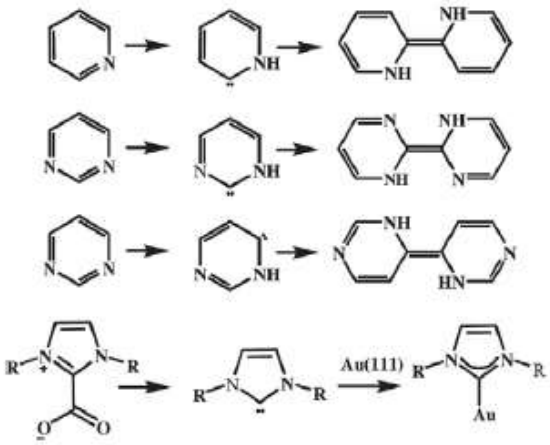
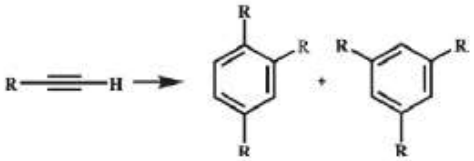
On-surface synthesis

N-heterocyclic carbenes formation and dimerization



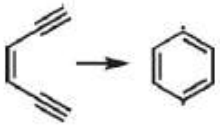
Glaser coupling

Alkyne cyclotrimerization

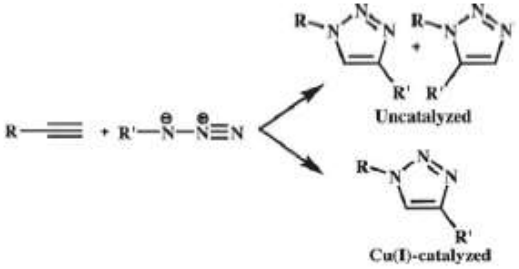


Metalated carbyne

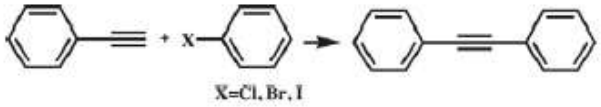
Bergman reaction



Azide–alkyne cycloaddition



Sonogashira coupling



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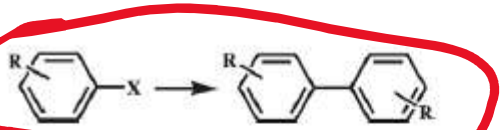
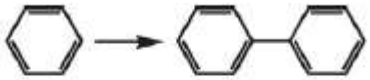
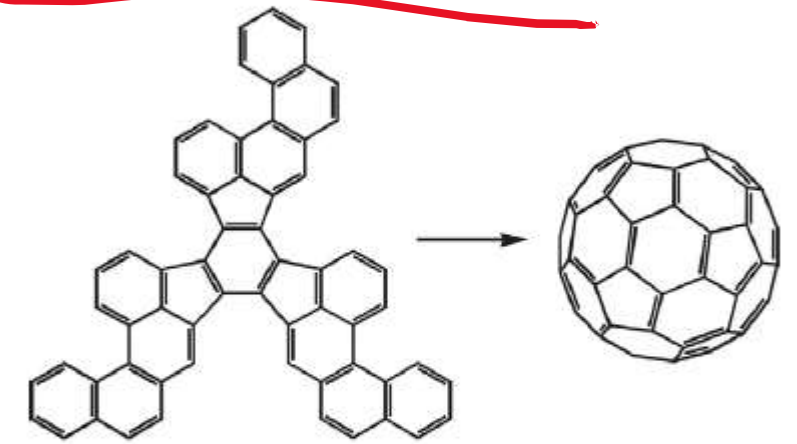
Dehalogenative homocoupling of terminal alkynyl bromides

Ullmann coupling





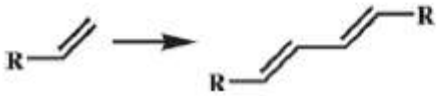
Aryl–aryl dehydrogenation coupling

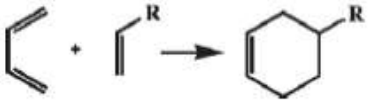
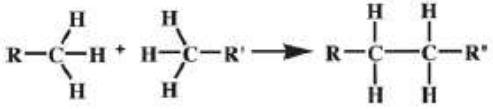
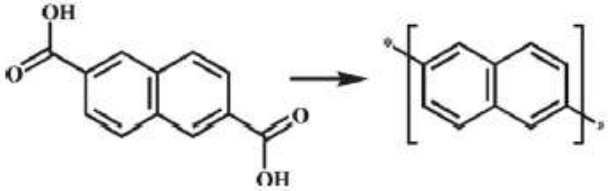
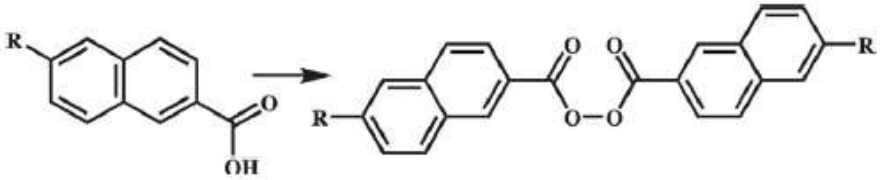
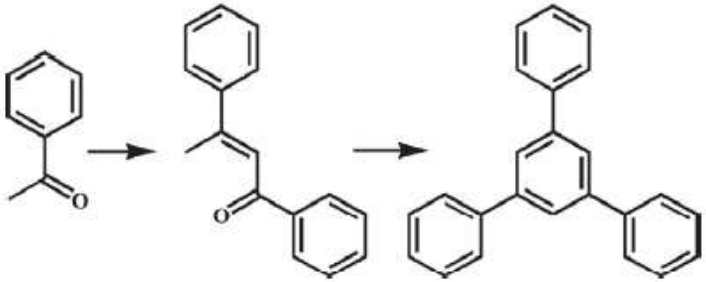
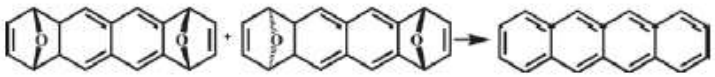


fullerene

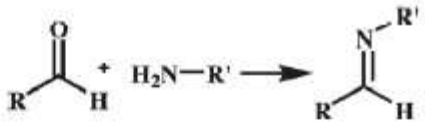
graphene nanoribbons

Dehydrogenative homocoupling of terminal alkene

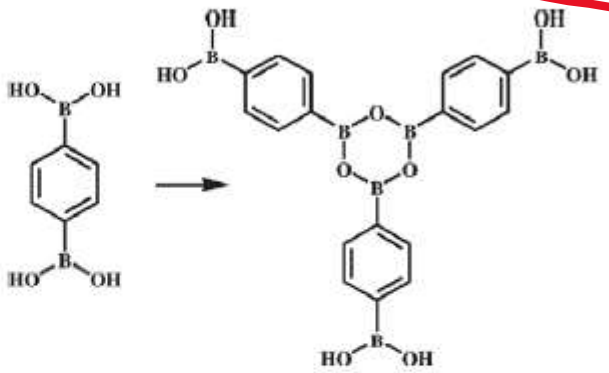


Dehalogenative homocoupling of terminal alkenyl bromides	
Diels–Alder reaction	
Wurtz coupling	
Linear alkane polymerization	
Decarboxylative polymerization	
Dehydrogenative coupling	
Dimerization and cyclotrimerization of acetyls	
Dealkylation of ethers to alcohols	
Reduction	

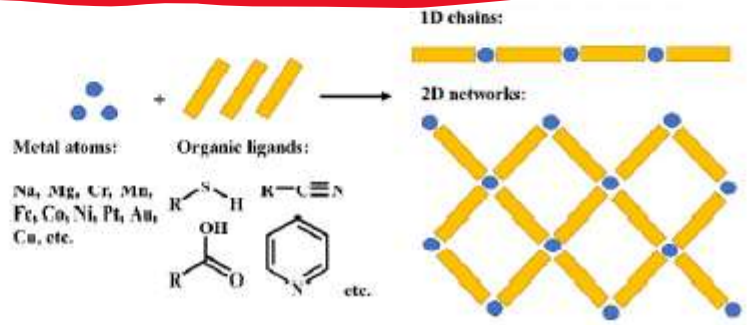
Schiff-base reaction (imine formation)



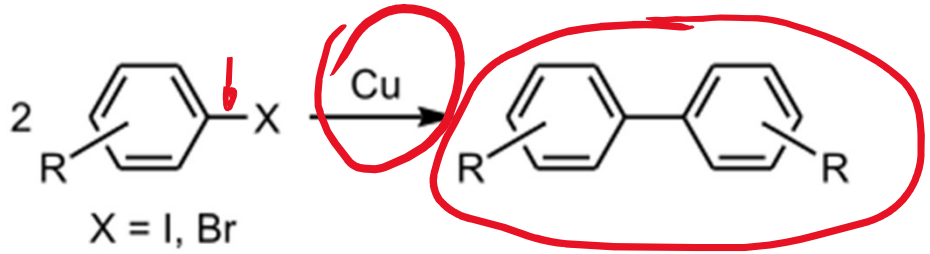
Boronic acid condensation



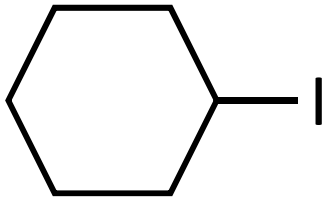
Surface confined
Metal–organic coordination

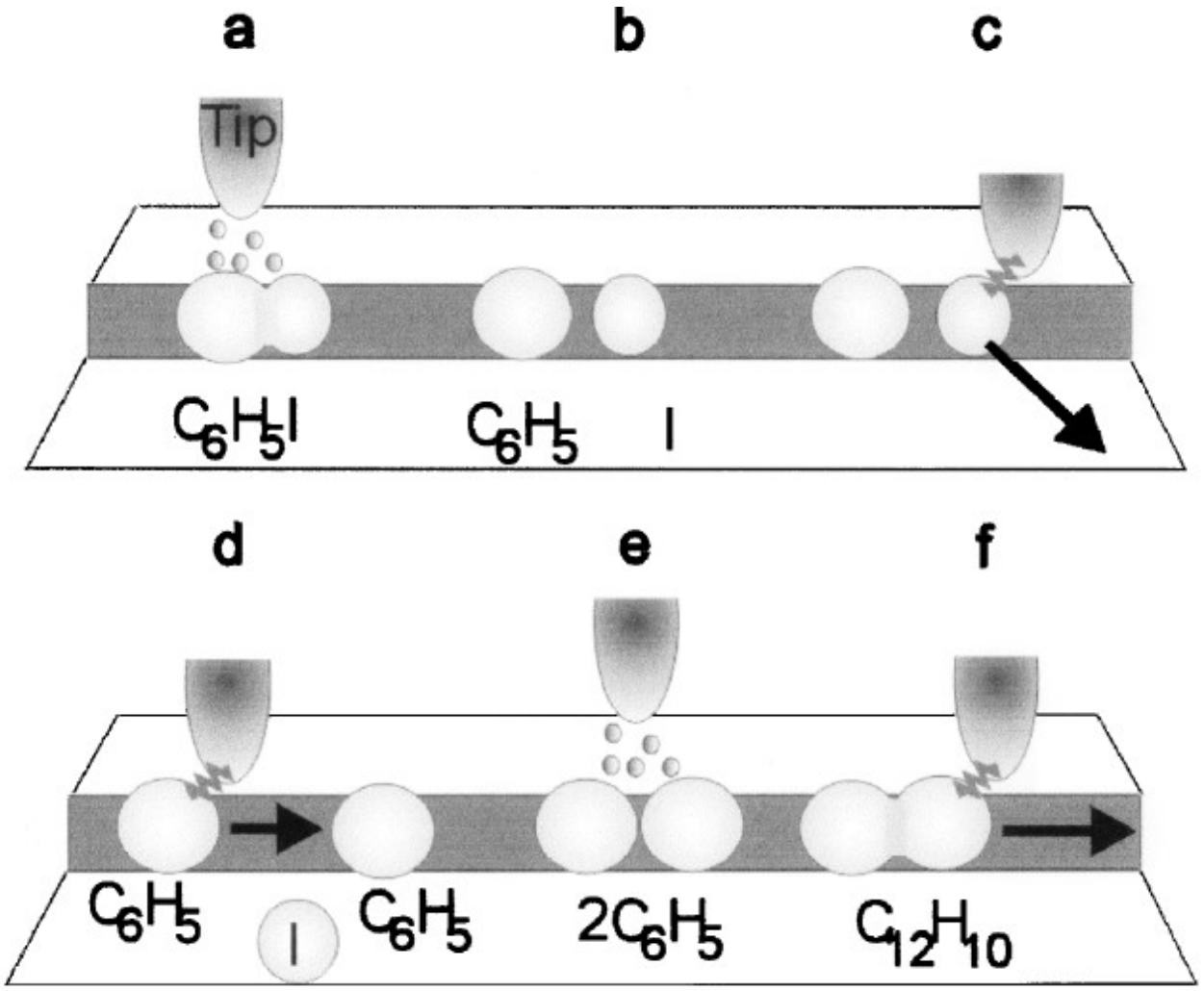


Reazione di Ullmann o Ullmann coupling



X alogeni, tipicamente Br

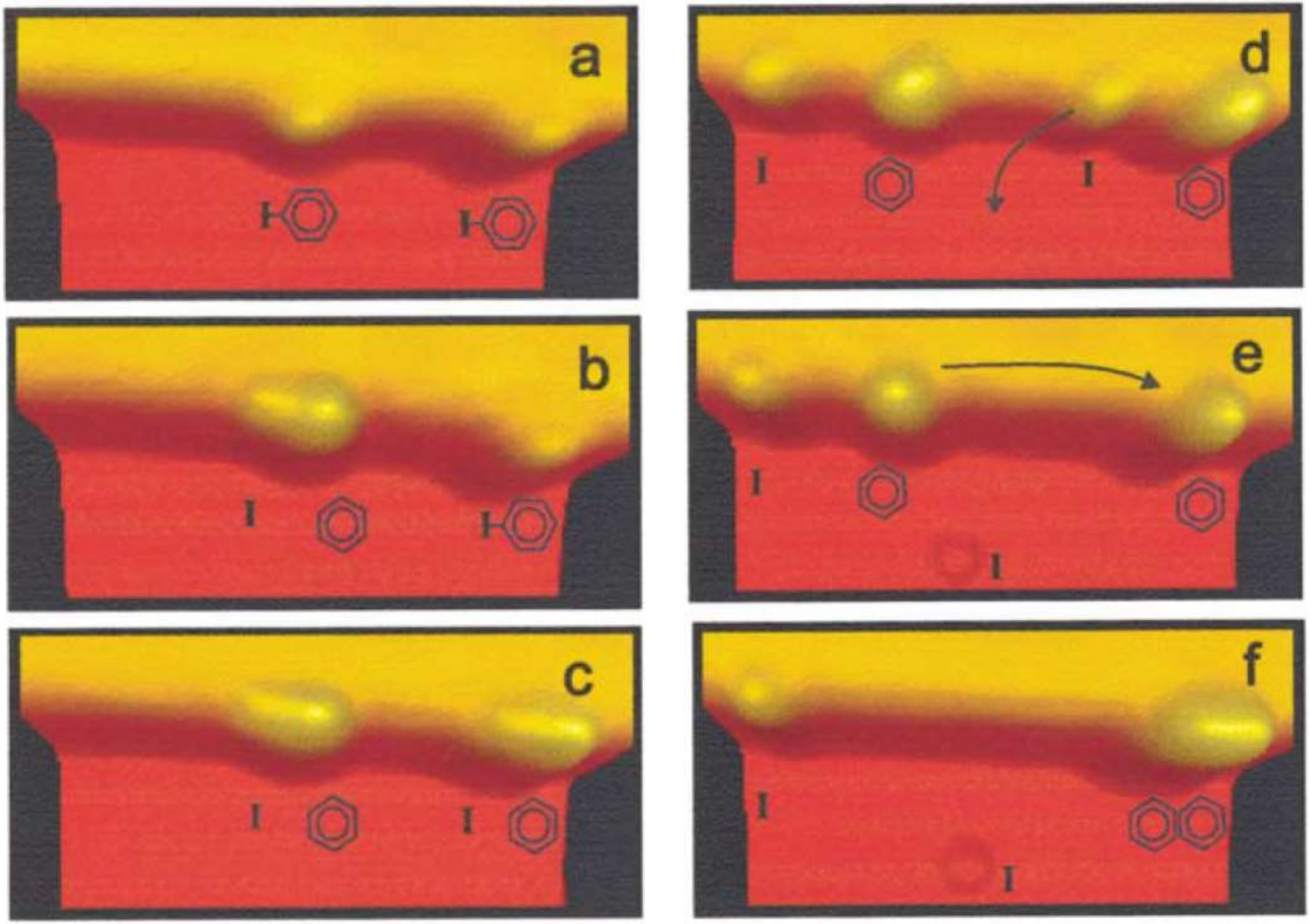


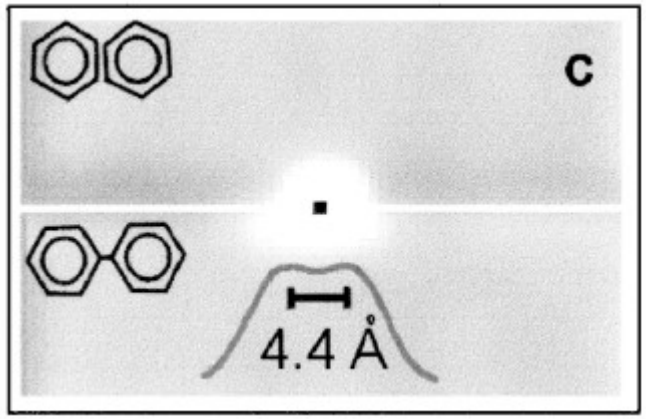


VOLUME 85, NUMBER 13 PHYSICAL REVIEW LETTERS 25 SEPTEMBER 2000

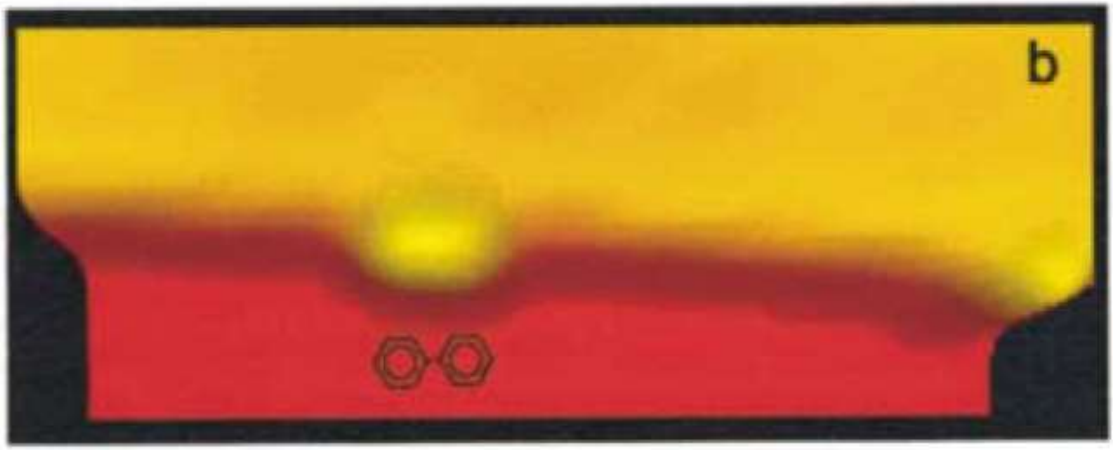
Inducing All Steps of a Chemical Reaction with the Scanning Tunneling Microscope Tip: Towards Single Molecule Engineering

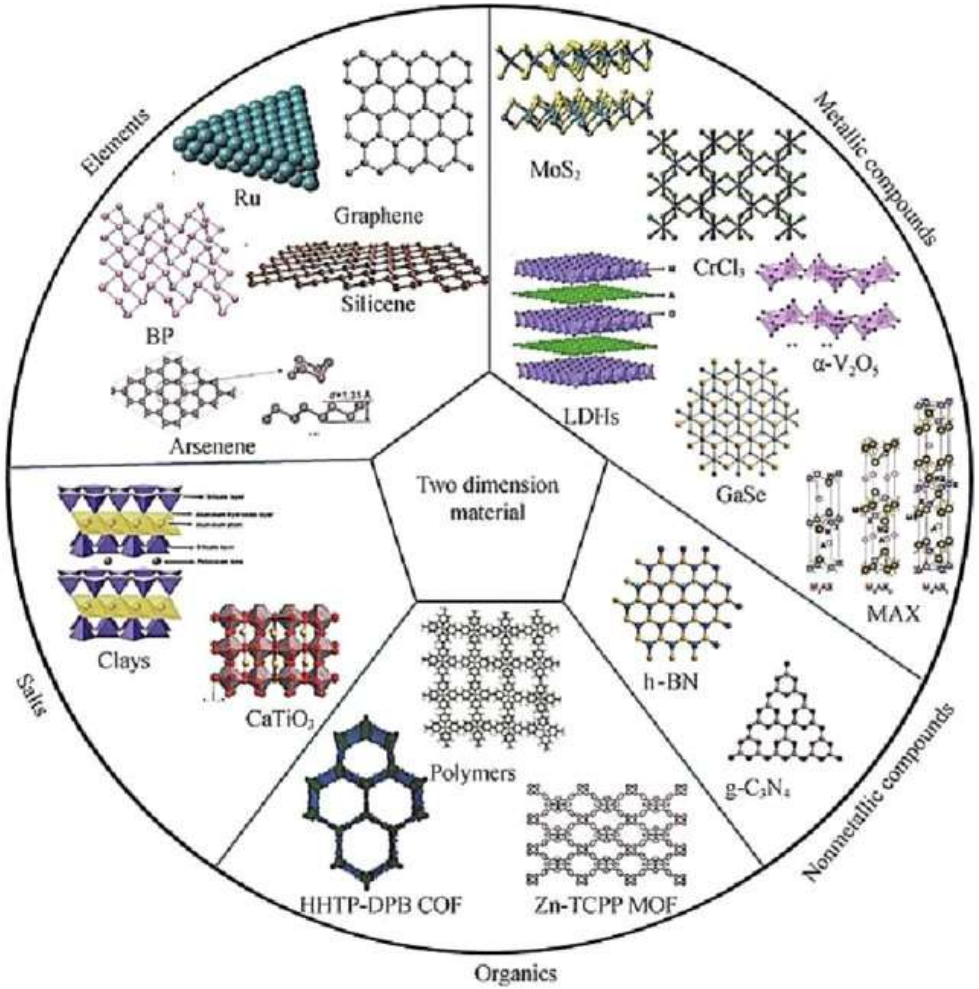
Saw-Wai Hla,[1,2,*] Ludwig Bartels,[1,†] Gerhard Meyer,[1] and Karl-Heinz Rieder[1]


a
b
c
d
e
f


c
4.4 Å

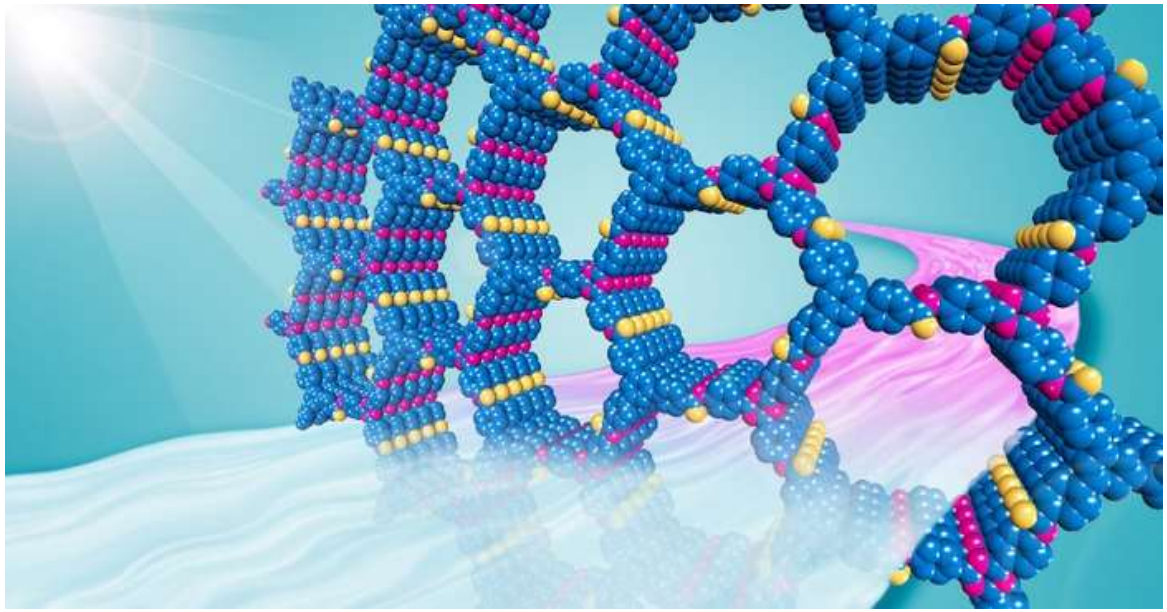

a


b

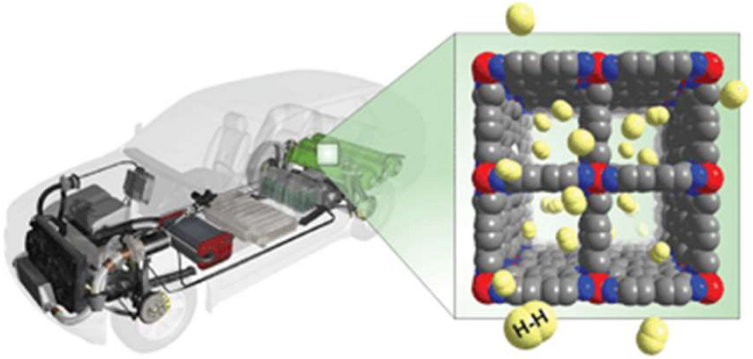


https://doi.org/10.1142/S1793292019300019

Covalent Organic Frameworks

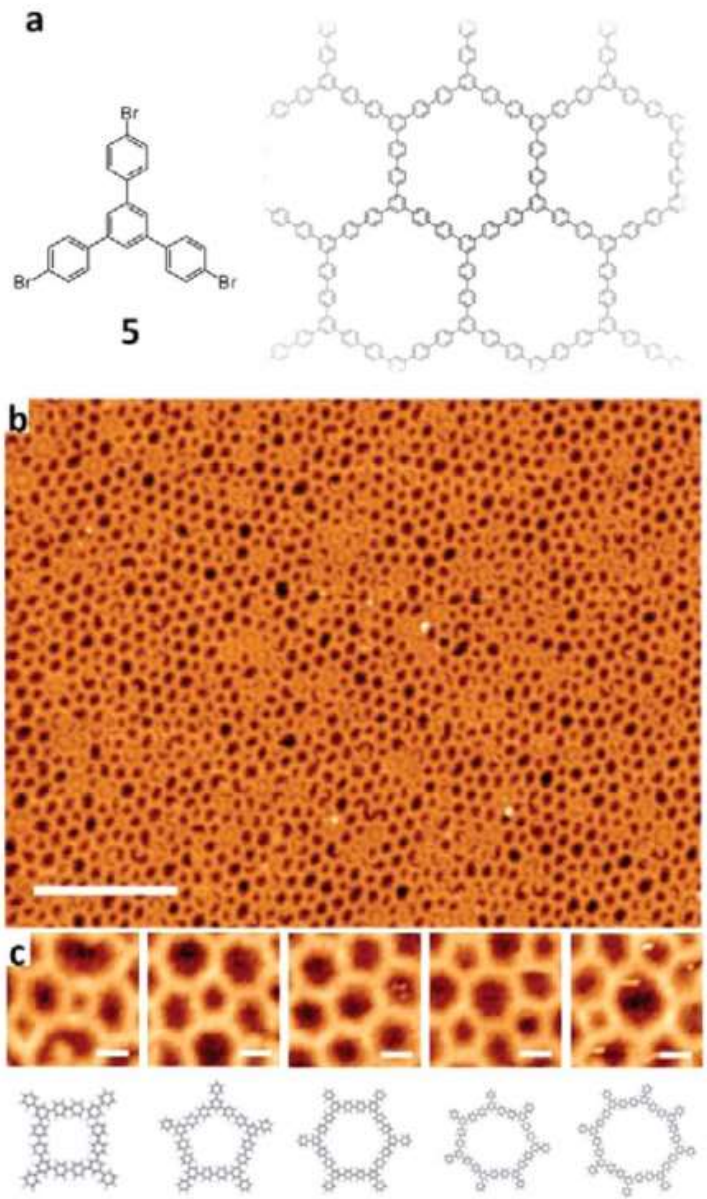


Storaging

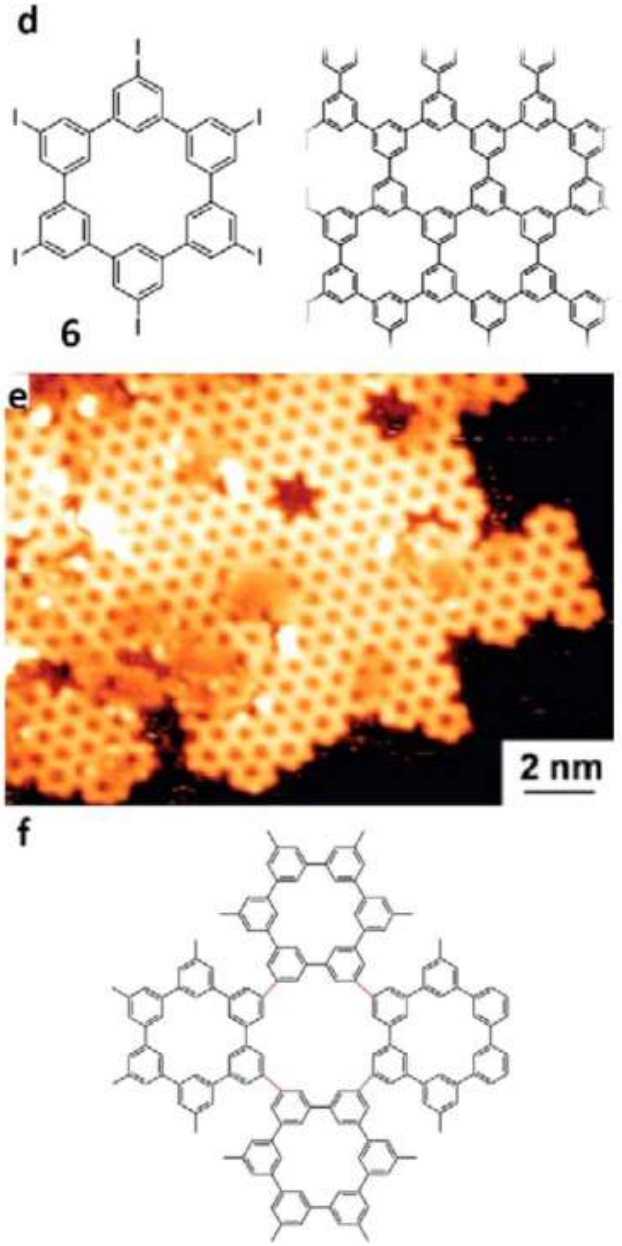


Fotocatalisi

La struttura del precursore determina la morfologia del 2D e la concentrazione di difetti

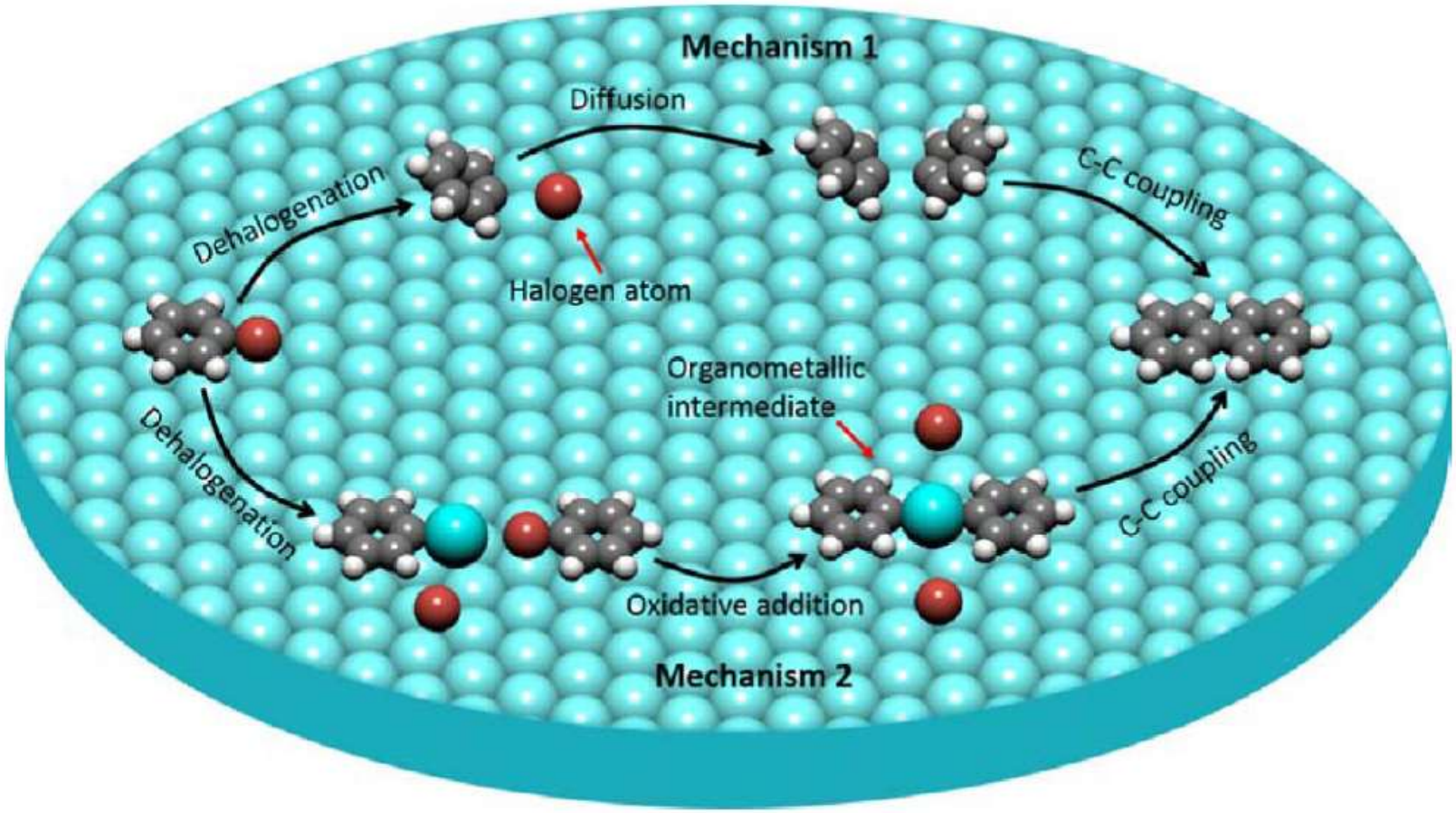


2D - COVALENT ORGANIC FRAMEWORK

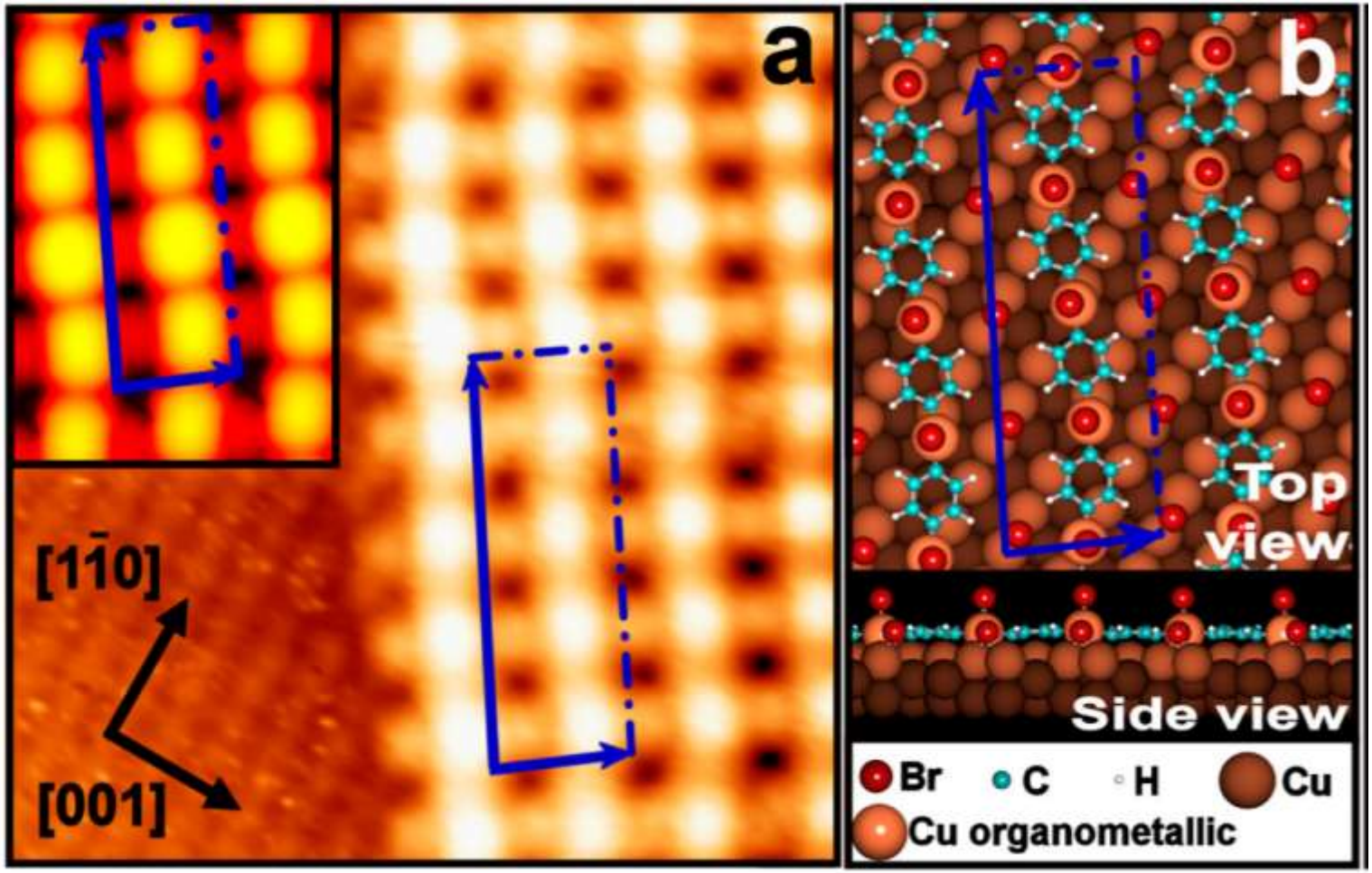


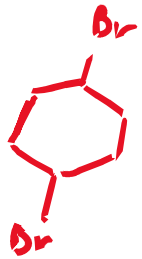
ACS Nano 2014, 8, 7880−7889.

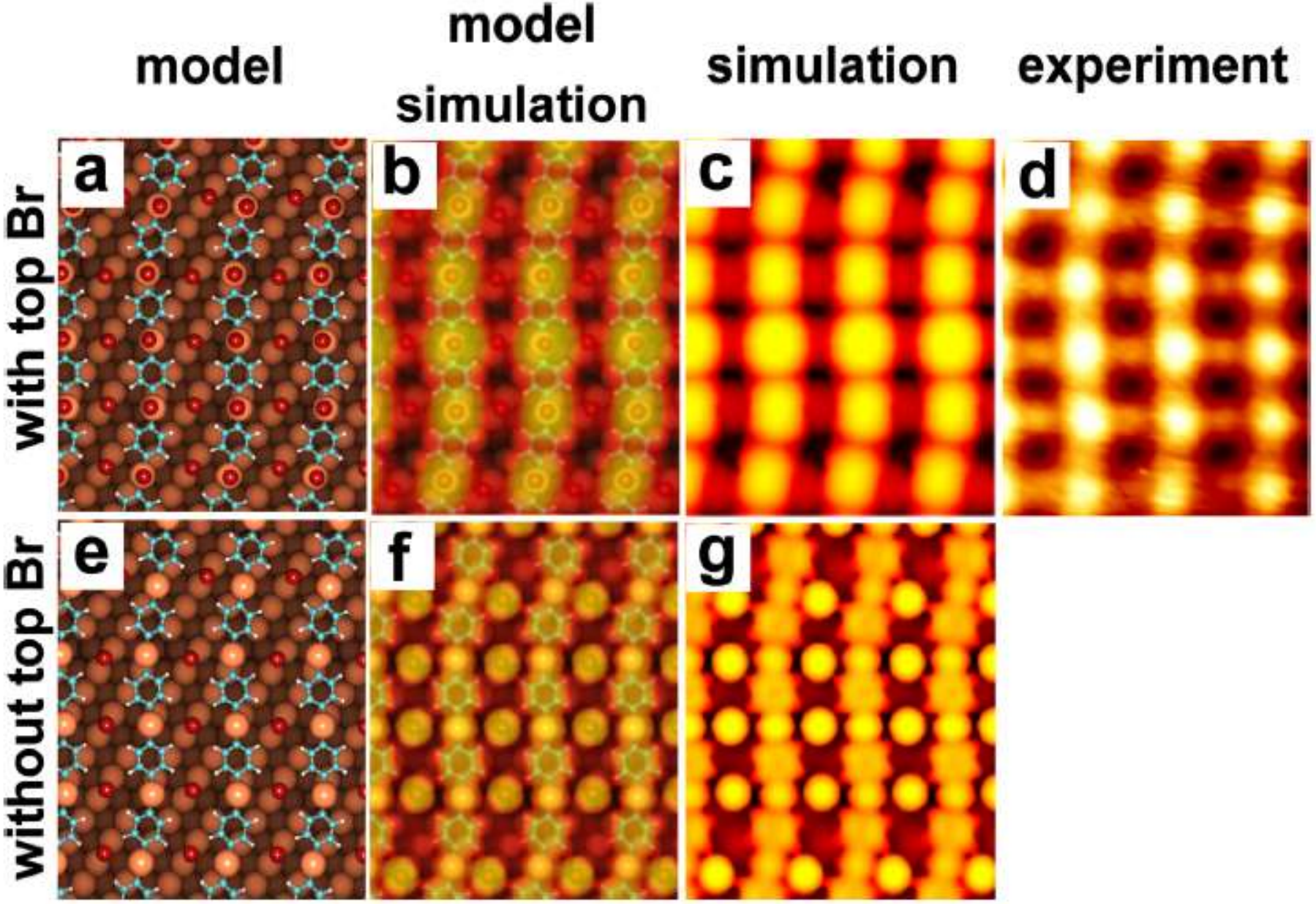
Chem. Commun. 2010, 46, 7157−7159.

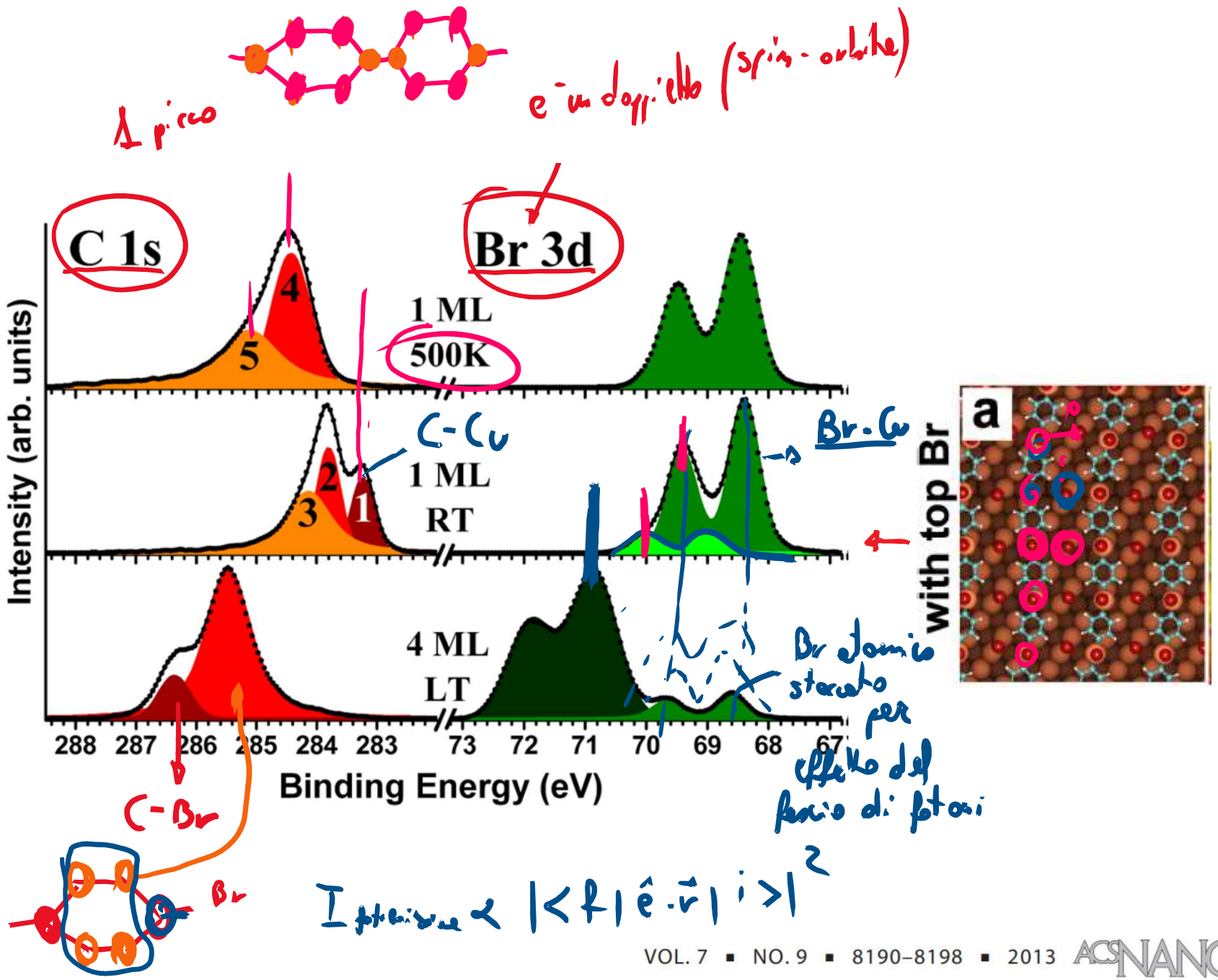


DOI: 10.1021/acs.accounts.5b00168
Acc. Chem. Res. 2015, 48, 2484−2494


a
b
[1$\bar{1}$0]
[001]
Top view
Side view
Br
C
H
Cu
Cu organometallic




model
model
simulation
simulation
experiment
with top Br
without top Br
a
b
c
d
e
f
g



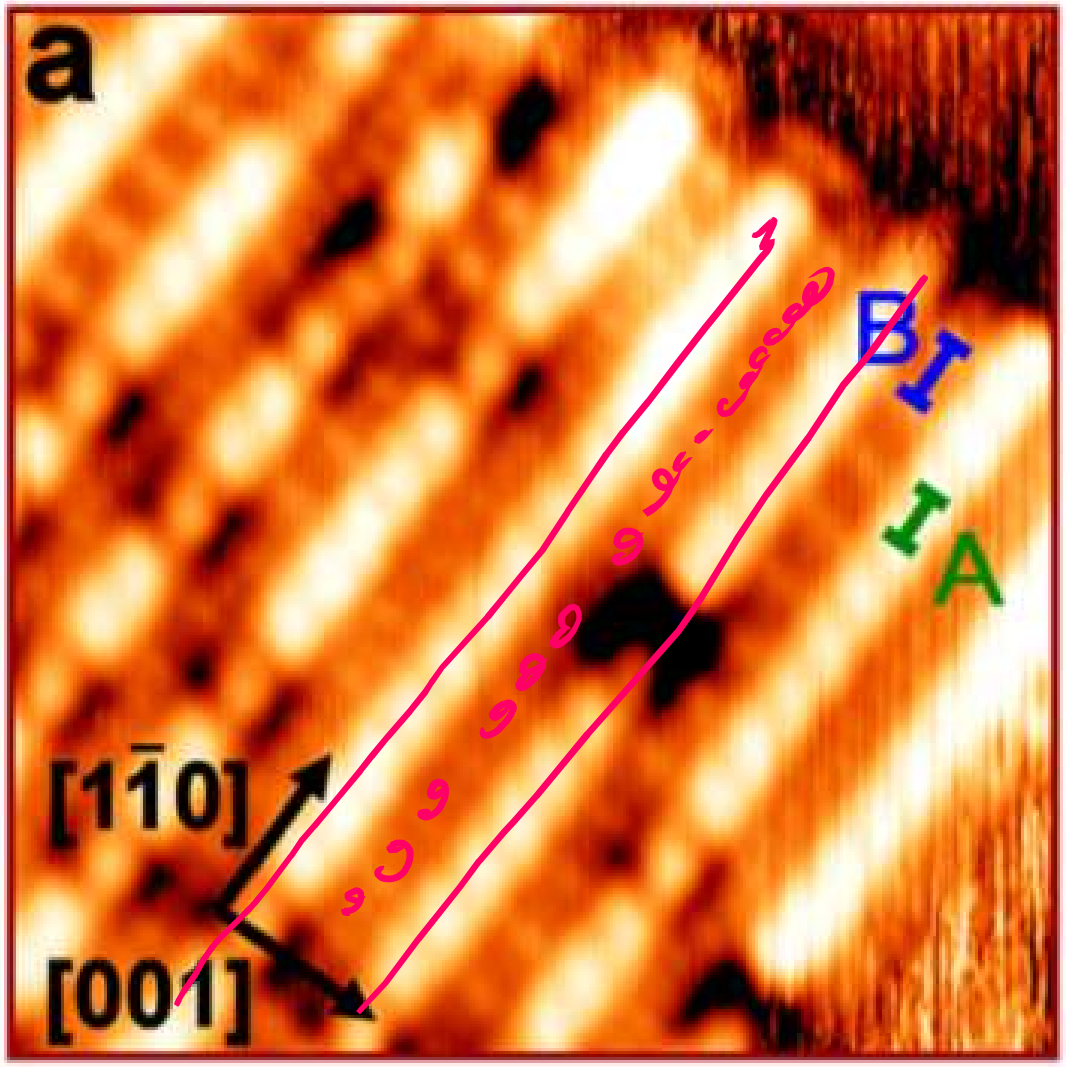
Δ picco

è un doppietto (spin-orbita)

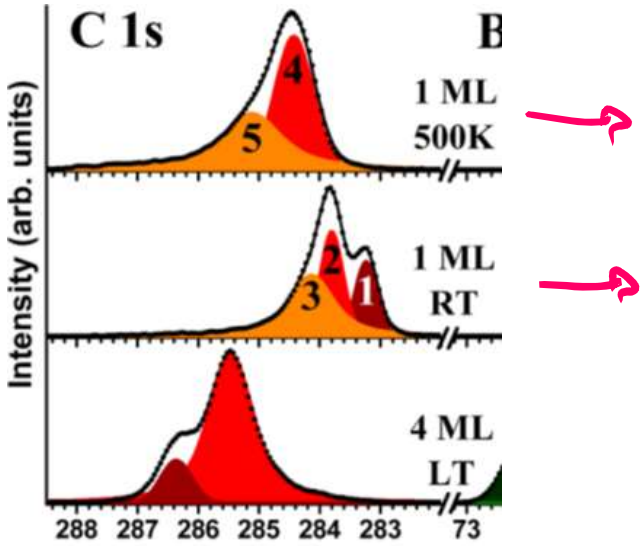
Br atomico strappato per effetto del fascio di fotoni

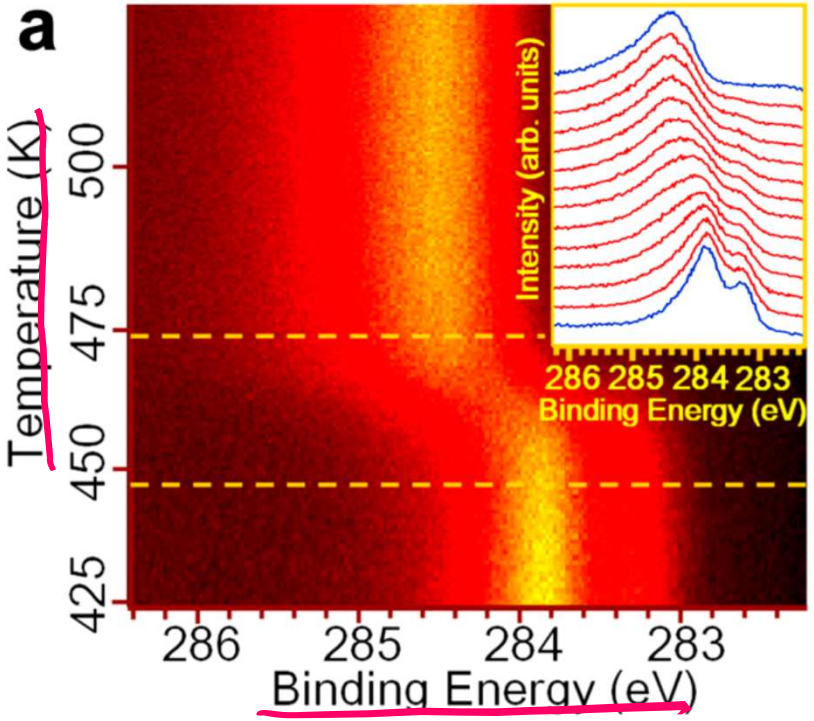
$I_{fotoelettrone} \propto |\langle f|\hat{e}\cdot\vec{r}|i\rangle|^2$

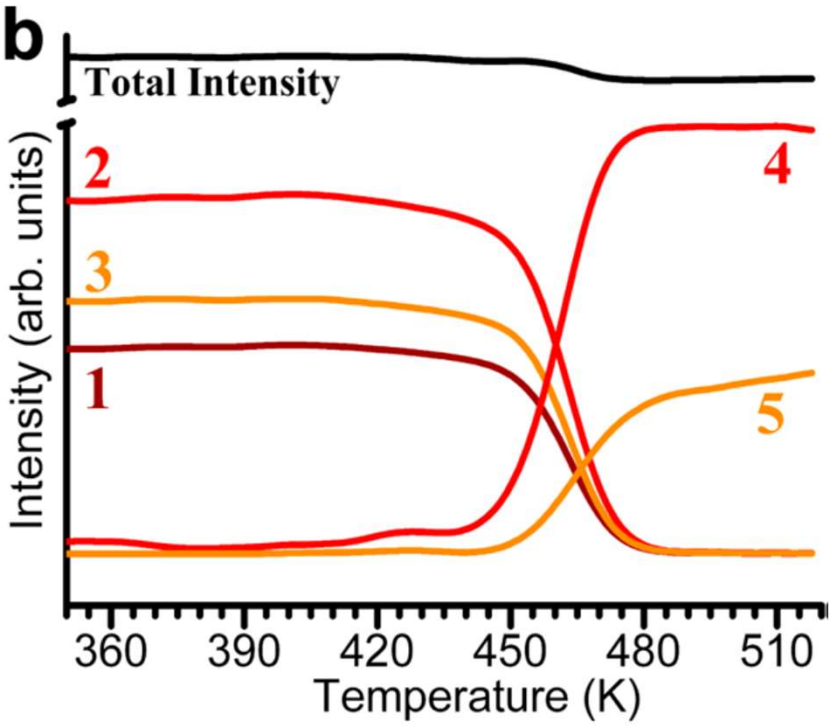
Annealing @ 500°C

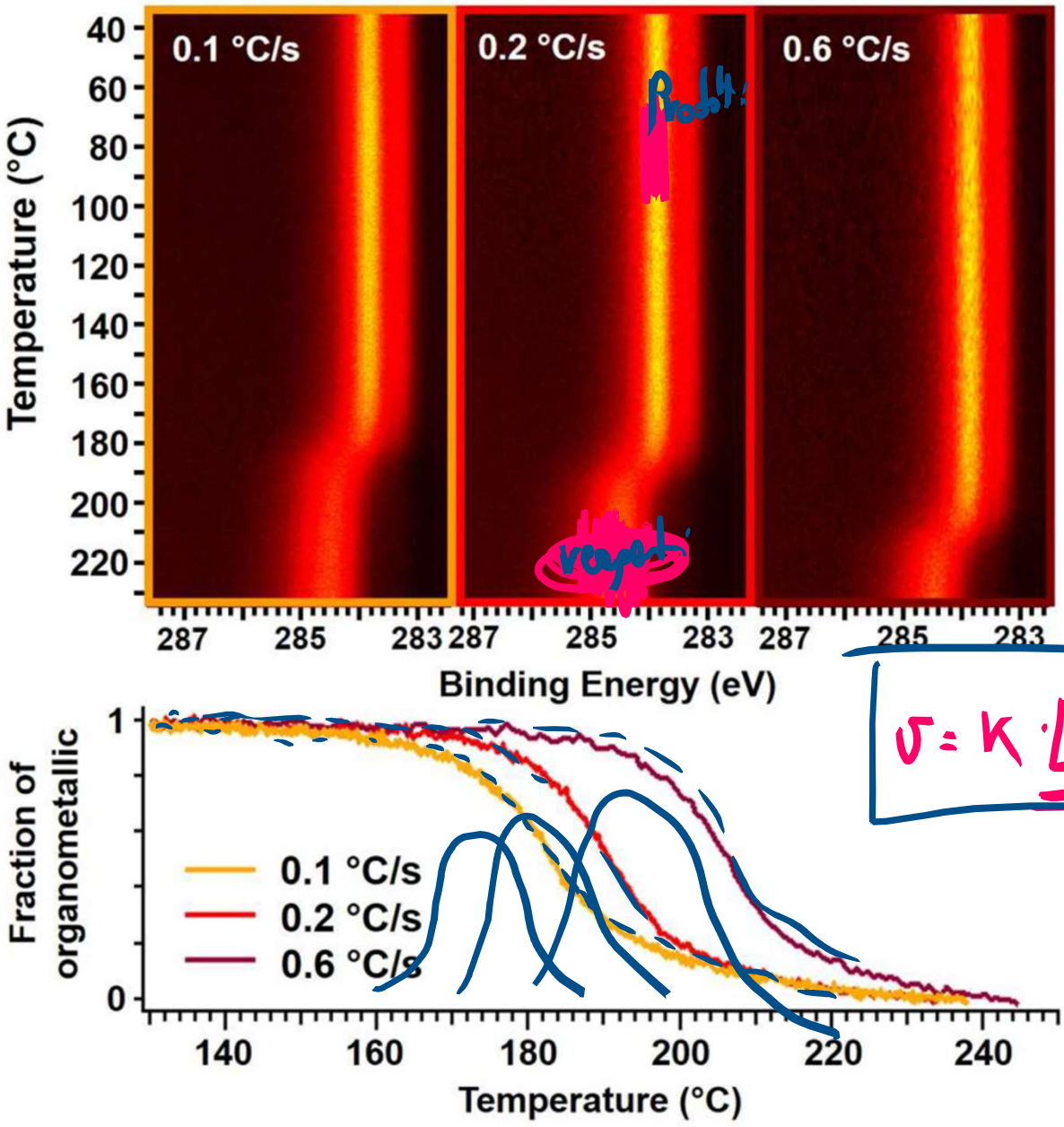


VOL. 7 ▪ NO. 9 ▪ 8190–8198 ▪ 2013 ACSNANO www.acsnano.org







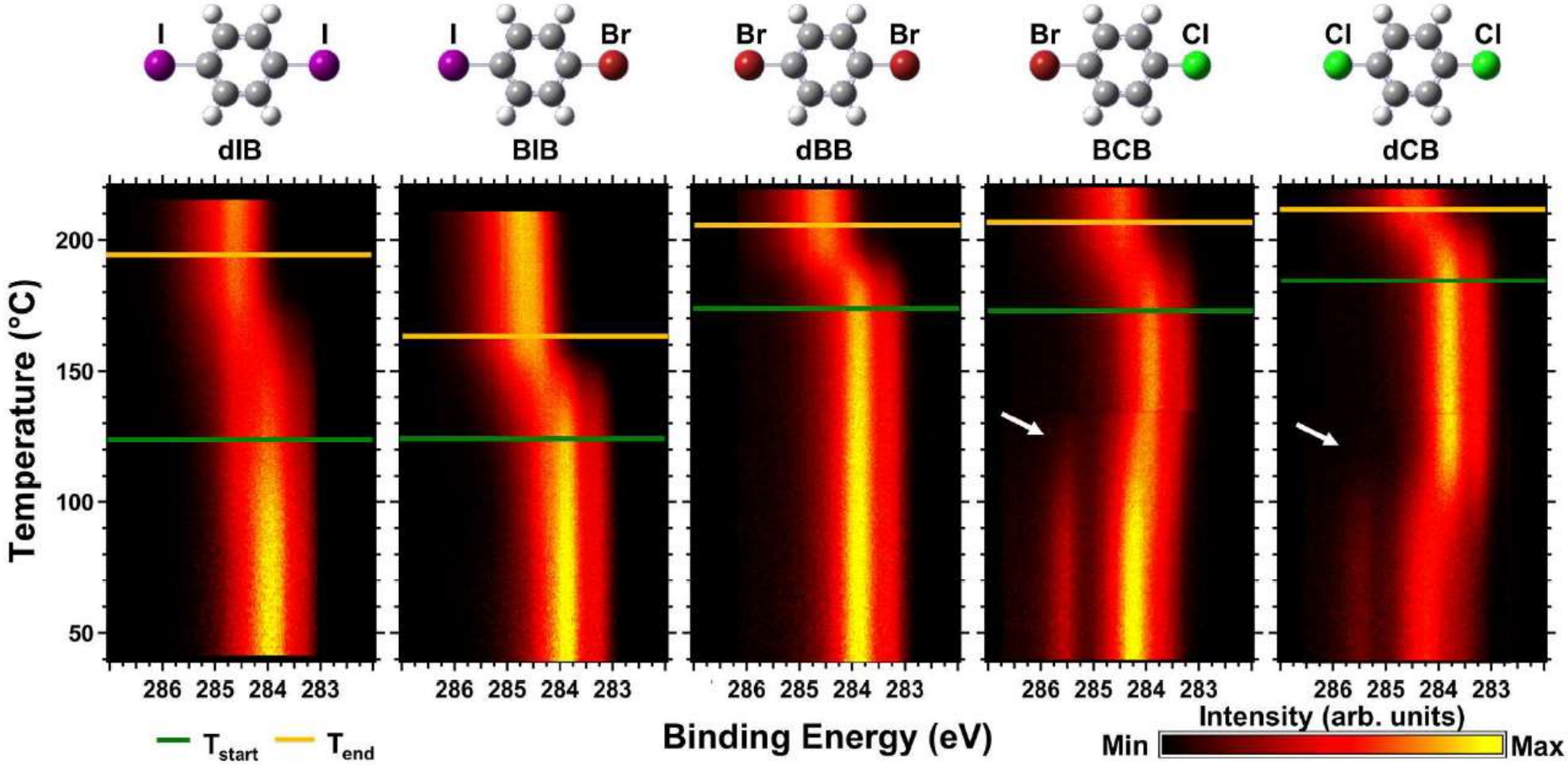


diversi rate di riscaldamento

studio della velocità di reazione

$$v = K \cdot [A]^n$$

$$\frac{d\,\sigma(t)}{dt}$$


I
I
dIB
I
Br
BIB
Br
Br
dBB
Br
Cl
BCB
Cl
Cl
dCB
Temperature (°C)
200
150
100
50
286 285 284 283
Binding Energy (eV)
T start
T end
Intensity (arb. units)
Min
Max

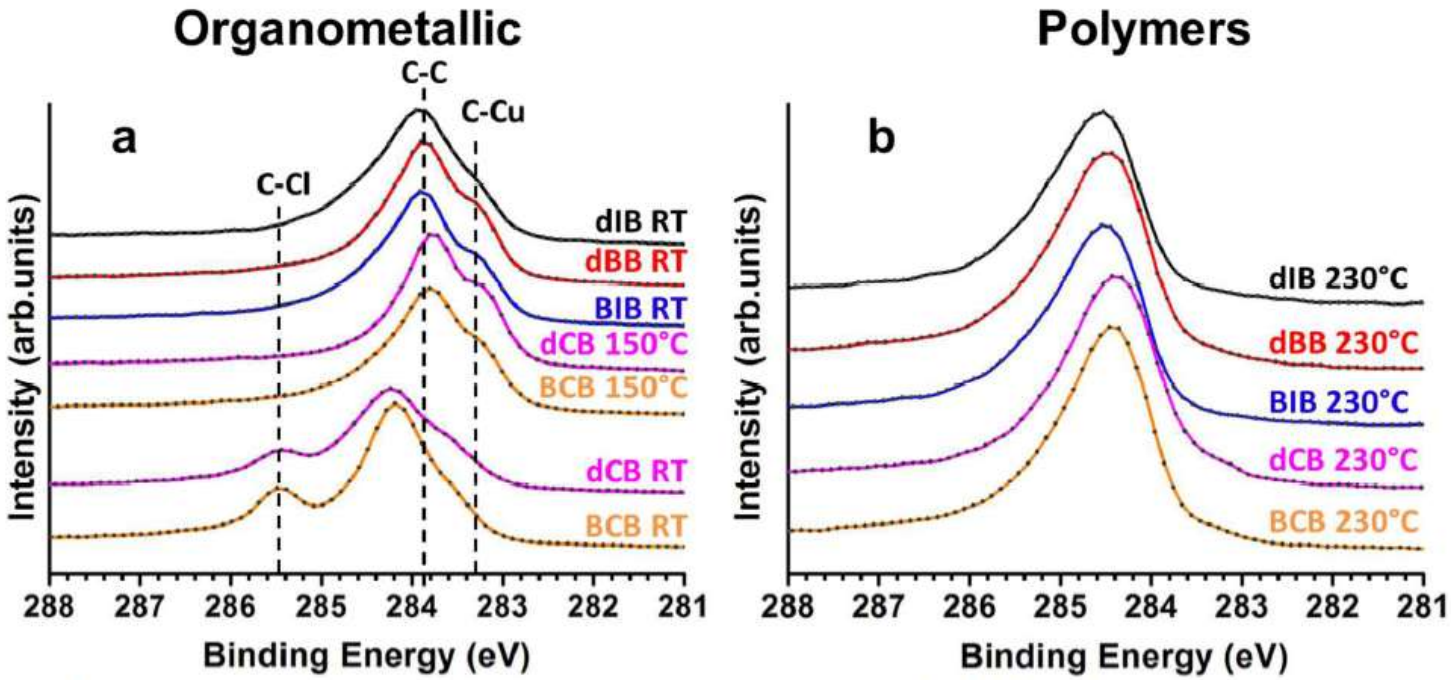
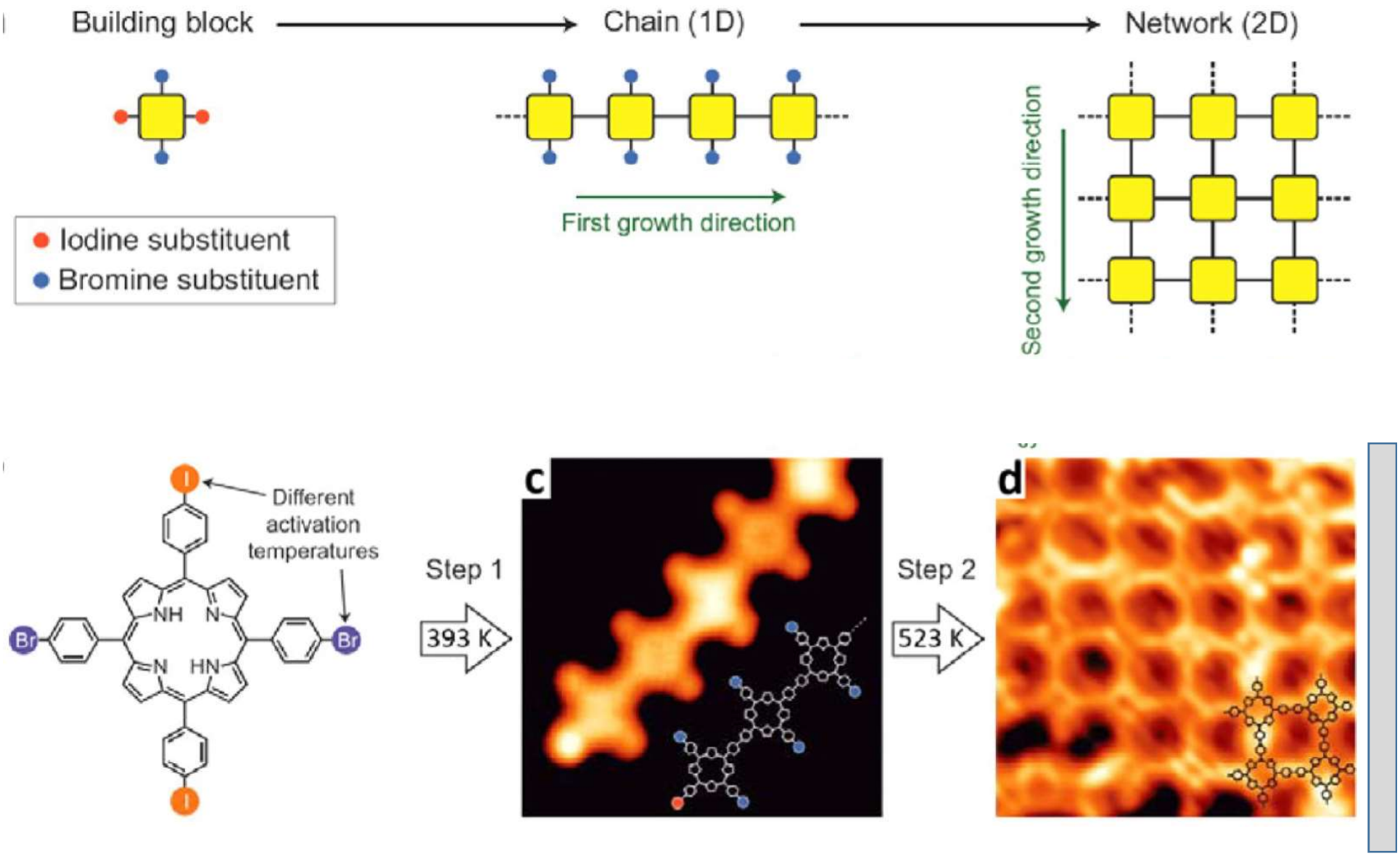


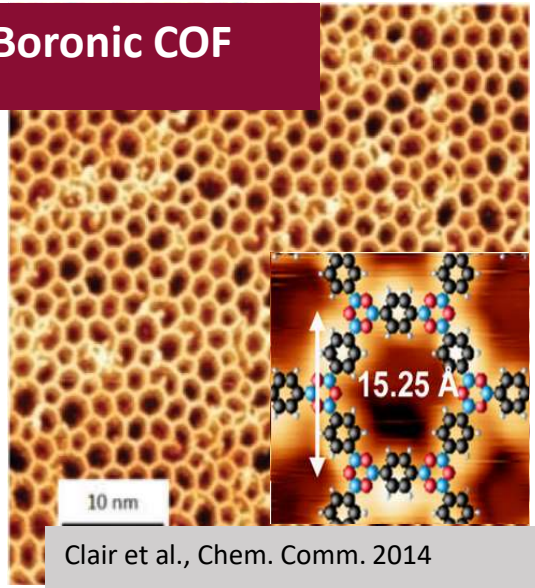
Figure 2. C 1s spectra for a saturated coverage of each precursor on Cu(110) for the organometallic (a) and polymer (b) phases.


Building block
Chain (1D)
Network (2D)
Iodine substituent
Bromine substituent
First growth direction
Second growth direction
Different activation temperatures
Step 1
393 K
Step 2
523 K
c
d

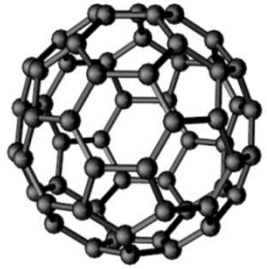
Boronic condensation

2D Covalent Organic Frameworks

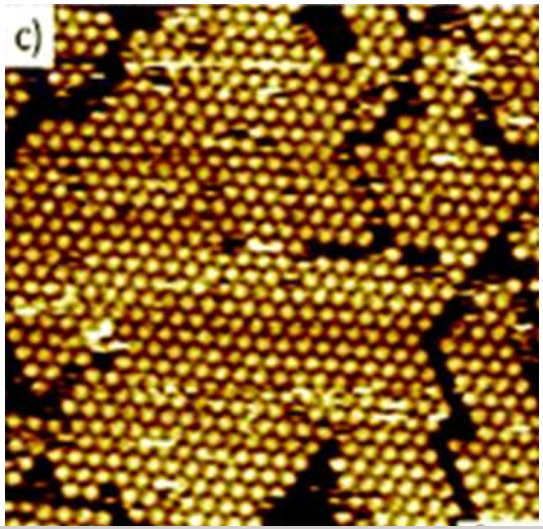
Boronic COF



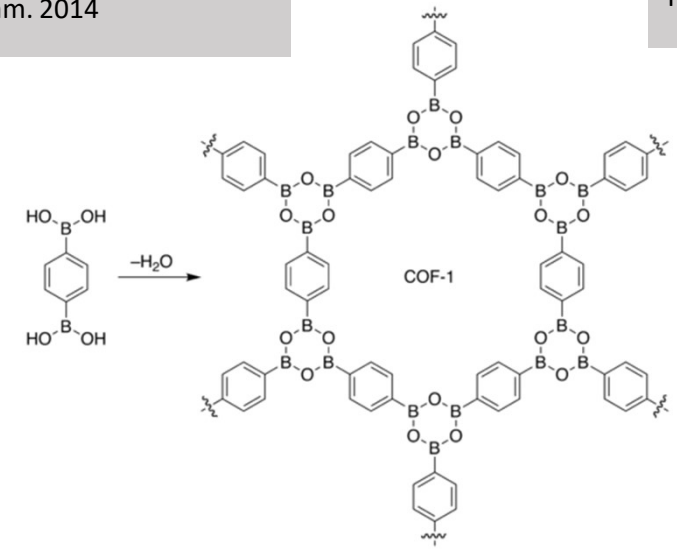
Clair et al., Chem. Comm. 2014

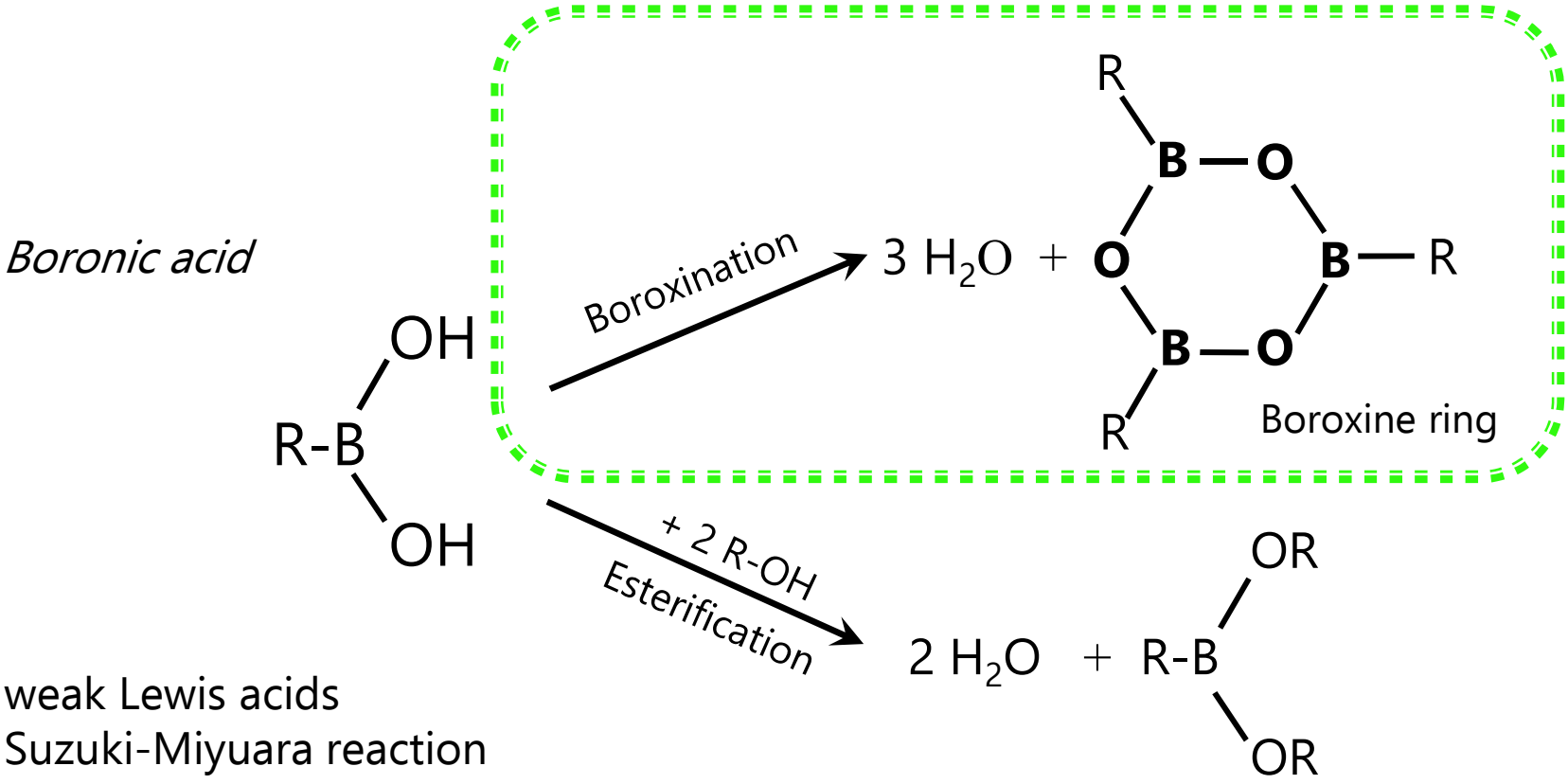


fullerene



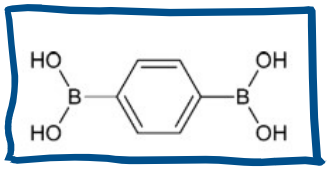
Plas et al., Chem. Comm. 2016





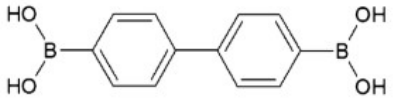
weak Lewis acids
Suzuki-Miyuara reaction
detection of sugars
molecular imprinting

1

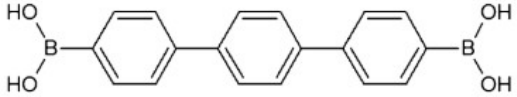


evaporabile in UHV ✓

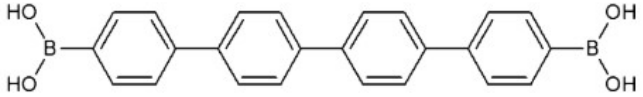
2



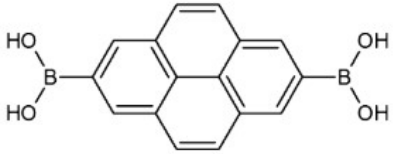
3



4



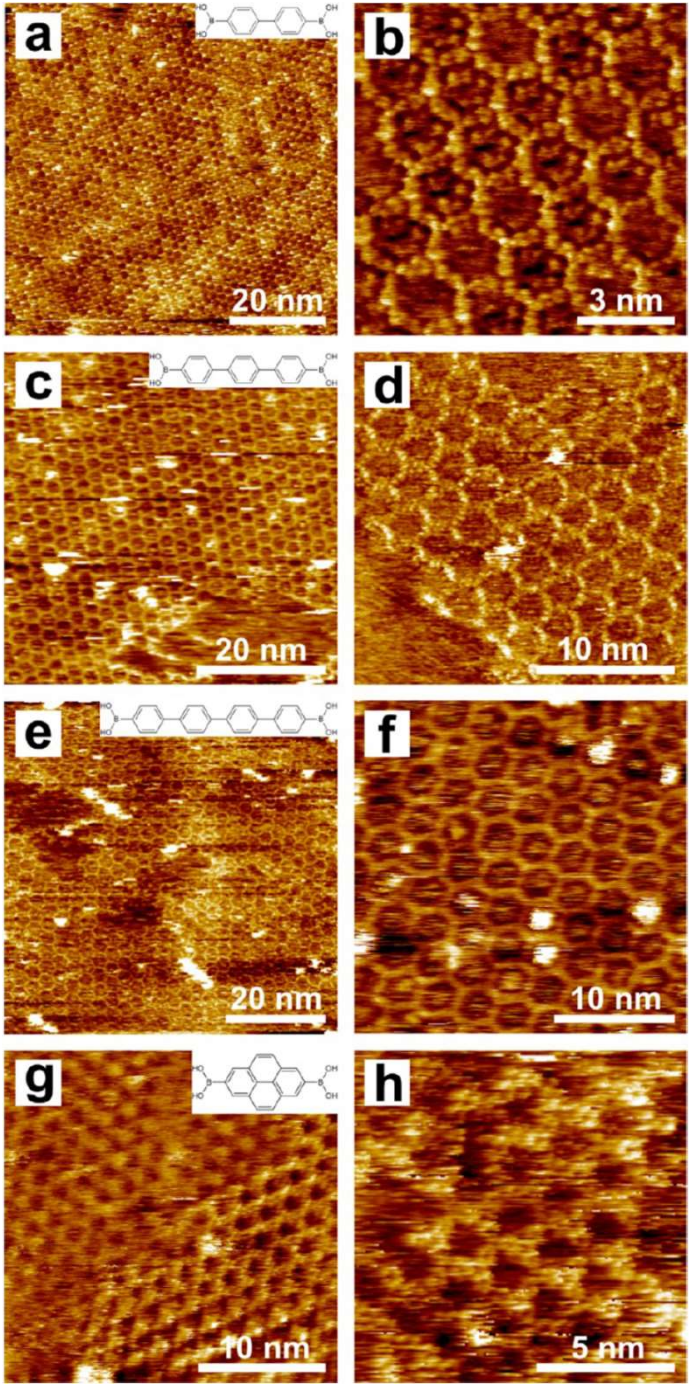
5



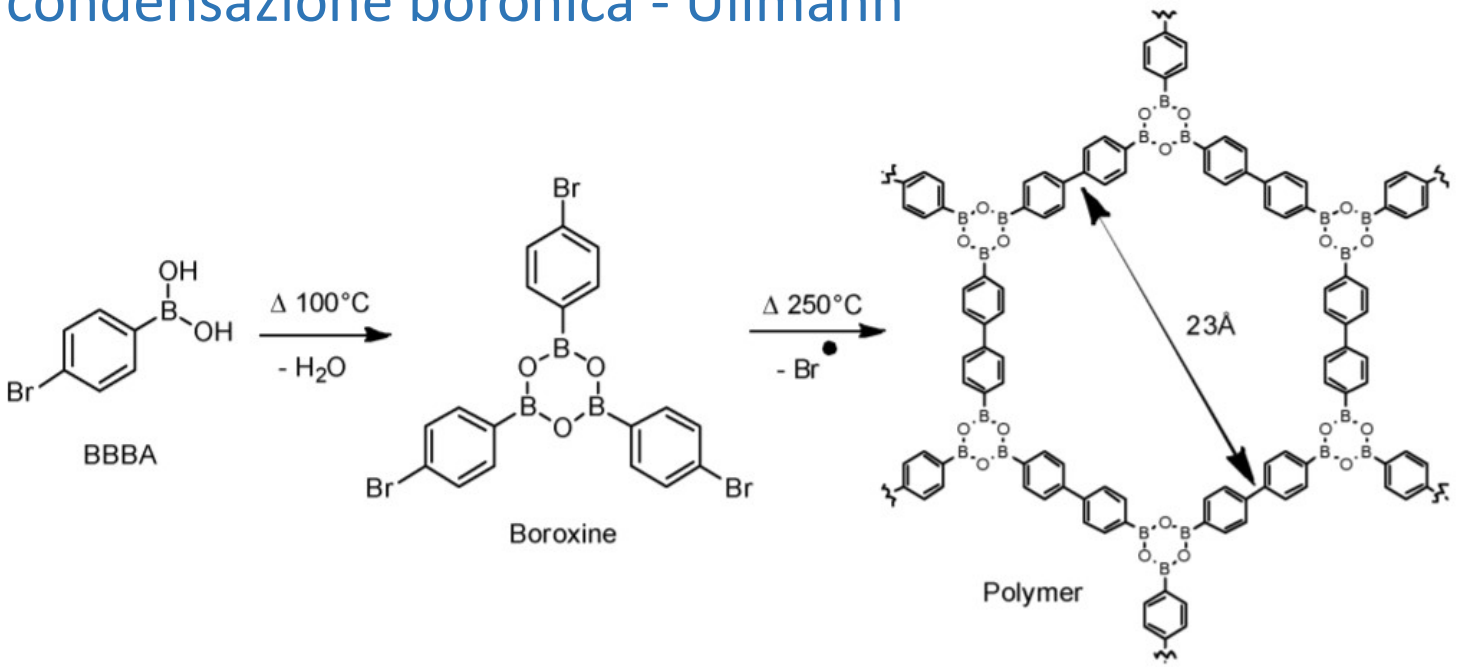
!! Se metto i precursori in un crogiolo e tento di sublimarli

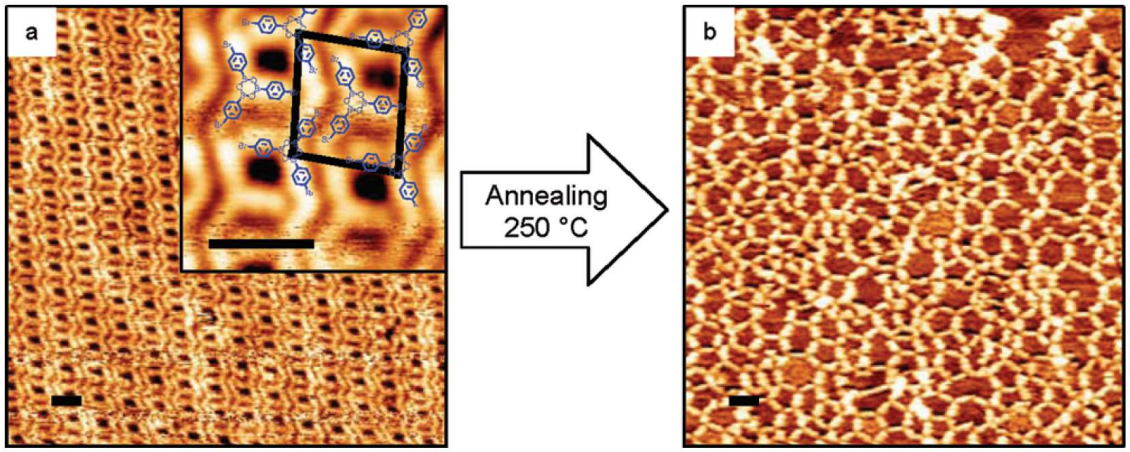
→ Condensano nel crogiolo

→ preparazione in soluzione

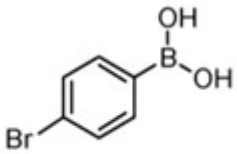


Sequenza condensazione boronica - Ullmann



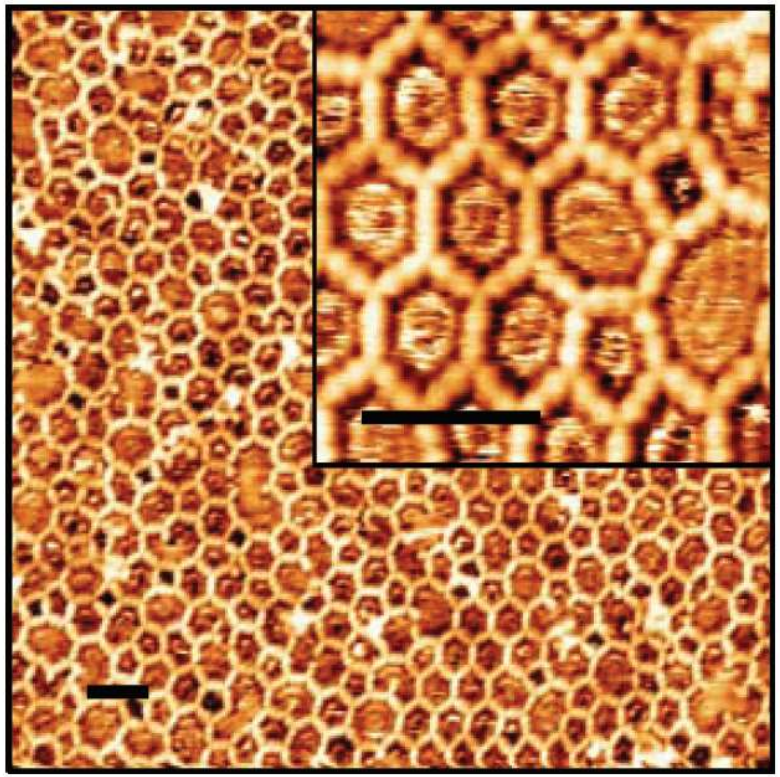


J. Phys. Chem. C 2012, 116, 4819–4823



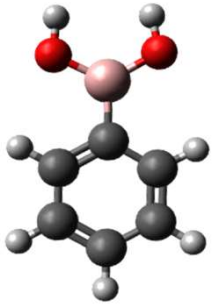
BBBA

Ts=250°C

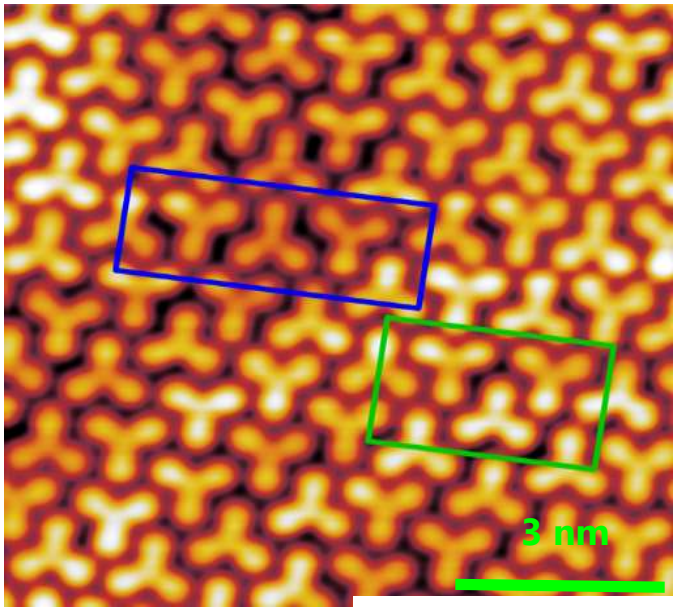


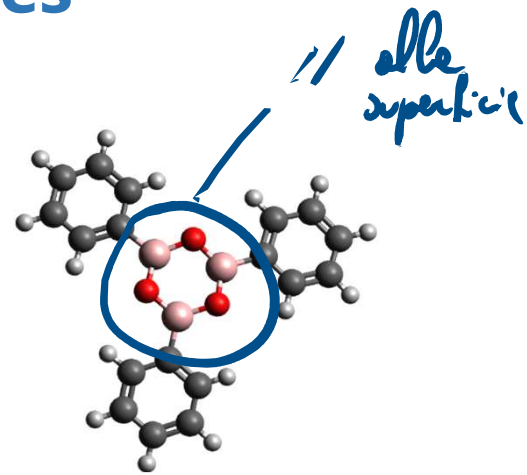
J. Phys. Chem. C 2012, 116, 4819–4823

Boroxine macromolecules

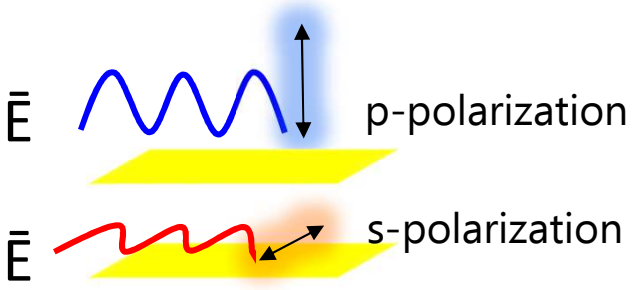


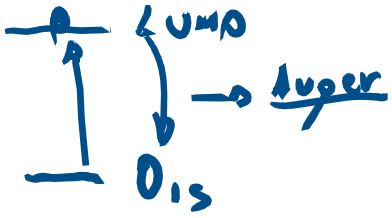
Phenylboronic acid
on Au(111)

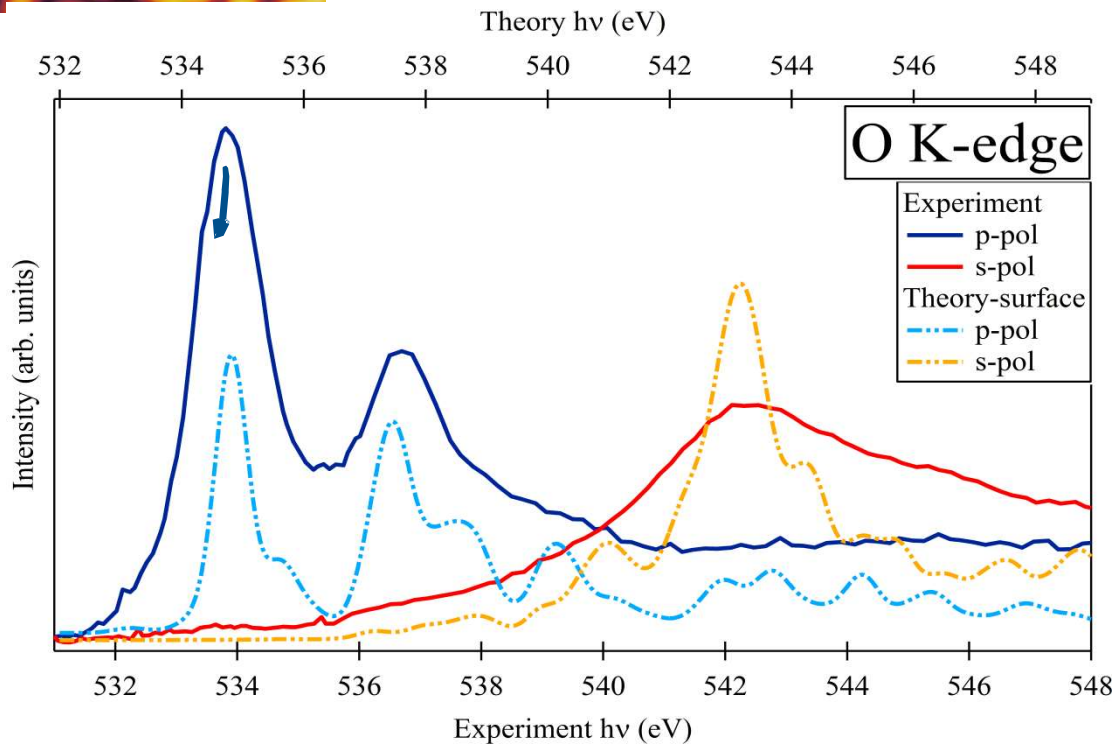




On surface synthesis
Triphenylboroxine





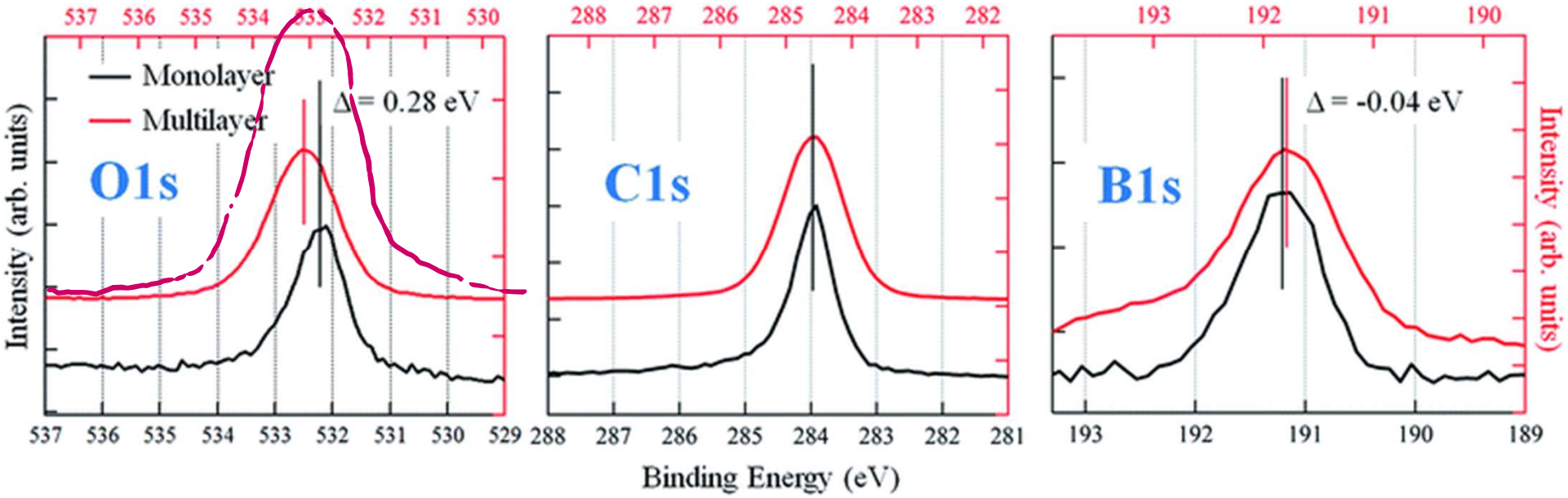


Chem. Sci., 2017, 8, 3789-3798

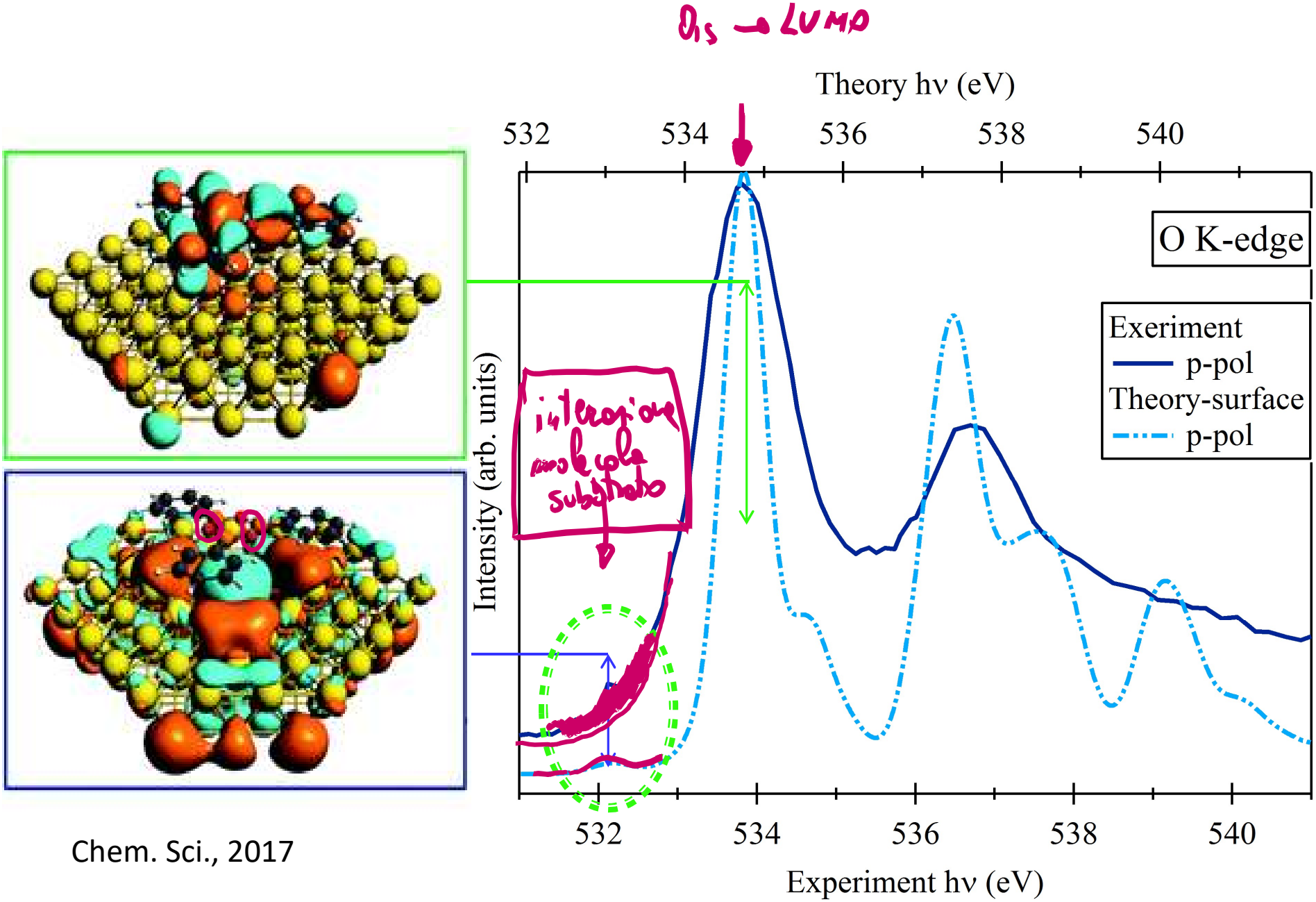
$T < -50°C$ → cresce multilayer del precursore

Il rapporto $\frac{O_{1s}}{B_{1s}}$ sia maggiore sul multilayer

$h\nu$ la probabilità di fotoemissione da un certo livello (O_{1s}, B_{1s} ...) dipende dalla cross section ($\sigma_{O_{1s}}$, $\sigma_{B_{1s}}$)

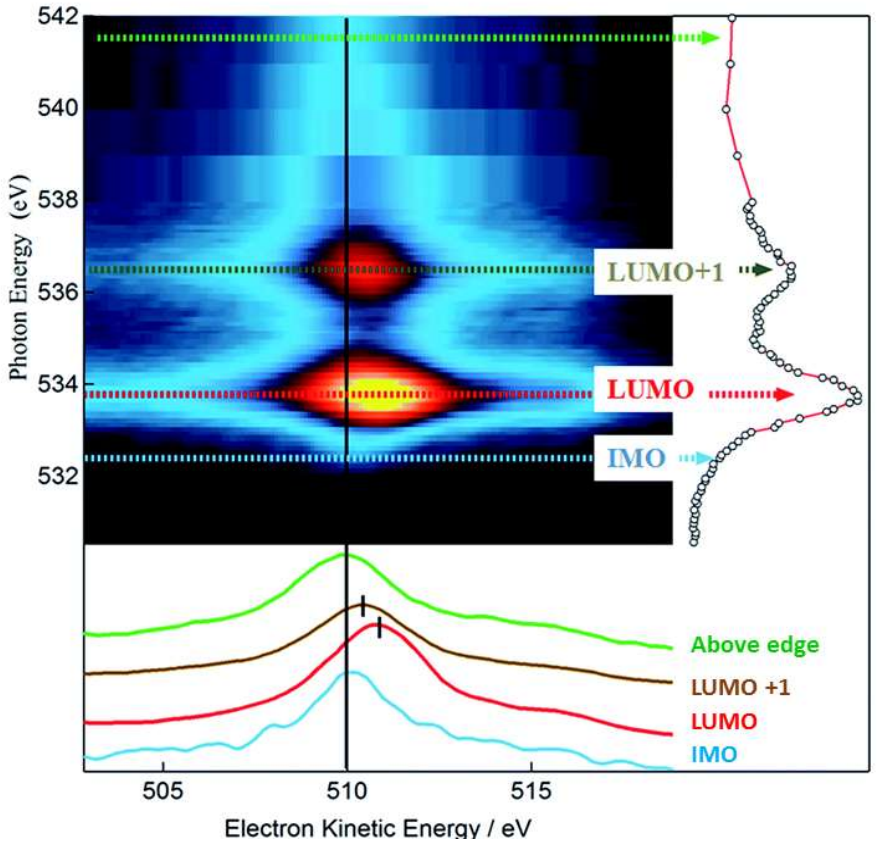


Chem. Sci., 2017, 8, 3789-3798



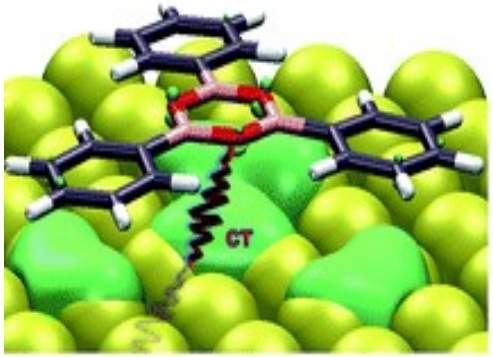
Chem. Sci., 2017

O k-edge RESPES: IMO promotes ultra-fast charge delocalization

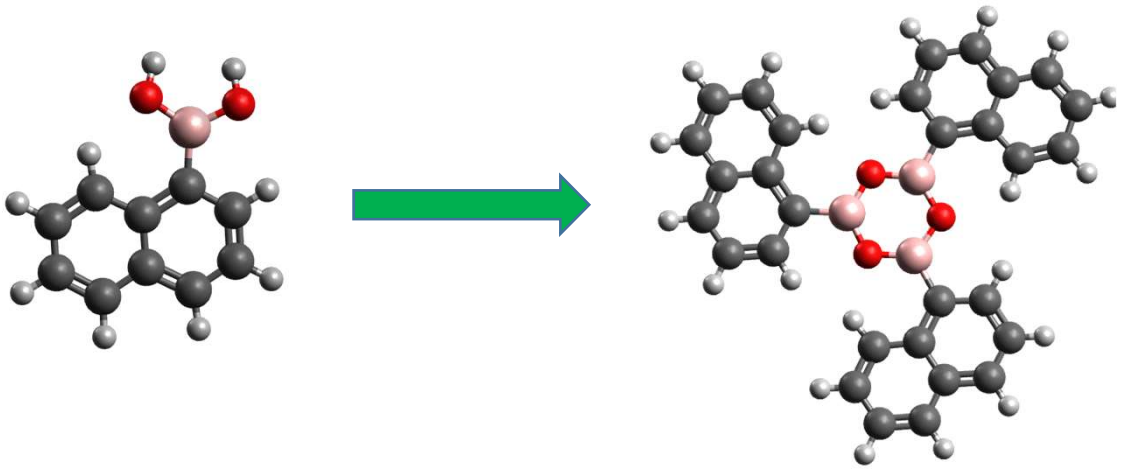


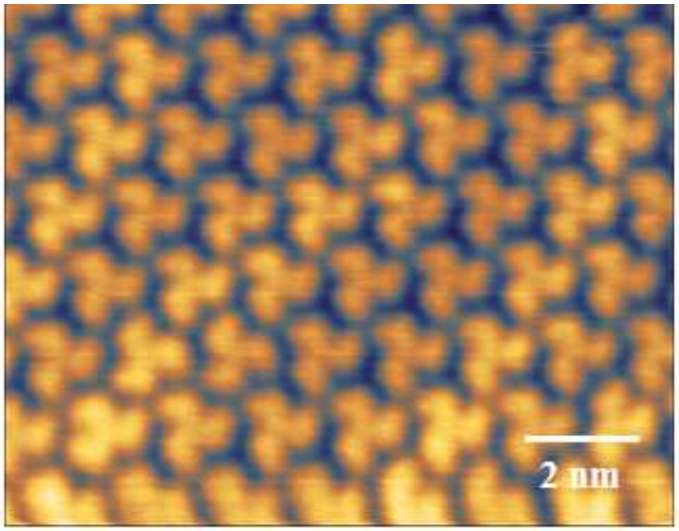
platforms for

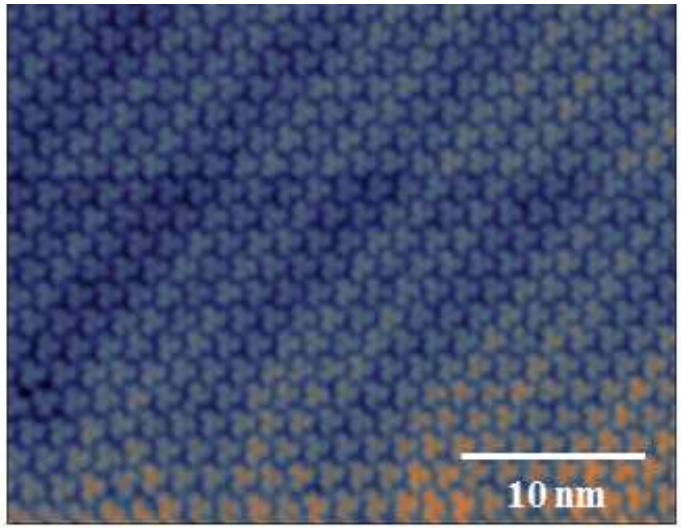
ultrafast charge transfer

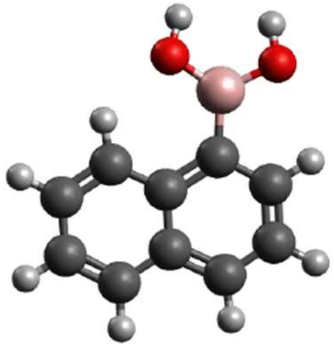


Toffoli et al., Chem. Sci., 2017, **8**, 3789-3798

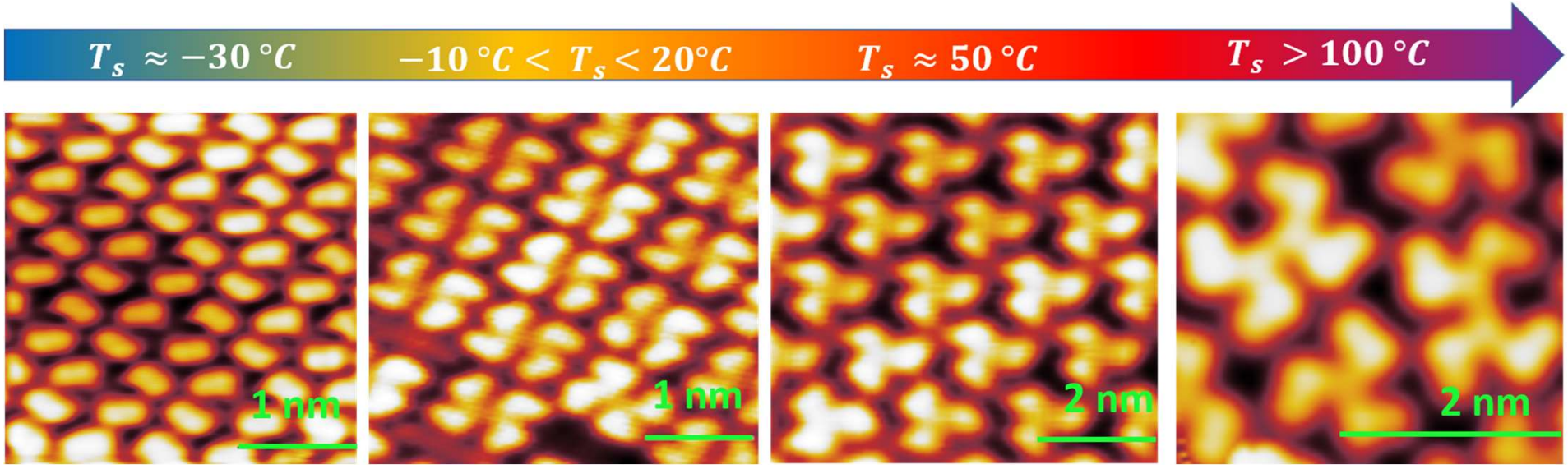


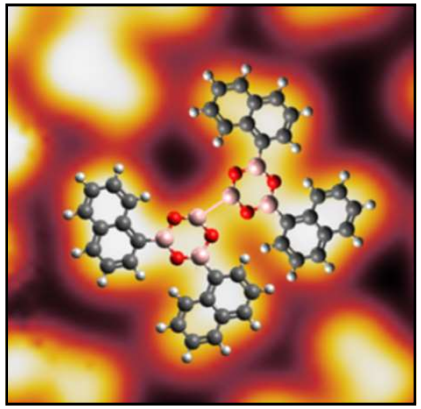

2 nm

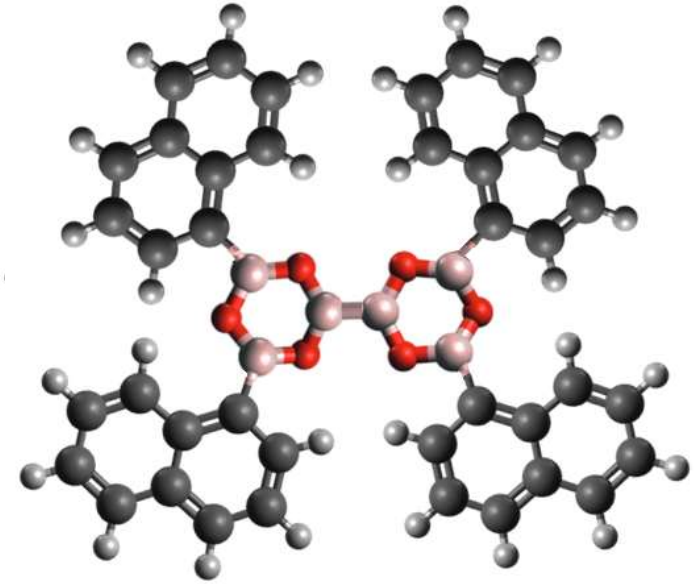

10 nm

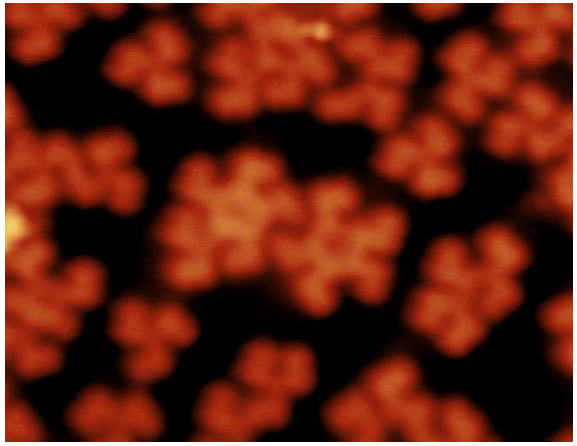


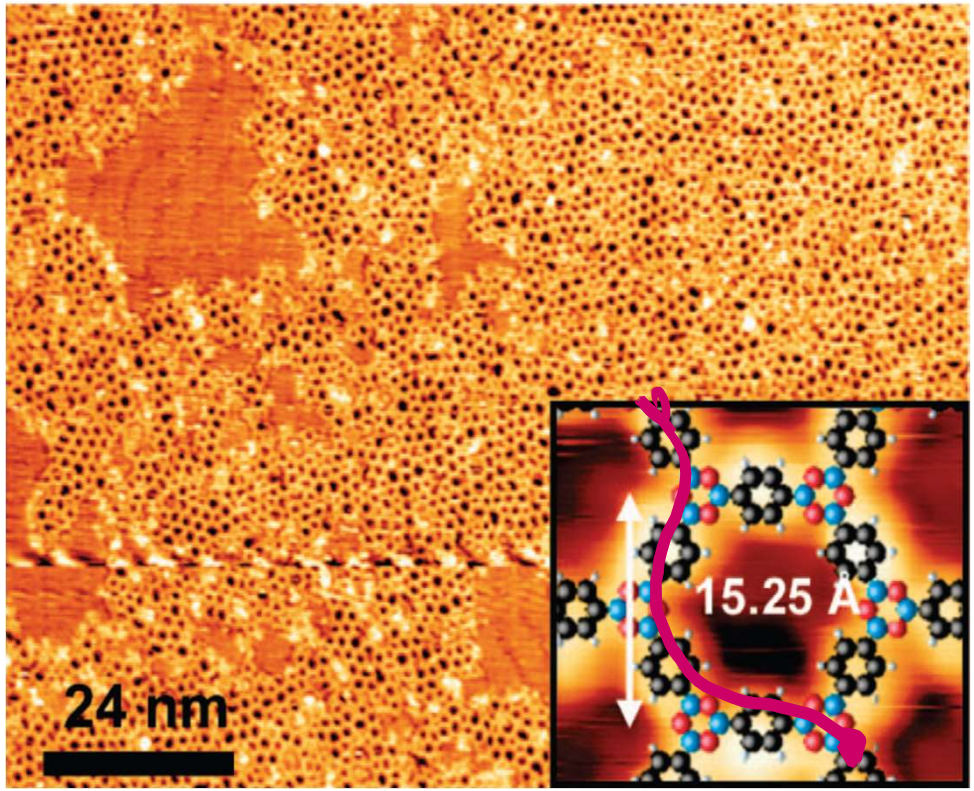
NBA su Au(111)











T. Faury et al., J. Phys. Chem. C 2012, 116, 4819−4823

non c'è la formazione di orbitali estesi

↓

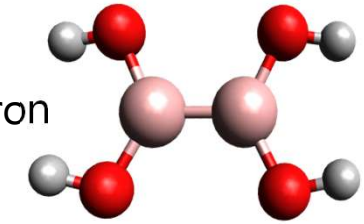
non c'è formazione di bande

DFT calculations:
Boroxine rings break the aromaticity of phenyl rings

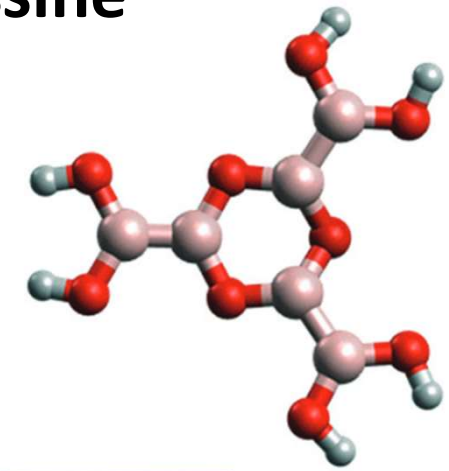
R. Wang, X. Zhang, S. Wang, G. Fu, J. Wang,
Phys.Chem.Chem.Phys.,2016,18,1258

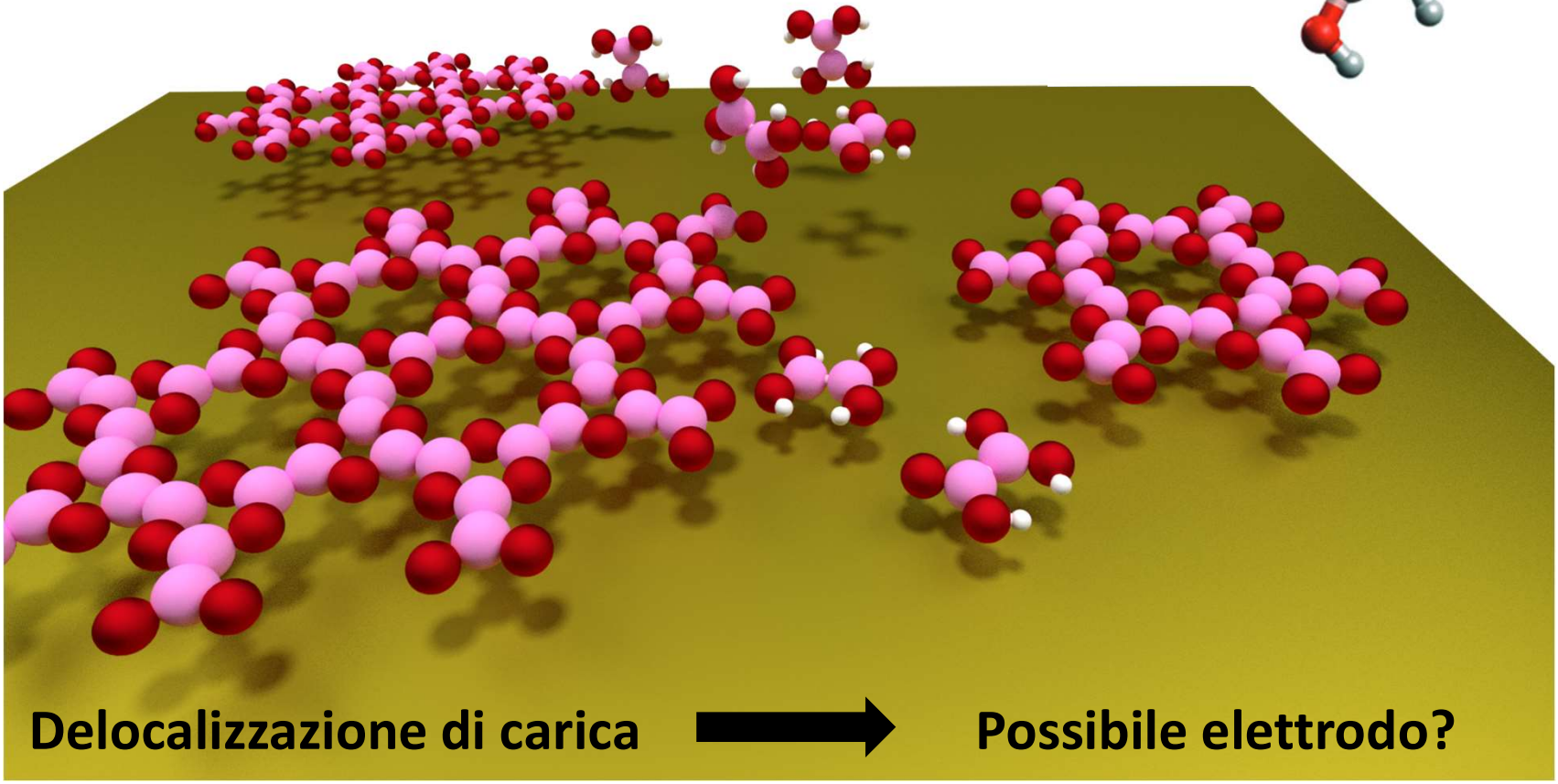
Framework di borossine

THDB
Tetra**h**ydroxy**di**b**o**ron

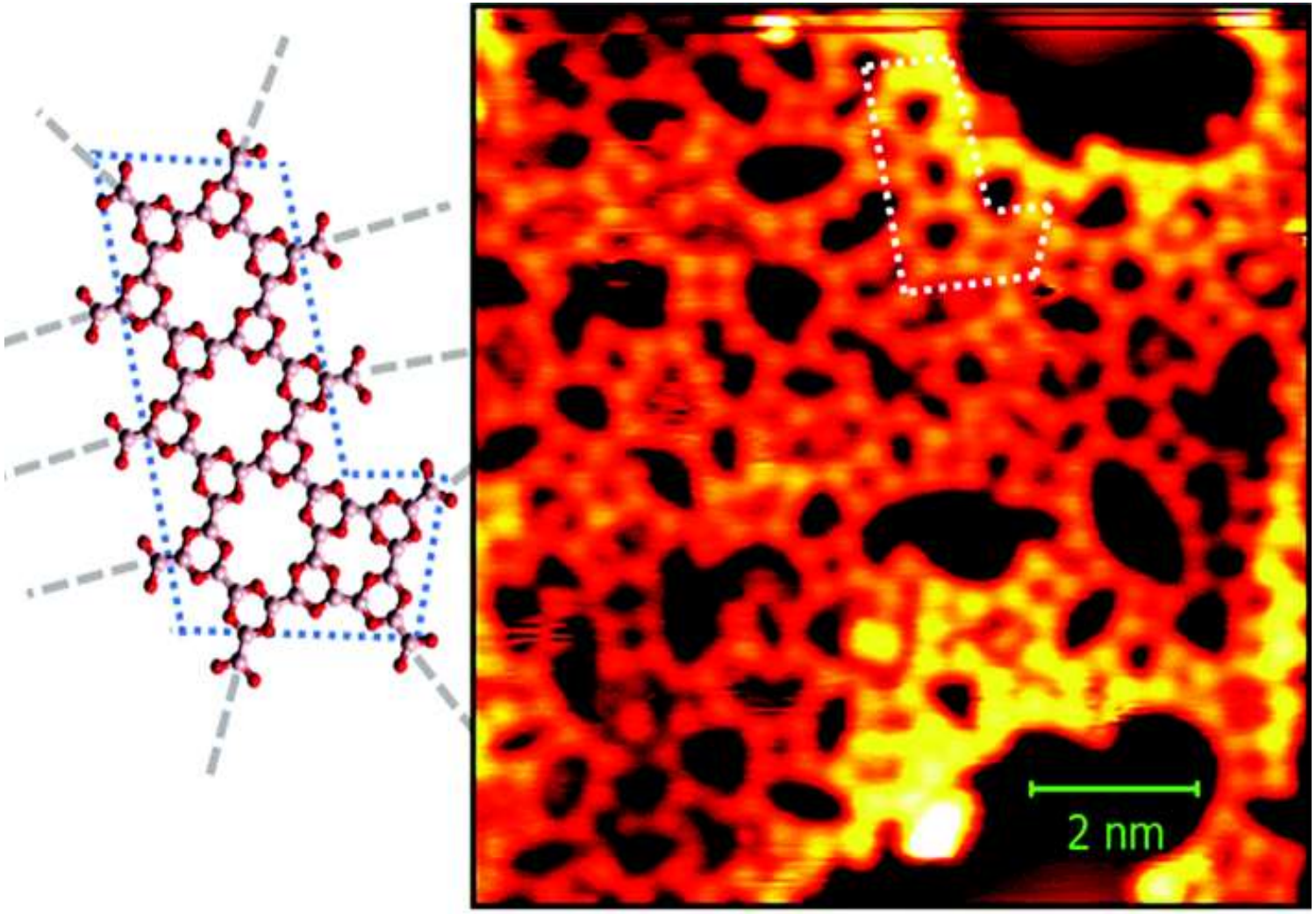


B
O
H





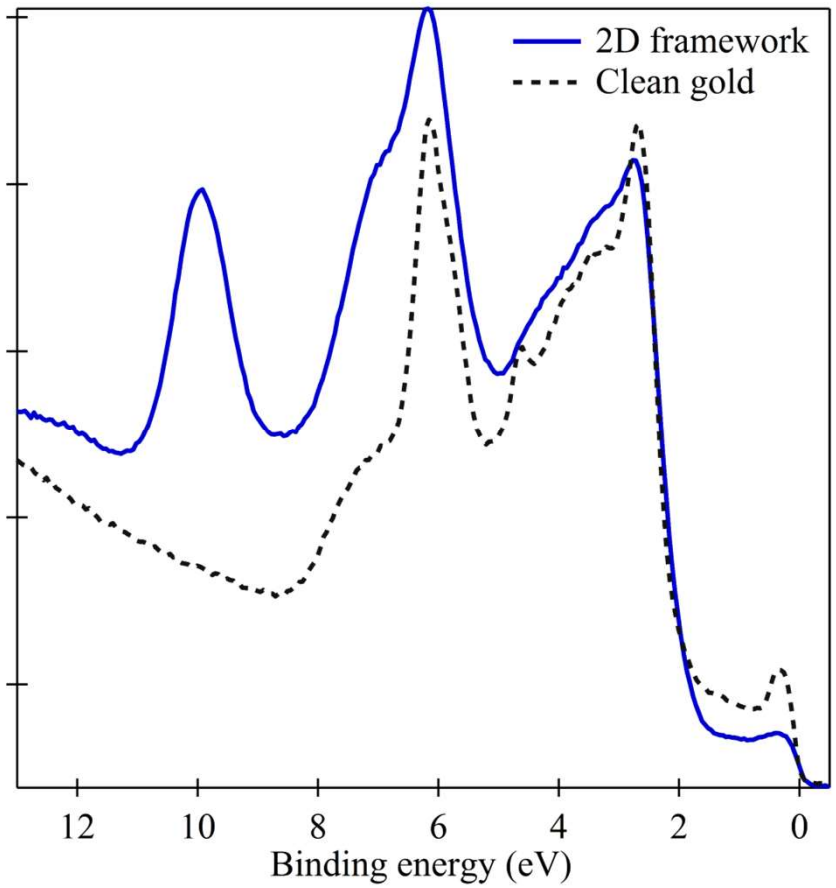
Chem. Commun., 2018

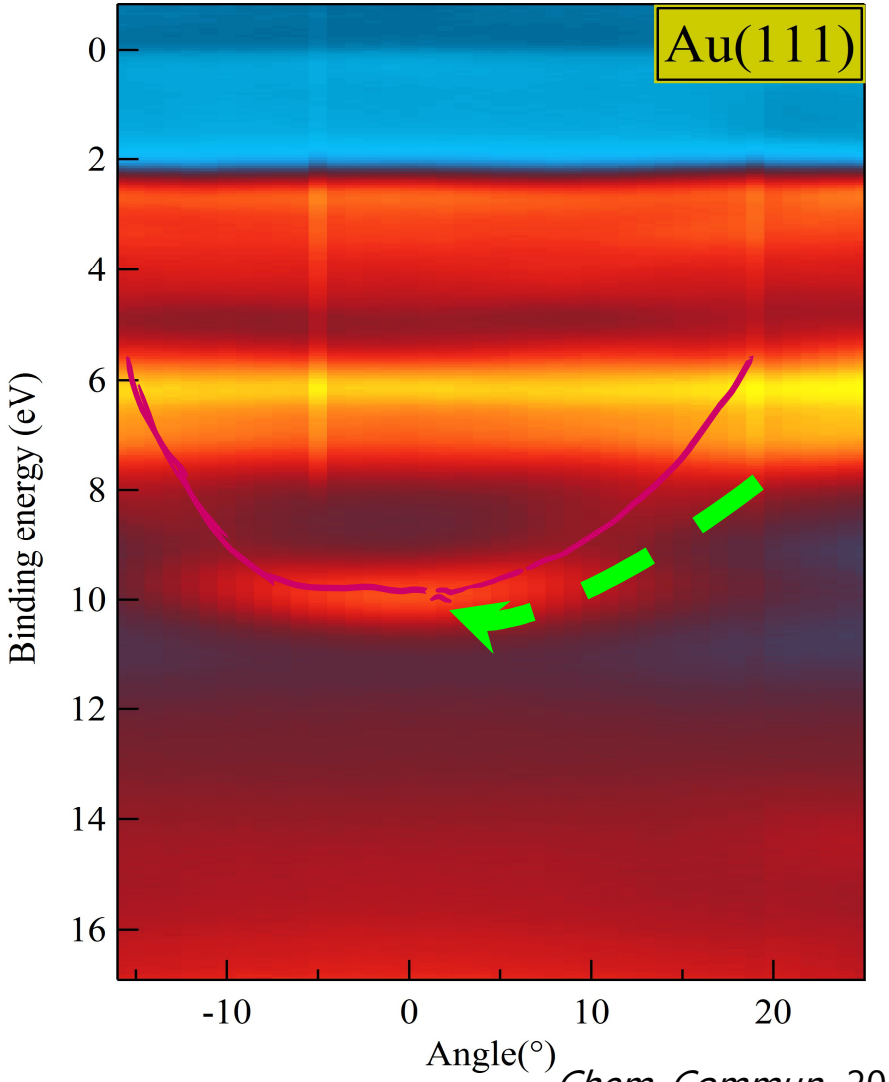


vitreous morphology

Proliferation of defects

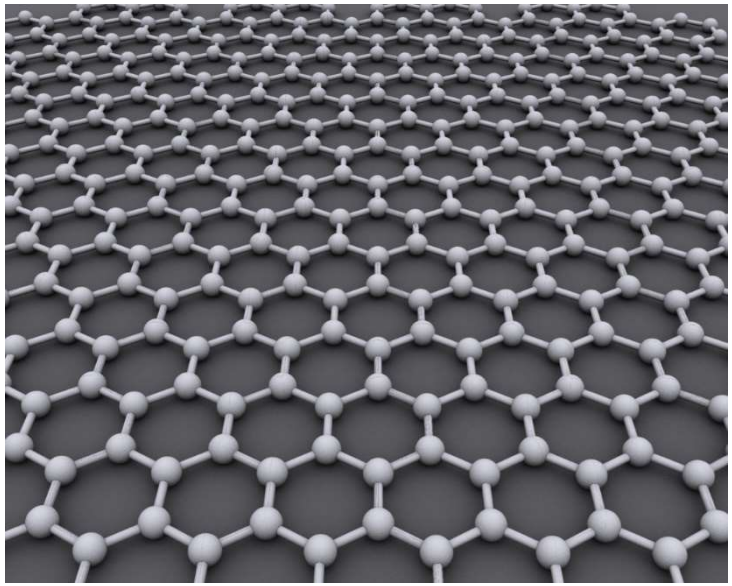
Chem. Commun., 2018

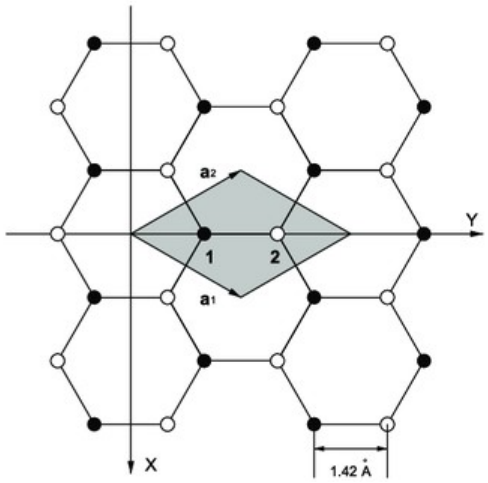


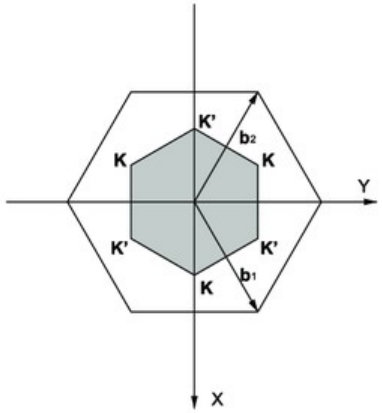


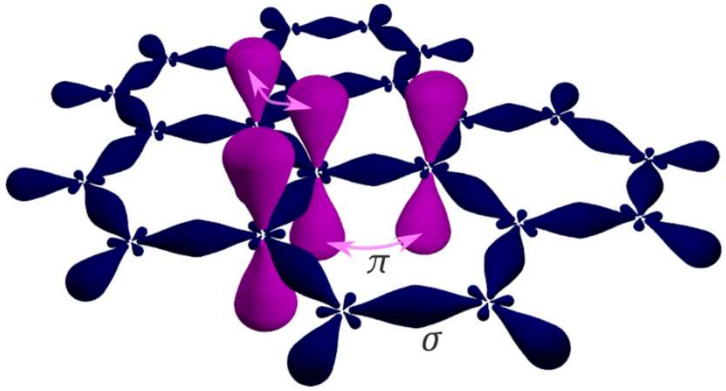
Chem. Commun., 2018

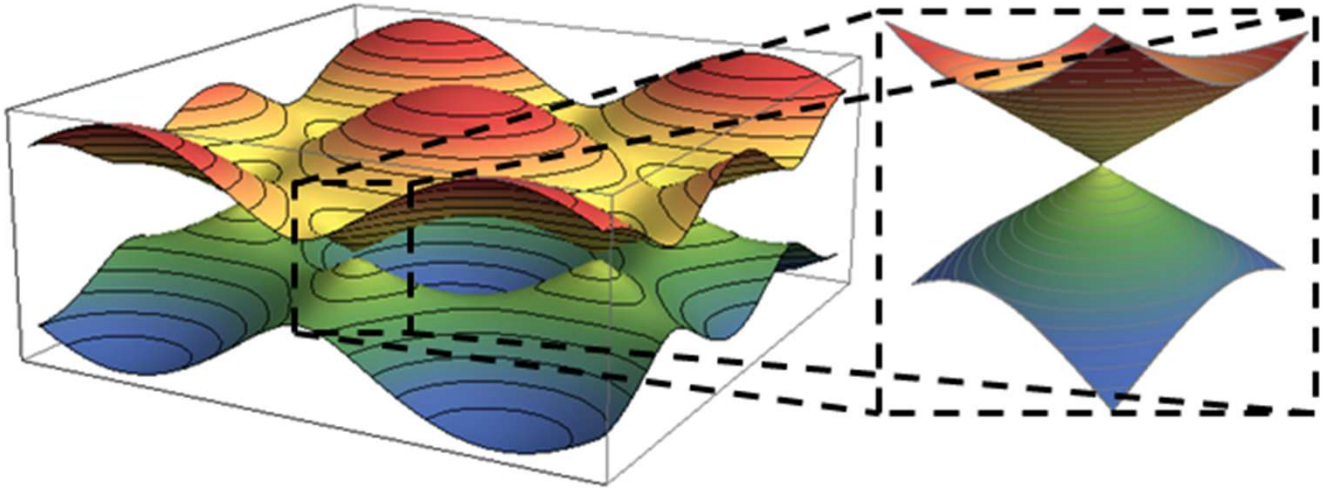
Band dispersion at room temperature – electron delocalization

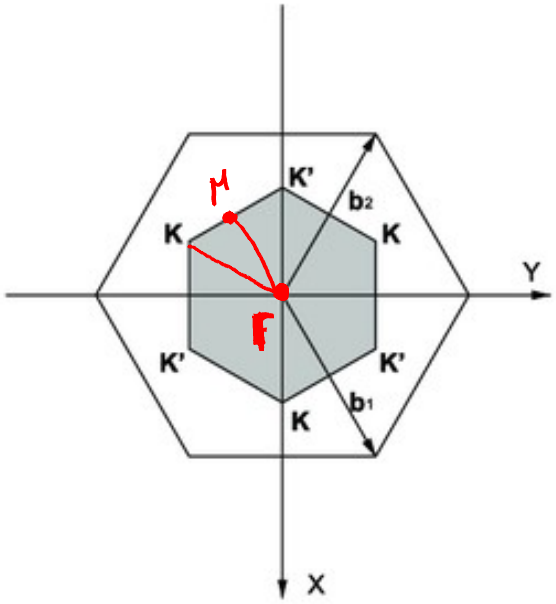


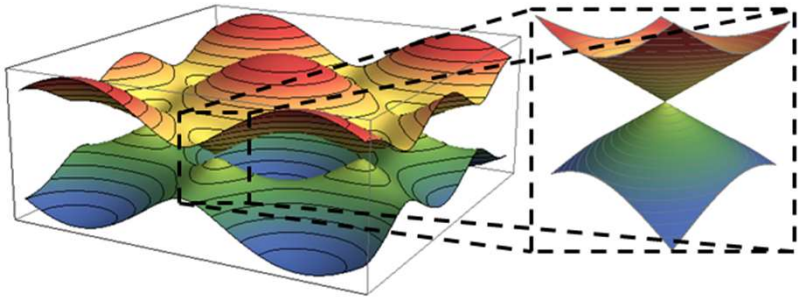

a2
a1
1
2
Y
X
1.42 Å

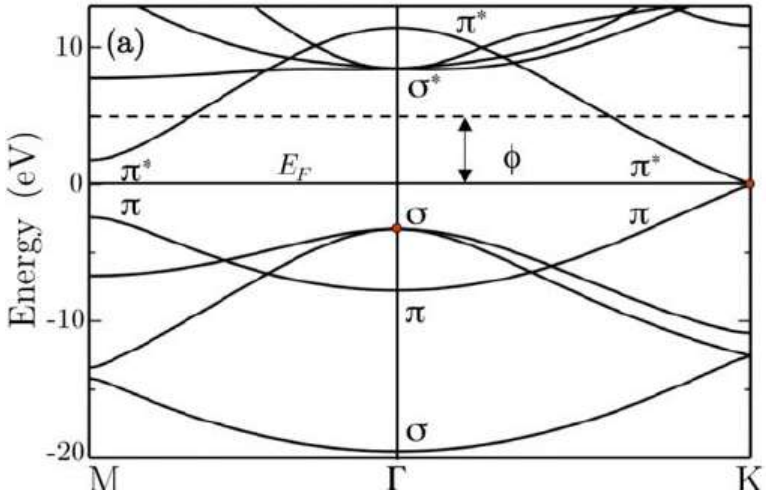

K'
b2
K
K
Y
K'
K'
K
b1
X

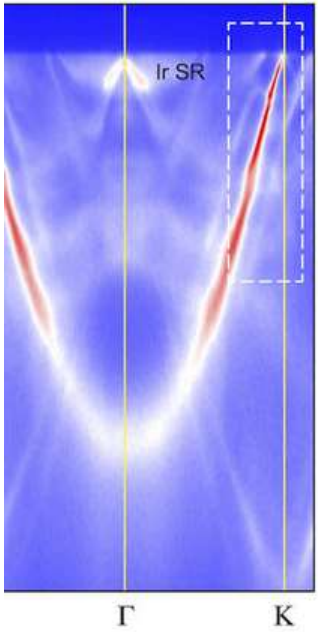

π
σ

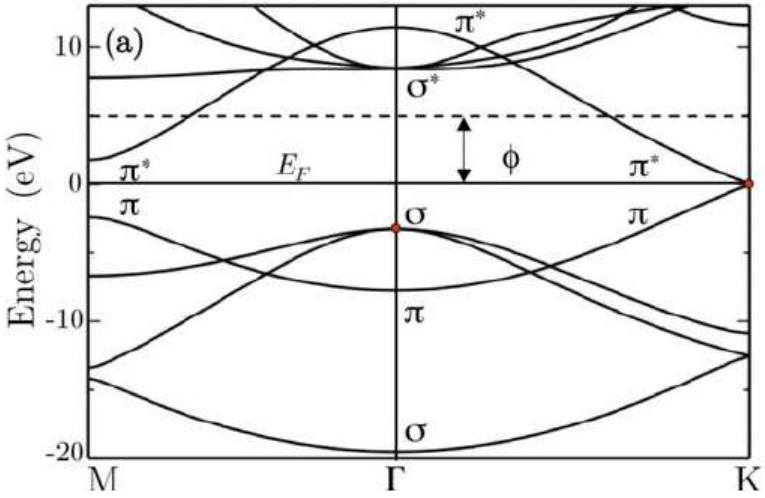



M
K'
b2
K
K
Y
Γ
K'
K'
b1
K
X



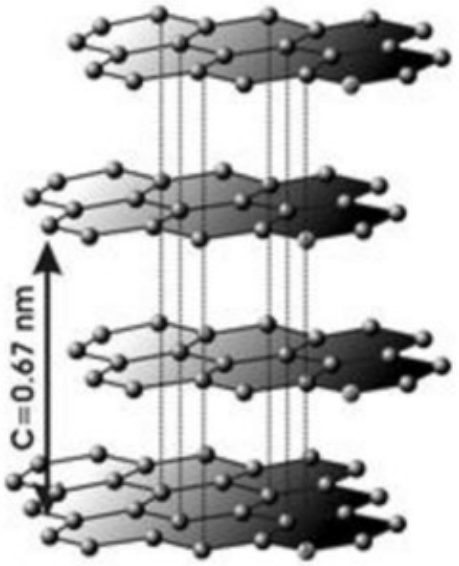

(a)
10
0
-10
-20
Energy (eV)
π*
σ*
ϕ
π*
π*
E_F
π
σ
π
π
σ
M
Γ
K

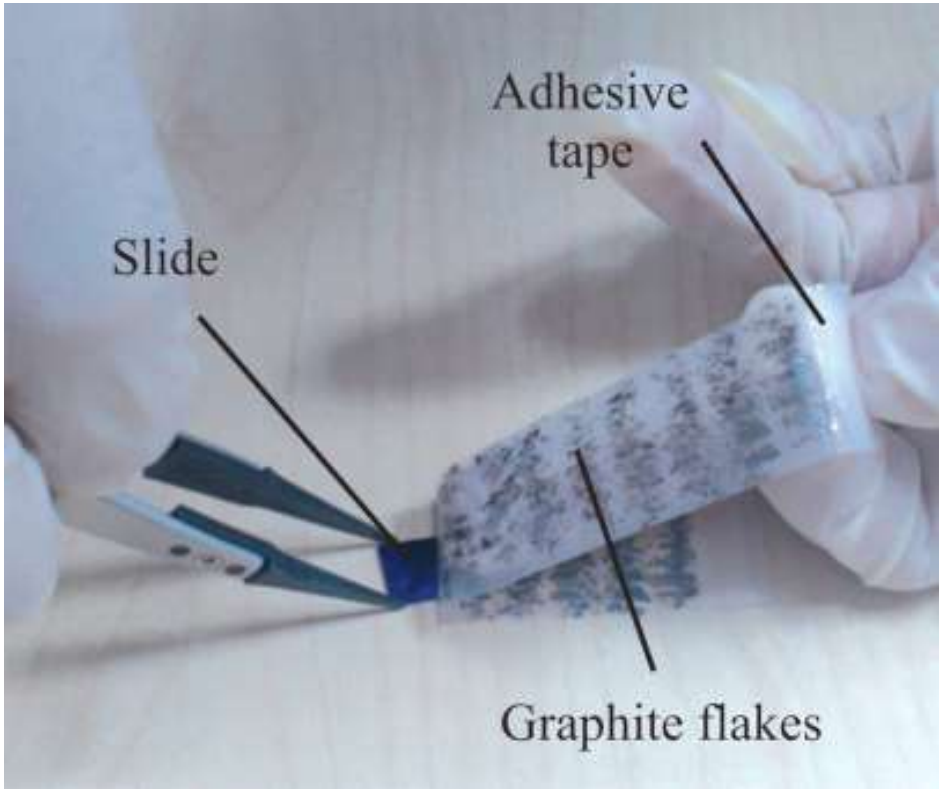




•Journal of Physics Condensed Matter 2015 27(30)

Sintesi di grafene

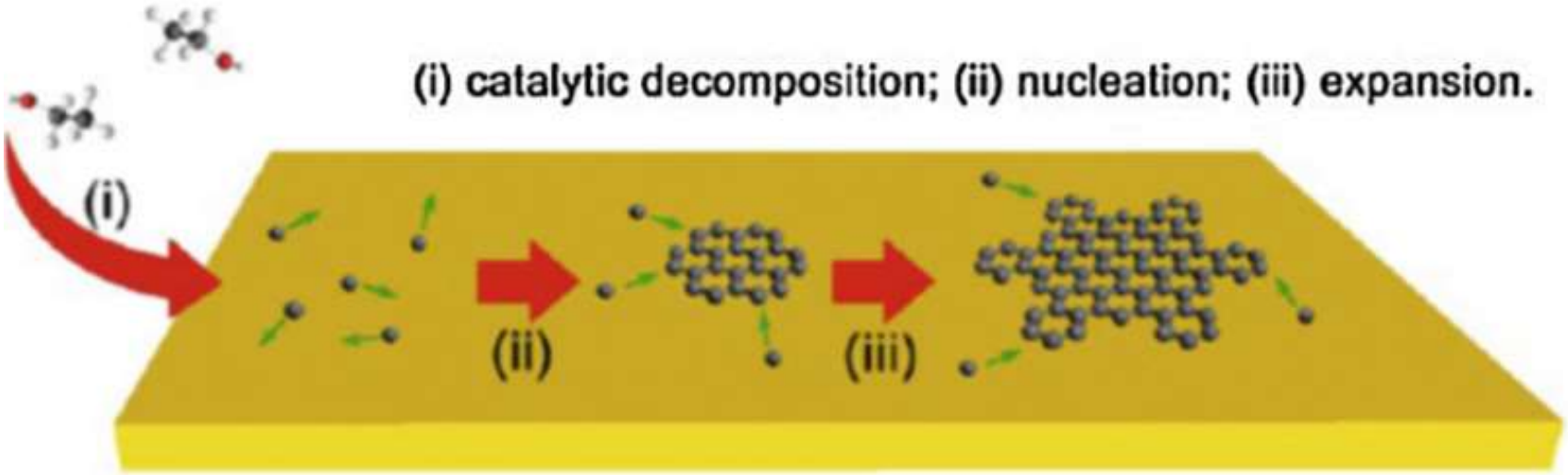



Adhesive
tape
Slide
Graphite flakes


Andre Geim

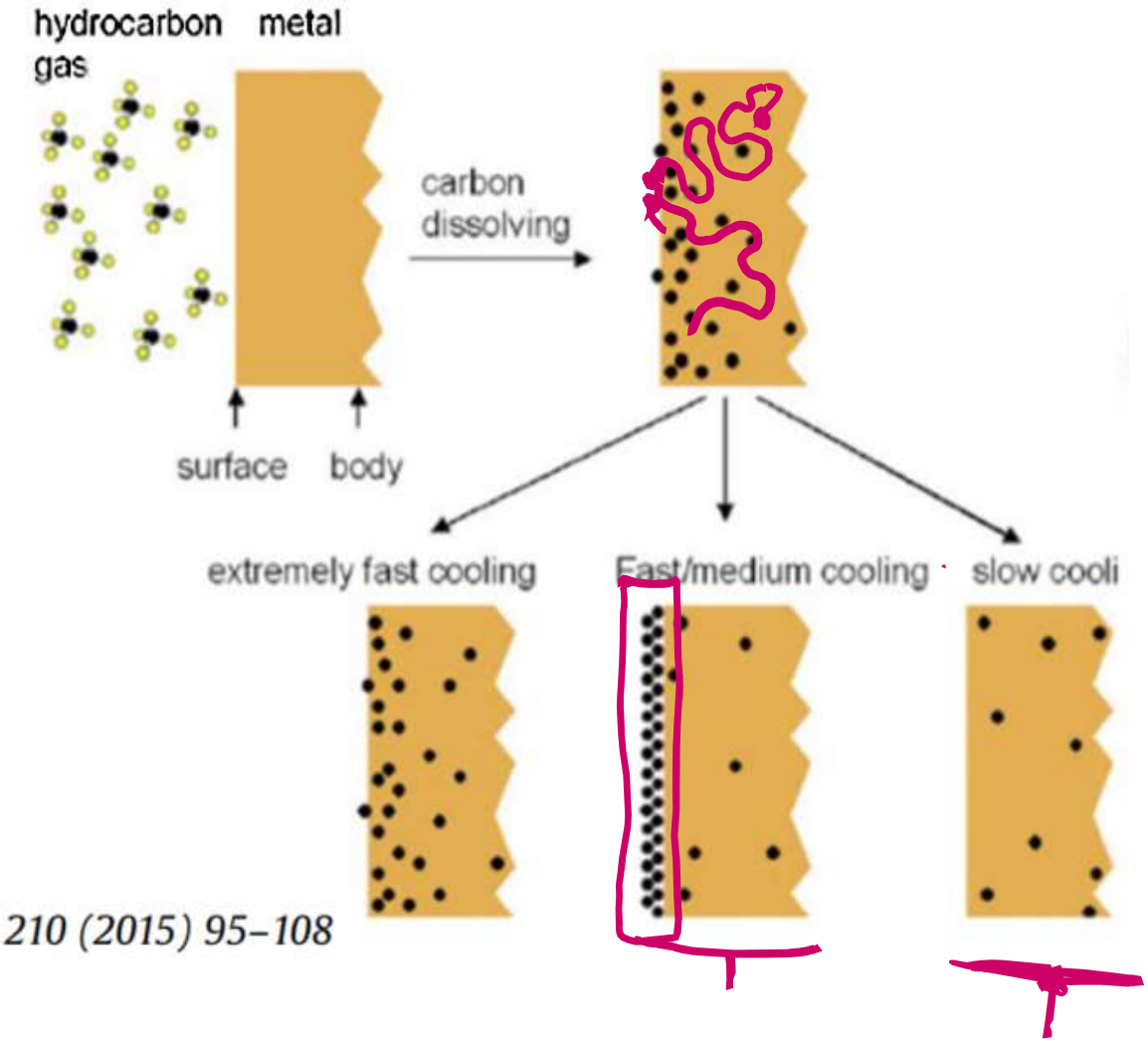
Chemical Vapour Deposition

Cu (111), 1000 °C



X. Chen et al./Synthetic Metals 210 (2015) 95–108

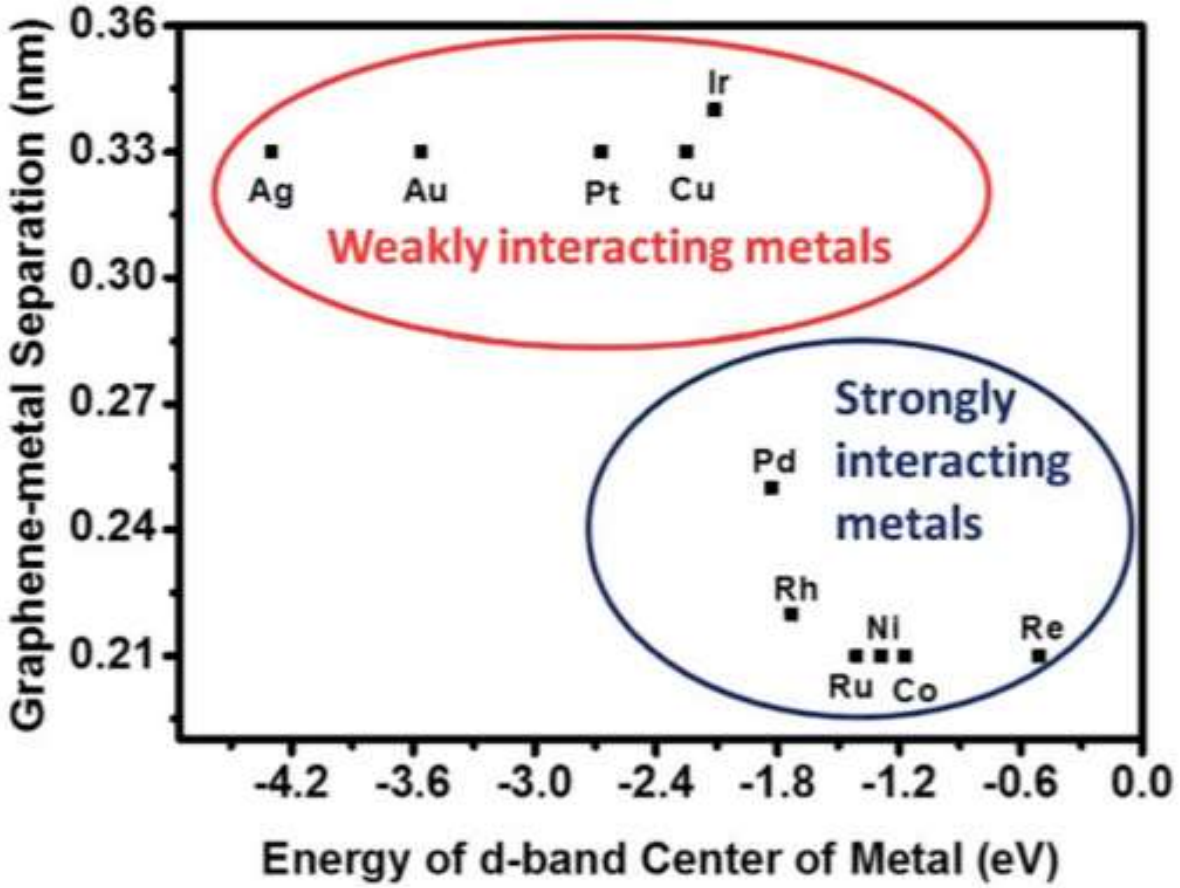
Ni(111)

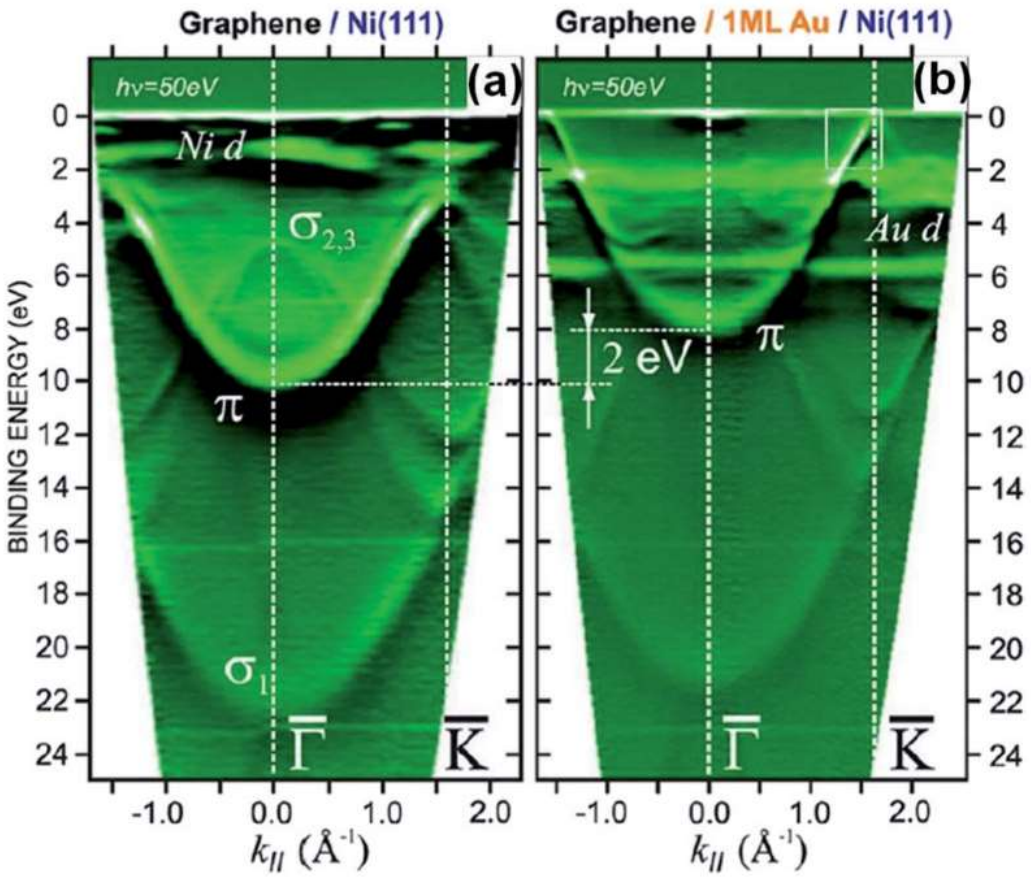


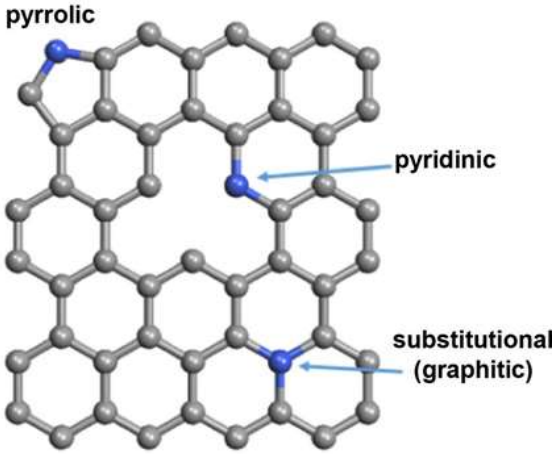
X. Chen et al./Synthetic Metals 210 (2015) 95–108

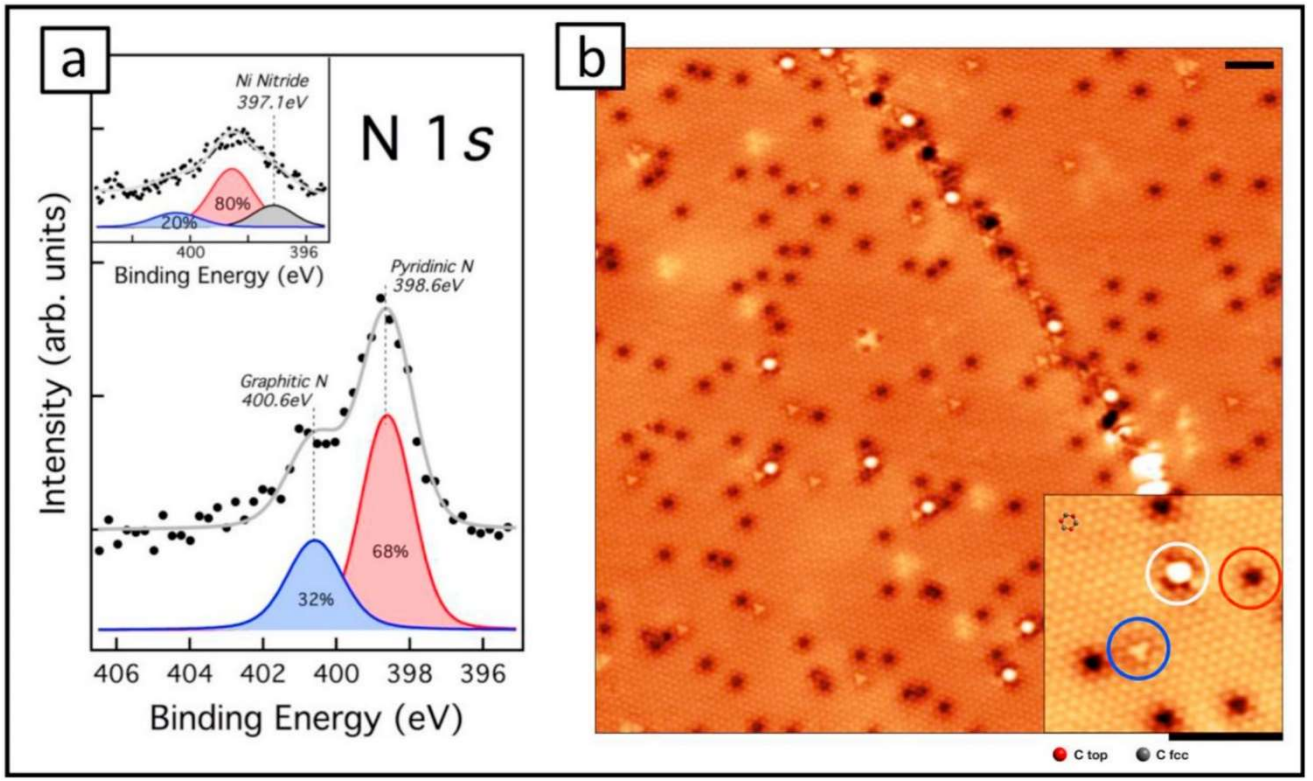
Table 1 Carbon solubilities (atom%) in different transition metals at 1000 °C according to ref. 17

Metal	Carbon solubility (atom%) at 1000 °C
Co	3.41
Ni	2.03
Cu	0.04
Ru	1.56
Rh	0.89
Pd	5.98
Ag	0.01
Re	4.39
Ir	1.35
Pt	1.76
Au	0.01

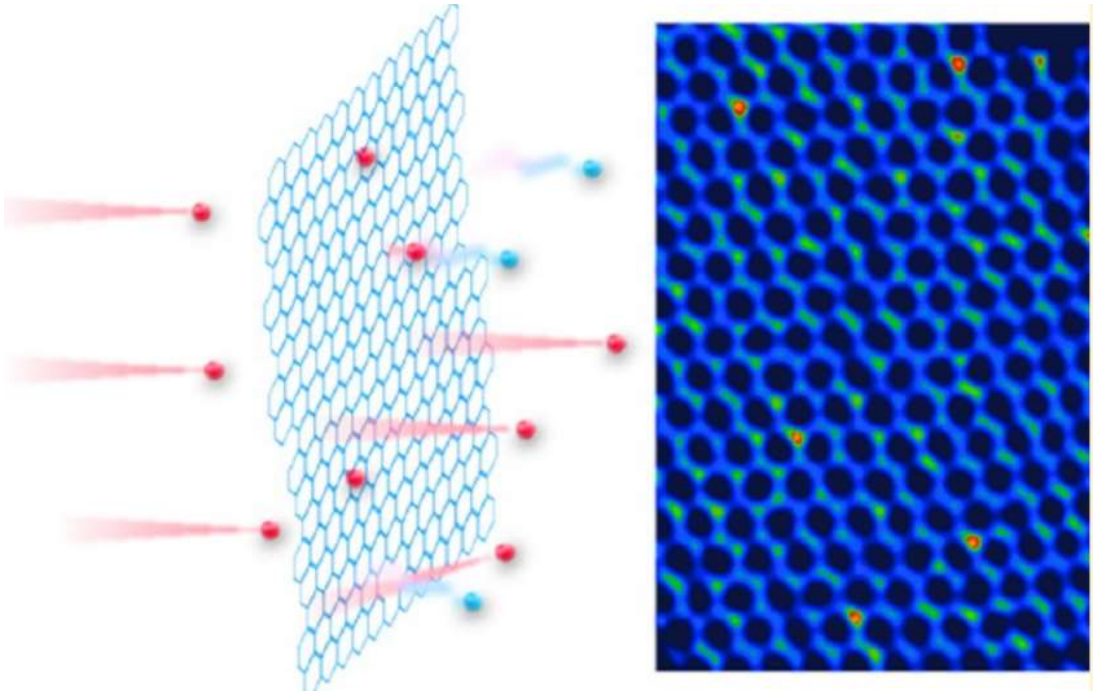

Graphene-metal Separation (nm)
0.36
0.33
0.30
0.27
0.24
0.21
Ag
Au
Pt
Cu
Ir
Weakly interacting metals
Strongly interacting metals
Pd
Rh
Ni
Ru
Co
Re
-4.2
-3.6
-3.0
-2.4
-1.8
-1.2
-0.6
0.0
Energy of d-band Center of Metal (eV)

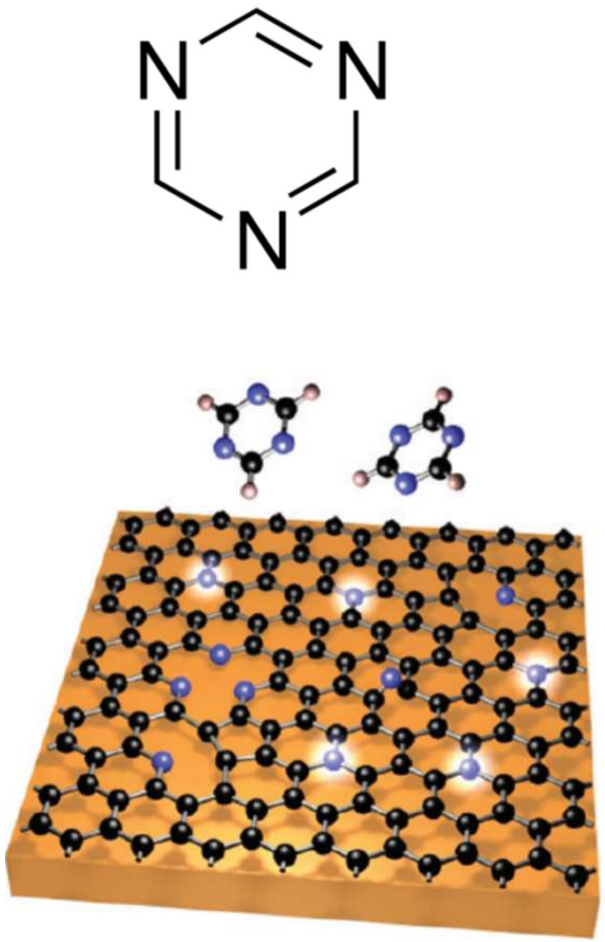

Graphene / Ni(111)
Graphene / 1ML Au / Ni(111)
hν=50eV
hν=50eV
(a)
(b)
Ni d
σ2,3
π
σ1
Au d
2 eV
Γ̄
K̄
Γ̄
K̄
BINDING ENERGY (eV)
0
2
4
6
8
10
12
14
16
18
20
22
24
-1.0
0.0
1.0
2.0
kII (Å-1)
kII (Å-1)

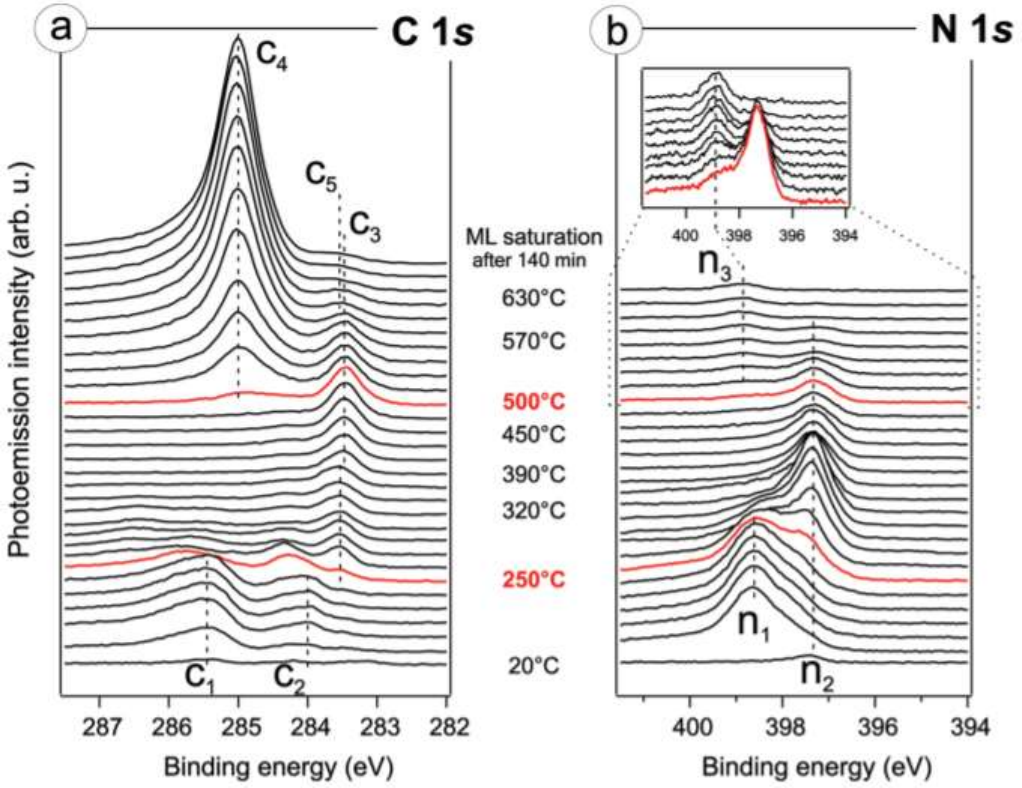




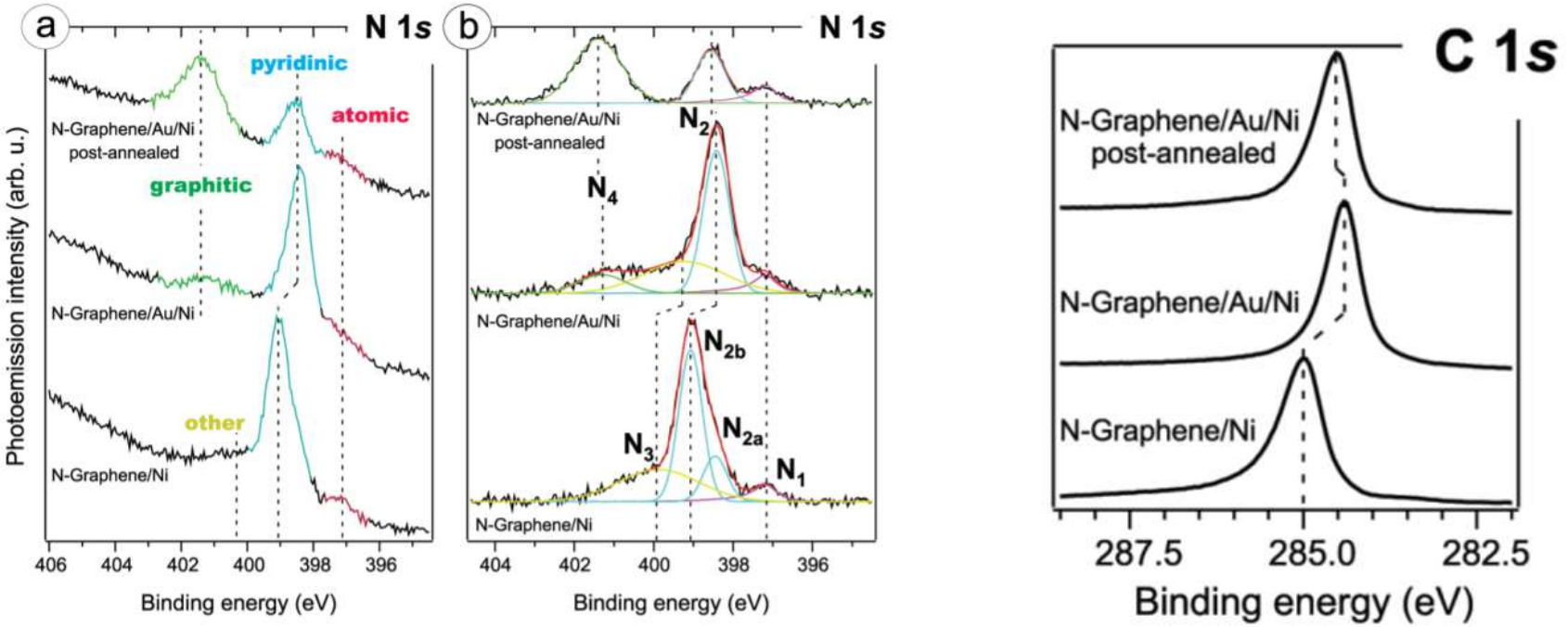
Carbon 171 (2021) 704–710



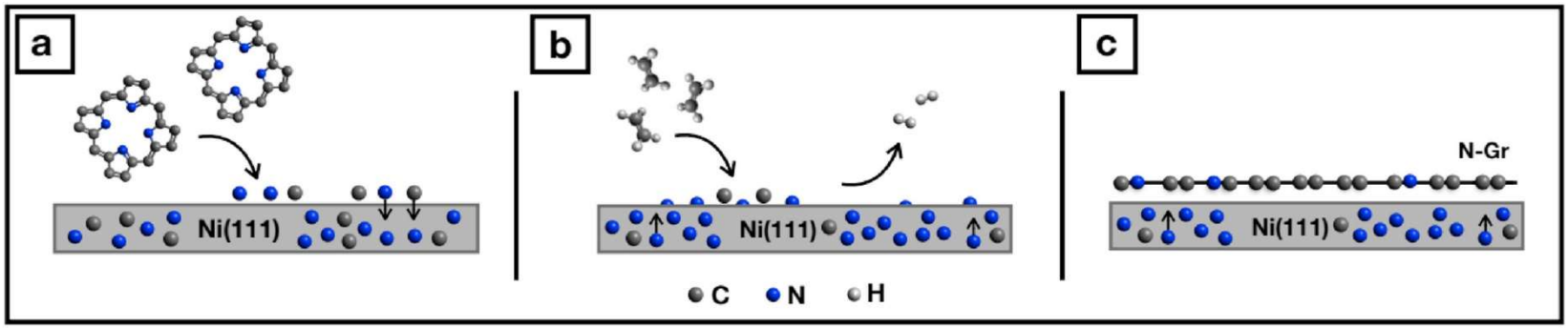




Nano Lett. 2011, 11, 5401–5407

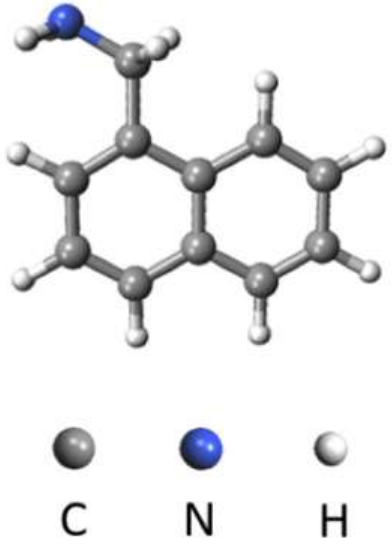


Nano Lett. 2011, 11, 5401–5407

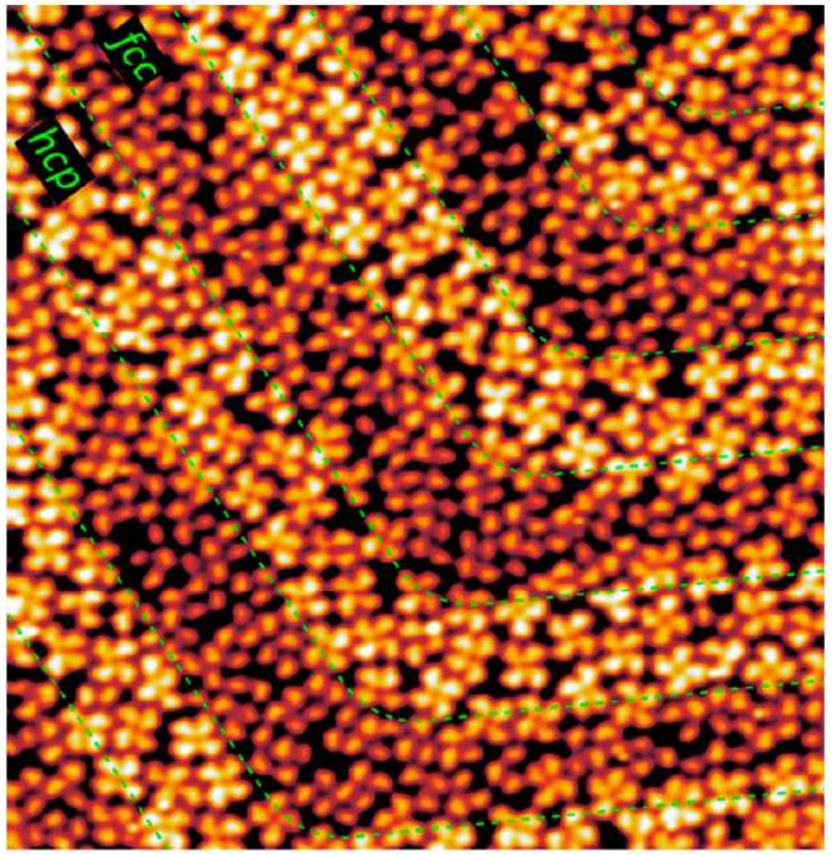


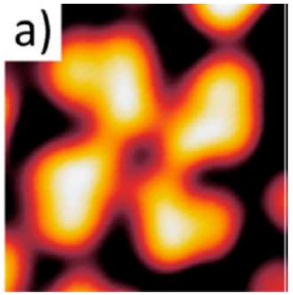
Carbon 171 (2021) 704–710

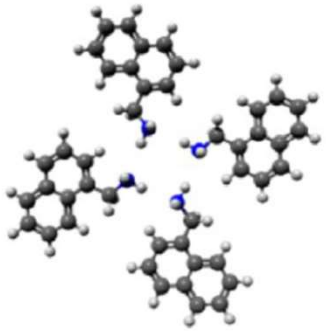
Naphthylmethyl amine (NMA)



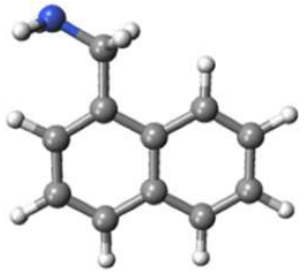
on Au(111)



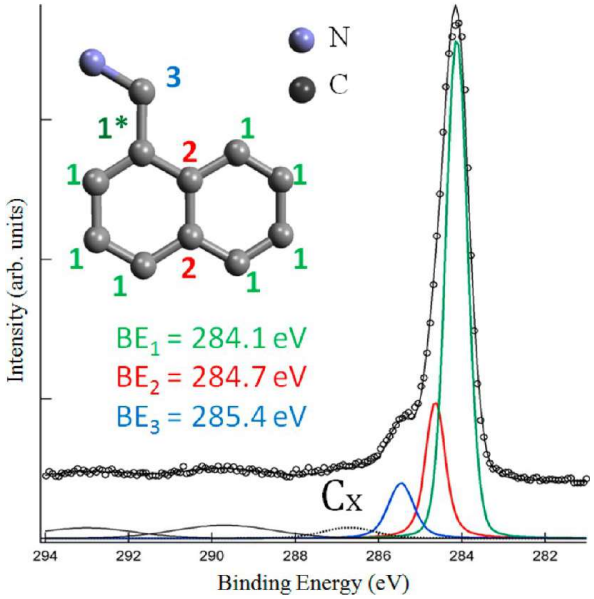


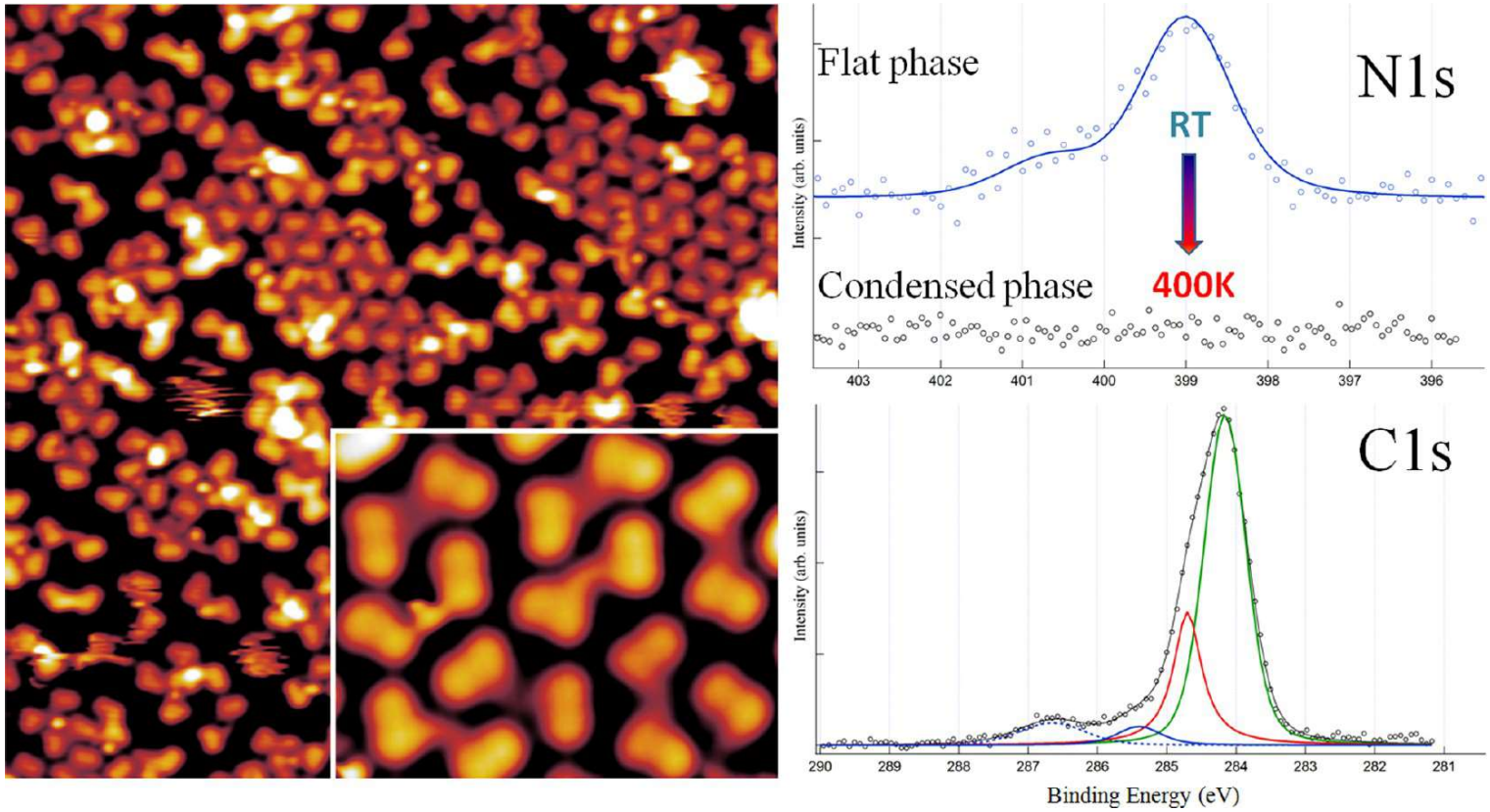


J. Phys. Chem. C 2016, 120, 11, 6104–6115

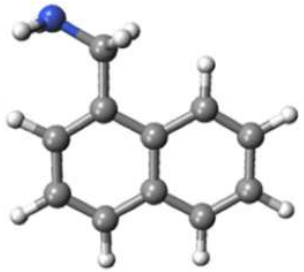


on Au(111)

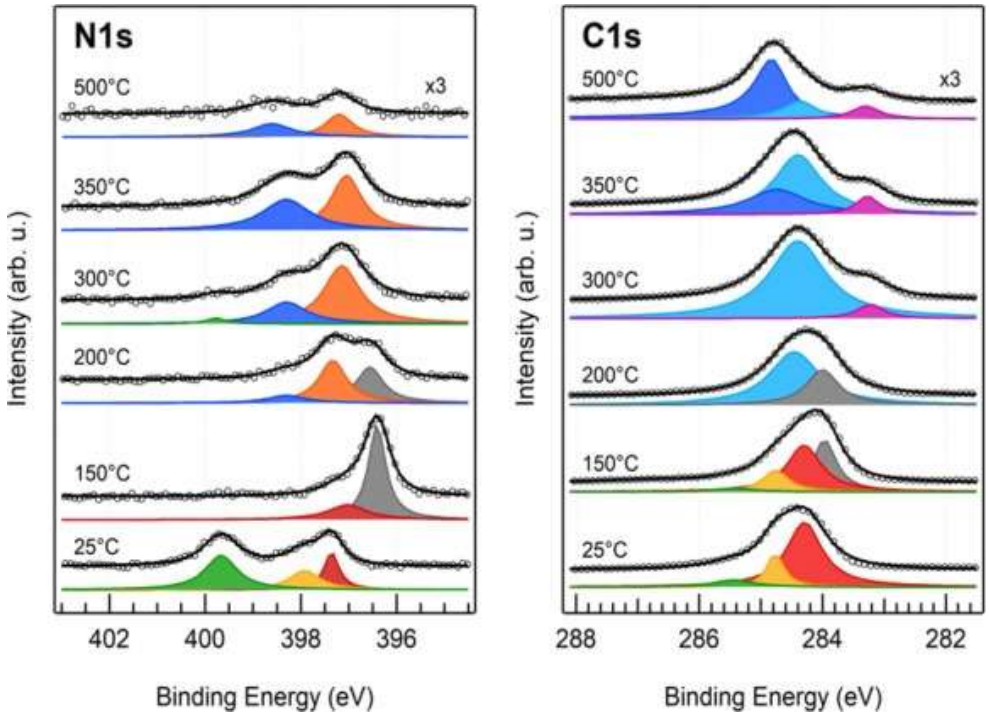

N
C
3
1*
2
1
1
1
1
2
1
1
1
BE1 = 284.1 eV
BE2 = 284.7 eV
BE3 = 285.4 eV
Cx
Intensity (arb. units)
294
292
290
288
286
284
282
Binding Energy (eV)



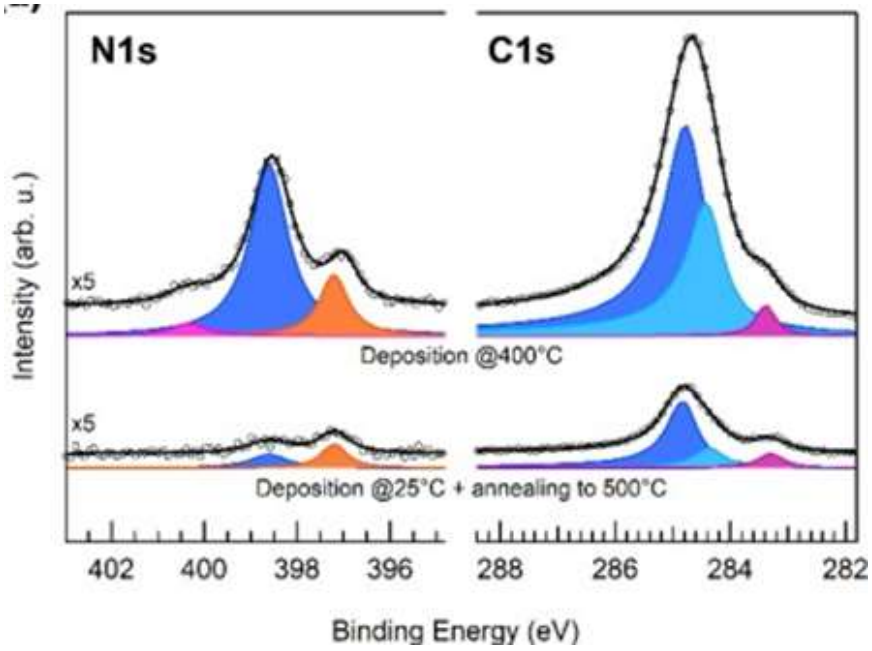
J. Phys. Chem. C 2016, 120, 11, 6104–6115



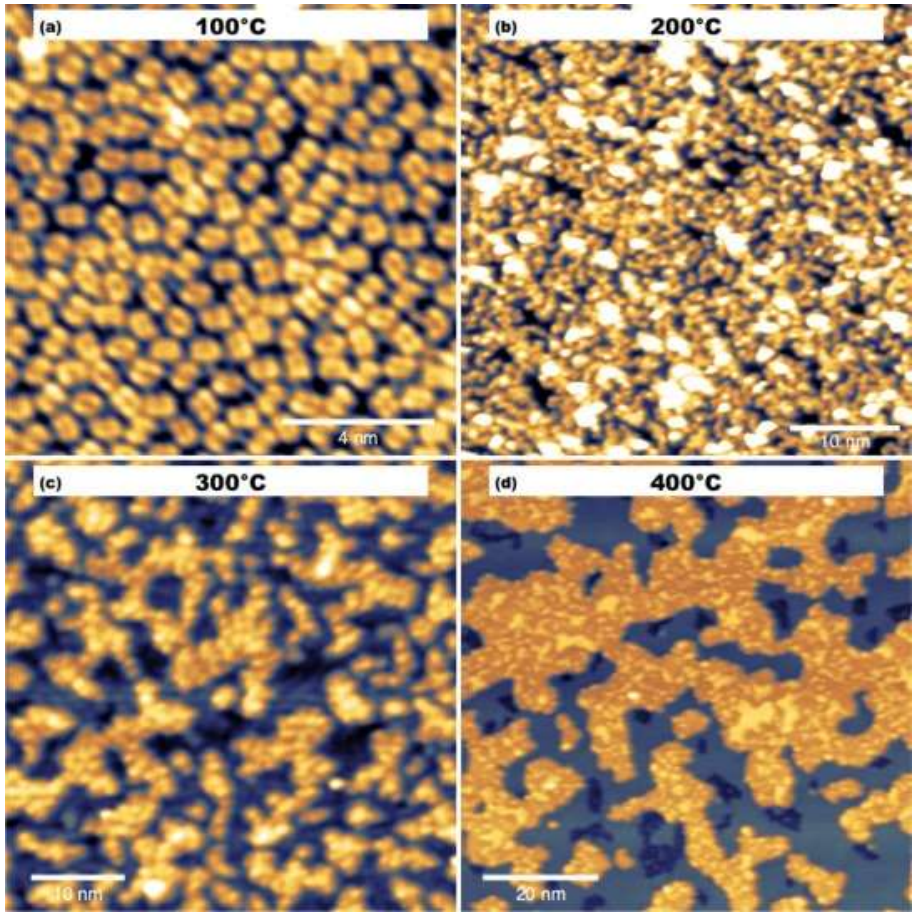
on Ni(111)



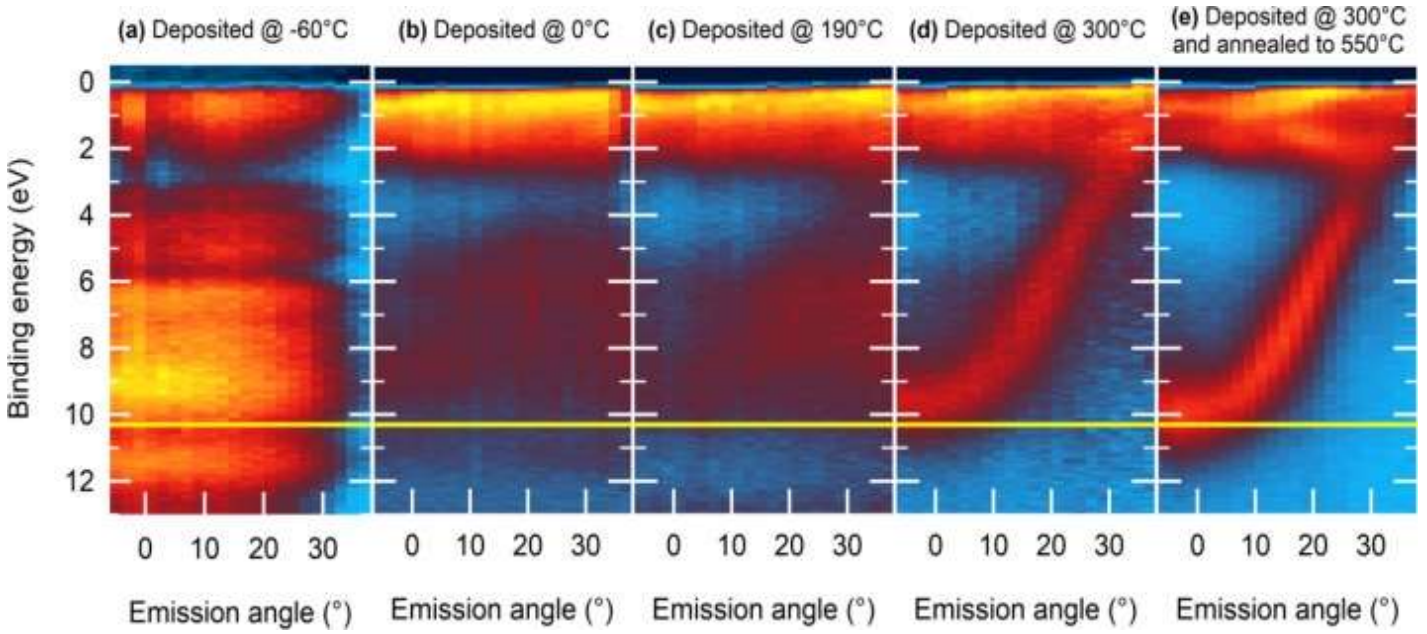
Costantini et al., FlatChem 24 (2020) 100205



Costantini et al., FlatChem 24 (2020) 100205



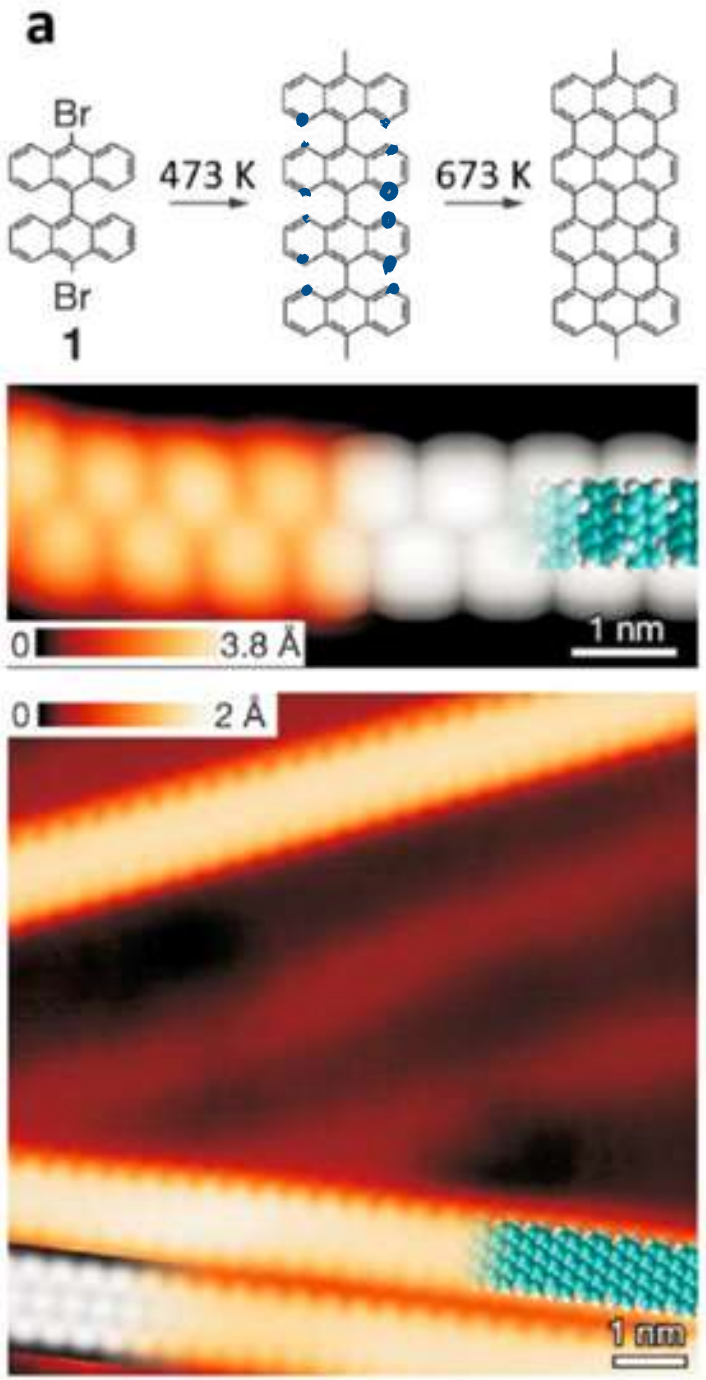
Costantini et al., FlatChem 24 (2020) 100205



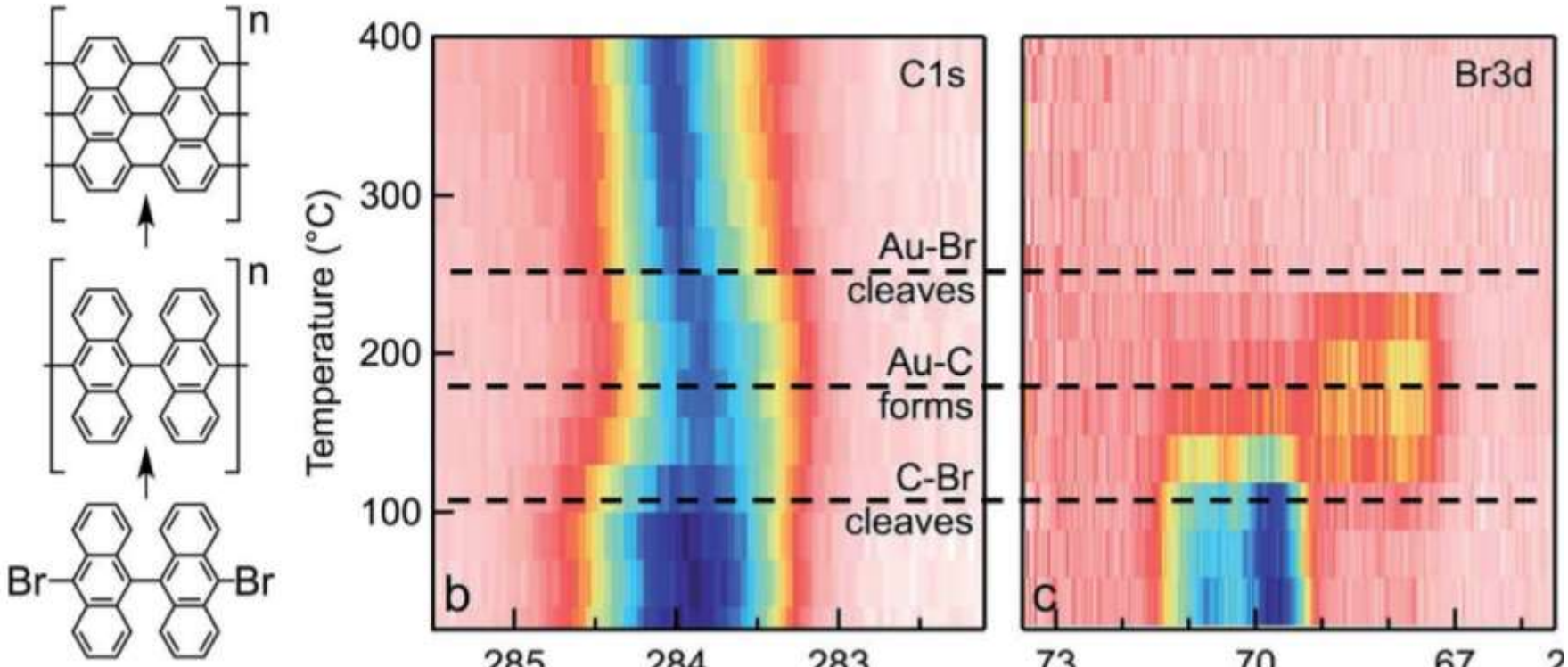
Costantini et al., FlatChem 24 (2020) 100205

Sintesi in sequenza:

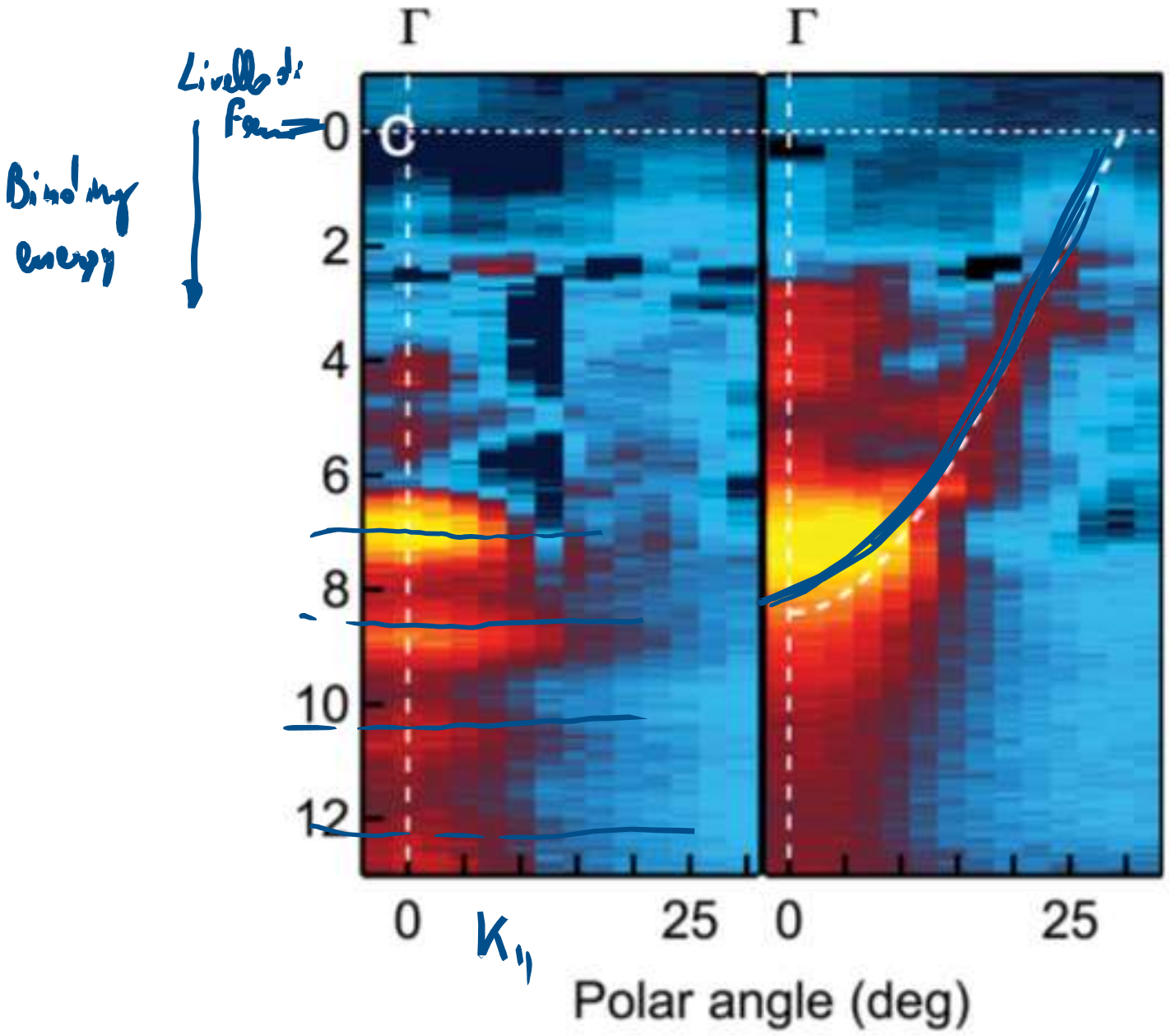
1. Ullmann
2. Cyclodehydrogenation



Nature 2010, 466, 470–473



bande électronique E(k)


Γ
Γ
Binding energy
0
2
4
6
8
10
12
0
25
0
25
$k_{//}$
Polar angle (deg)