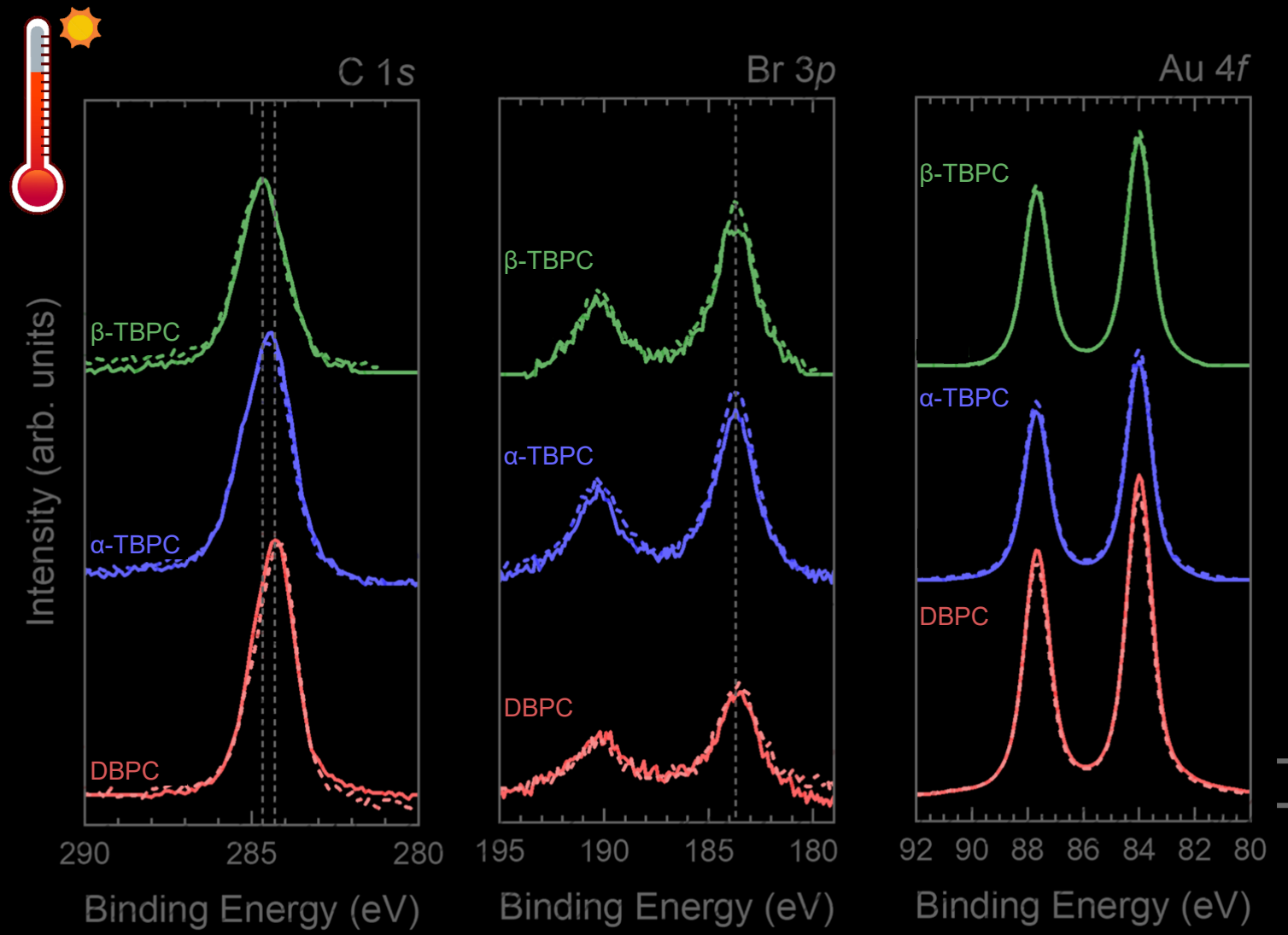


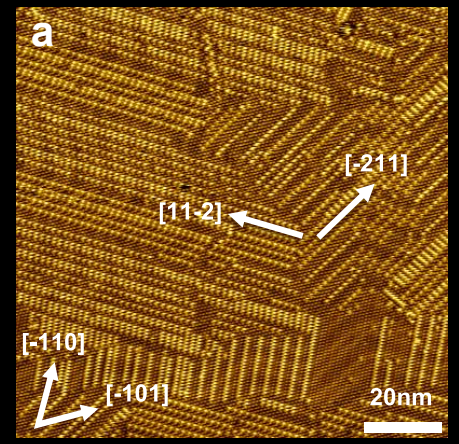
α-TBPC

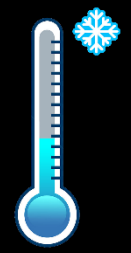


DBPC









Intensity of the XPS peaks are the same for ML and multilayer

Small shift between the molecules with four bromines with respect the one with two

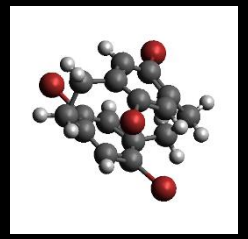
ML

Multilayer

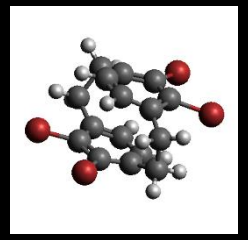
A. Caporale – antonio.caporale@uniroma2.it

XPS: Multilayer in liquid N_2

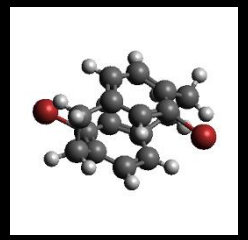
β-TBPC

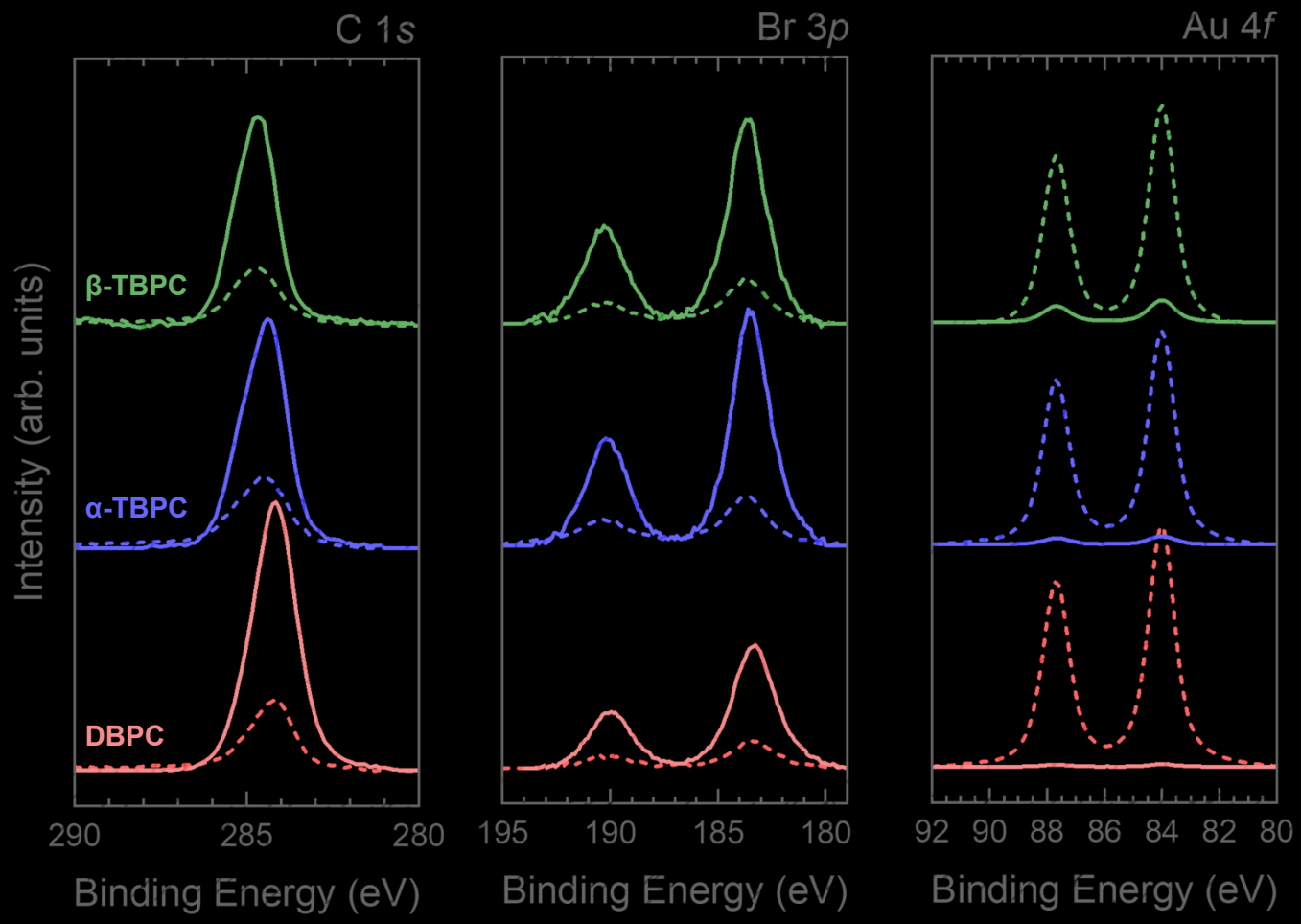


α-TBPC



DBPC





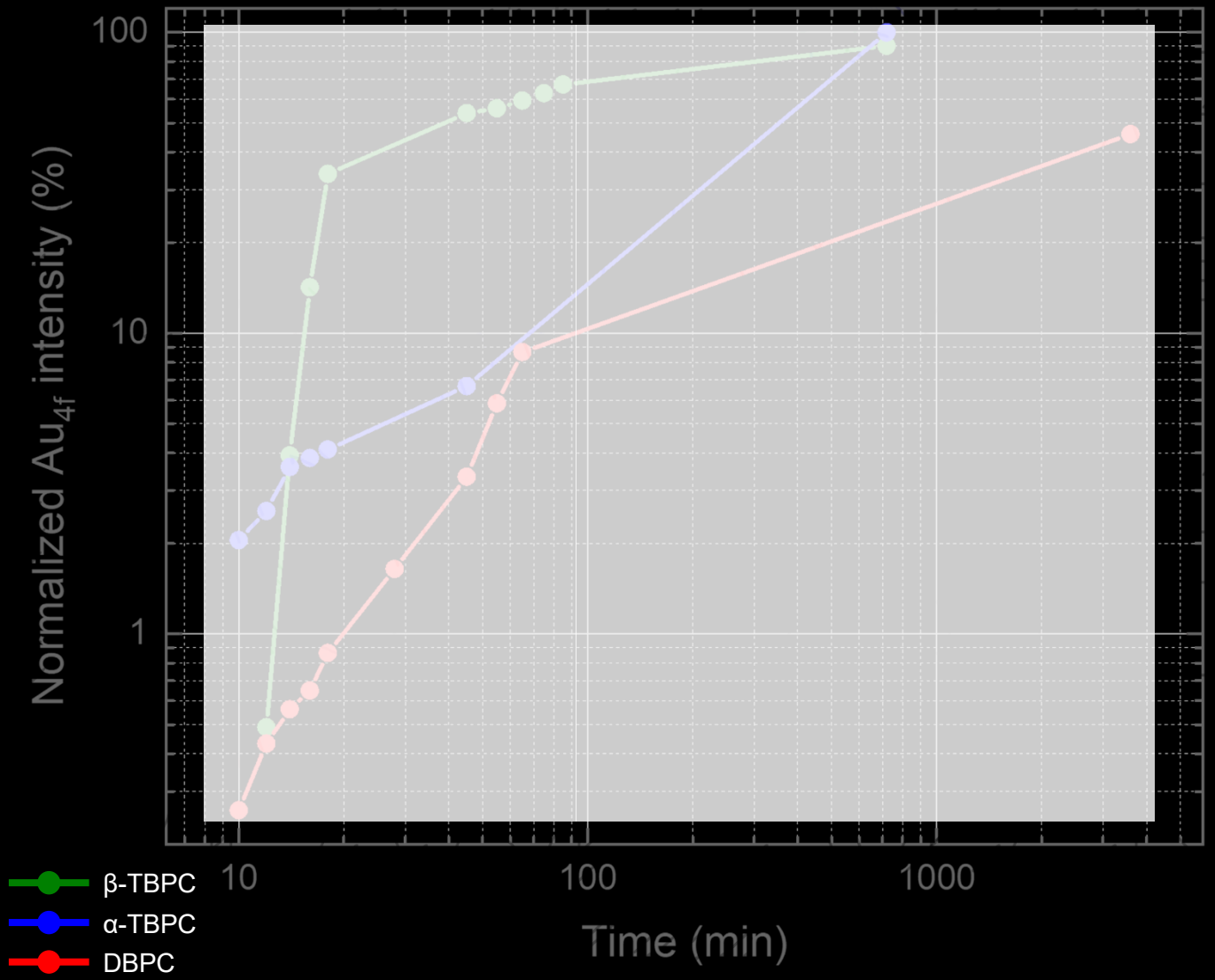
The solid lines are referred to a Au(111) kept at 273K during evaporation

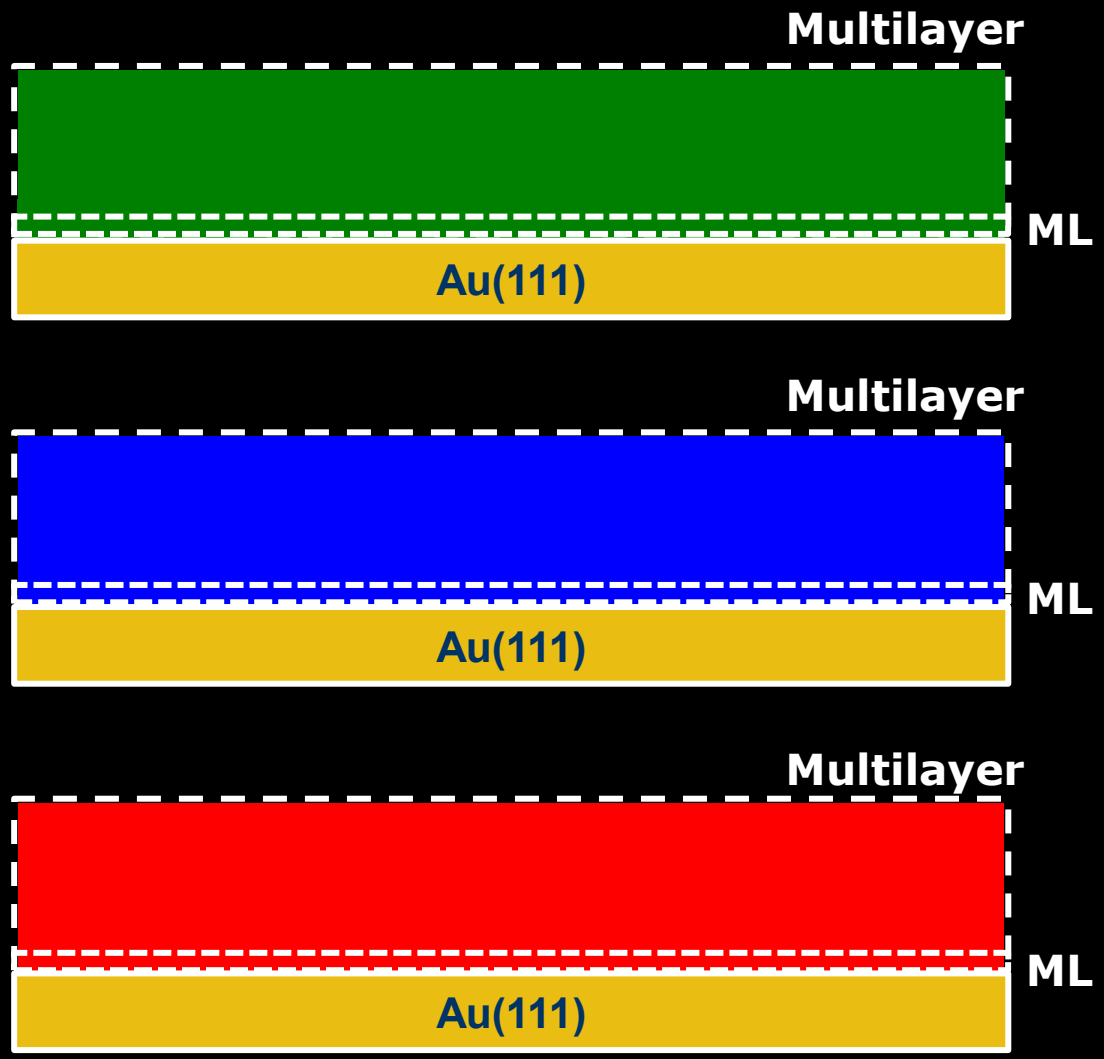
Multilayer can be attached evaporating with the substrate cold

ML or Multilayer at RT

Multilayer

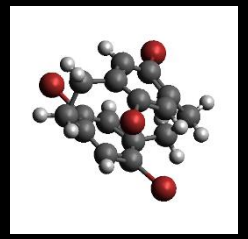
Time behaviour



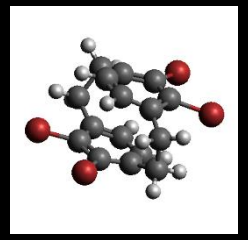


XPS: after 24 hours

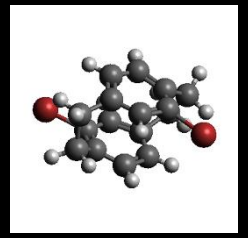
β-TBPC

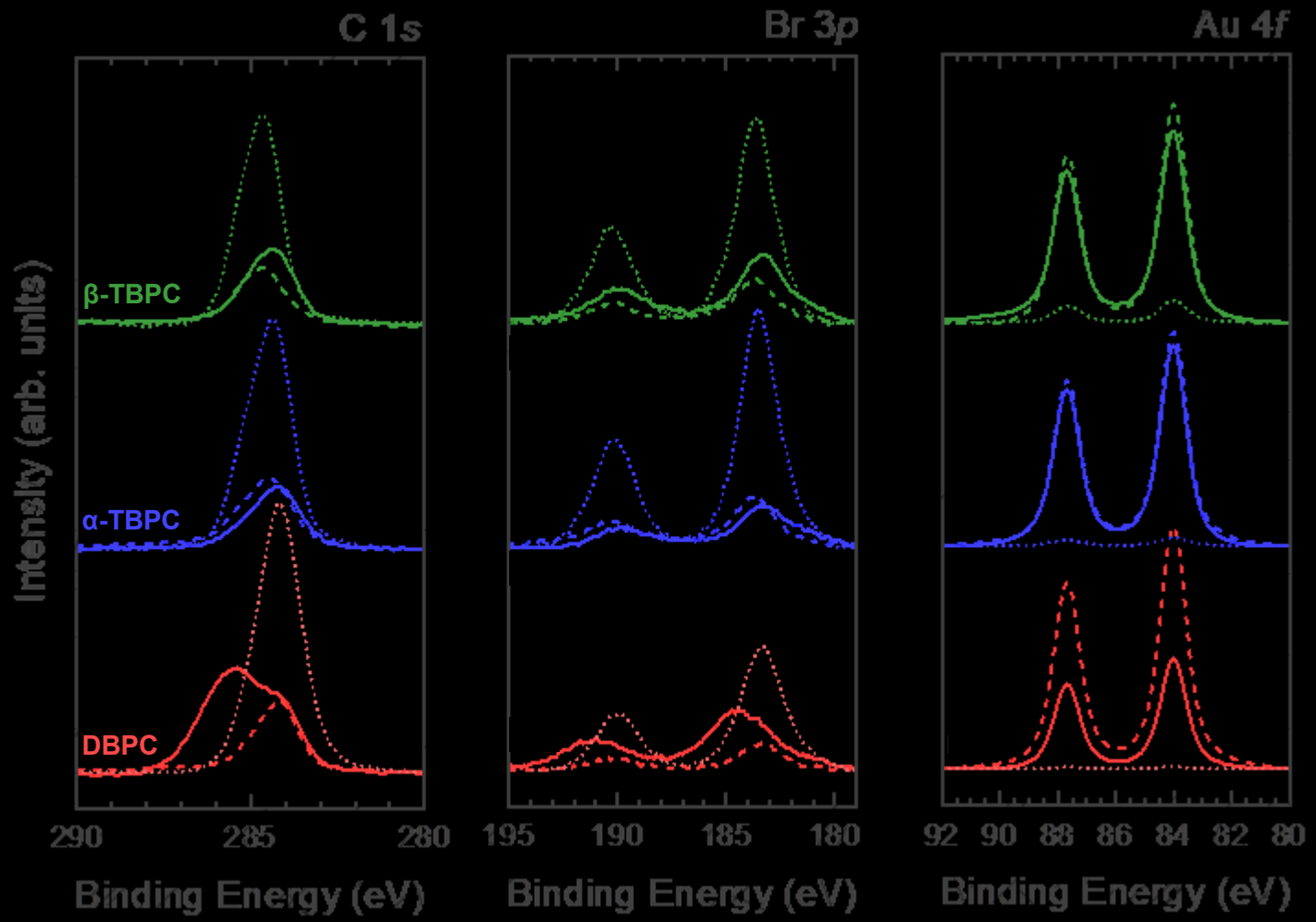


α-TBPC



DBPC





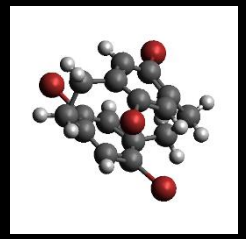
ML

After 24 hrs

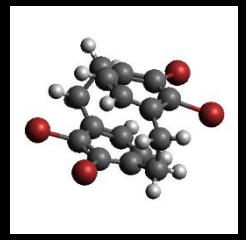
Initial multilayer

UPS: ML vs Multilayer

β-TBPC



α-TBPC



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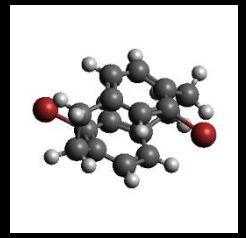

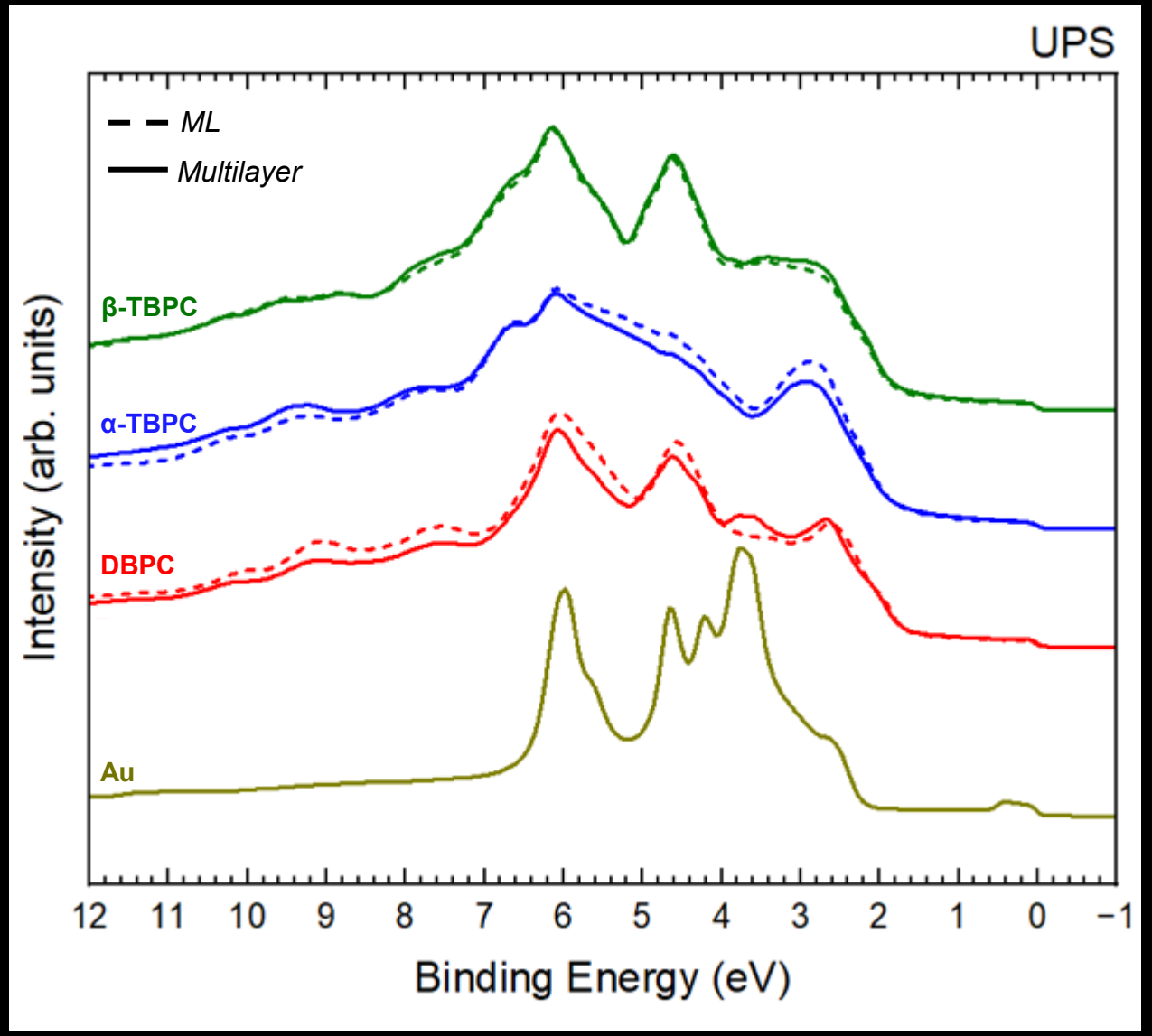

ML and multilayer have roughly the same behaviour

The three molecules behave differently, especially the α-TBPC, which present different feature at around 4.4eV and 2.5eV