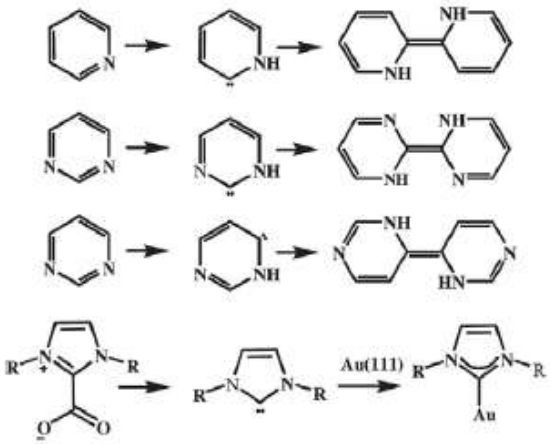
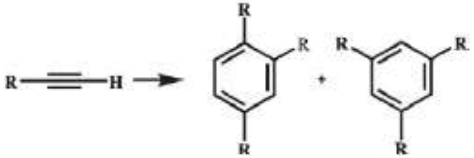
On-surface synthesis

N-heterocyclic carbenes formation and dimerization



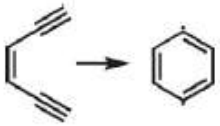
Glaser coupling

Alkyne cyclotrimerization

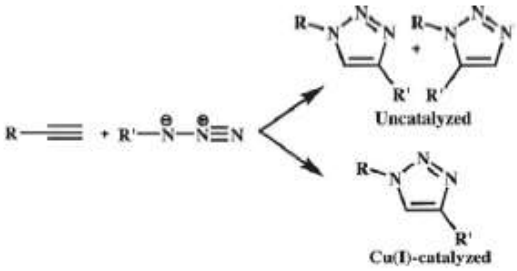


Metalated carbyne

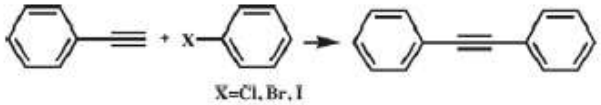
Bergman reaction



Azide–alkyne cycloaddition



Sonogashira coupling



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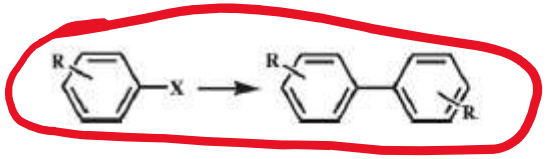
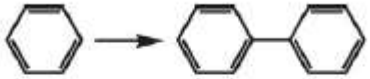
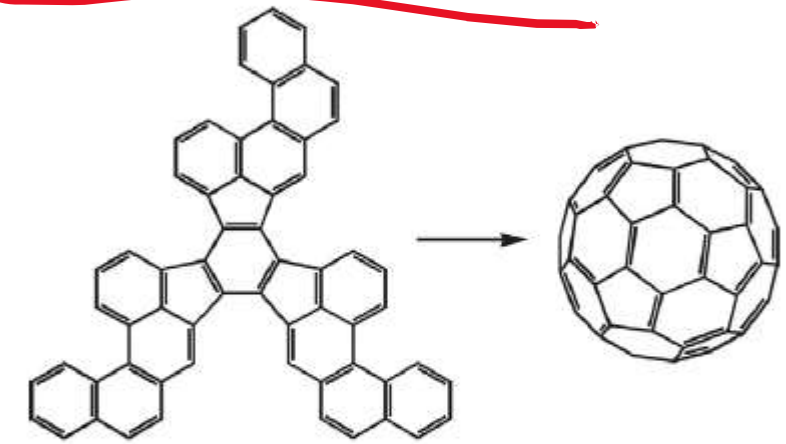
Dehalogenative homocoupling of terminal alkynyl bromides

Ullmann coupling

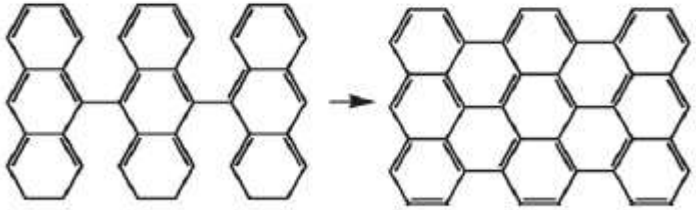




Aryl–aryl dehydrogenation coupling

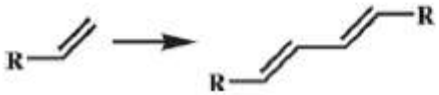


fullerene



graphene nanoribbons

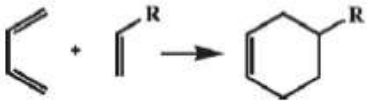
Dehydrogenative homocoupling of terminal alkene



Nano Today 13 (2017) 77–96

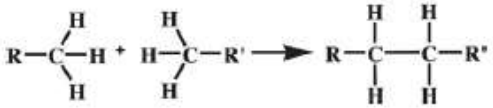
Dehalogenative homocoupling of terminal alkenyl bromides

Diels–Alder reaction

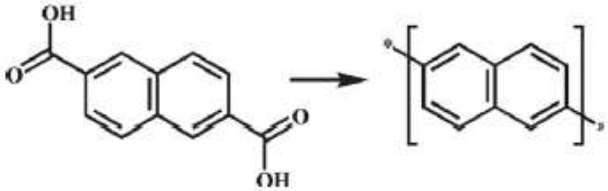


Wurtz coupling

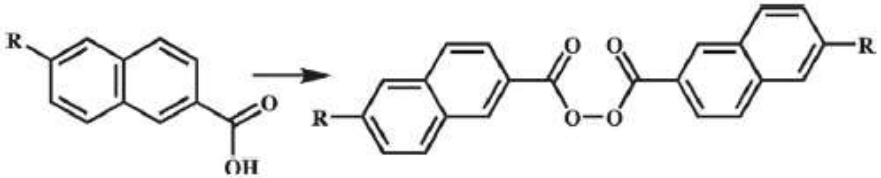
Linear alkane polymerization



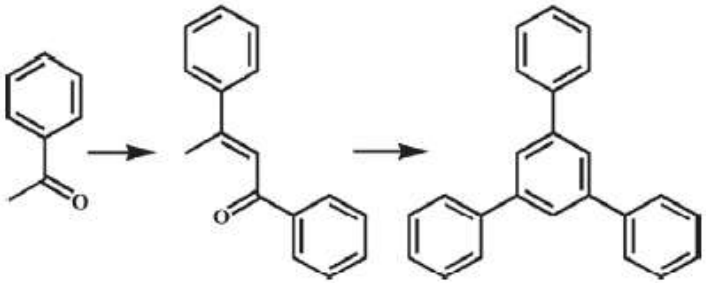
Decarboxylative polymerization



Dehydrogenative coupling

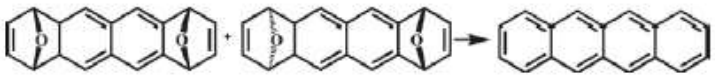


Dimerization and cyclotrimerization of acetyls

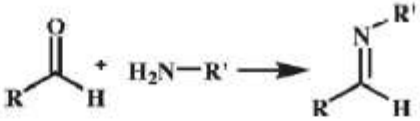


Dealkylation of ethers to alcohols

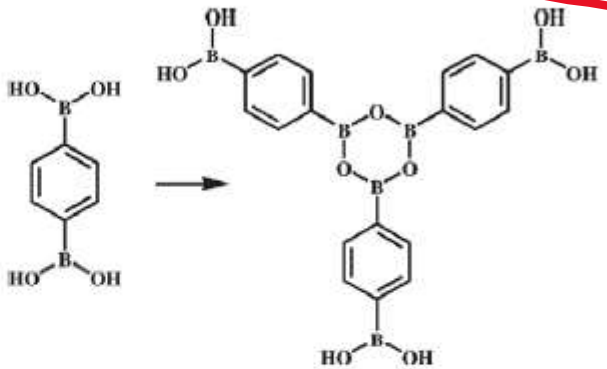
Reduction



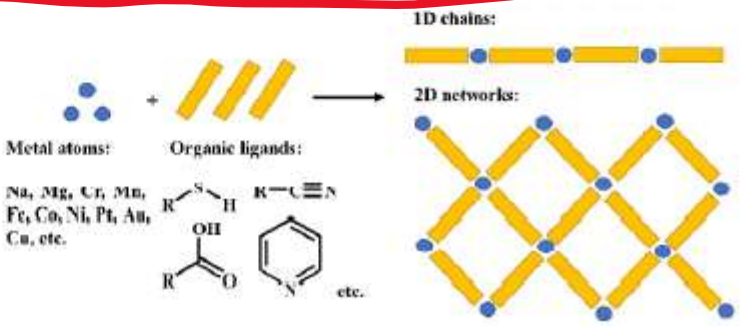
Schiff-base reaction (imine formation)



Boronic acid condensation

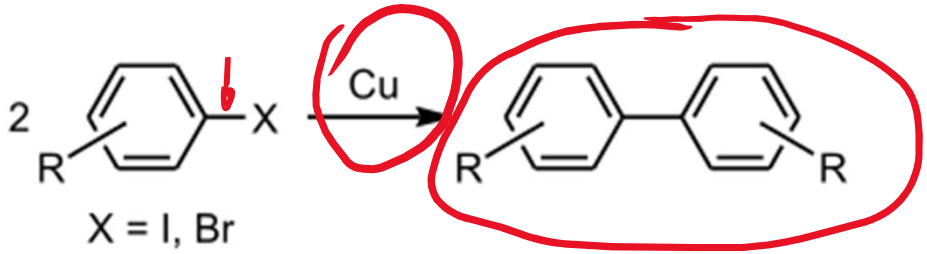


Surface confined
Metal–organic coordination

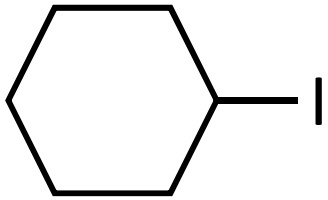


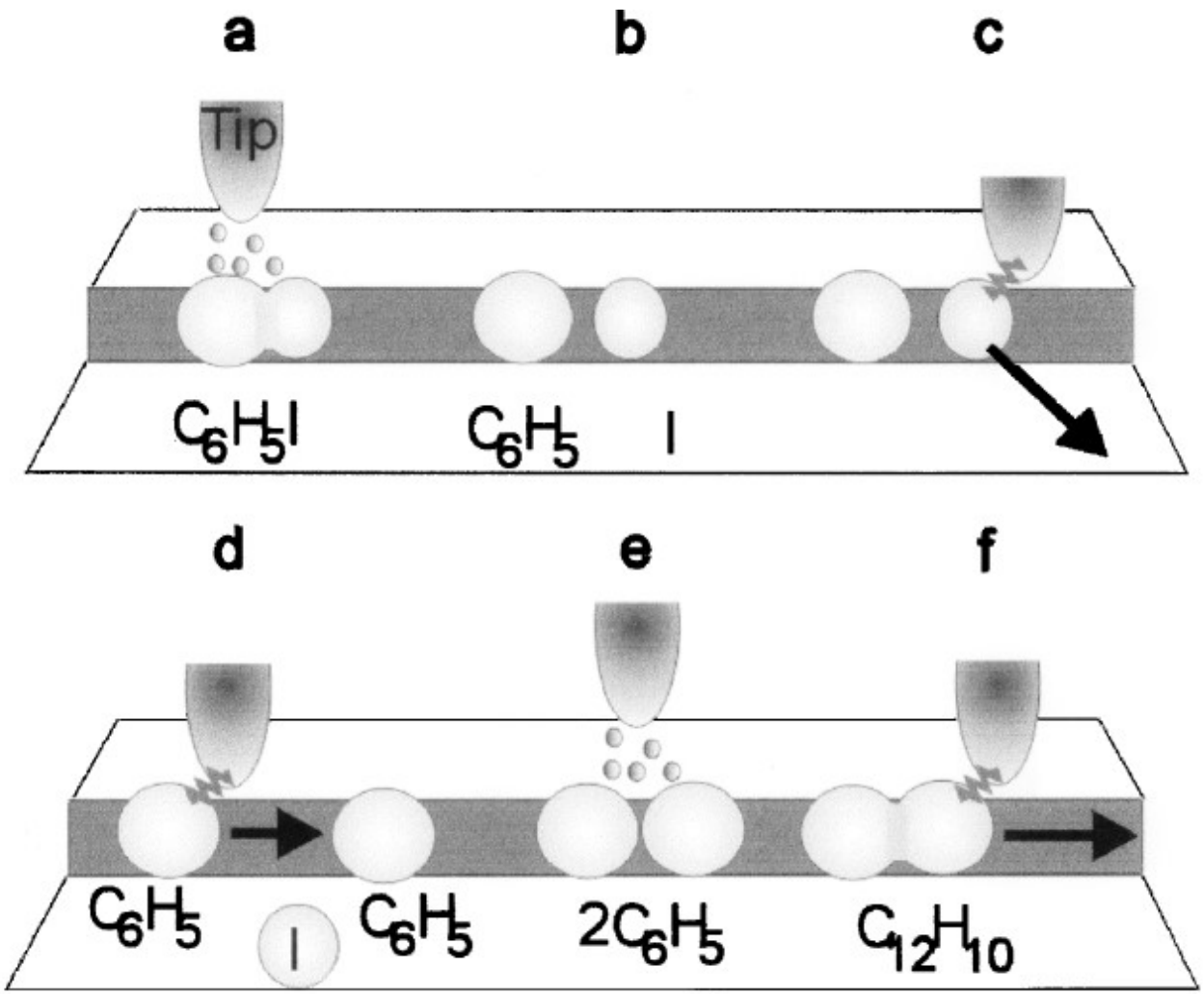
Nano Today 13 (2017) 77–96

Reazione di Ullmann o Ullmann coupling



X alogeni, tipicamente Br

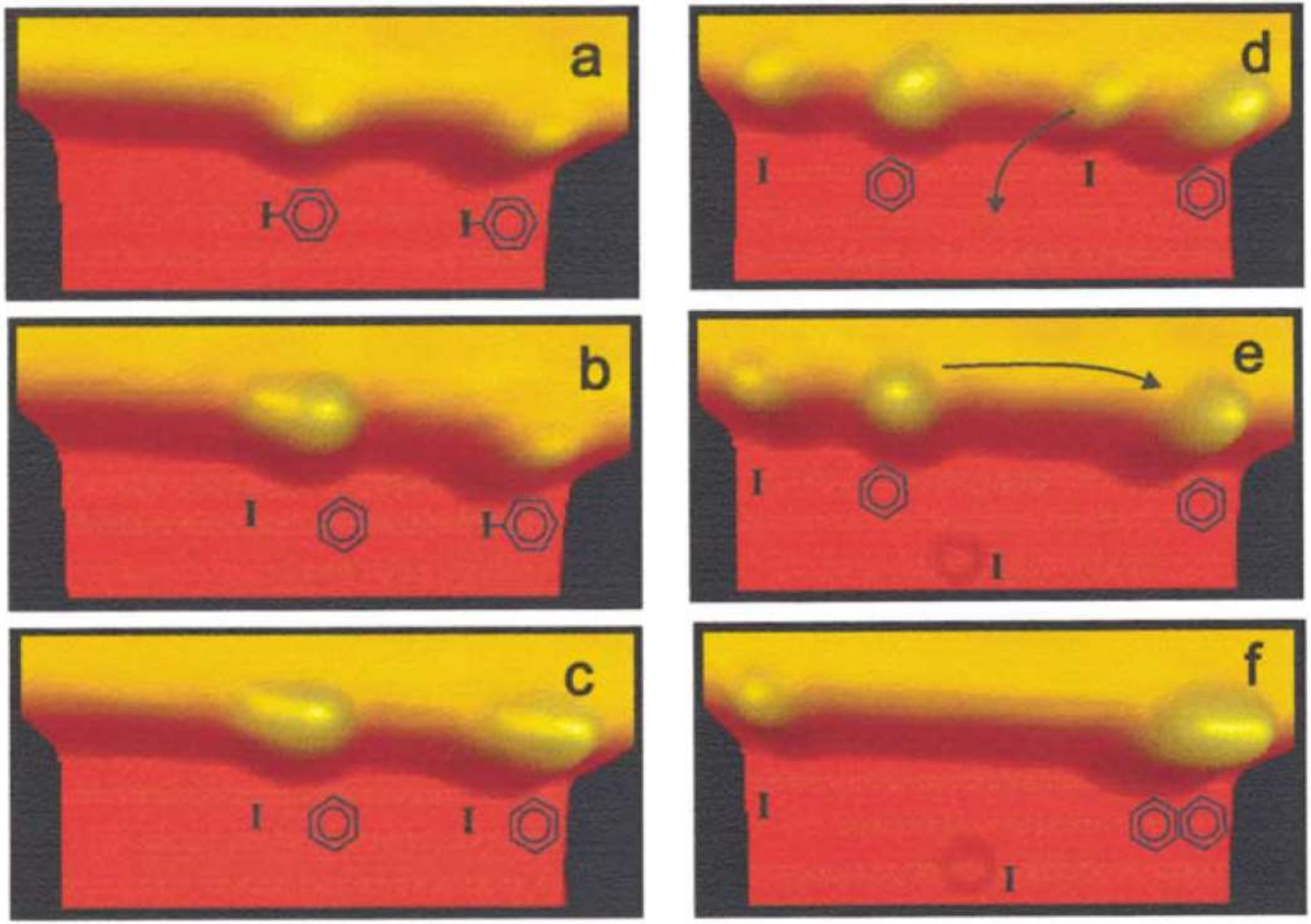


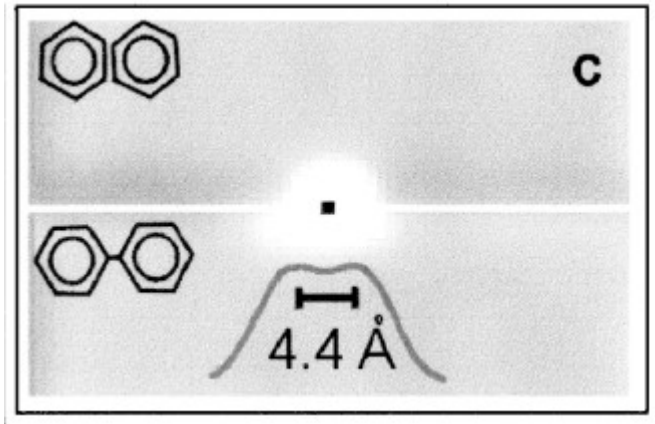


VOLUME 85, NUMBER 13 PHYSICAL REVIEW LETTERS 25 SEPTEMBER 2000

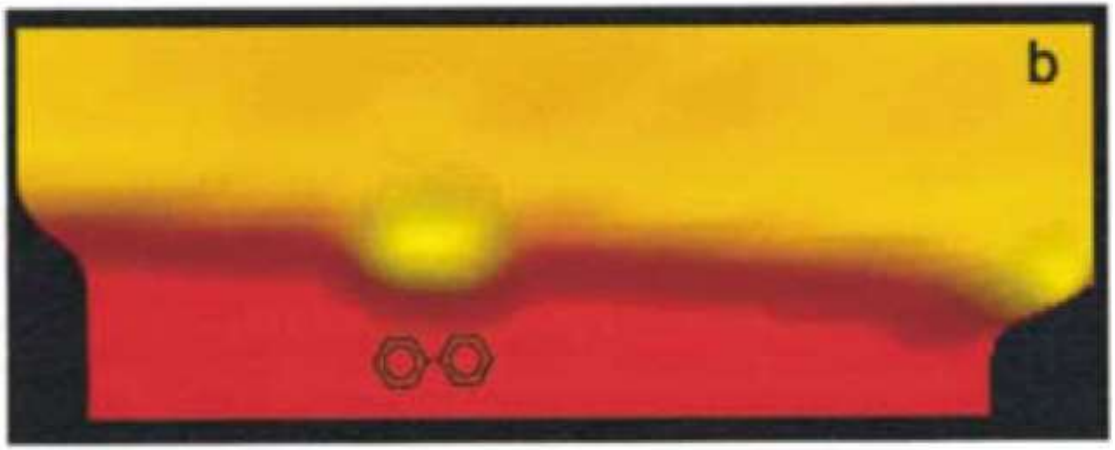
Inducing All Steps of a Chemical Reaction with the Scanning Tunneling Microscope Tip: Towards Single Molecule Engineering

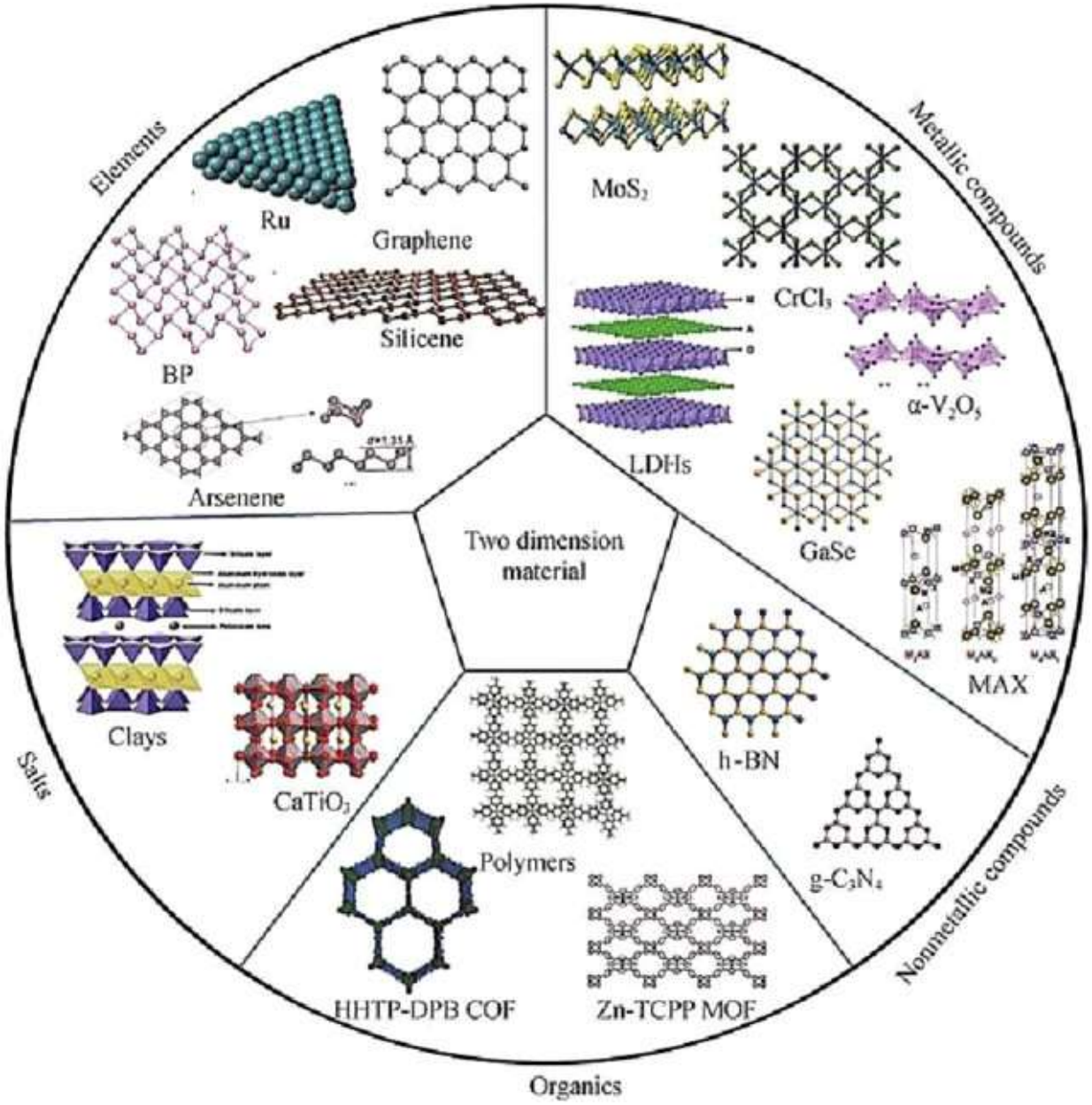
Saw-Wai Hla,[1,2,*] Ludwig Bartels,[1,†] Gerhard Meyer,[1] and Karl-Heinz Rieder[1]


a
b
c
d
e
f


c
4.4 Å

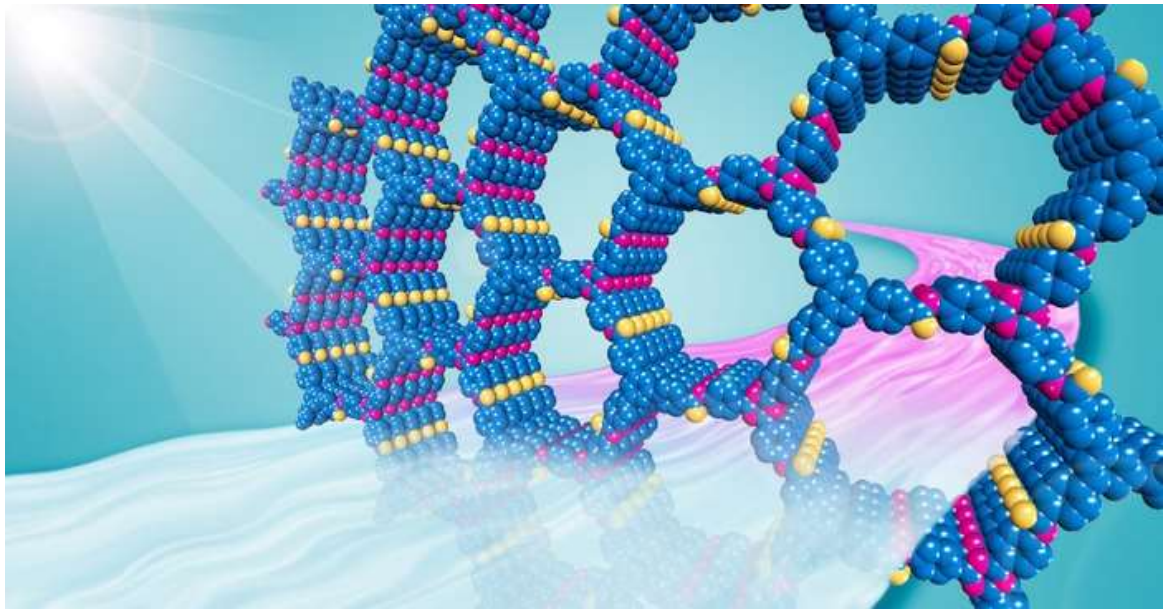

a


b

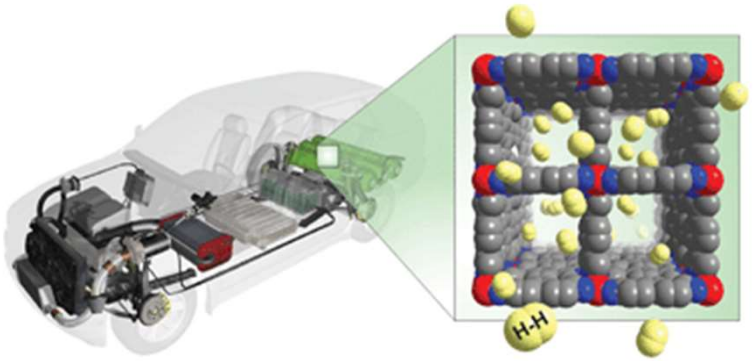


https://doi.org/10.1142/S1793292019300019

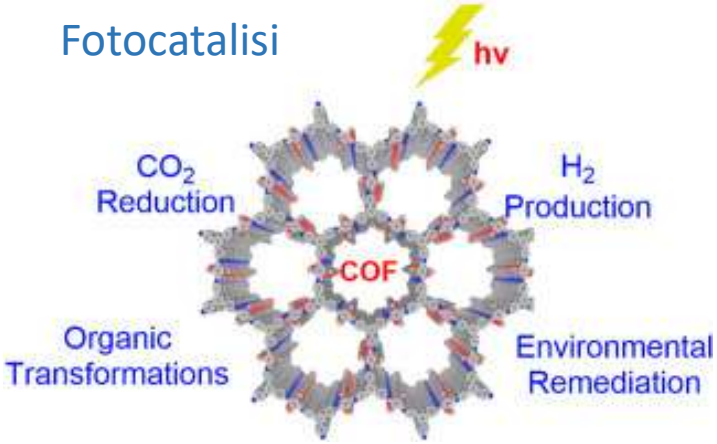
Covalent Organic Frameworks



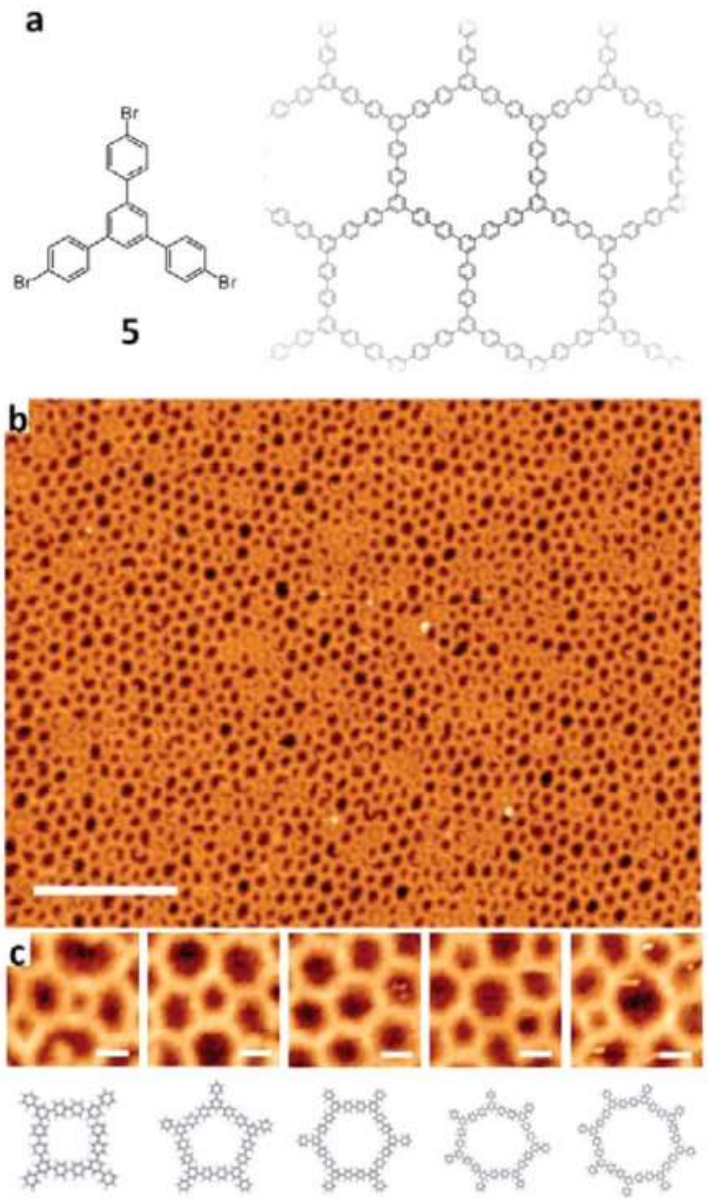
Storaging



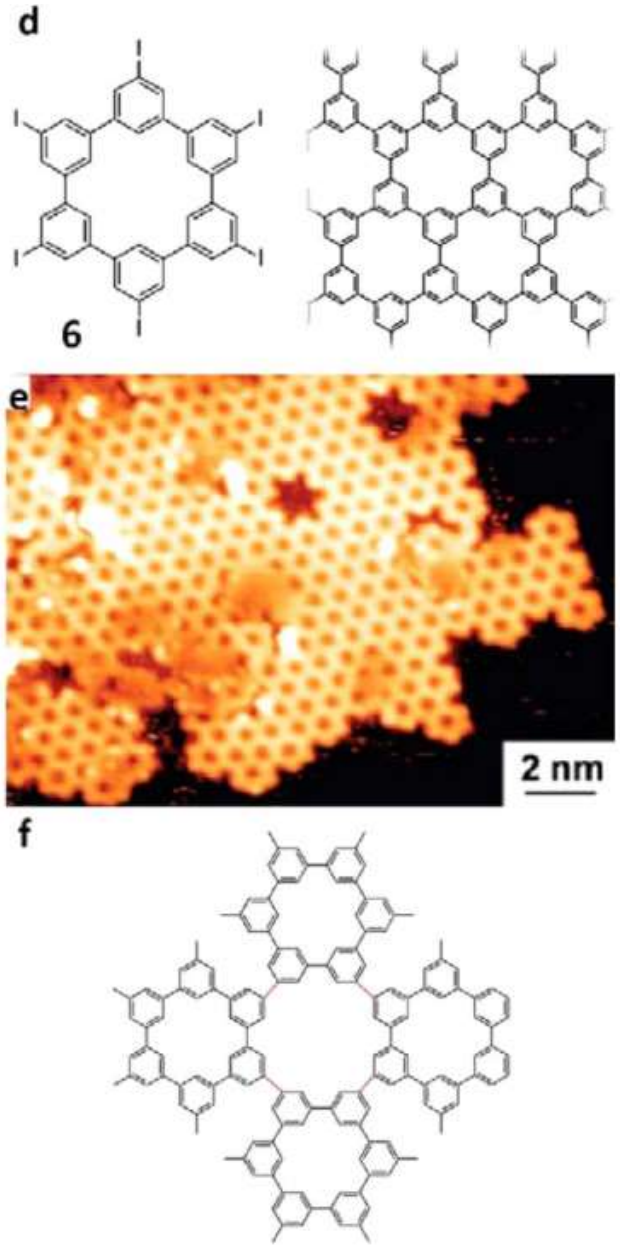
Fotocatalisi



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

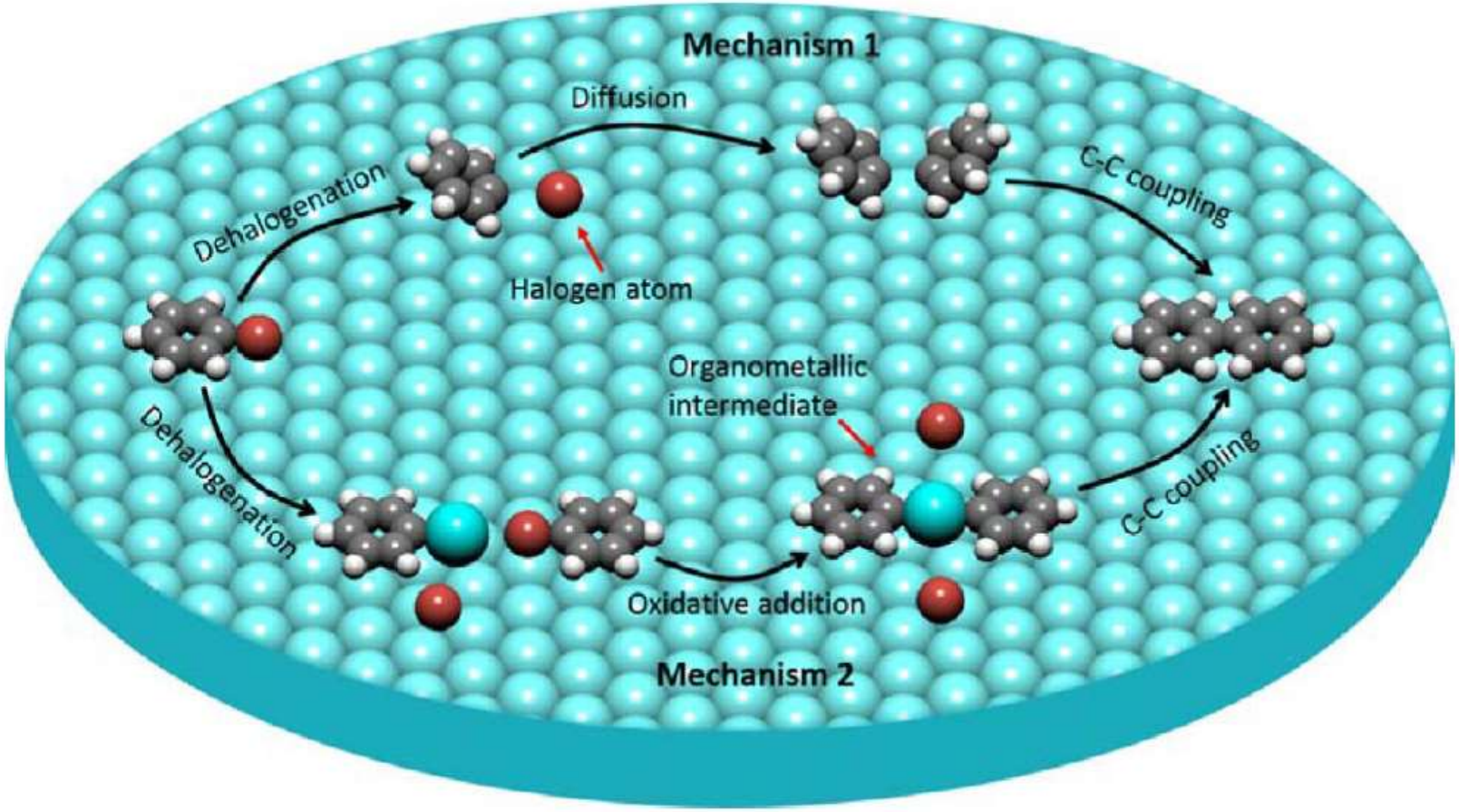


2D - COVALENT ORGANIC FRAMEWORK



ACS Nano 2014, 8, 7880−7889.

Chem. Commun. 2010, 46, 7157−7159.



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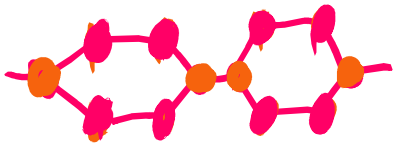
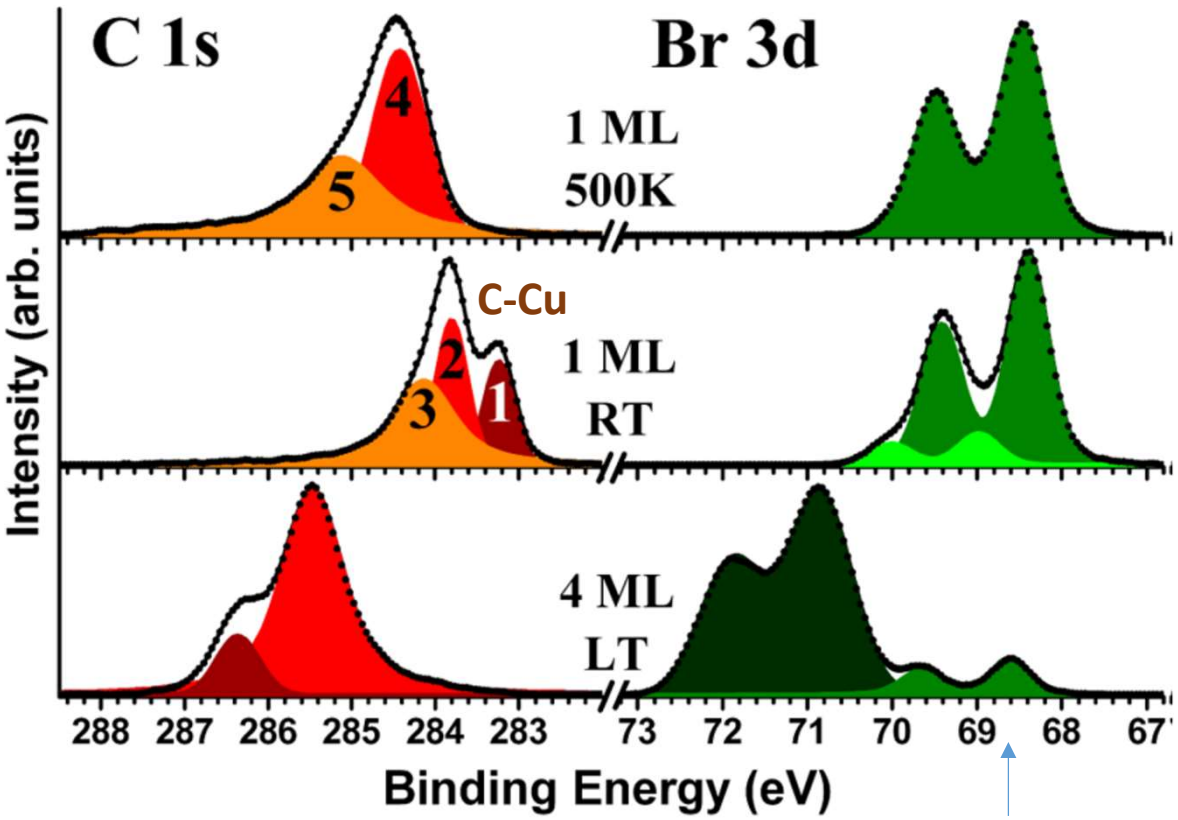
Acc. Chem. Res. 2015, 48, 2484−2494





Br atomico

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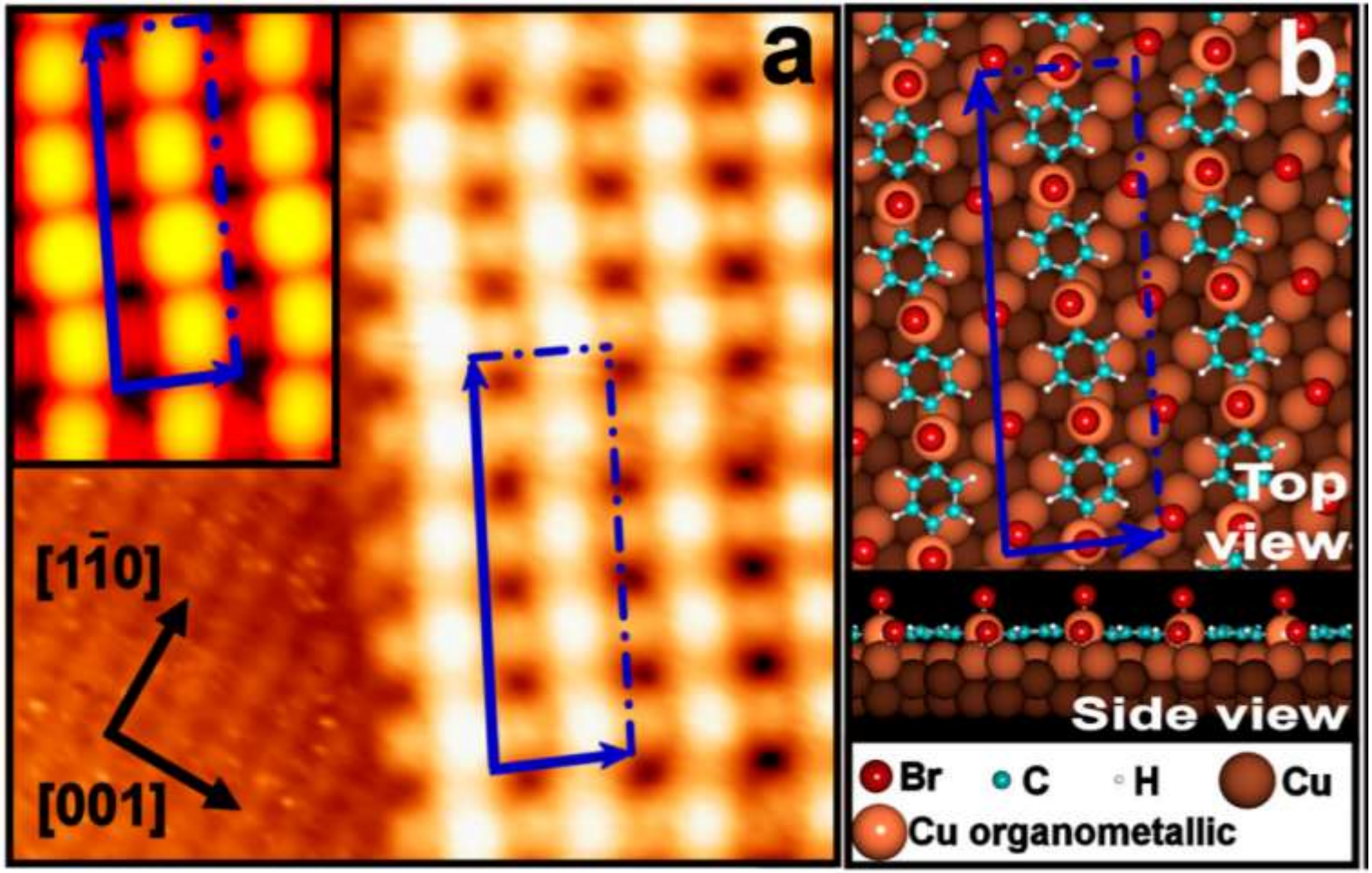
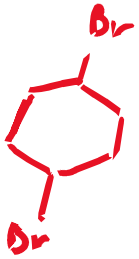
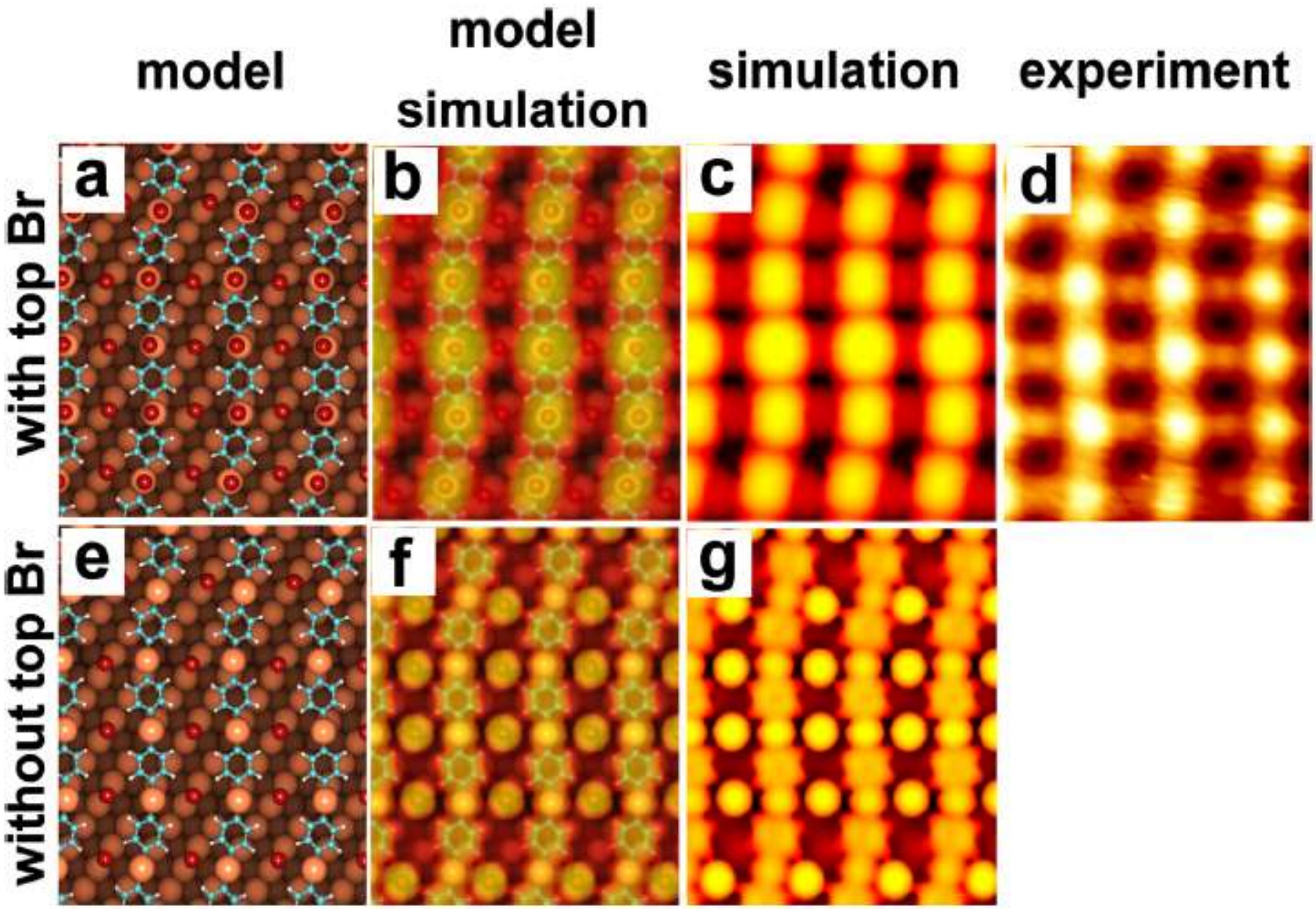
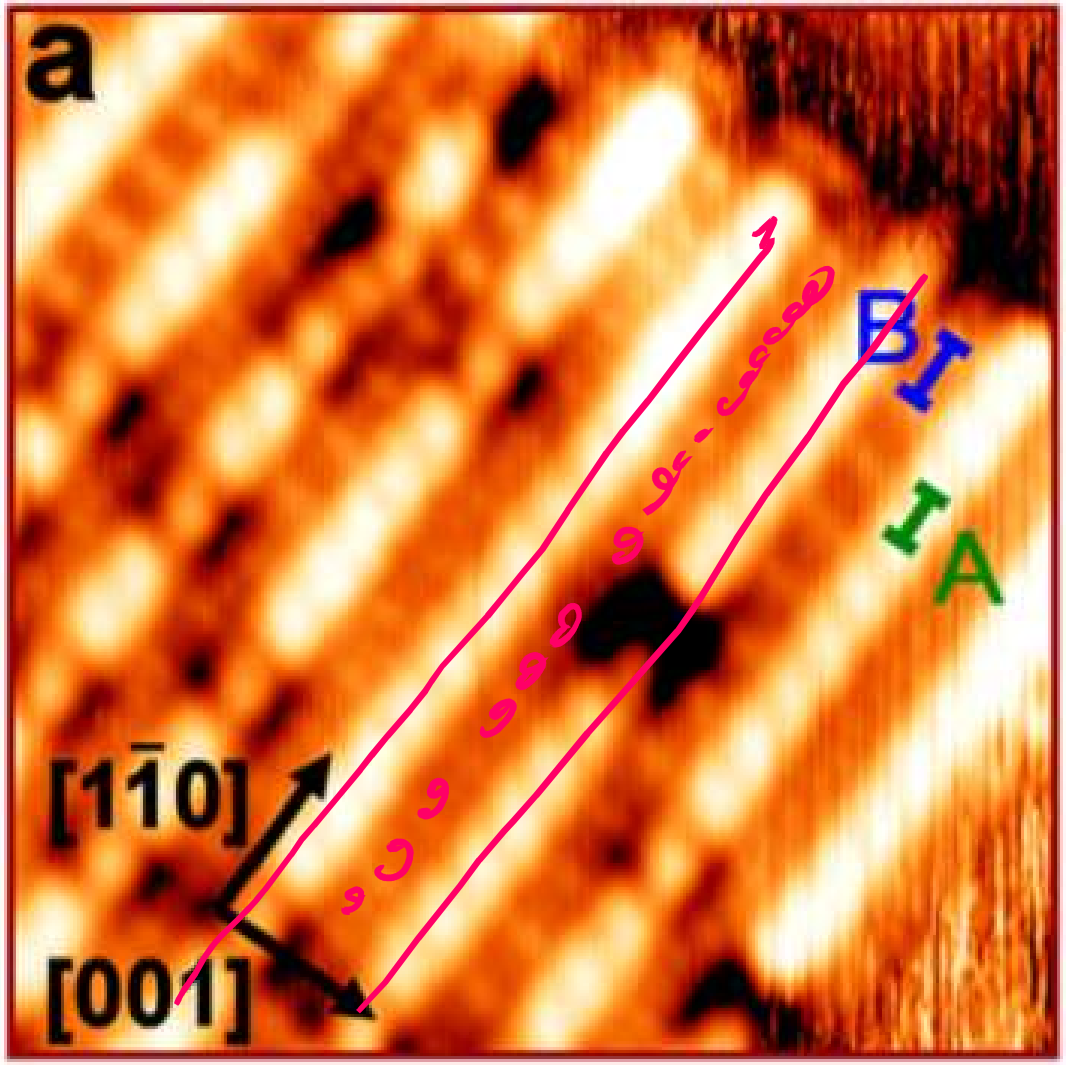

a
[1$\bar{1}$0]
[001]
b
Top view
Side view
Br
C
H
Cu
Cu organometallic


Br
Br


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

Annealing @ 500°C



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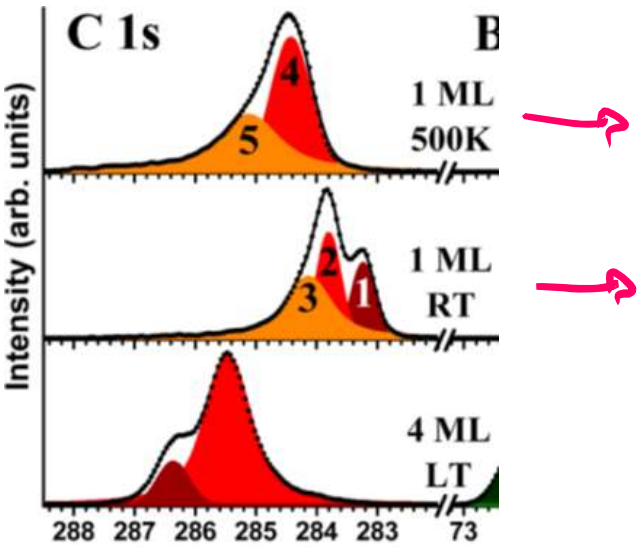
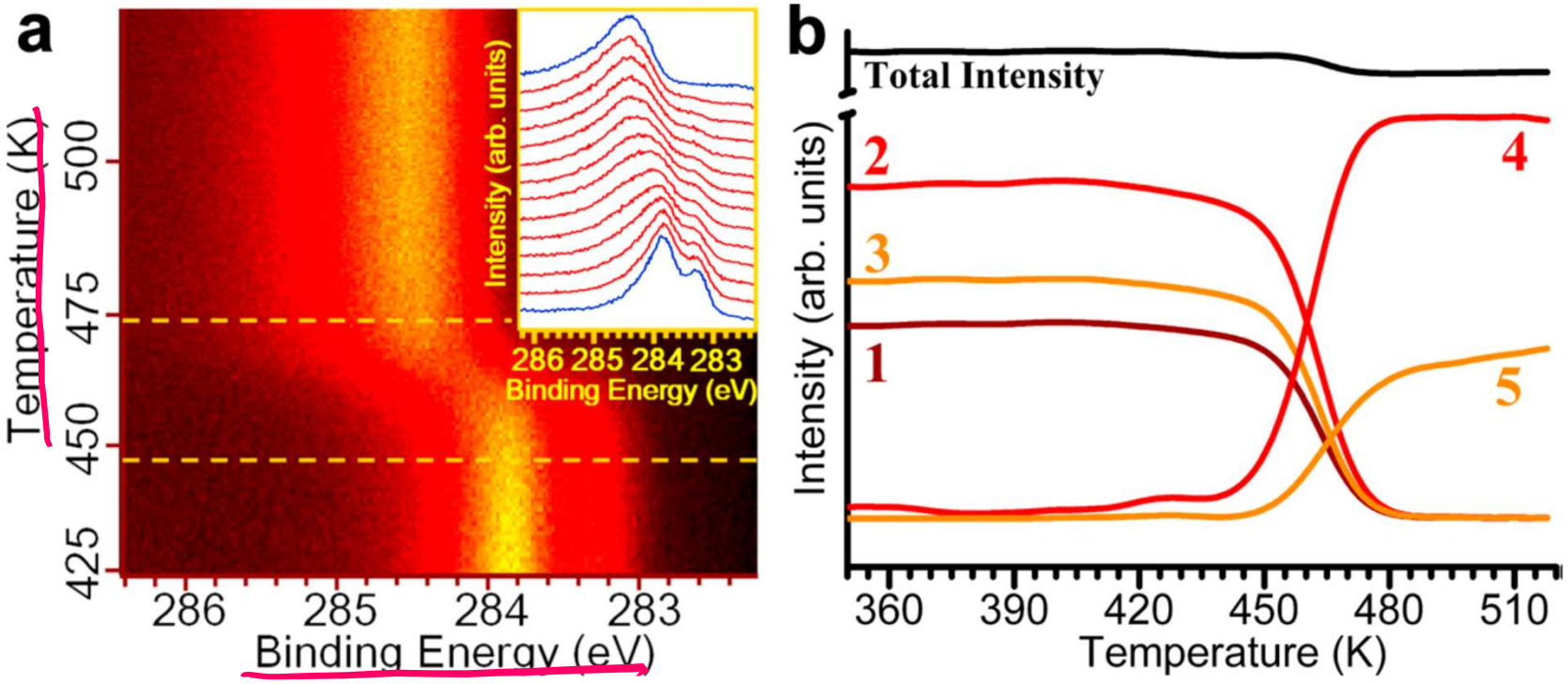
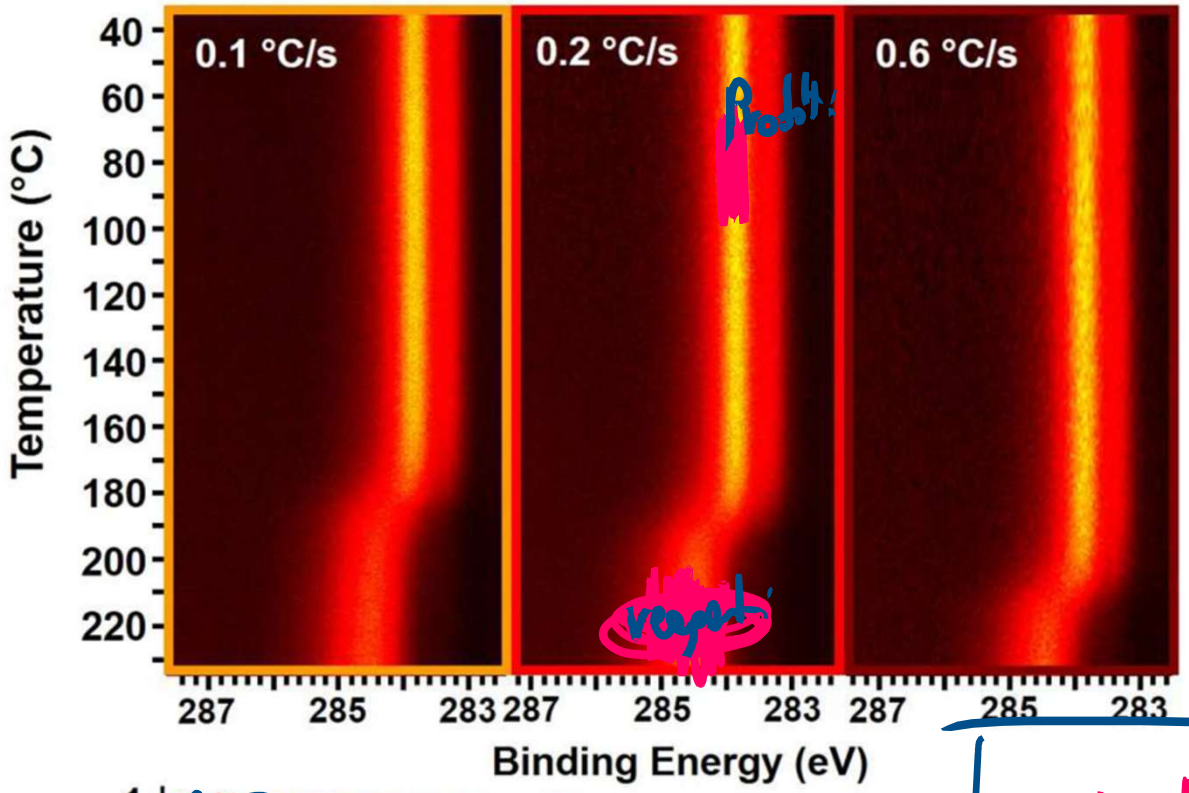
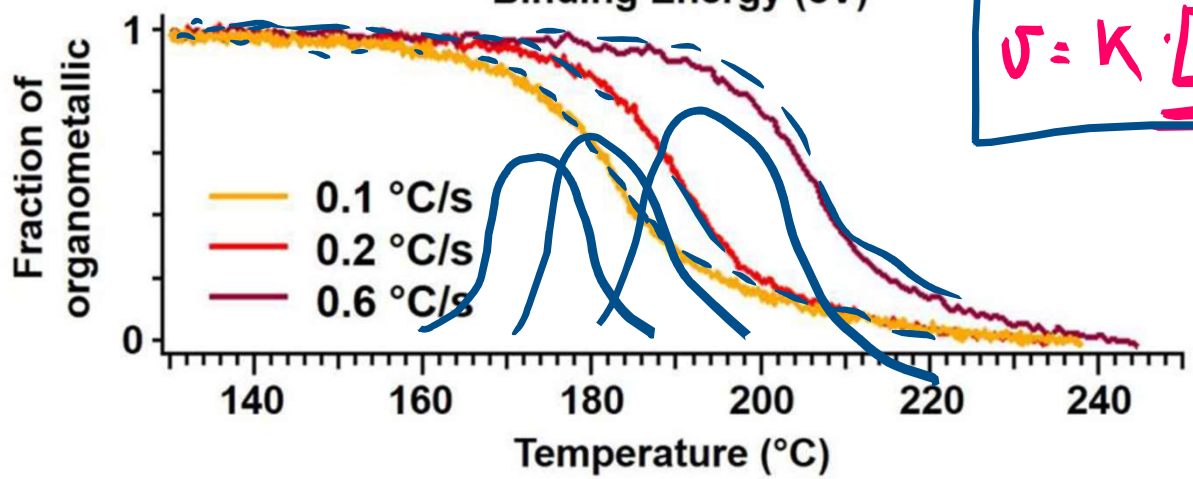






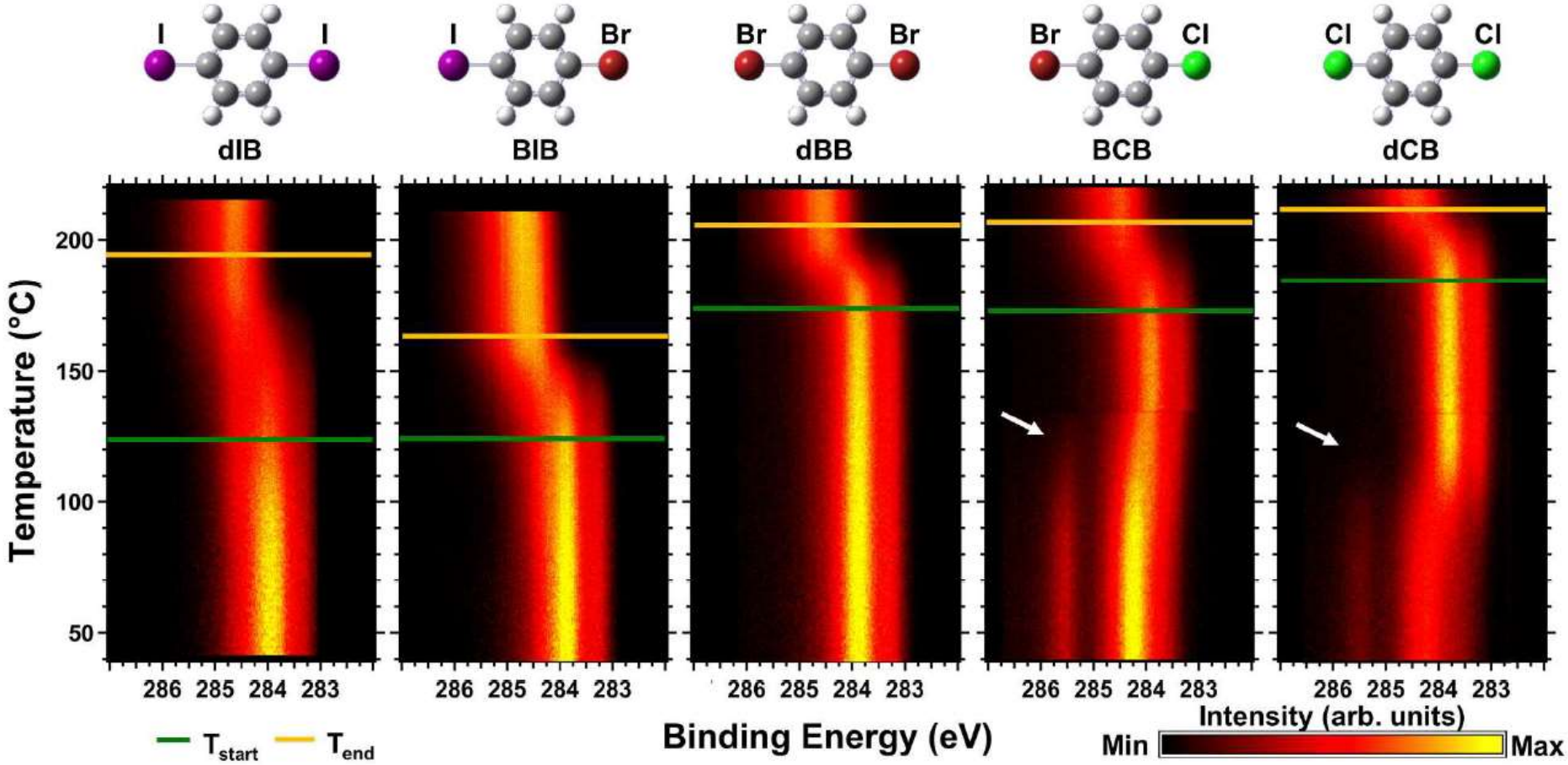
diversi rate di riscaldamento

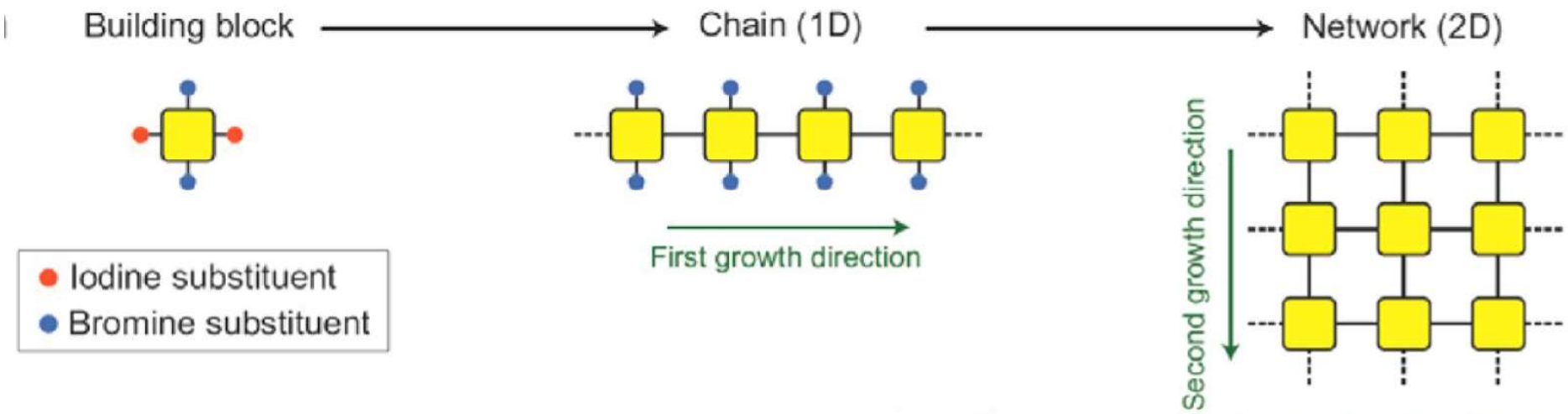
studio della velocità di reazione

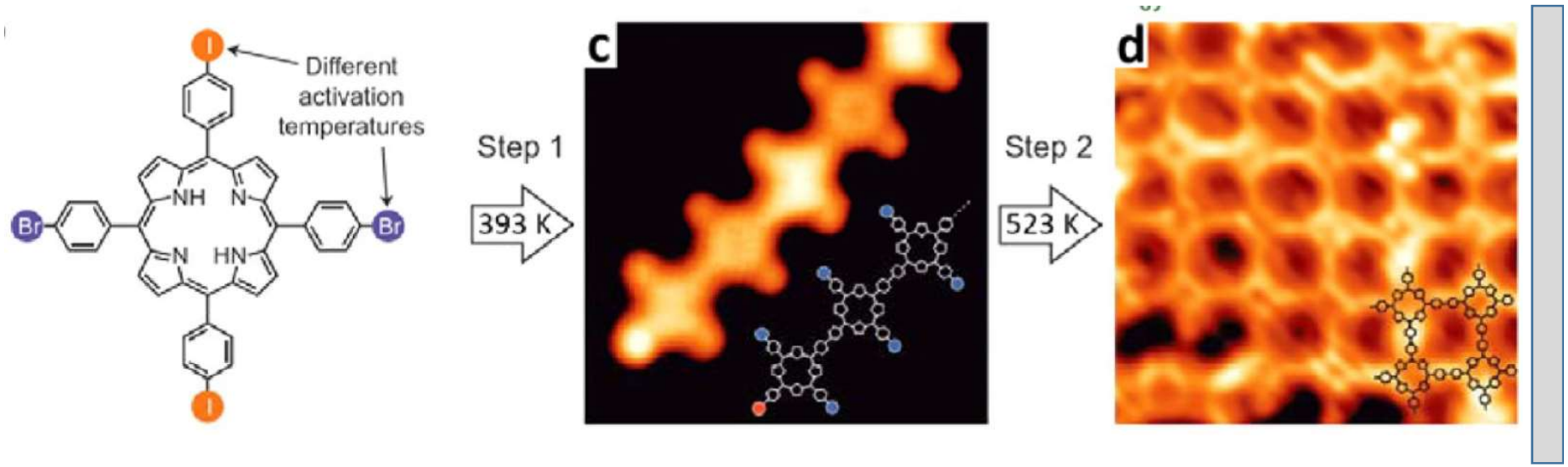


$$v = K \cdot [A]^n$$

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

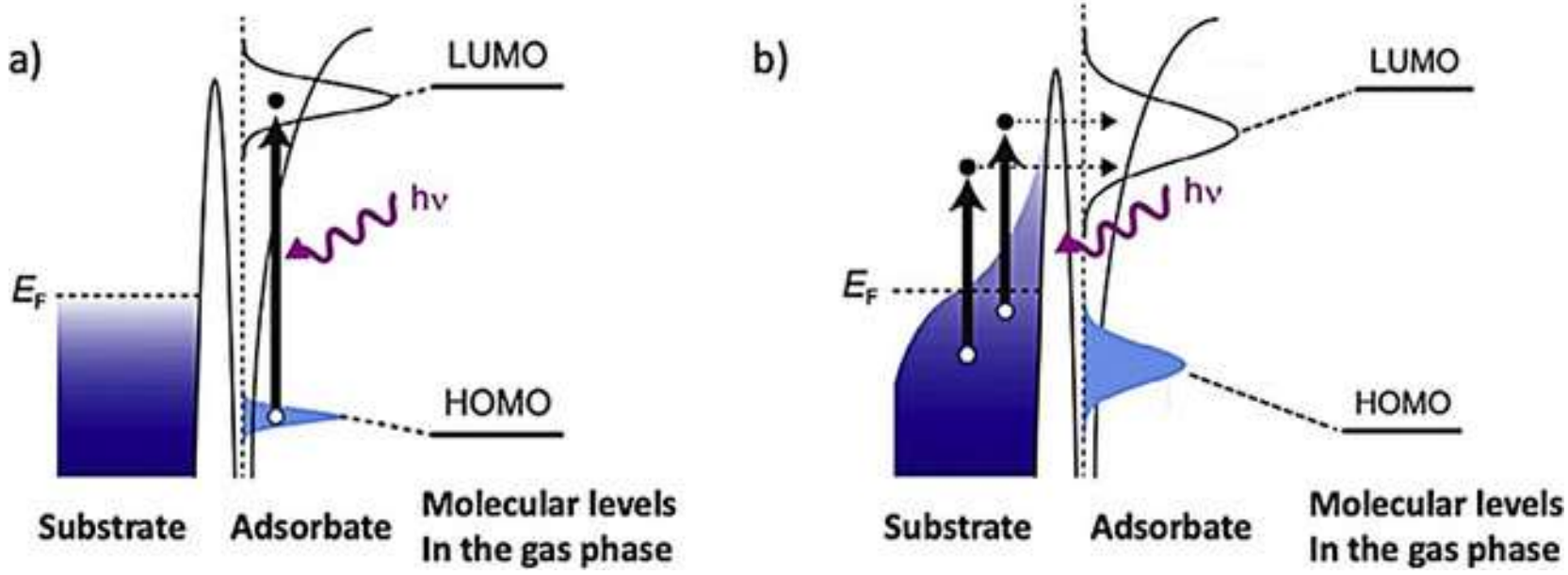

I
I
dIB
I
Br
BIB
Br
Br
dBB
Br
Cl
BCB
Cl
Cl
dCB
Temperature (°C)
200
150
100
50
286 285 284 283
Binding Energy (eV)
T_{start}
T_{end}
Intensity (arb. units)
Min
Max


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

Sintesi foto-indotta

Molecole sulla superficie possono modificare la loro struttura elettronica se illuminate (UV o visibile), a seguito di due possibili processi: eccitazione interna (ADS,adsorbate excitation) o popolazione del LUMO con elettroni del substrato (HEA Hot Electron Attachment).

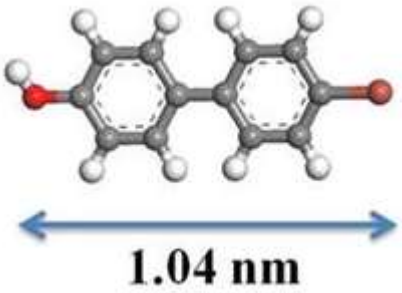


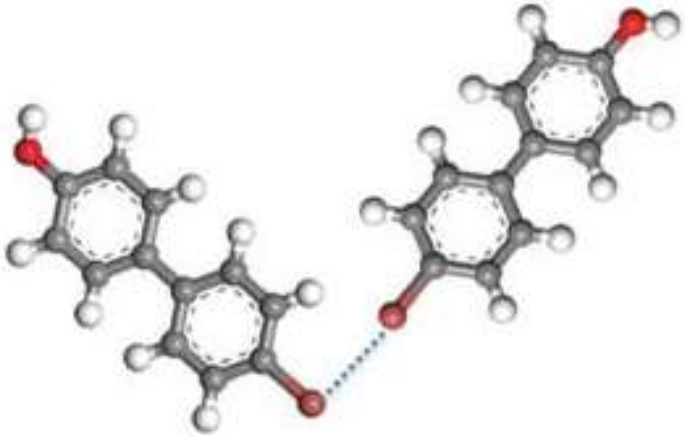
ChemPubSoc Europe
DOI: 10.1002/cphc.201900312
CHEMPHYSCHEM Minireviews

Photochemistry Highlights on On-Surface Synthesis

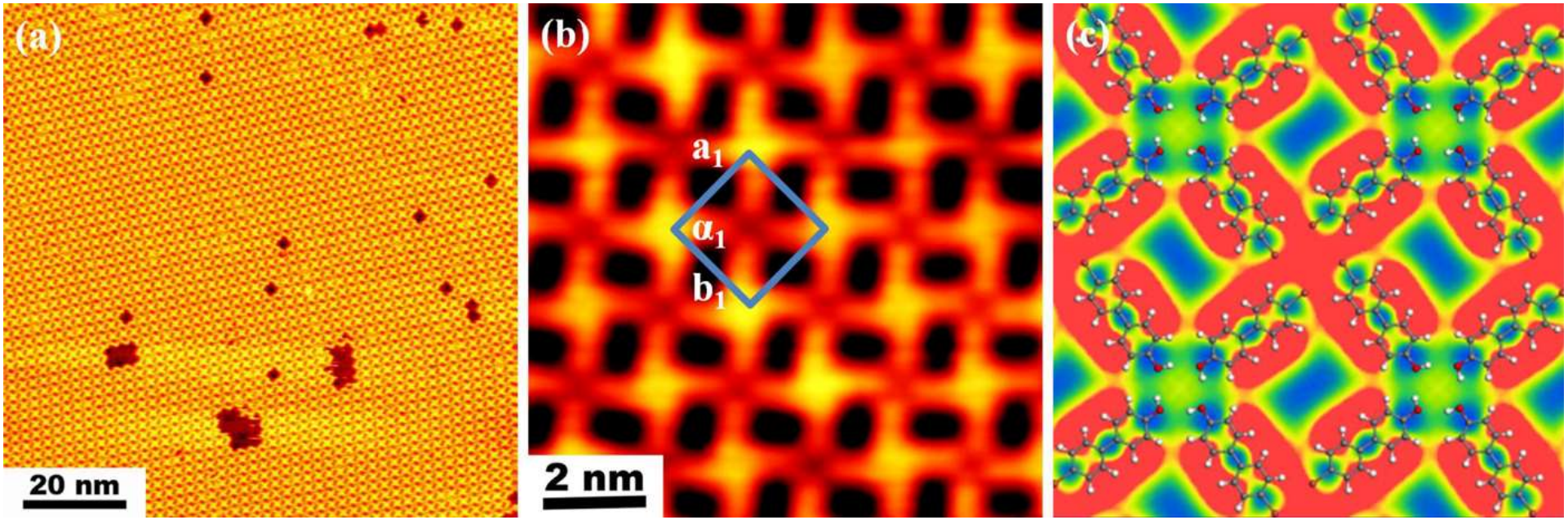
F. Palmino,[a] C. Loppacher,[b] and F. Chérioux*[a]

4-bromo-4’-hydroxybiphenyl



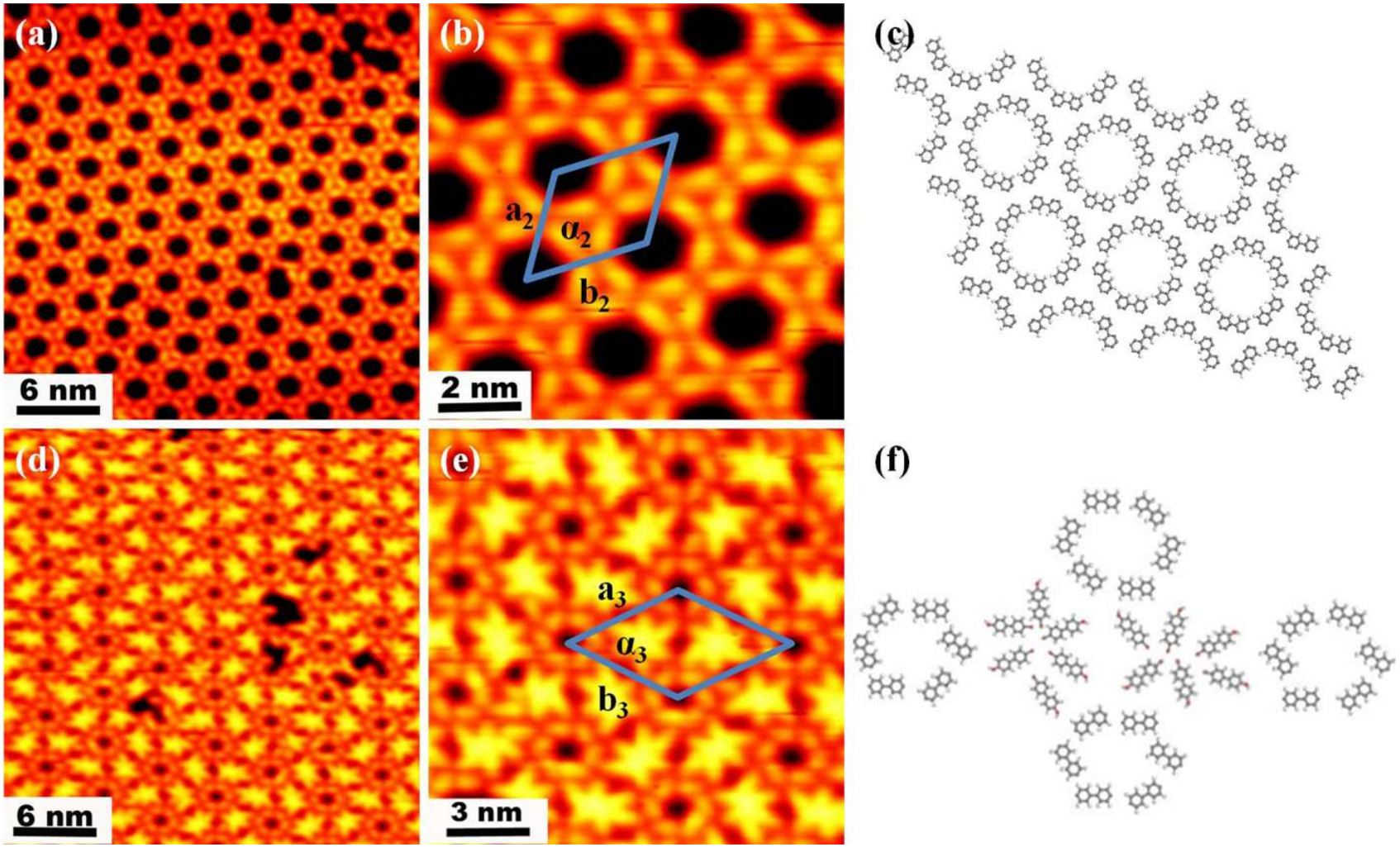


Le molecole dosate su Ag(111), temperatura campione 80K, autoassemblano formando un network basato su legami idrogeno e alogeno



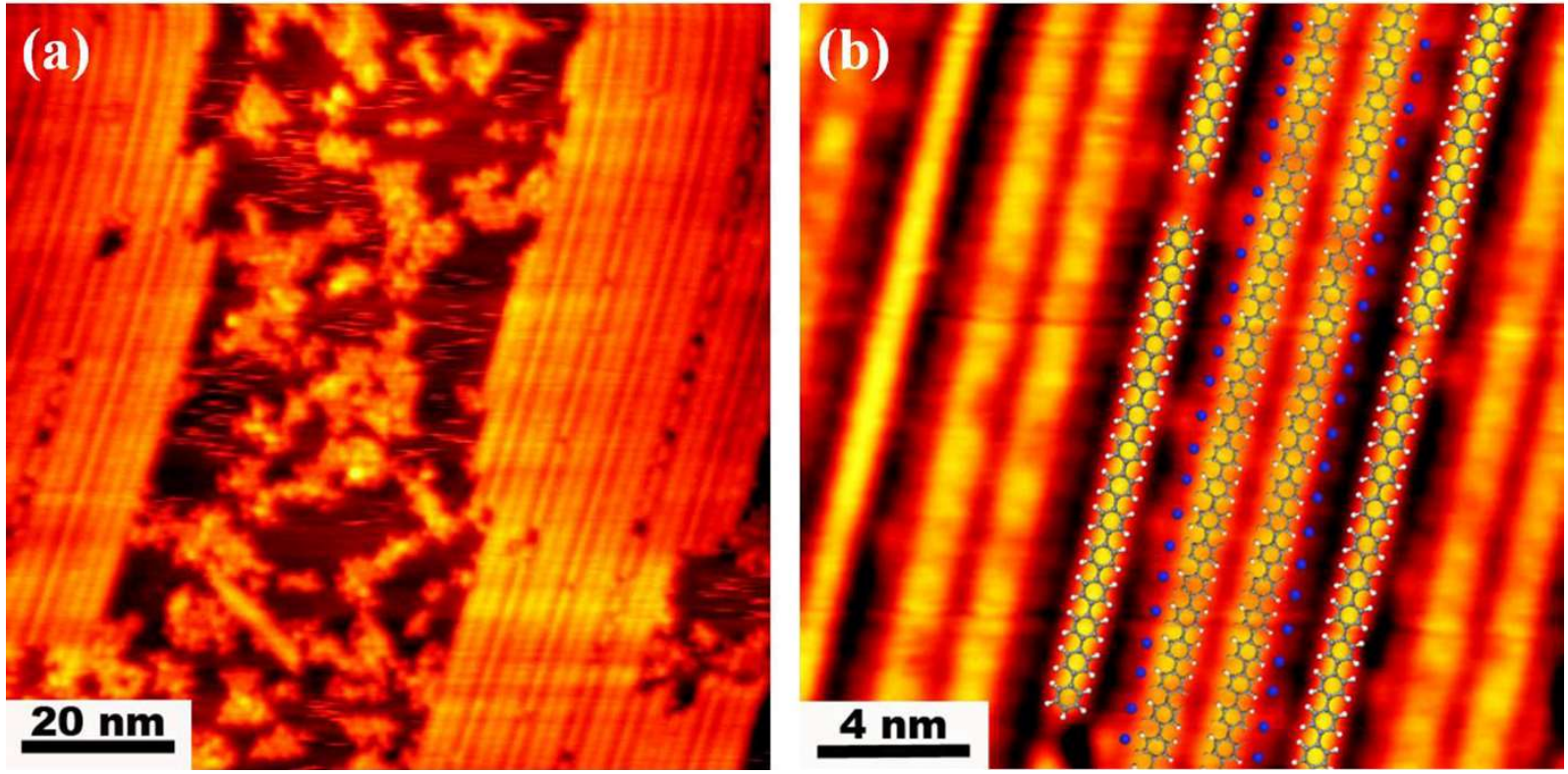
J. Chem. Phys. 142, 101902 (2015)

Illuminazione UV (266 nm, 10 min): si formano biradicali e ho due fasi diverse sulla superficie

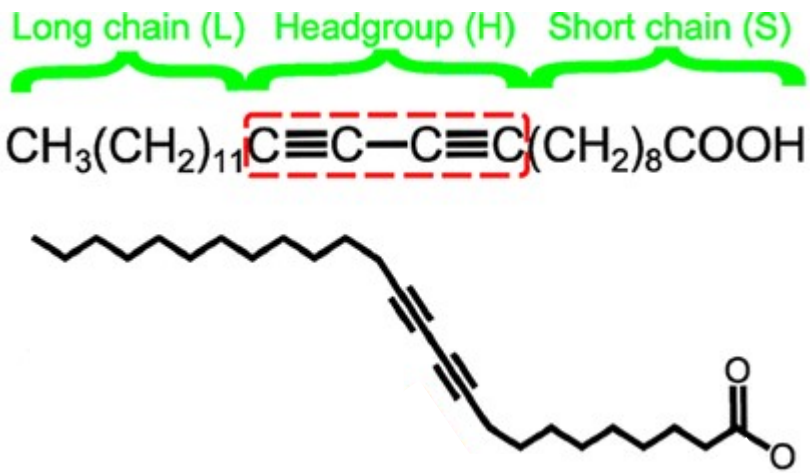


J. Chem. Phys. 142, 101902 (2015)

Scaldo a RT: polimerizzazione



J. Chem. Phys. 142, 101902 (2015)



10,12-pentacosadiynoic acid

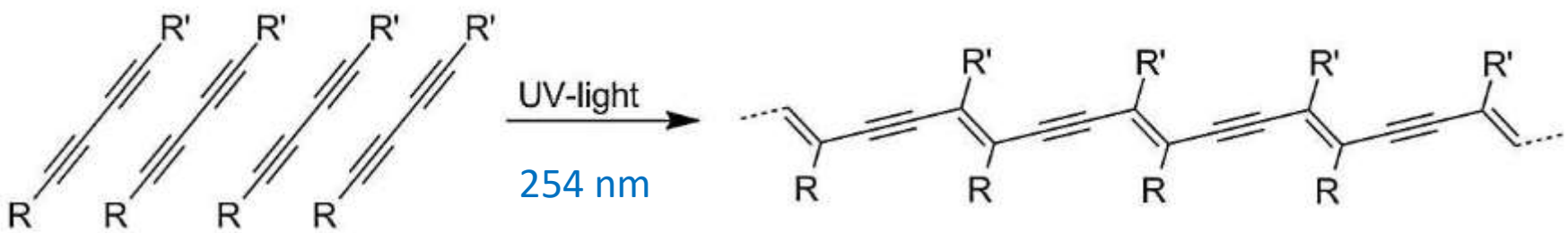
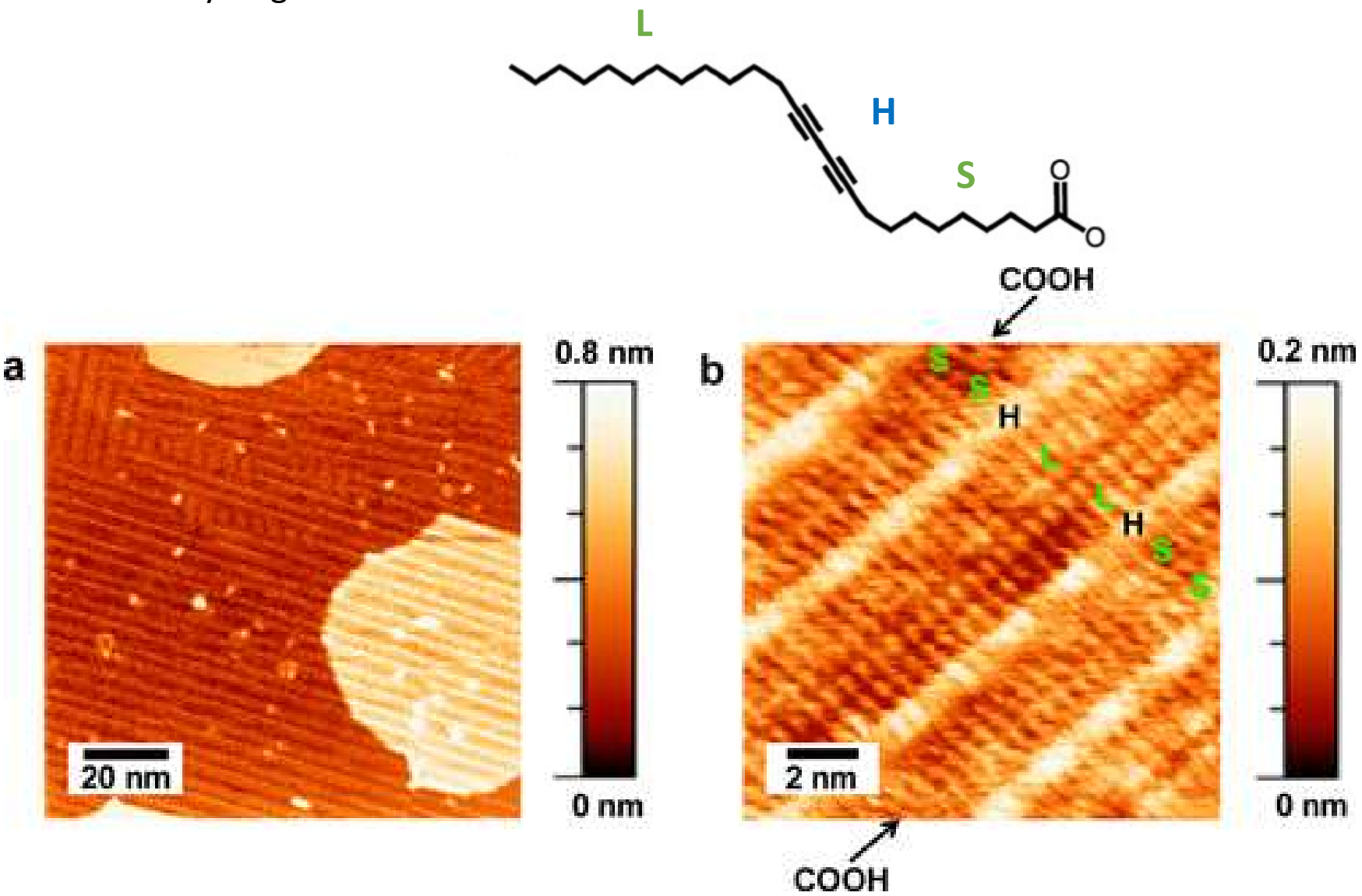


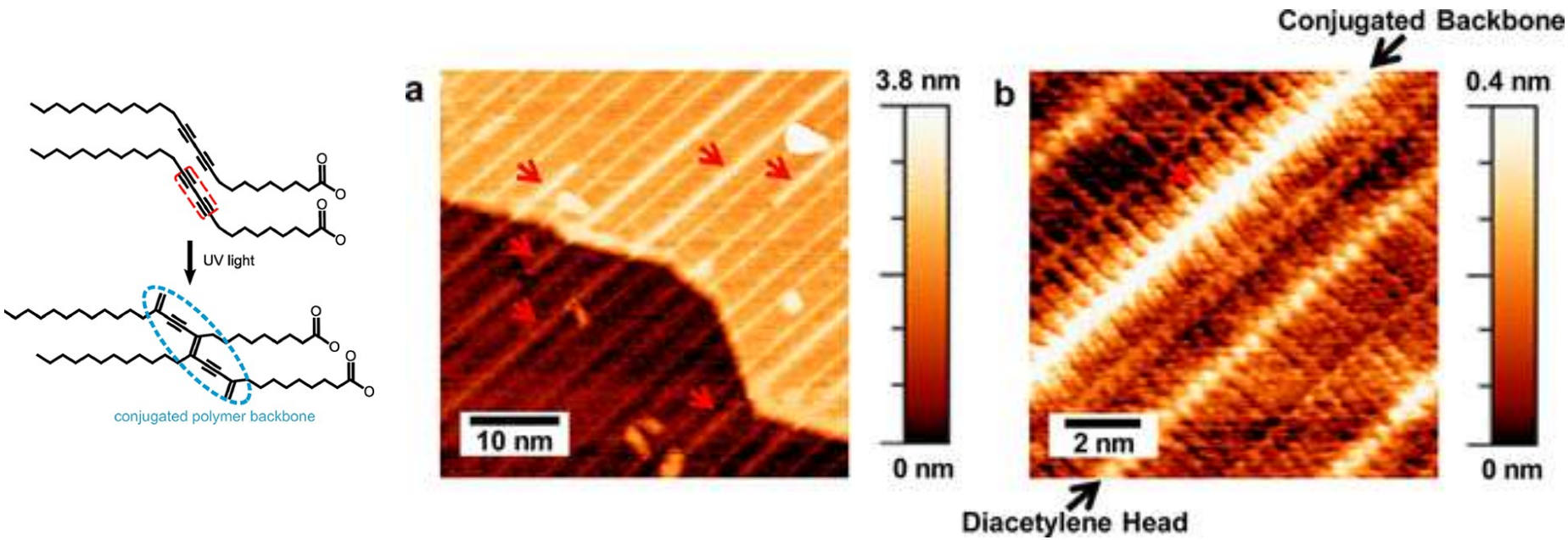
Figure 2. Schematic reaction of diacetylene after UV illumination.

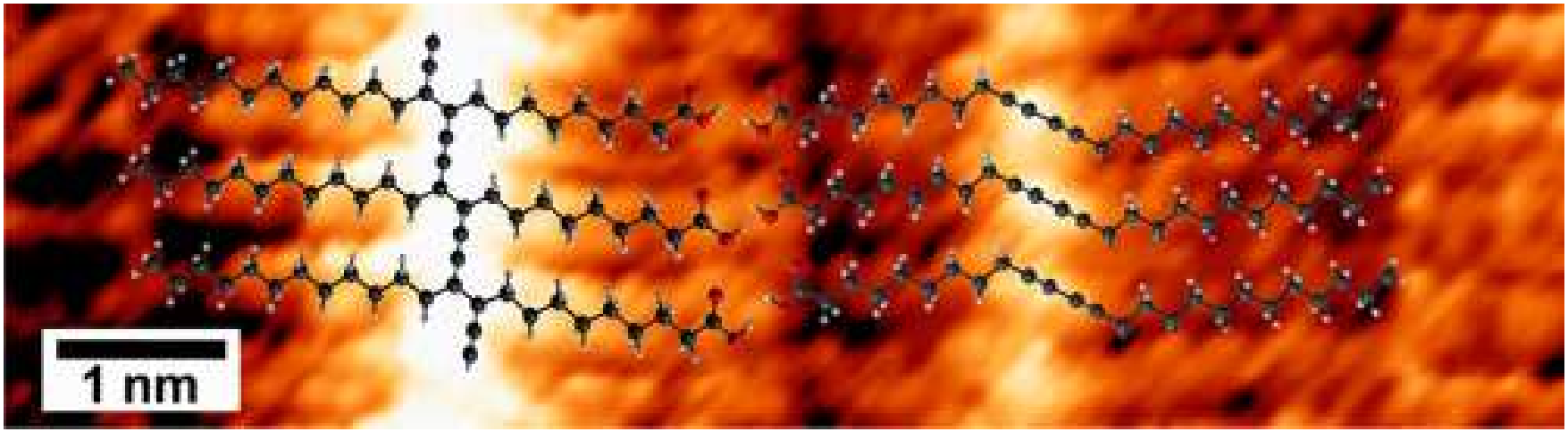
J. Am. Chem. Soc. 2012, 134, 40

Self-assembly su grafene:



J. Am. Chem. Soc. 2012, 134, 40





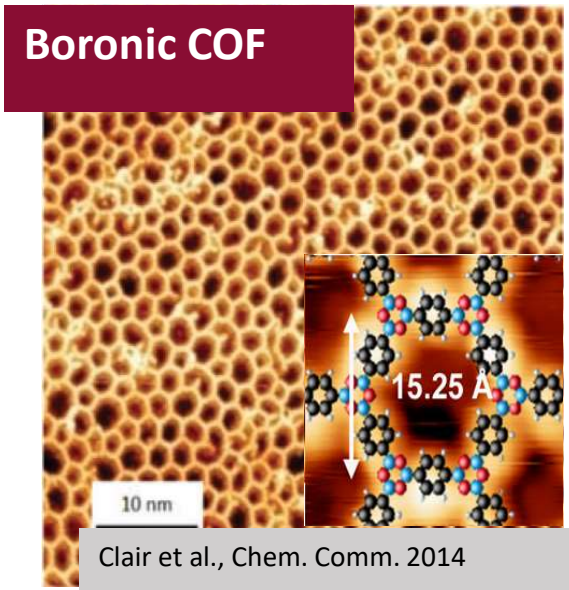
Qui, con la fotochimica, riesco a fare on-surface synthesis anche su un substrato poco reattivo come il grafene

J. Am. Chem. Soc. 2012, 134, 40

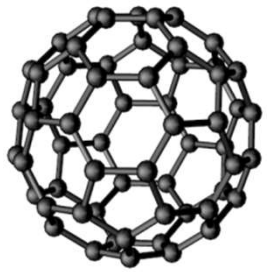
Boronic condensation

2D Covalent Organic Frameworks

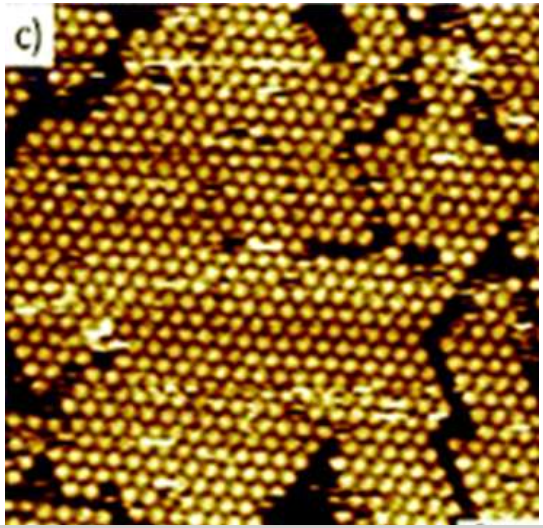
Boronic COF



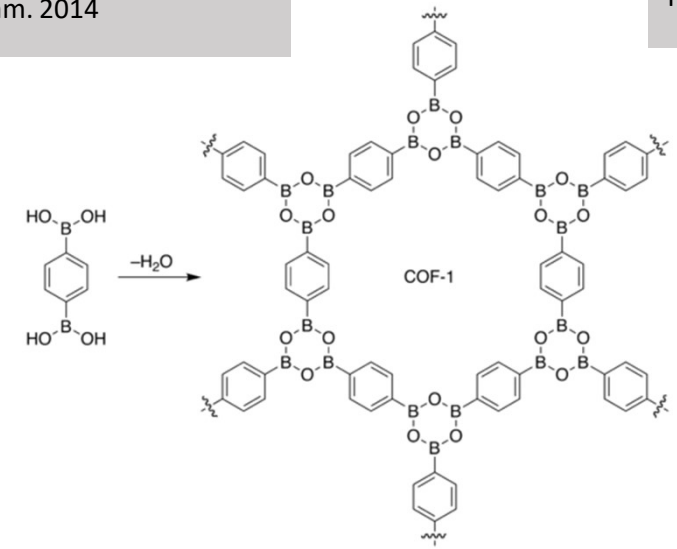
Clair et al., Chem. Comm. 2014



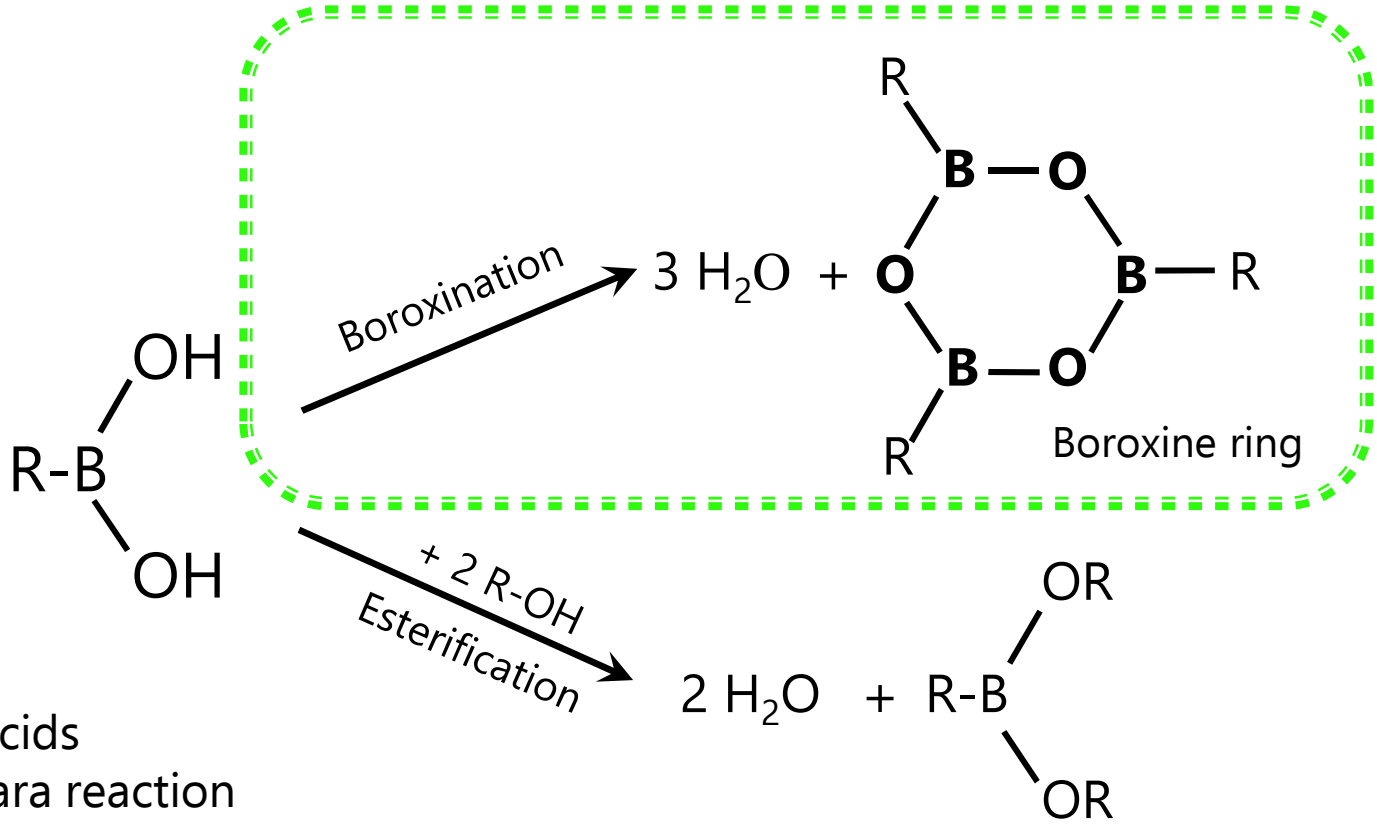
fullerene



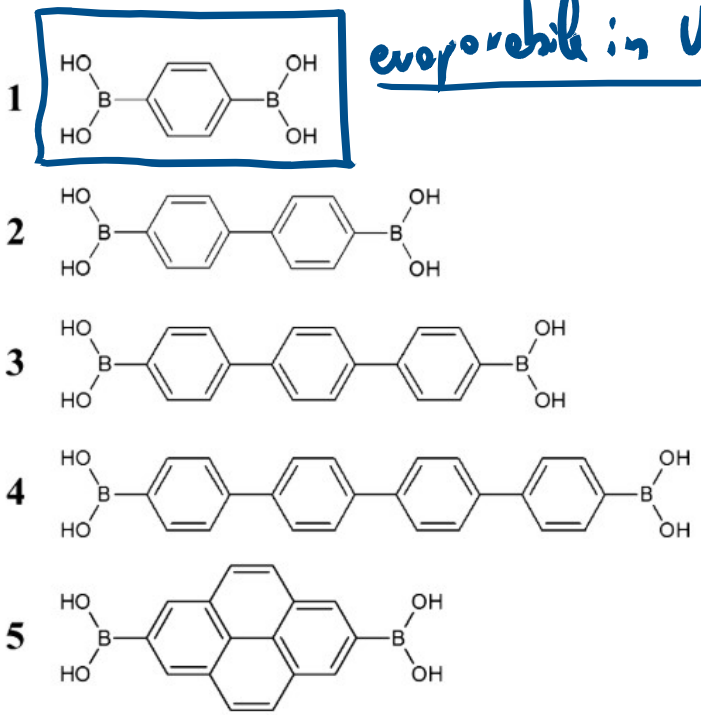
Plas et al., Chem. Comm. 2016



Boronic acid



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

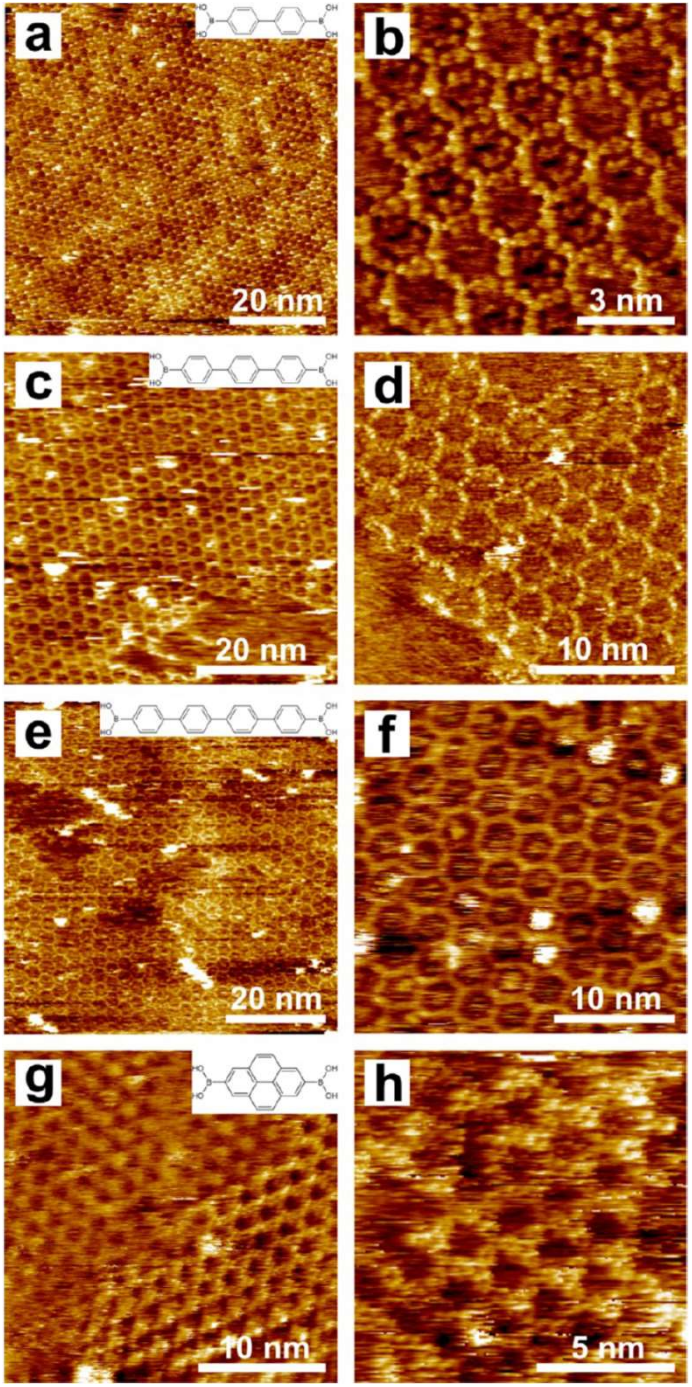


evaporabile in UHV

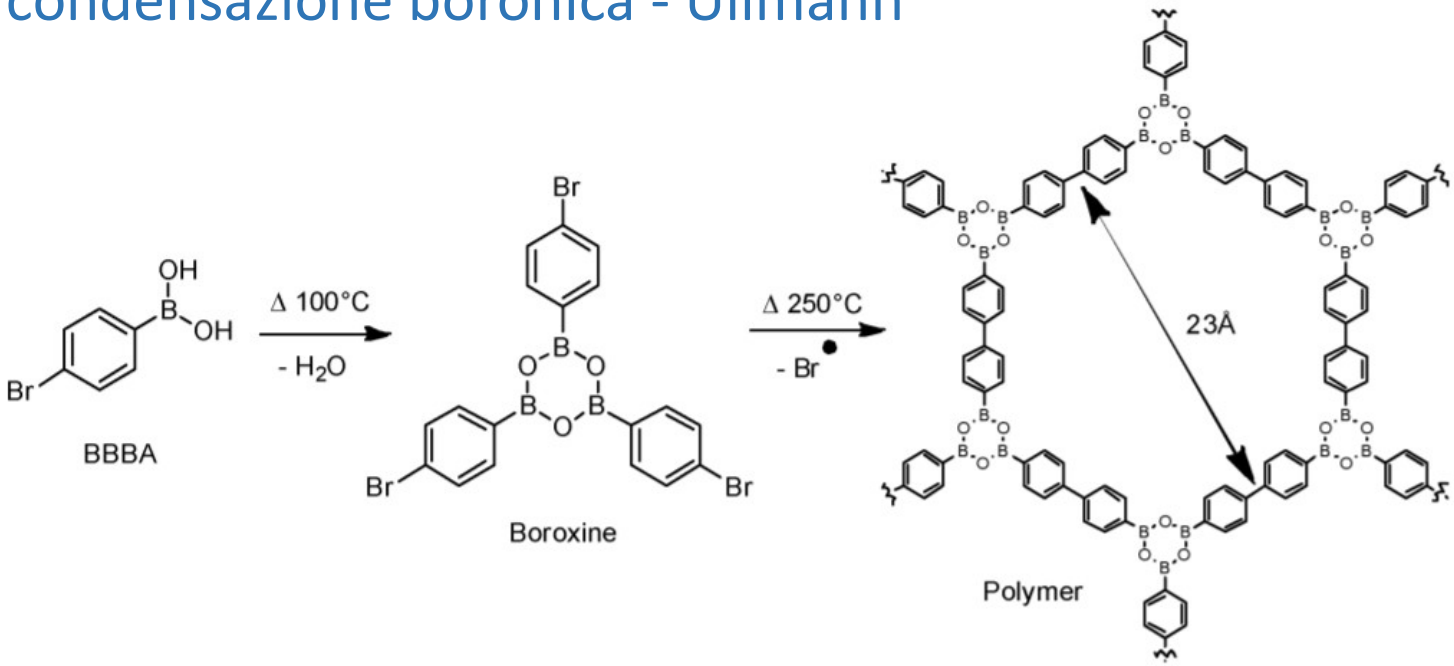
!! Se metto i precursori in un crogiolo e tutto di sublimarli

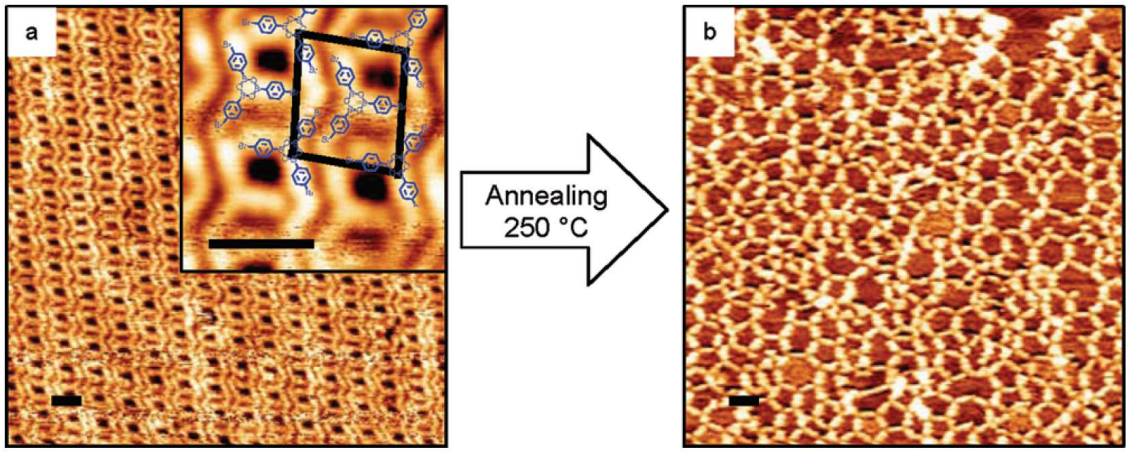
→ condensano nel crogiolo

→ preparazione in soluzione

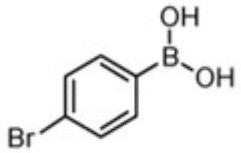


Sequenza condensazione boronica - Ullmann



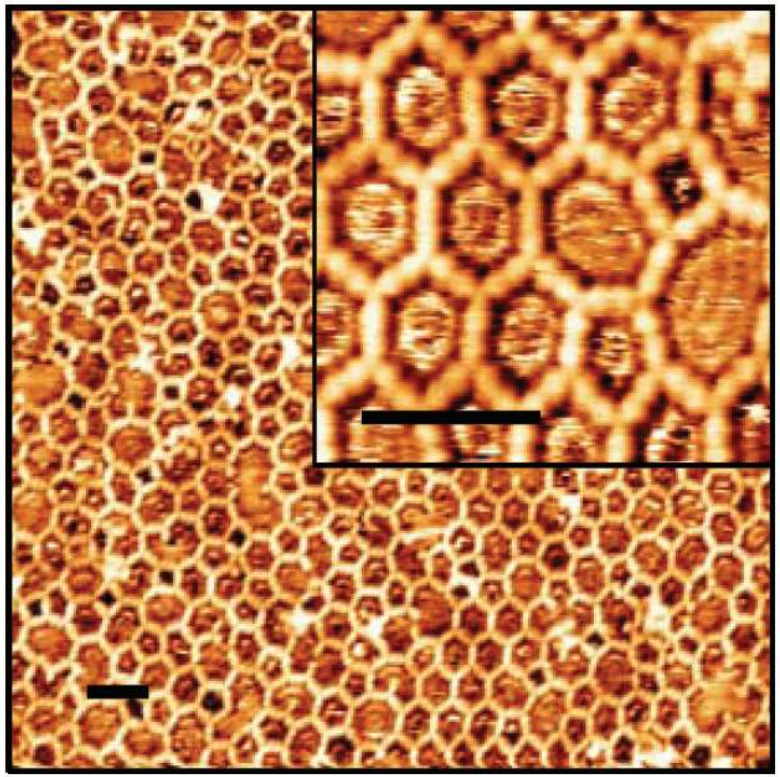


J. Phys. Chem. C 2012, 116, 4819–4823



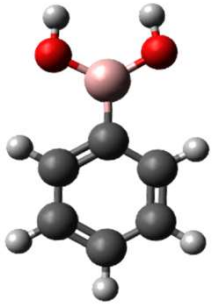
BBBA

Ts=250°C

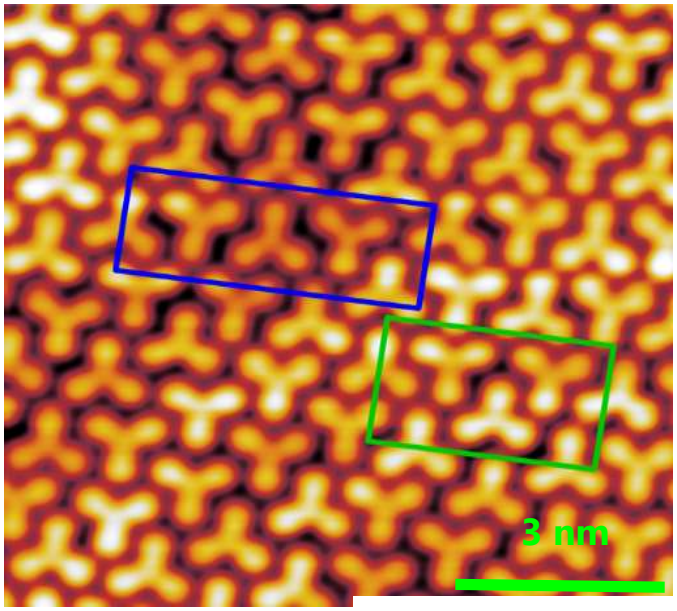


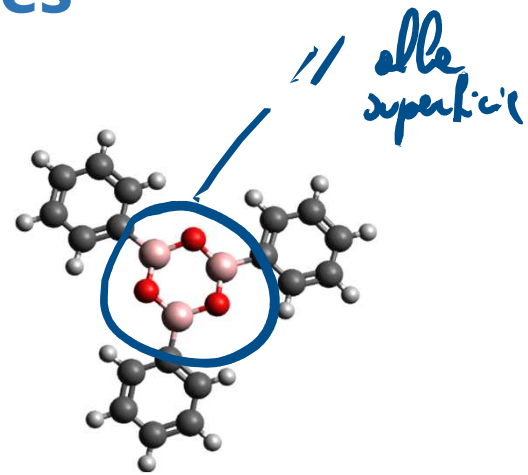
J. Phys. Chem. C 2012, 116, 4819–4823

Boroxine macromolecules

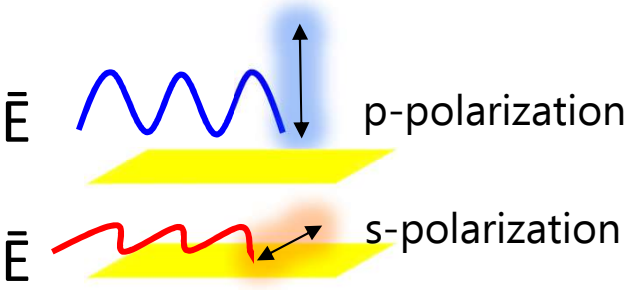


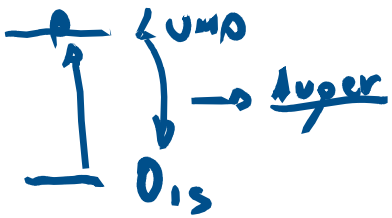
Phenylboronic acid
on Au(111)

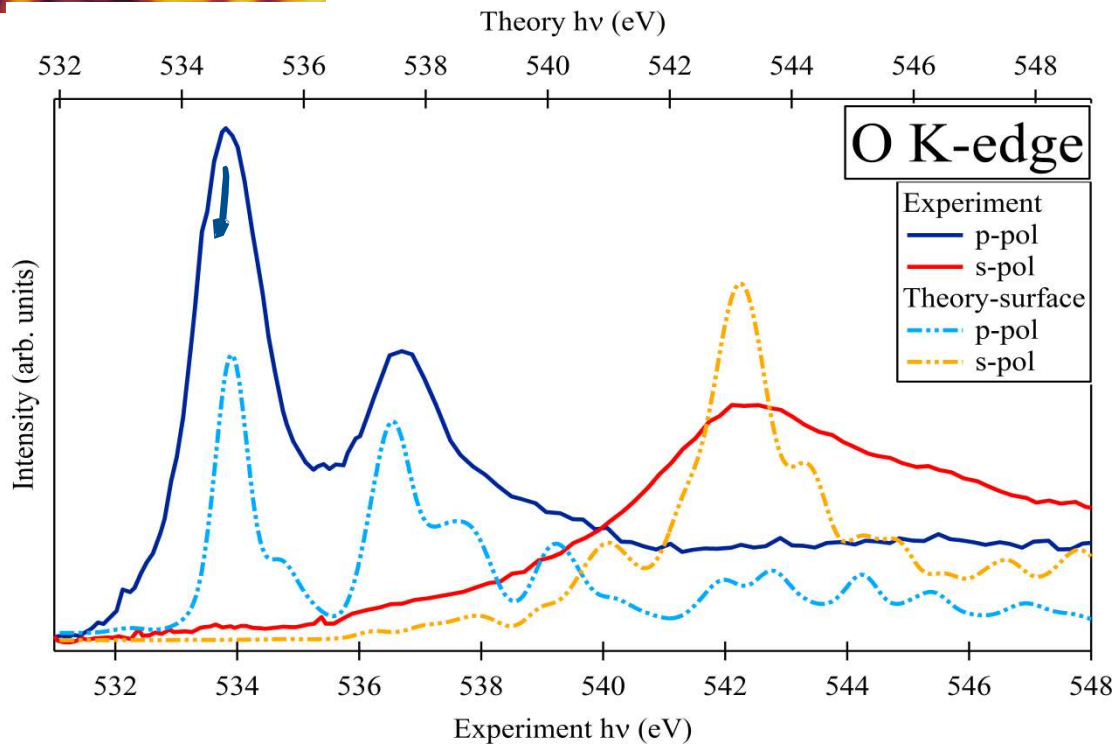




On surface synthesis
Triphenylboroxine





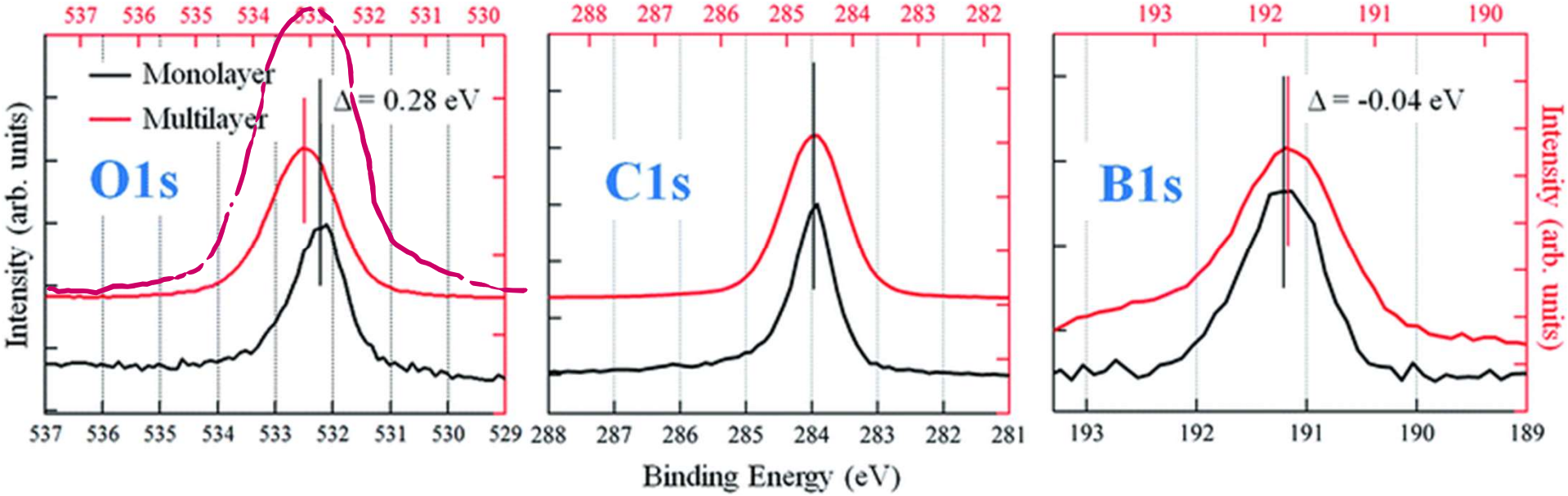


Chem. Sci., 2017, 8, 3789-3798

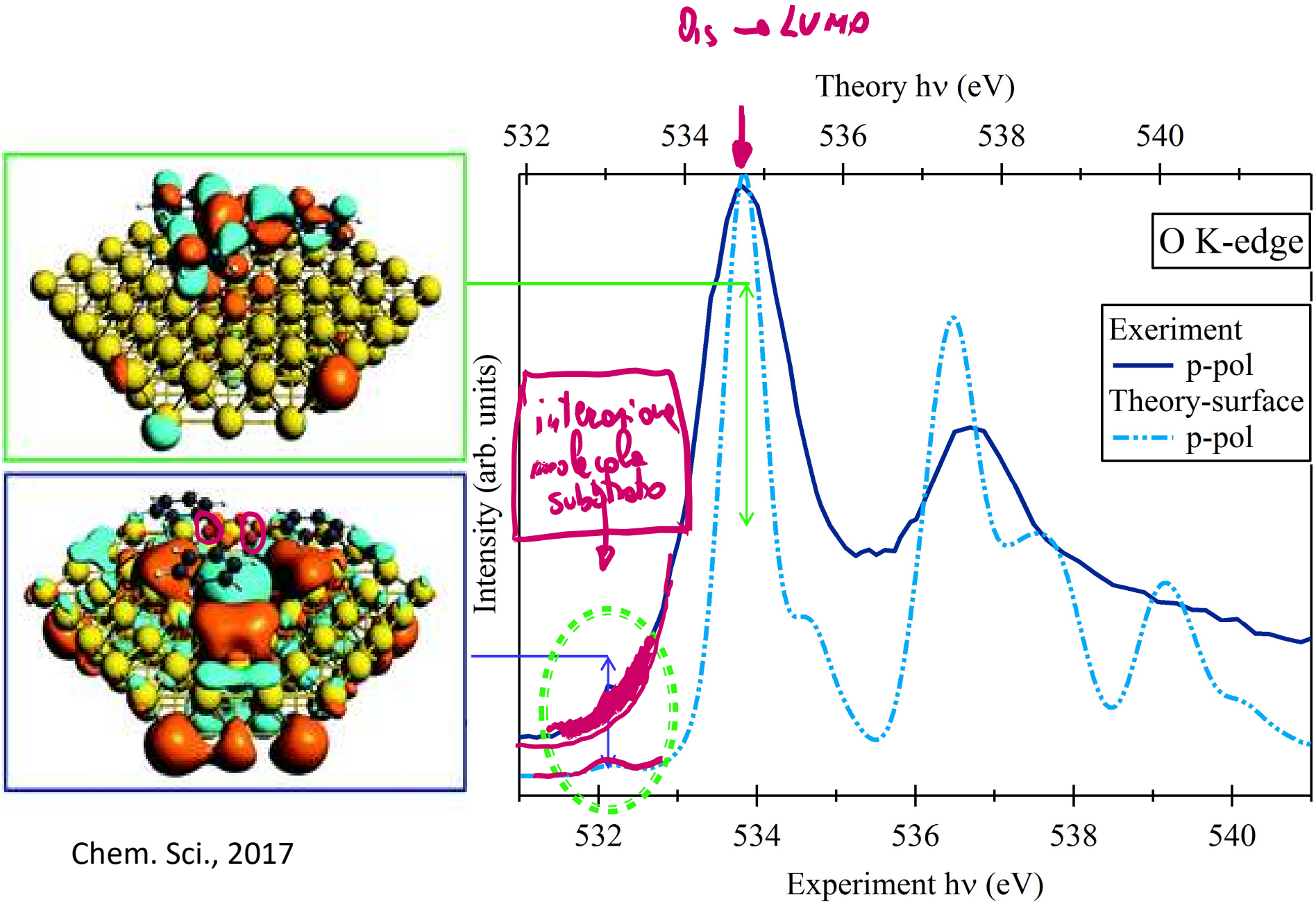
T < -50°C → crescita multilayer del precursore

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

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

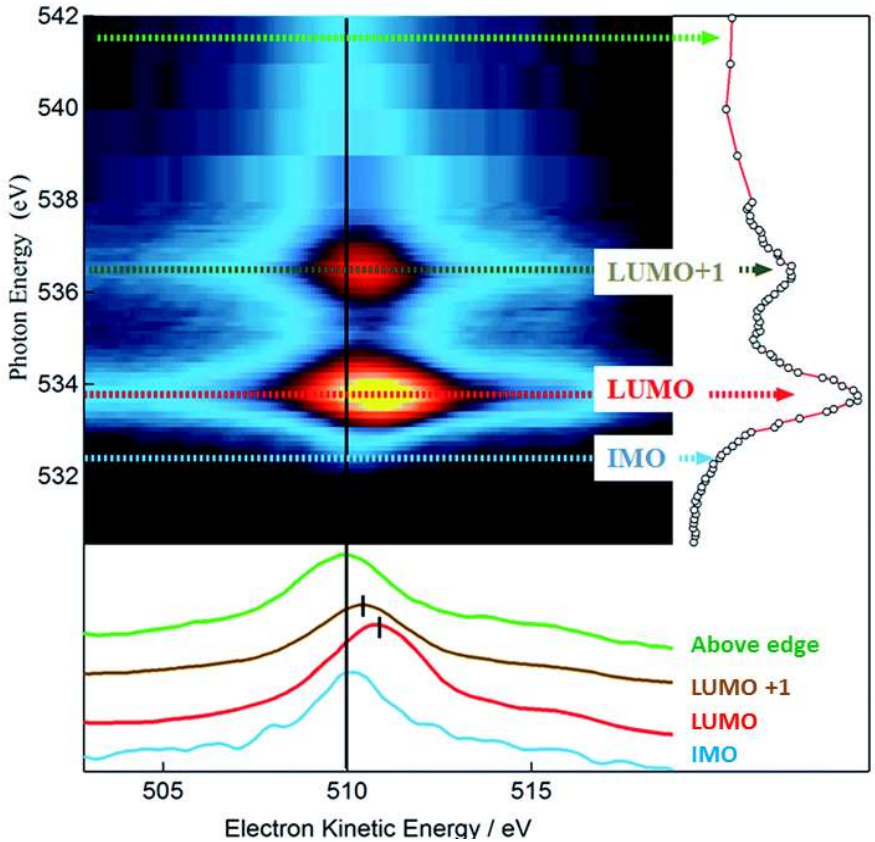


Chem. Sci., 2017, 8, 3789-3798



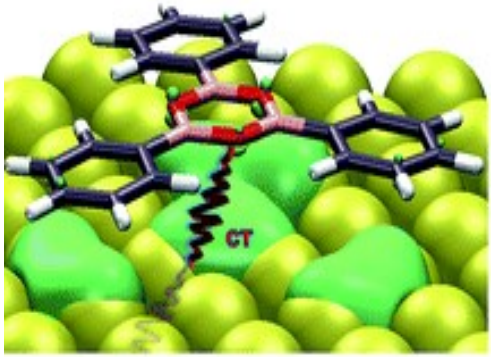
Chem. Sci., 2017

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

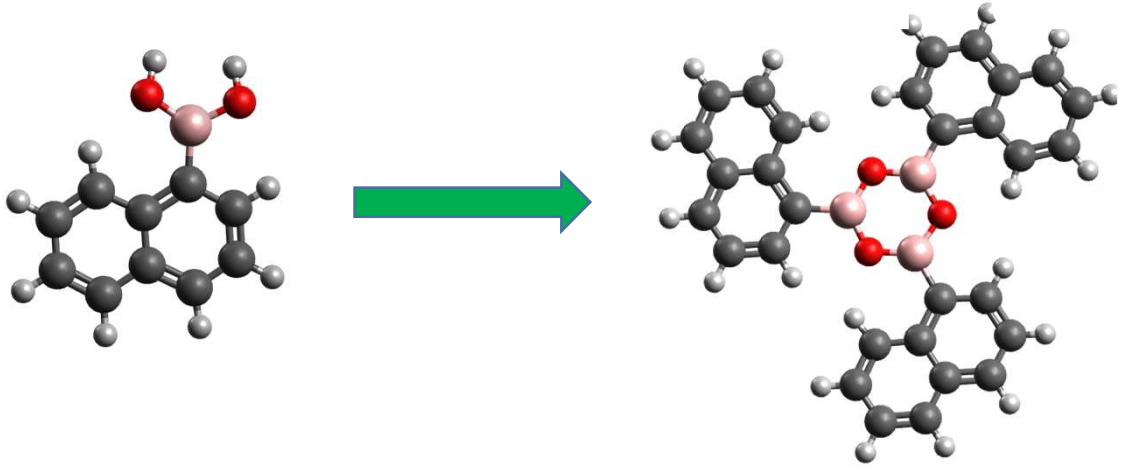


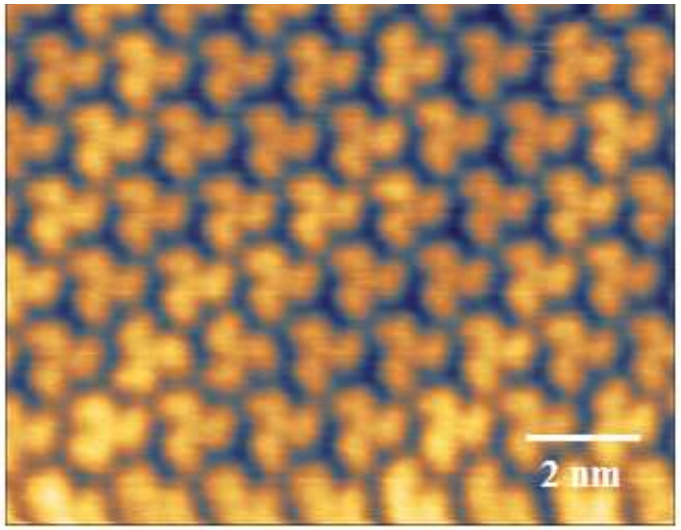
platforms for

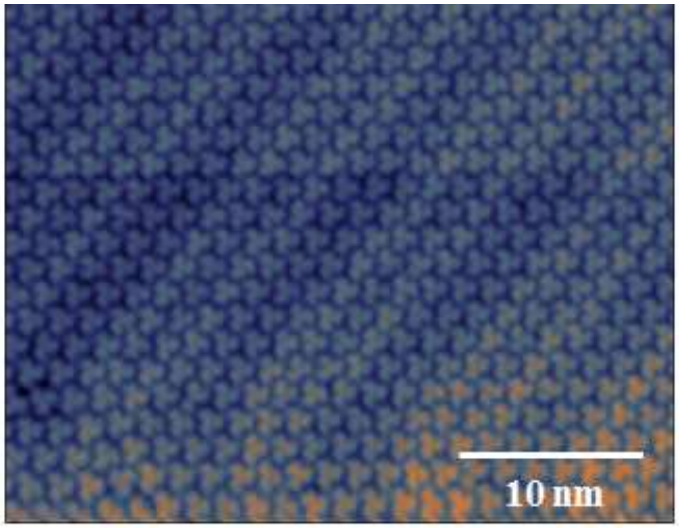
ultrafast charge transfer

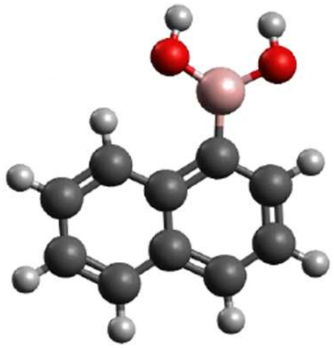


Toffoli et al., Chem. Sci., 2017, **8**, 3789-3798

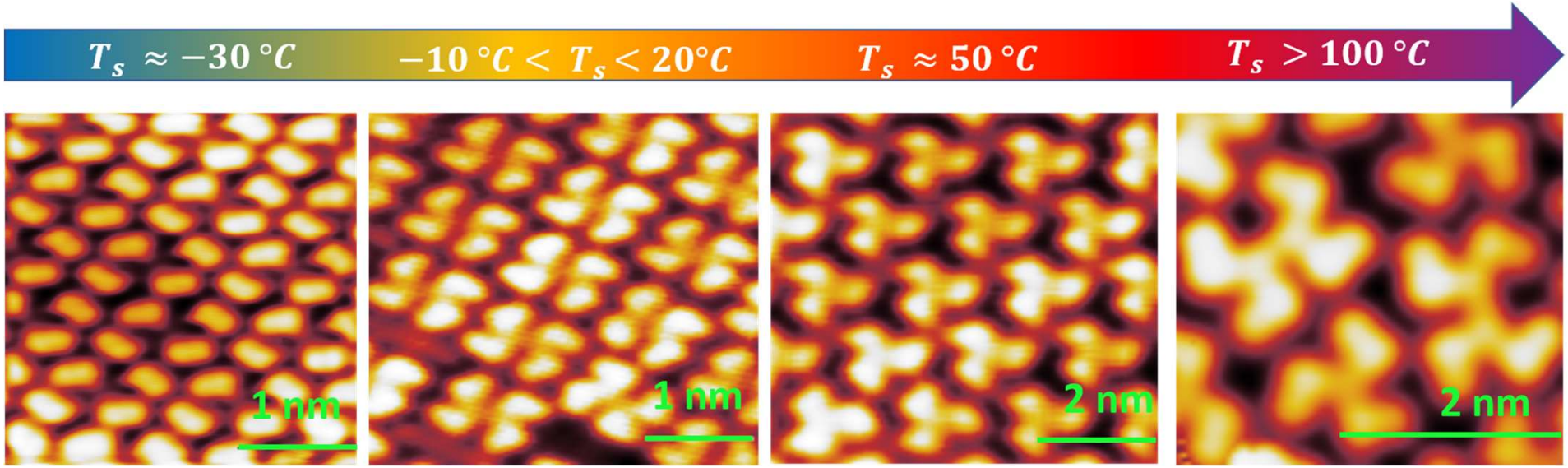


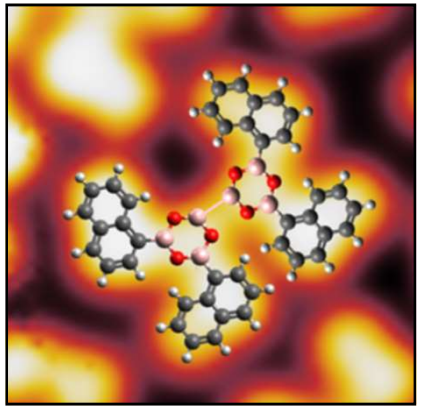

2 nm

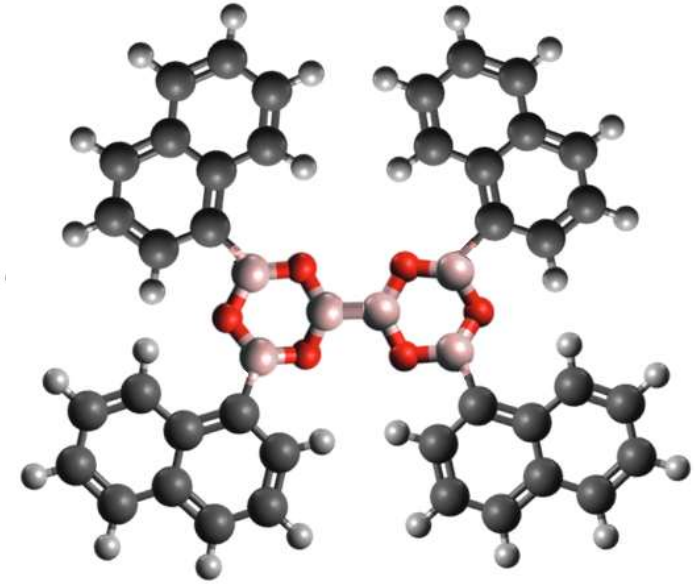

10 nm

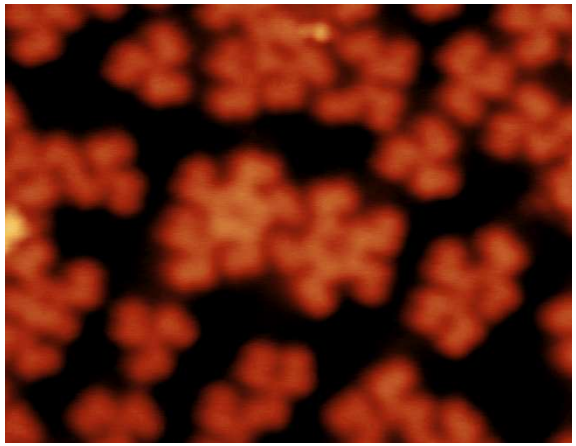


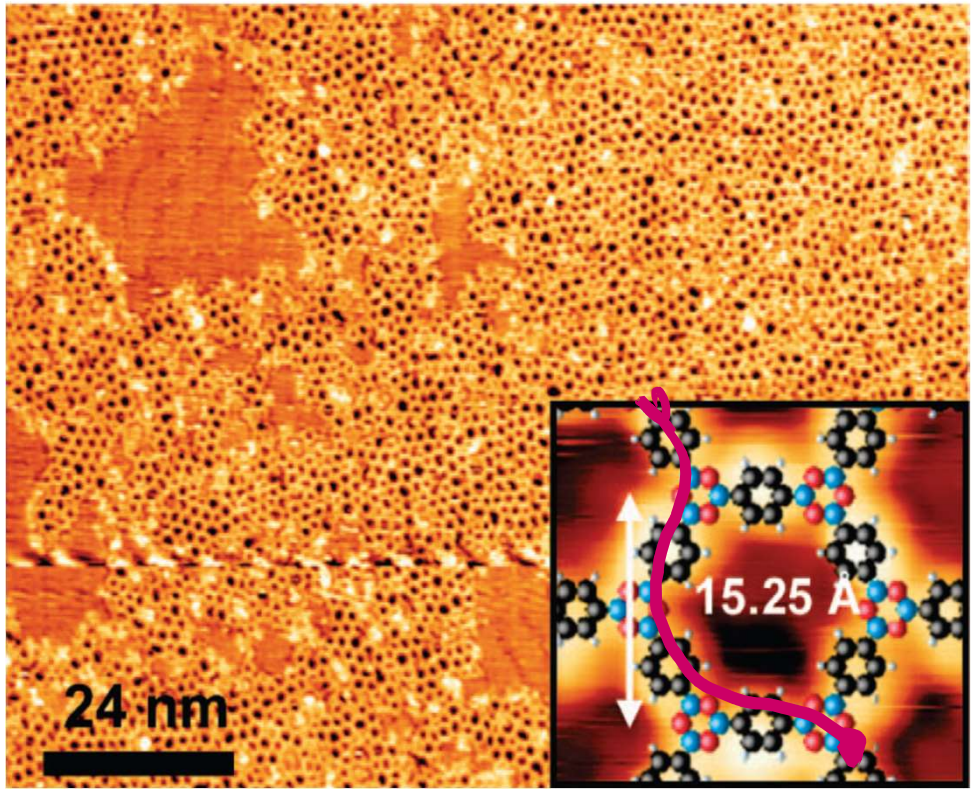
NBA su Au(111)











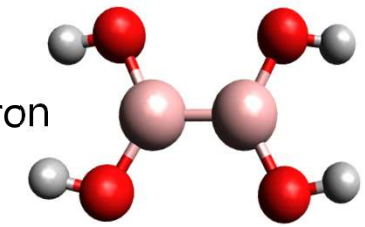
T. Faury et al., J. Phys. Chem. C 2012, 116, 4819−4823

DFT calculations:
Boroxine rings break the aromaticity of phenyl rings

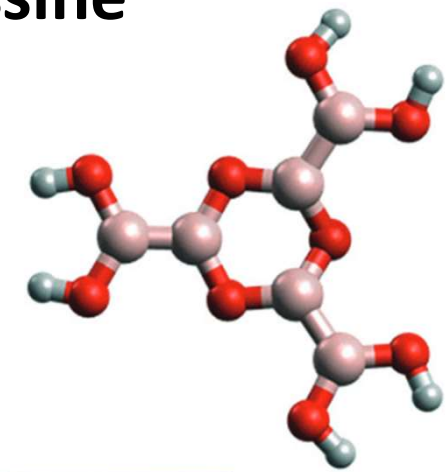
R. Wang, X. Zhang, S. Wang, G. Fu, J. Wang,
Phys.Chem.Chem.Phys.,2016,18,1258

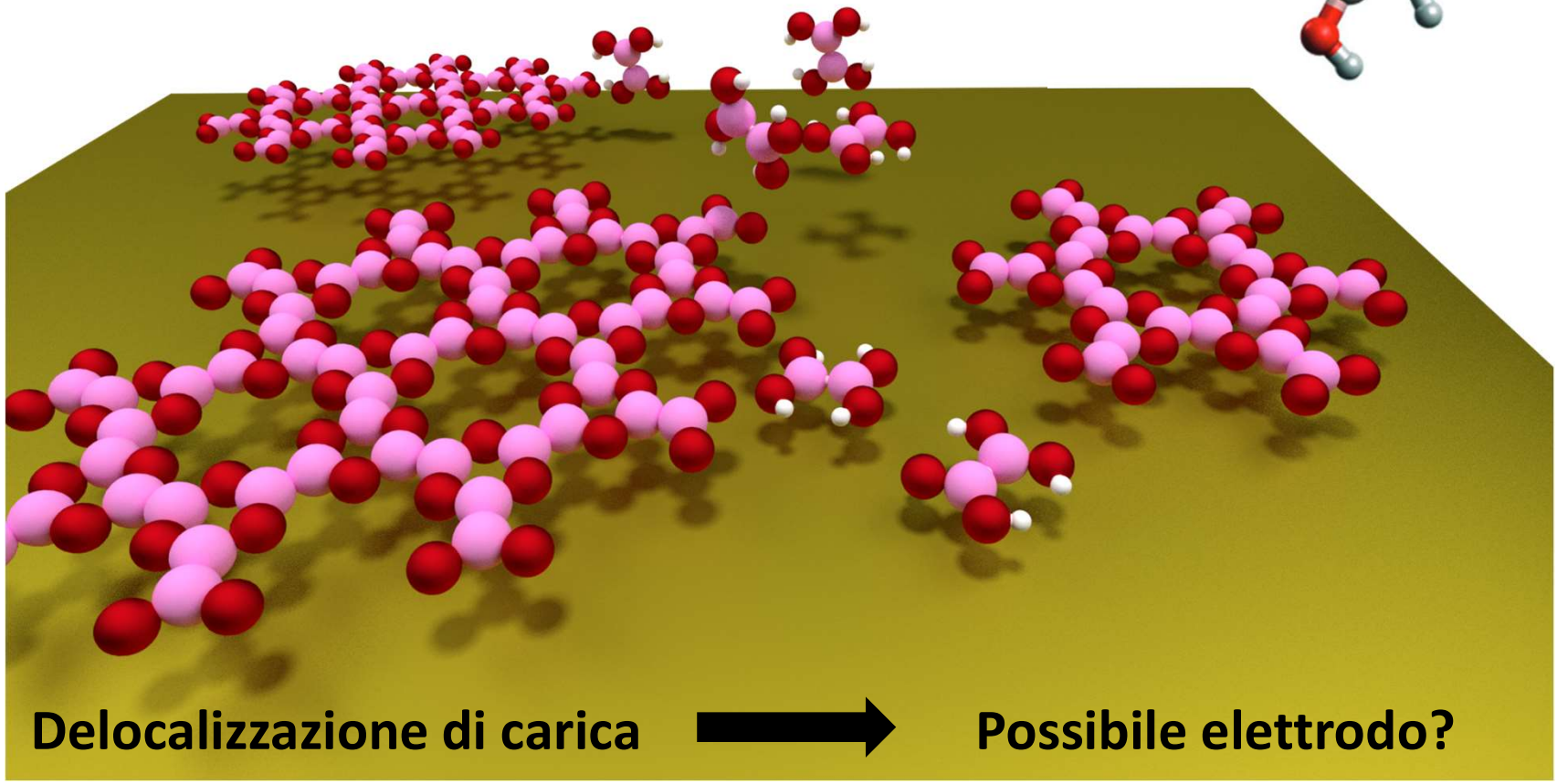
Framework di borossine

THDB
Tetra**h**ydroxy**di**boron

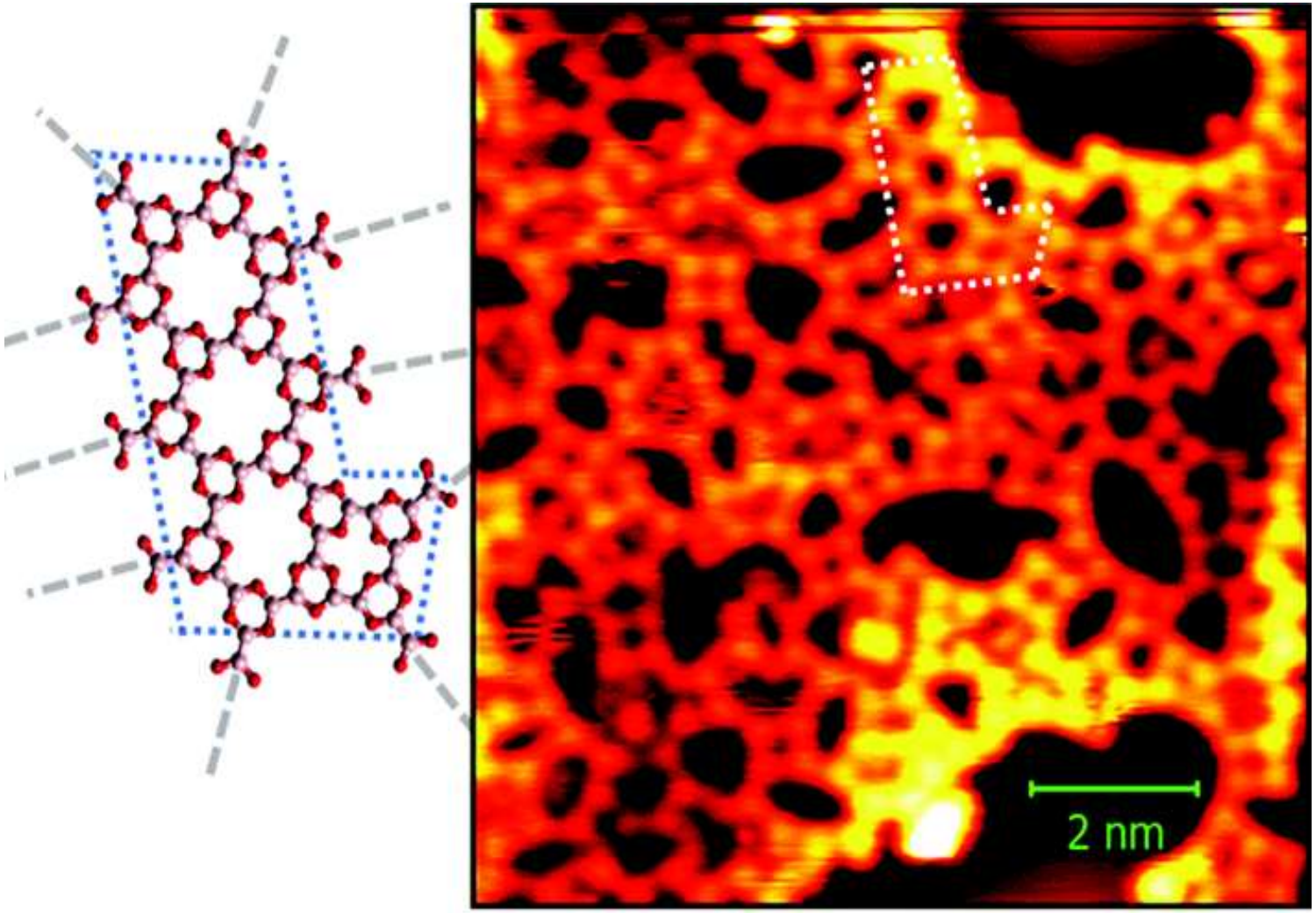


B
O
H





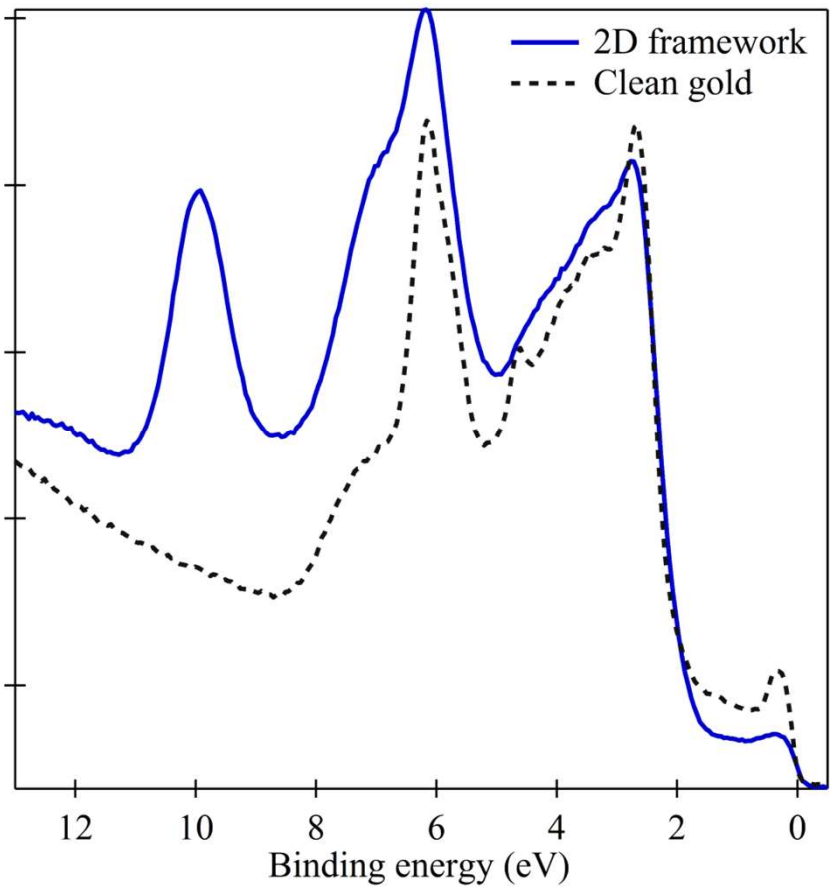
Chem. Commun., 2018

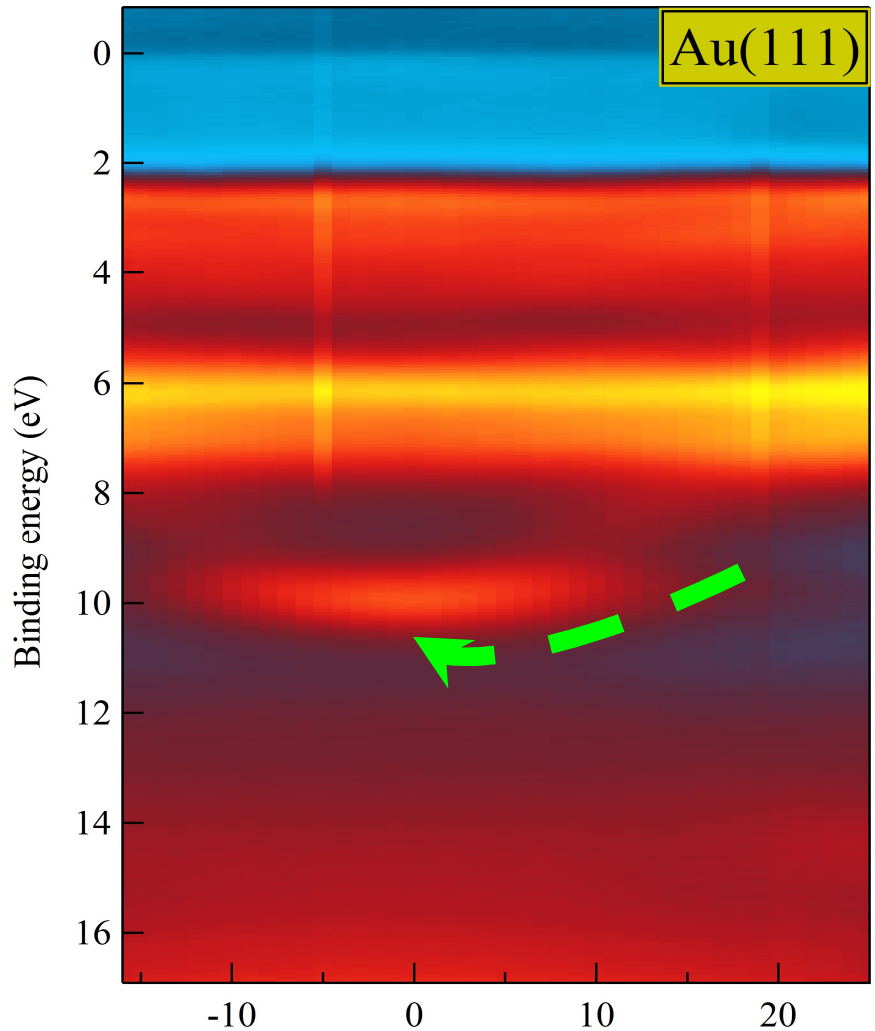


vitreous morphology

Proliferation of defects

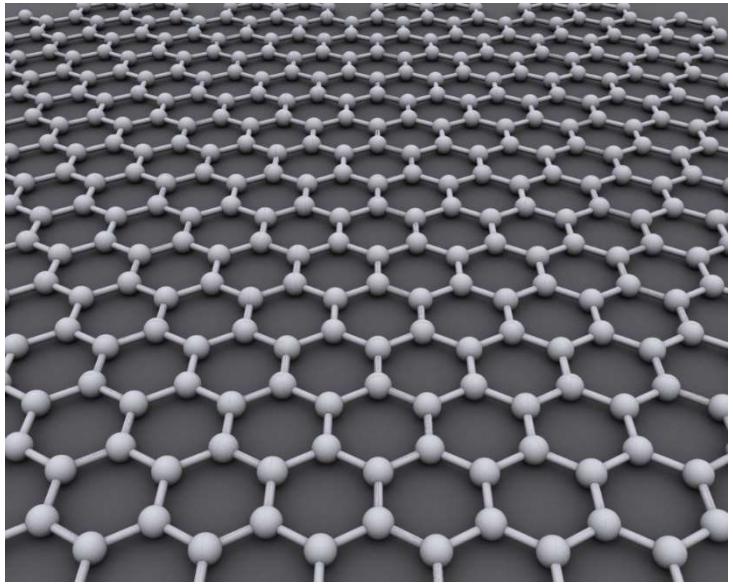
Chem. Commun., 2018

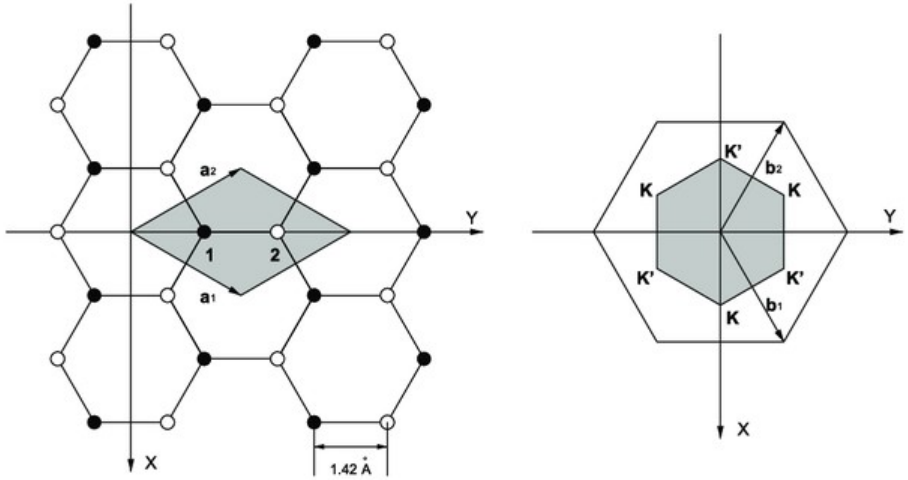


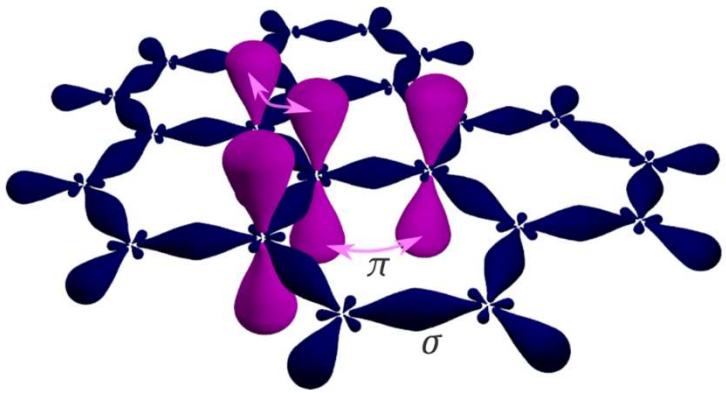


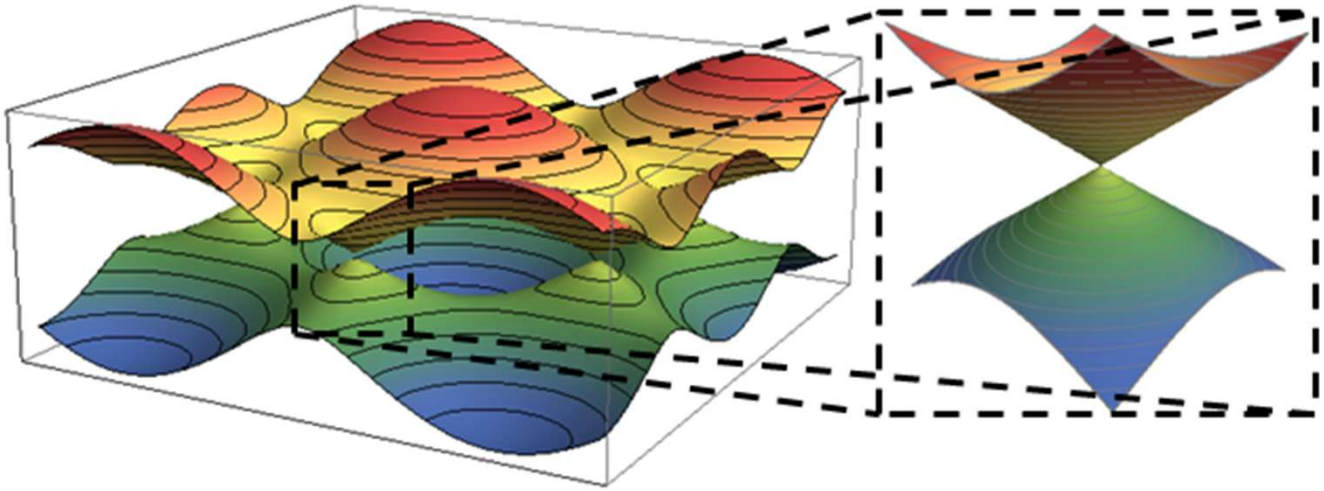
Chem. Commun., 2018

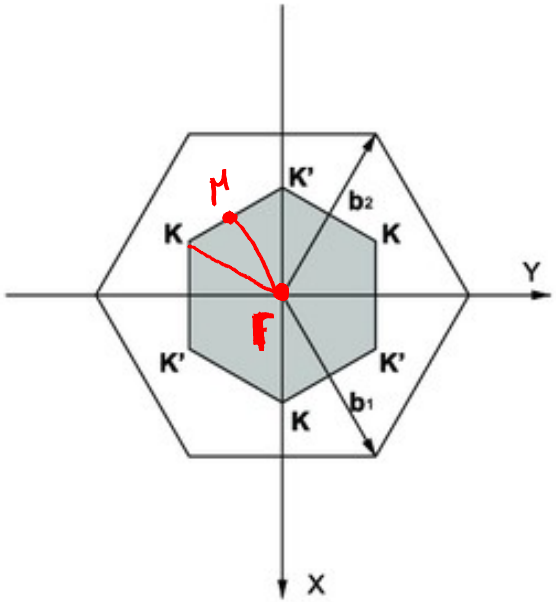
Band dispersion at room temperature – electron delocalization

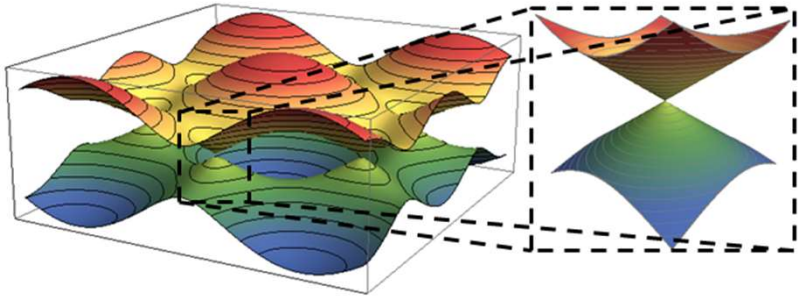


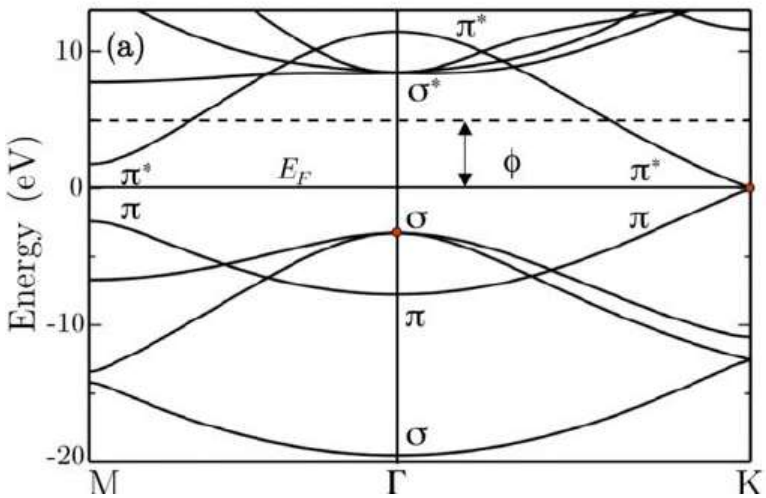

a2
a1
1
2
Y
X
1.42 Å
K'
K
b2
b1

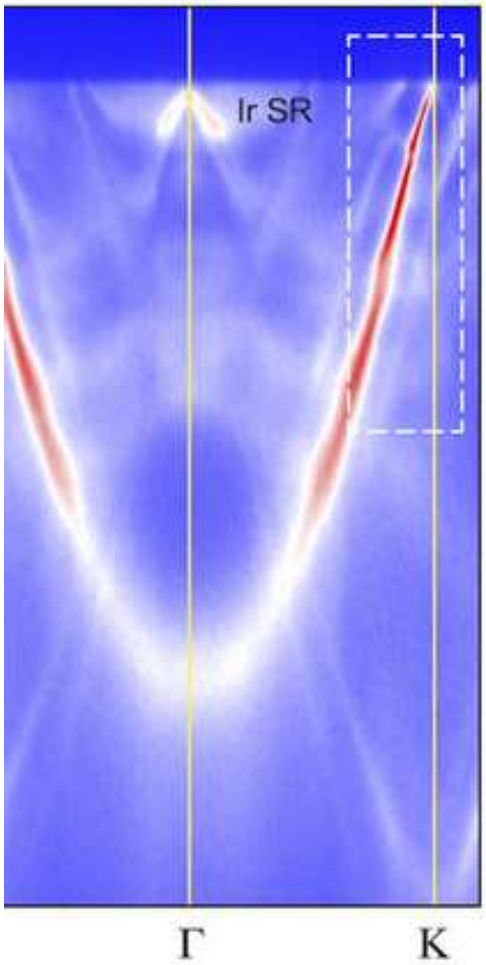

π
σ

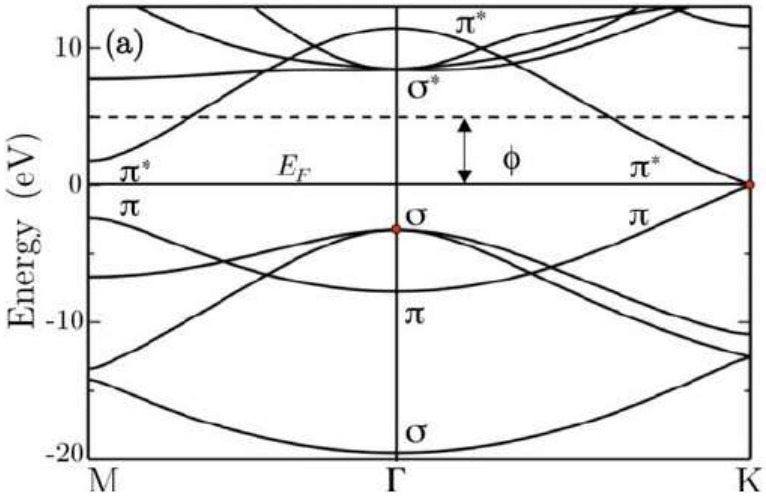



K'
b2
K
K
Y
Γ
K'
K'
b1
K
X
M



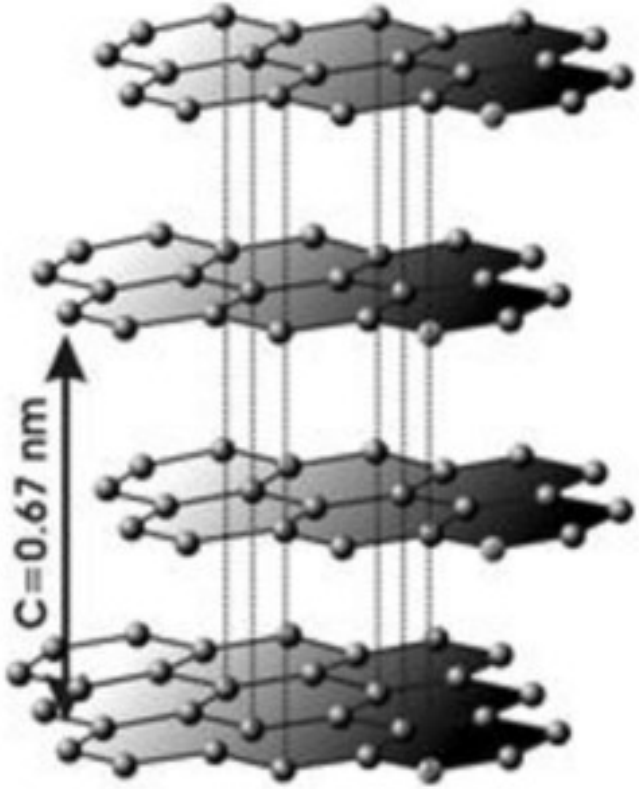

(a)
10
0
-10
-20
Energy (eV)
π*
σ*
π*
E_F
ϕ
π*
π
σ
π
π
σ
M
Γ
K

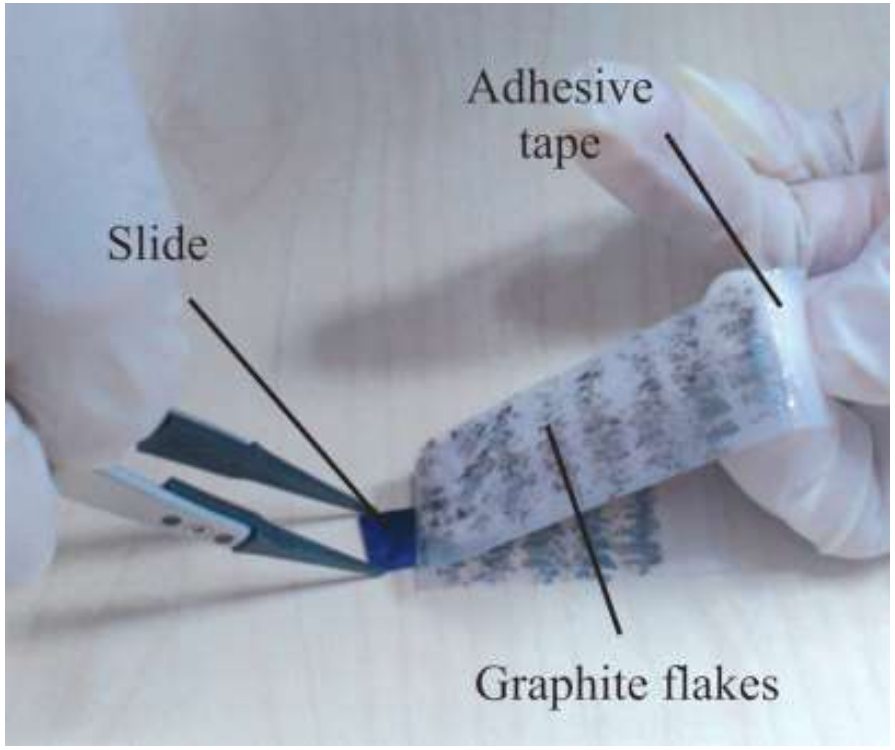




•Journal of Physics Condensed Matter 2015 27(30)

Sintesi di grafene

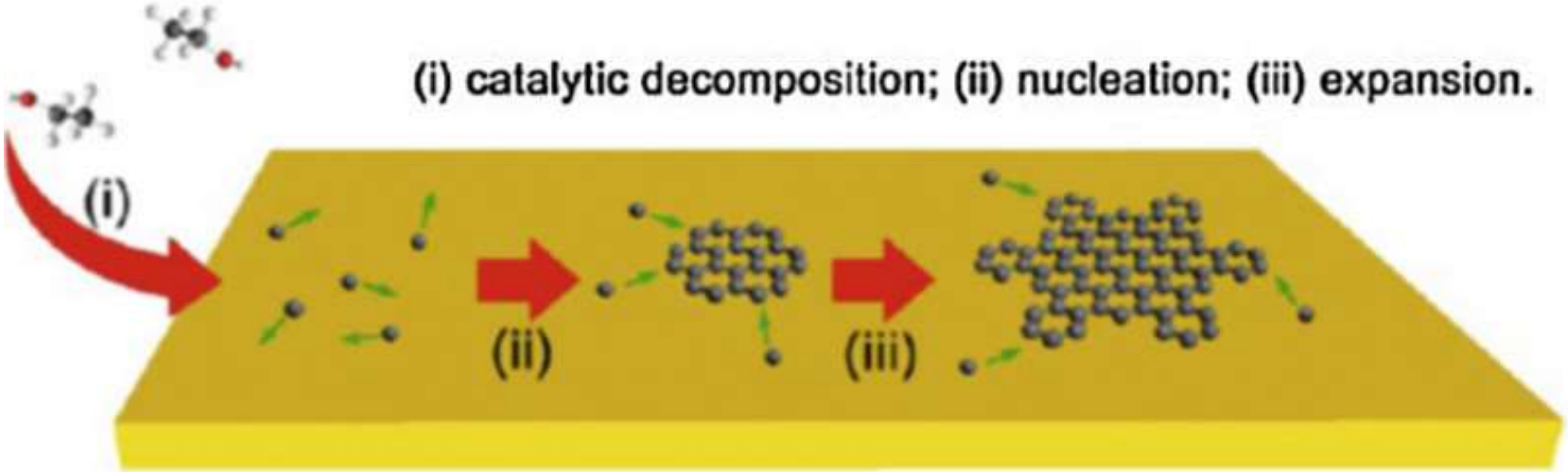



Adhesive
tape
Slide
Graphite flakes


Andre Geim

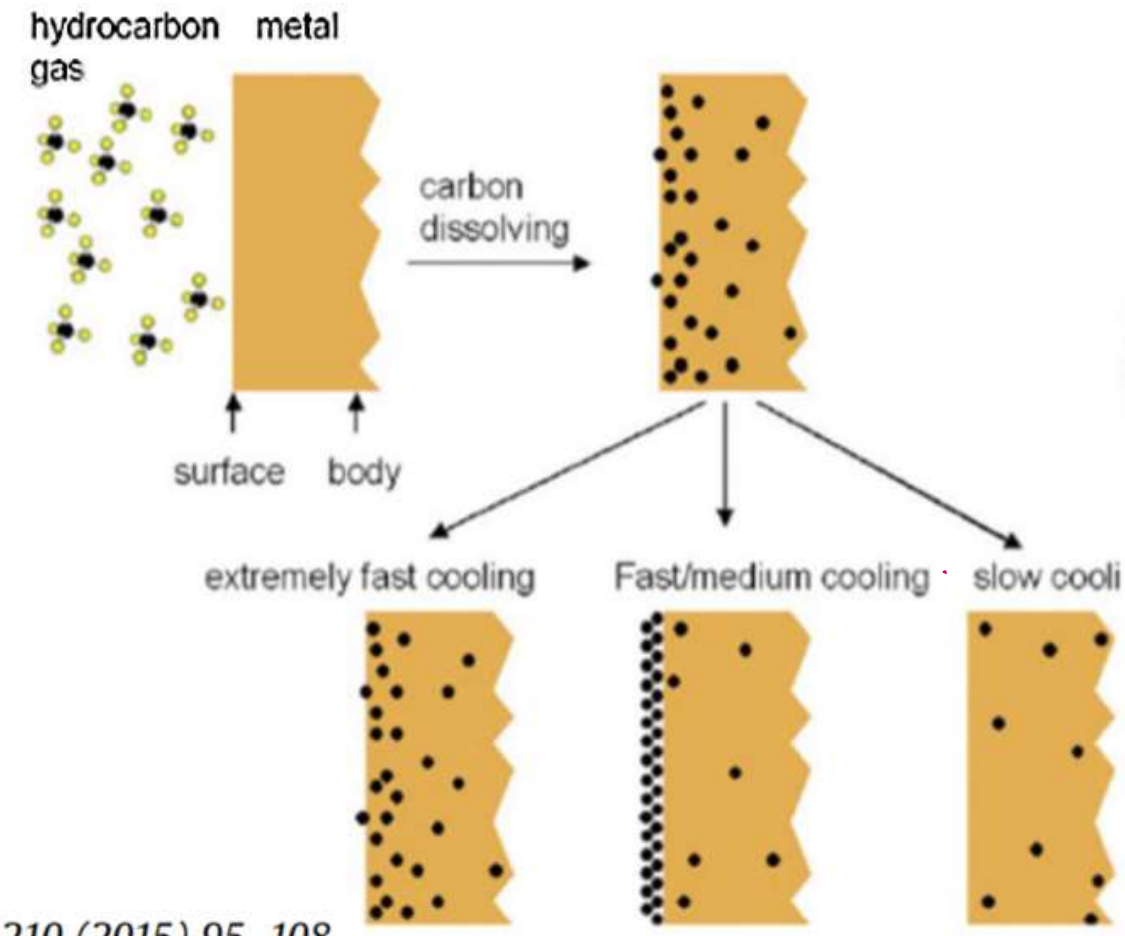
Chemical Vapour Deposition

Cu (111), 1000 °C



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

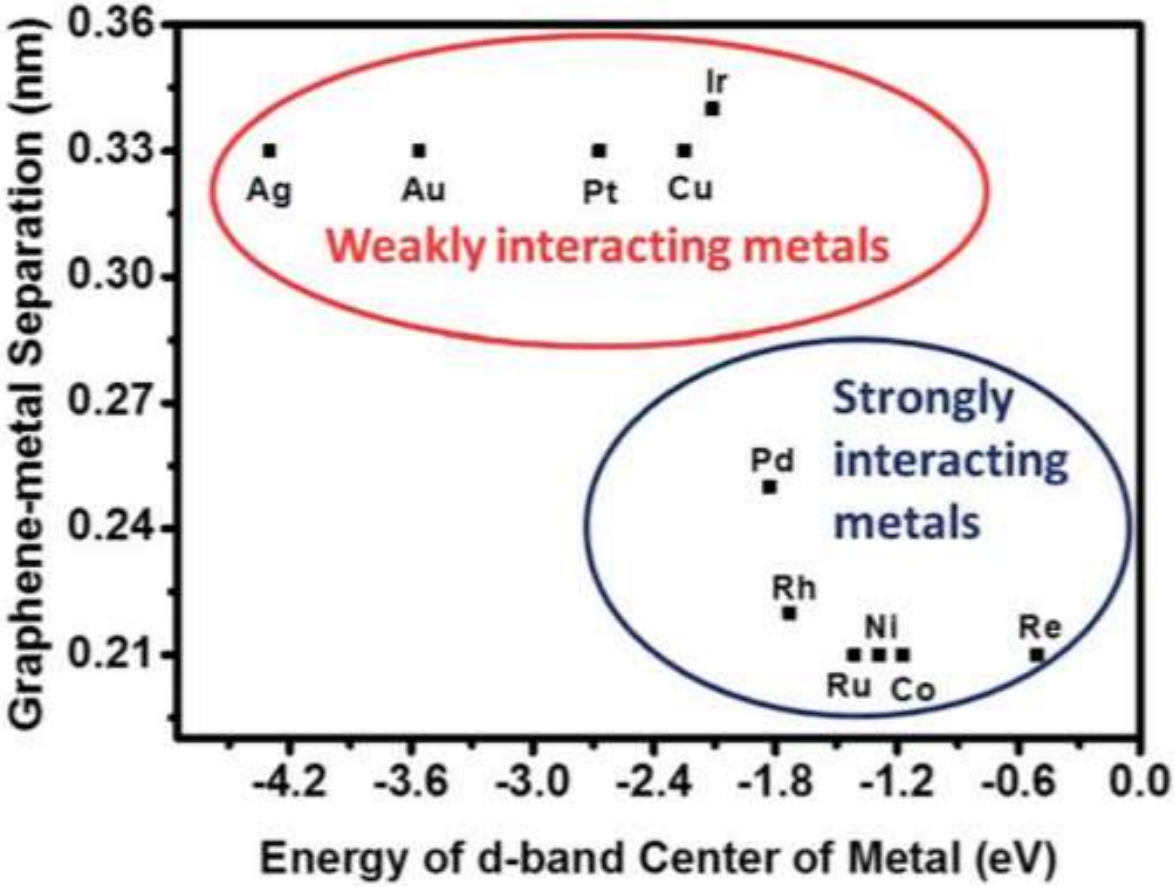
Ni(111)

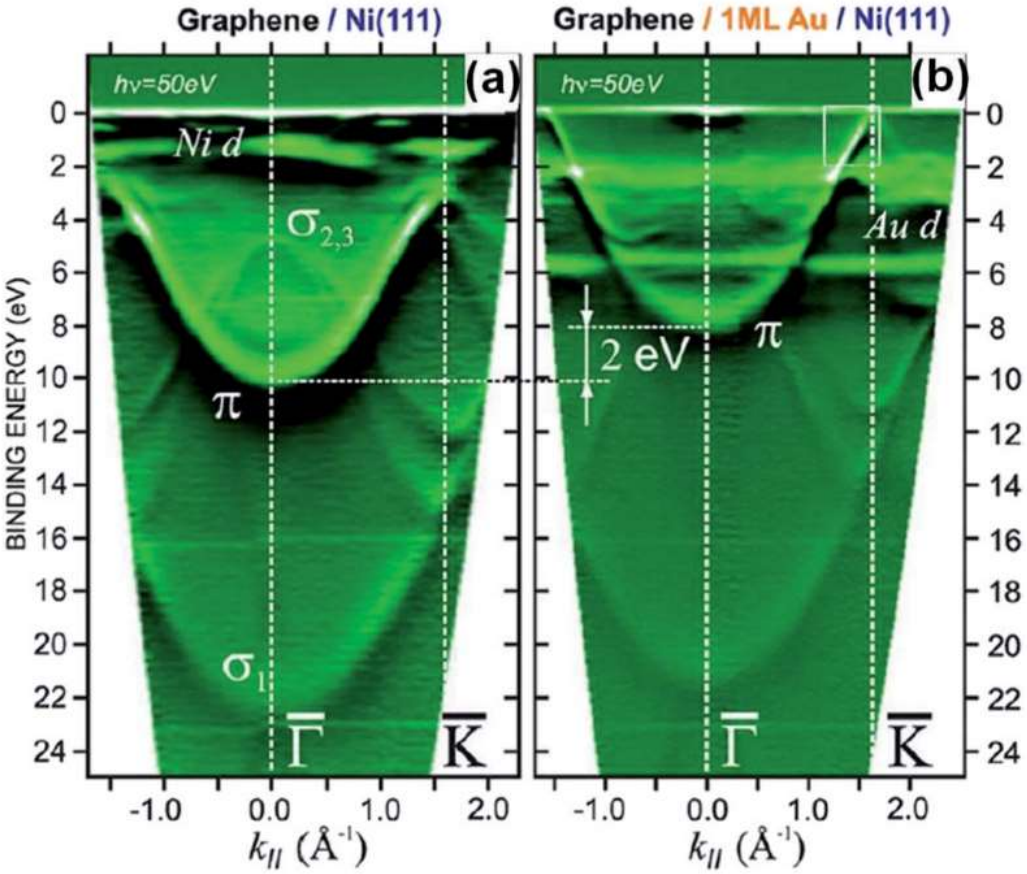


X. Chen et al. / Synthetic Metals 210 (2015) 95–108

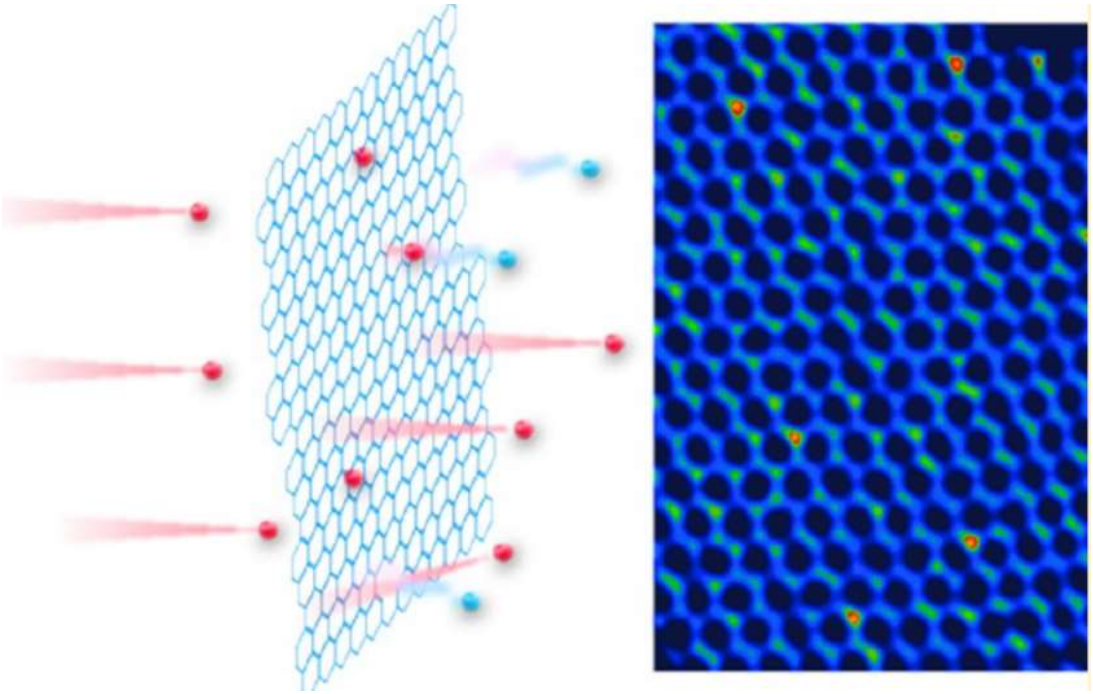
Table 1 Carbon solubilities (atom%) in different transition metals at 1000 °C according to ref. 17

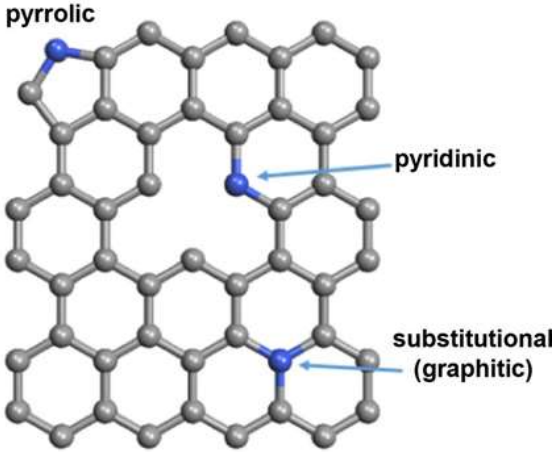
Metal	Carbon solubility (atom%) at 1000 °C
Co	3.41
Ni	2.03
Cu	0.04
Ru	1.56
Rh	0.89
Pd	5.98
Ag	0.01
Re	4.39
Ir	1.35
Pt	1.76
Au	0.01

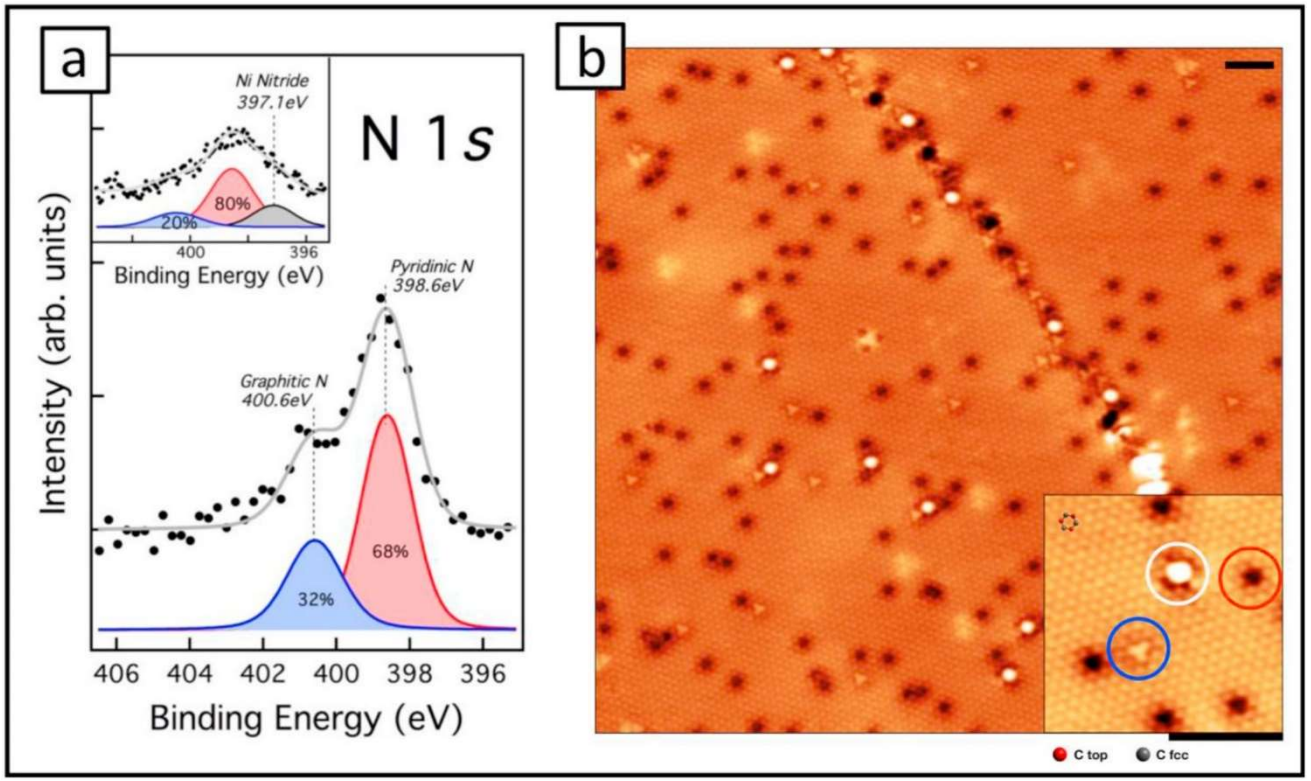

Graphene-metal Separation (nm)
0.36
0.33
0.30
0.27
0.24
0.21
Ir
Ag
Au
Pt
Cu
Weakly interacting metals
Strongly interacting metals
Pd
Rh
Ni
Re
Ru
Co
-4.2
-3.6
-3.0
-2.4
-1.8
-1.2
-0.6
0.0
Energy of d-band Center of Metal (eV)


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

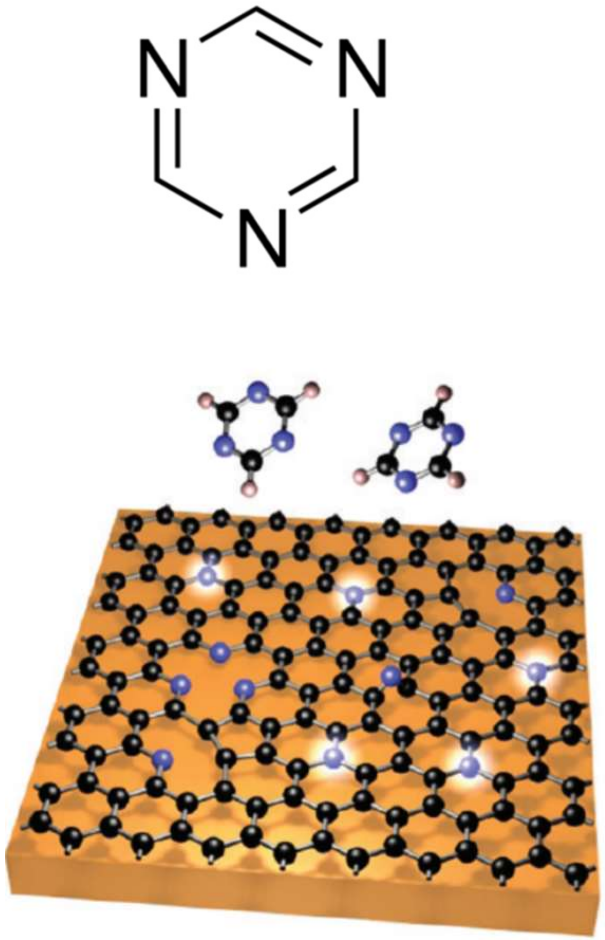
Doping di grafene Sostituire alcuni atomi di carbonio con atomi ad esembio di N o B permette di modificare la struttura elettronica del film.

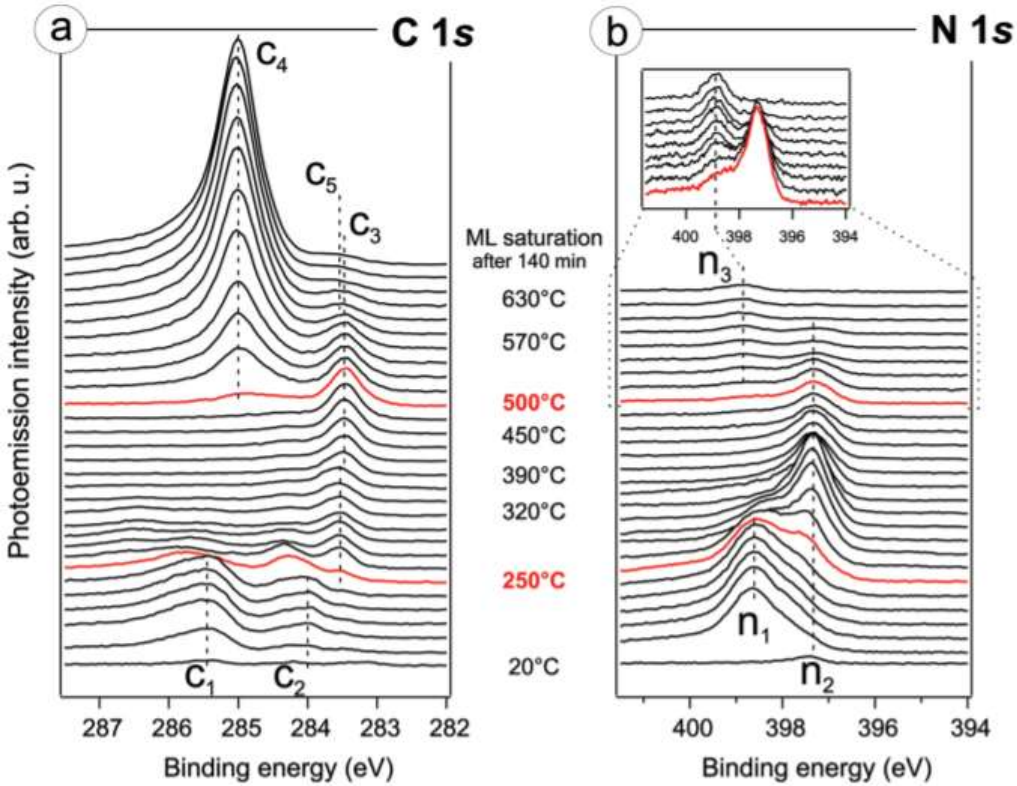




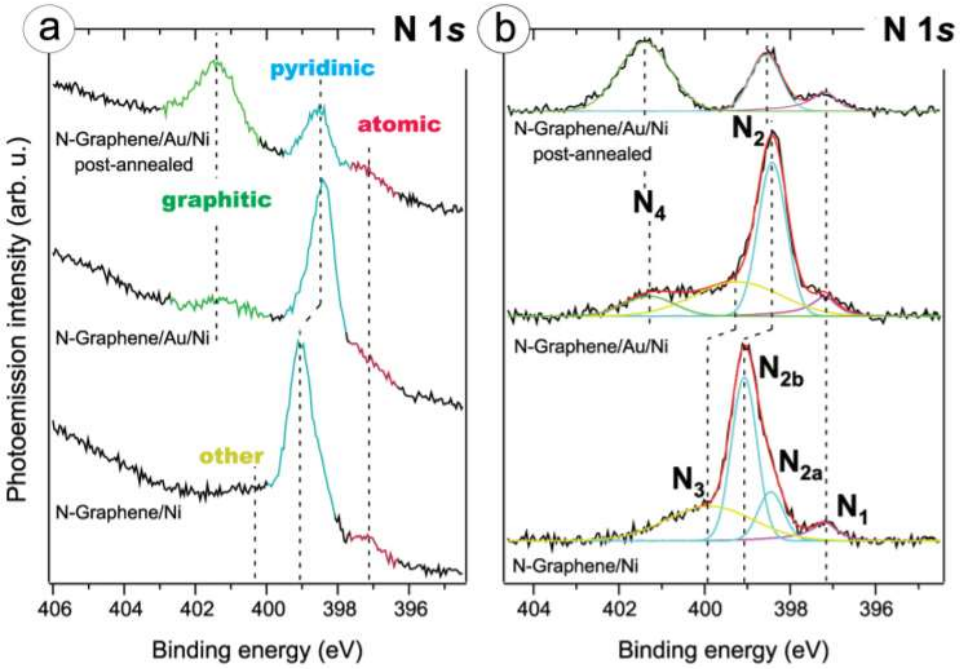


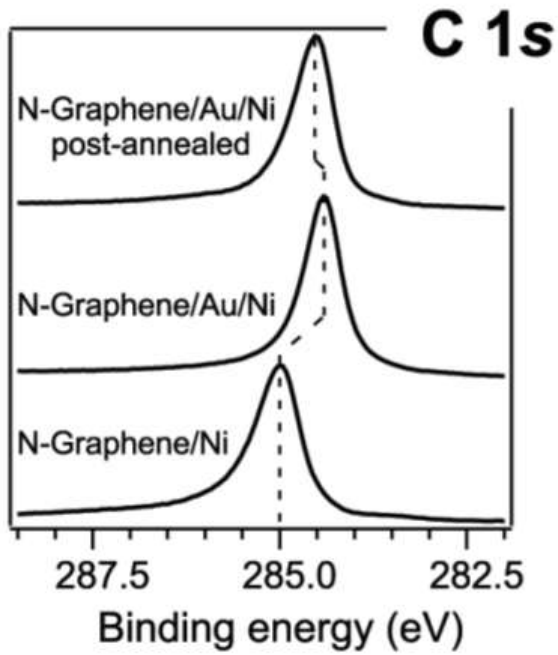
Carbon 171 (2021) 704–710



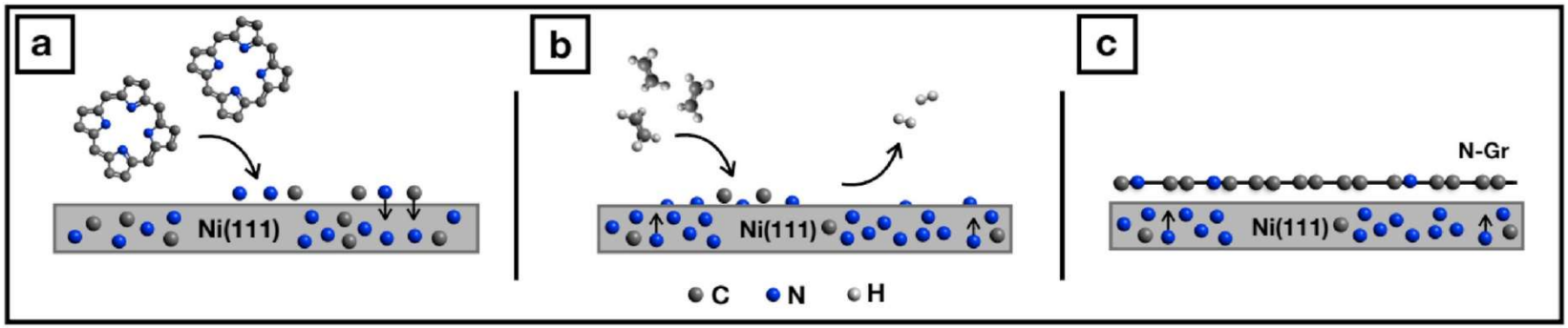


Nano Lett. 2011, 11, 5401–5407



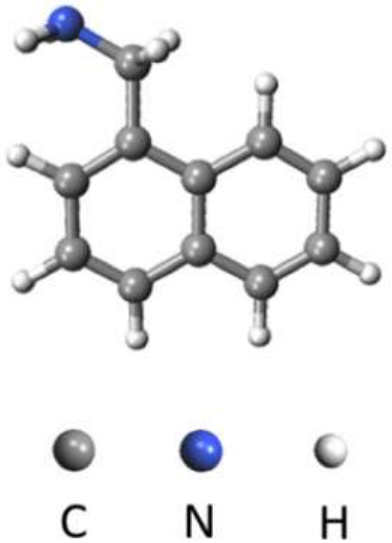


Nano Lett. 2011, 11, 5401–5407

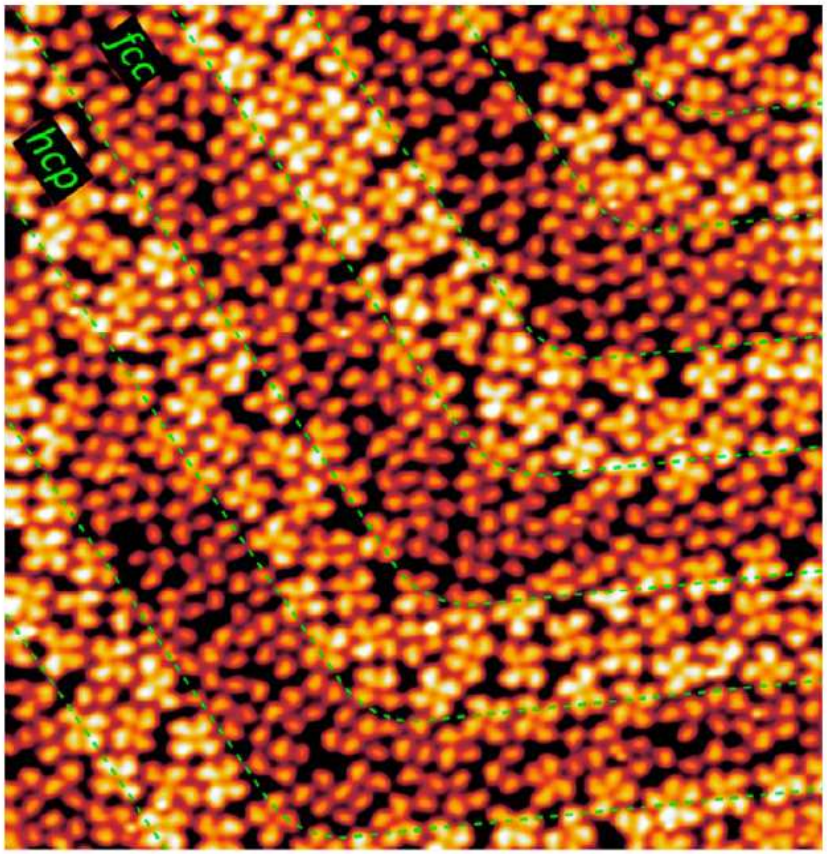


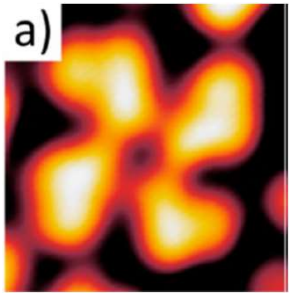
Carbon 171 (2021) 704–710

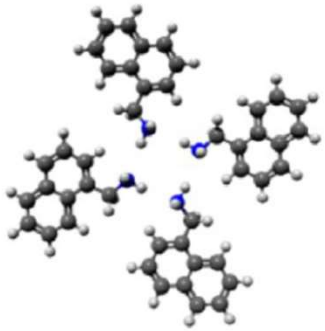
Naphthylmethyl amine (NMA)



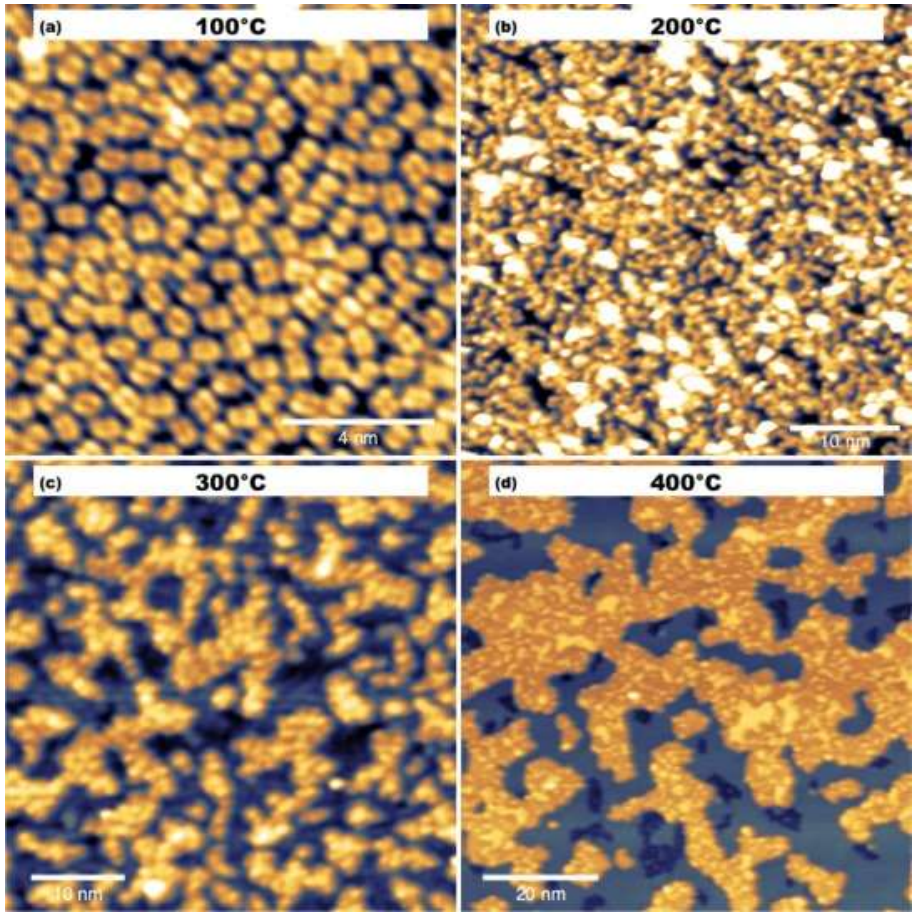
on Au(111)



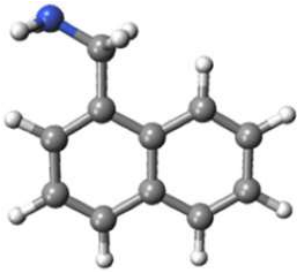




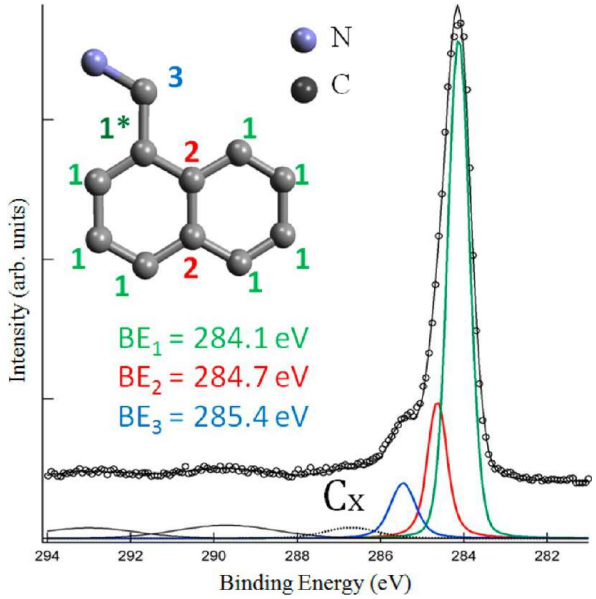
J. Phys. Chem. C 2016, 120, 11, 6104–6115

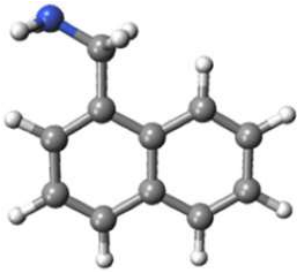


Costantini et al., FlatChem 24 (2020) 100205

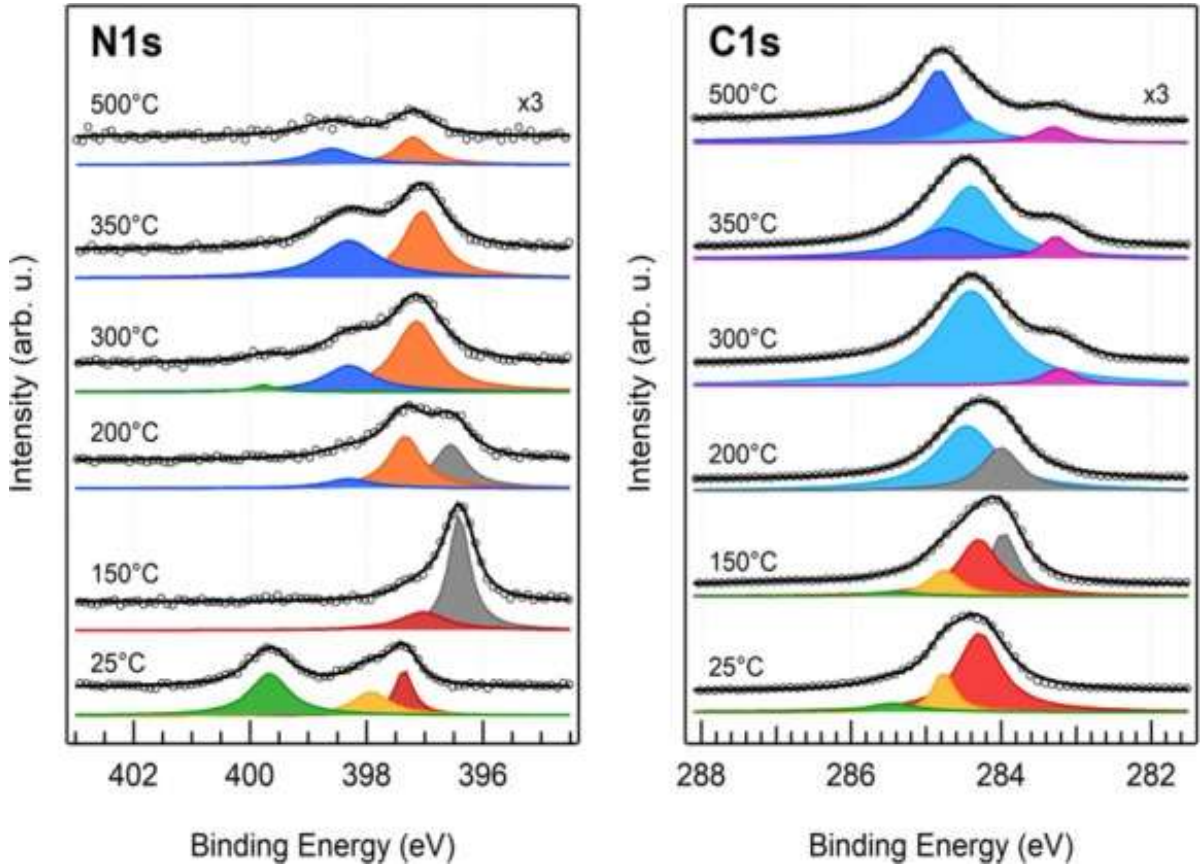


on Au(111)

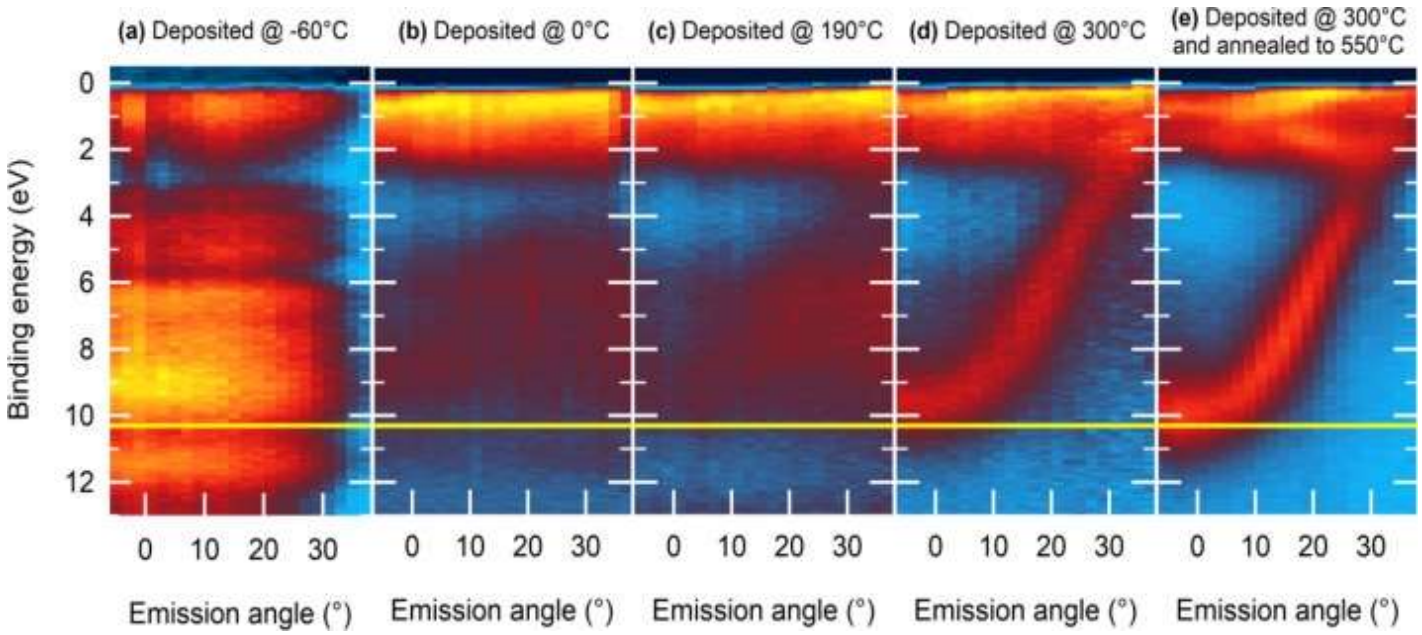

N
C
3
1*
2
1
1
1
1
1
2
1
1
1
BE1 = 284.1 eV
BE2 = 284.7 eV
BE3 = 285.4 eV
Cx
Intensity (arb. units)
294
292
290
288
286
284
282
Binding Energy (eV)



on Ni(111)



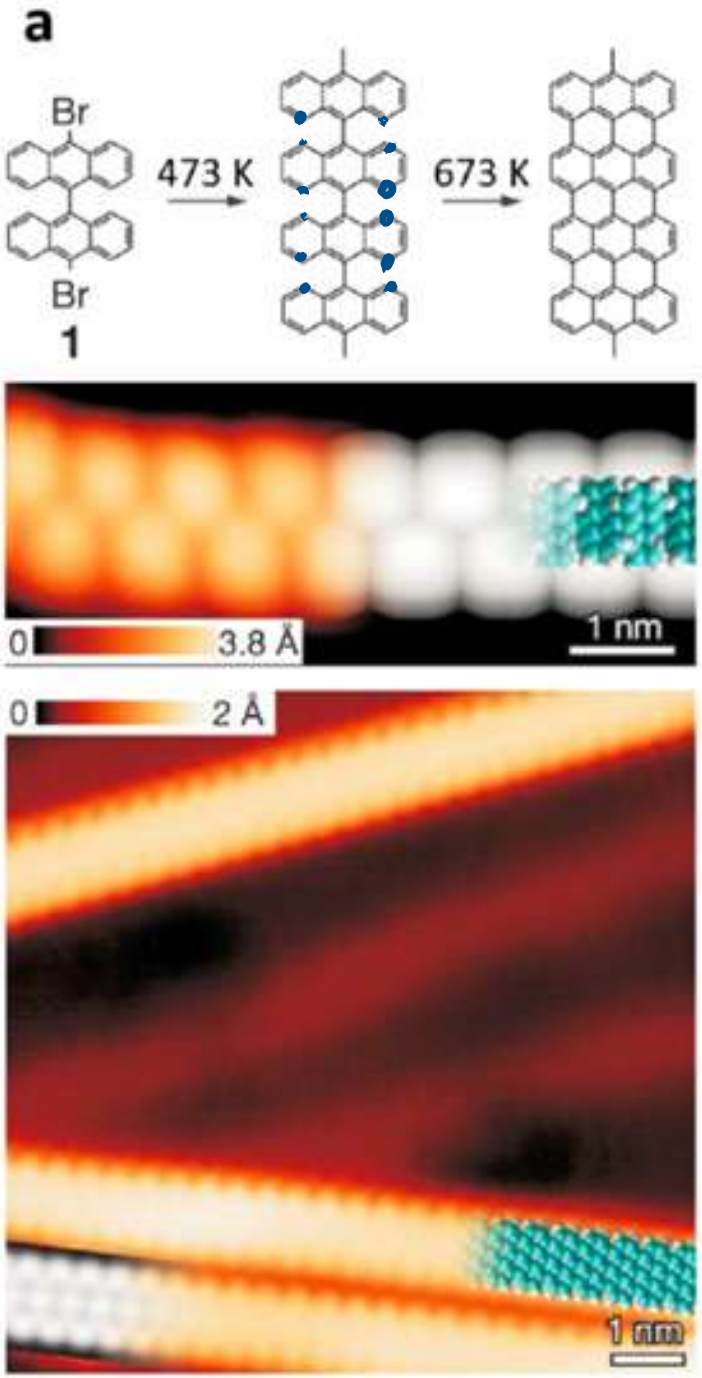
Costantini et al., FlatChem 24 (2020) 100205



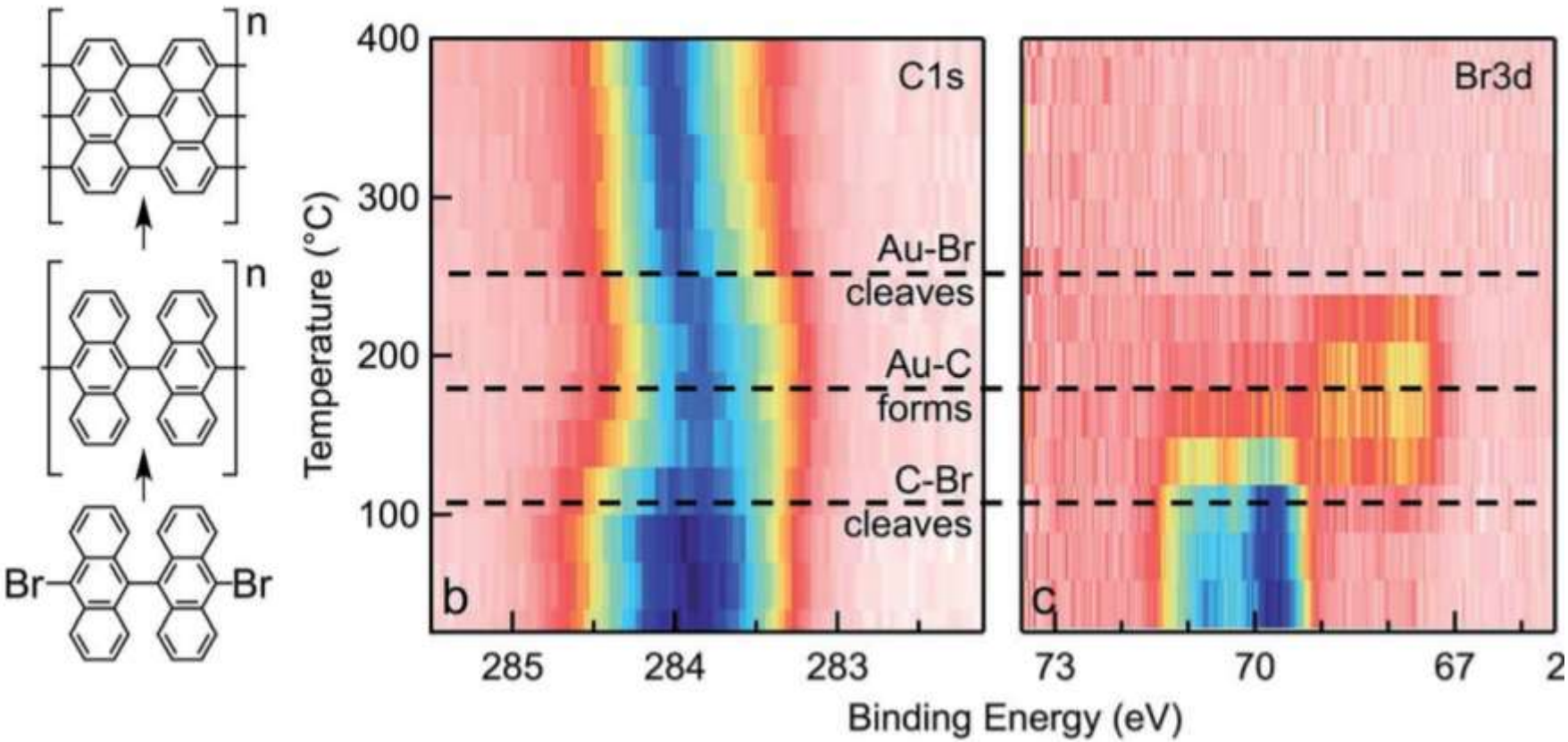
Costantini et al., FlatChem 24 (2020) 100205

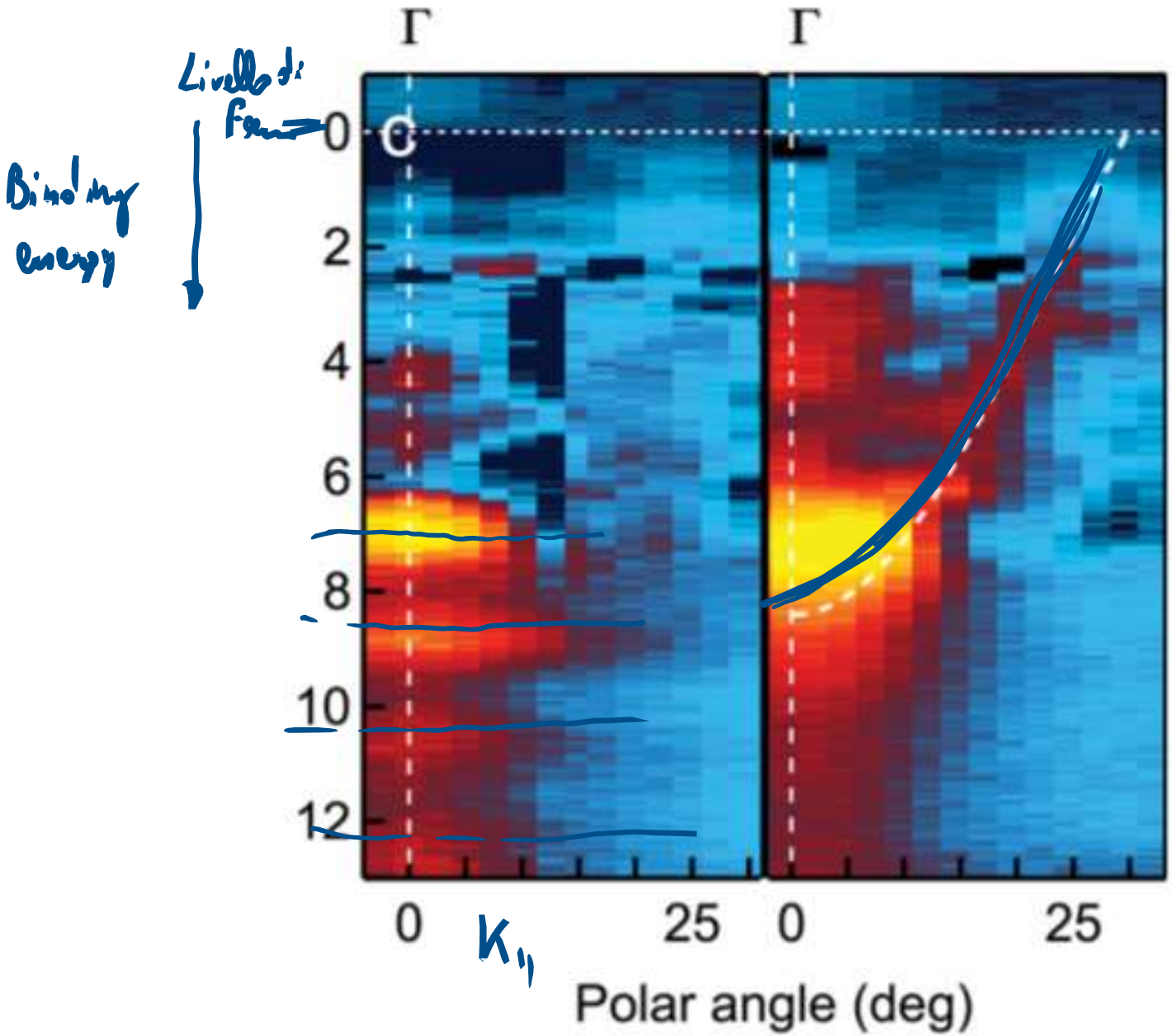
Sintesi in sequenza:

1. Ullmann
2. Cyclodehydrogenation

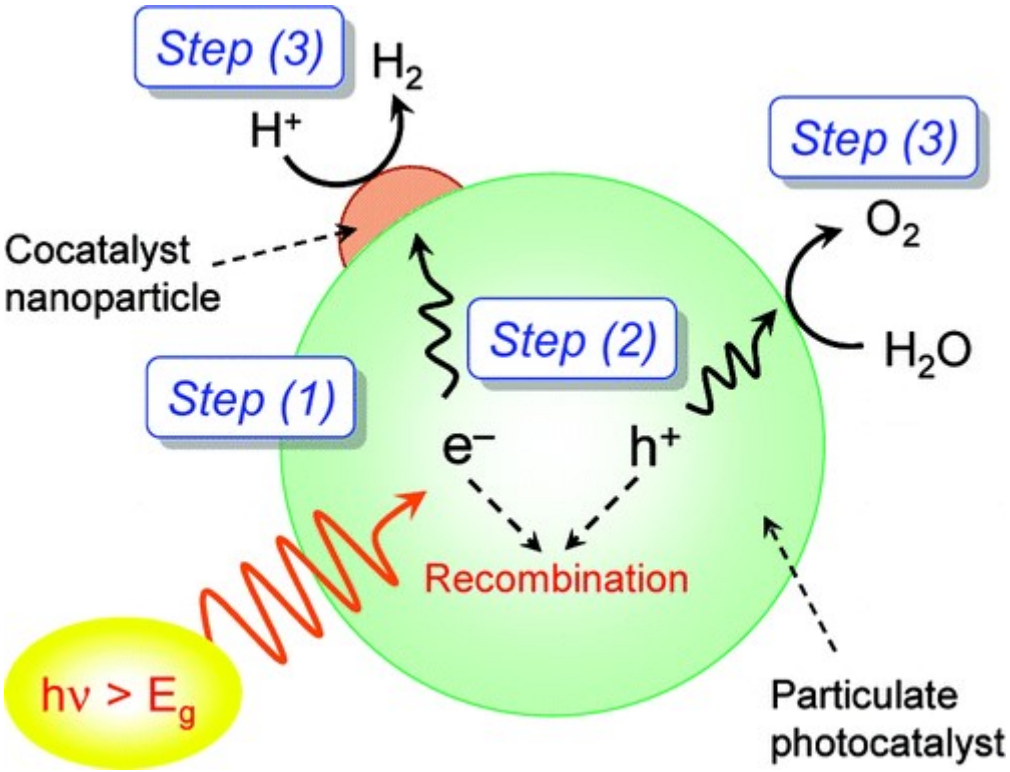


Nature 2010, 466, 470–473


n
n
Br
Br
400
300
200
100
Temperature (°C)
C1s
Br3d
Au-Br
cleaves
Au-C
forms
C-Br
cleaves
b
c
285
284
283
73
70
67
2
Binding Energy (eV)


Γ
Γ
Livello di Fermi
Binding energy
0
2
4
6
8
10
12
0
25
0
25
$K_{\parallel}$
Polar angle (deg)

Fotocatalisi per il processo di water-splitting

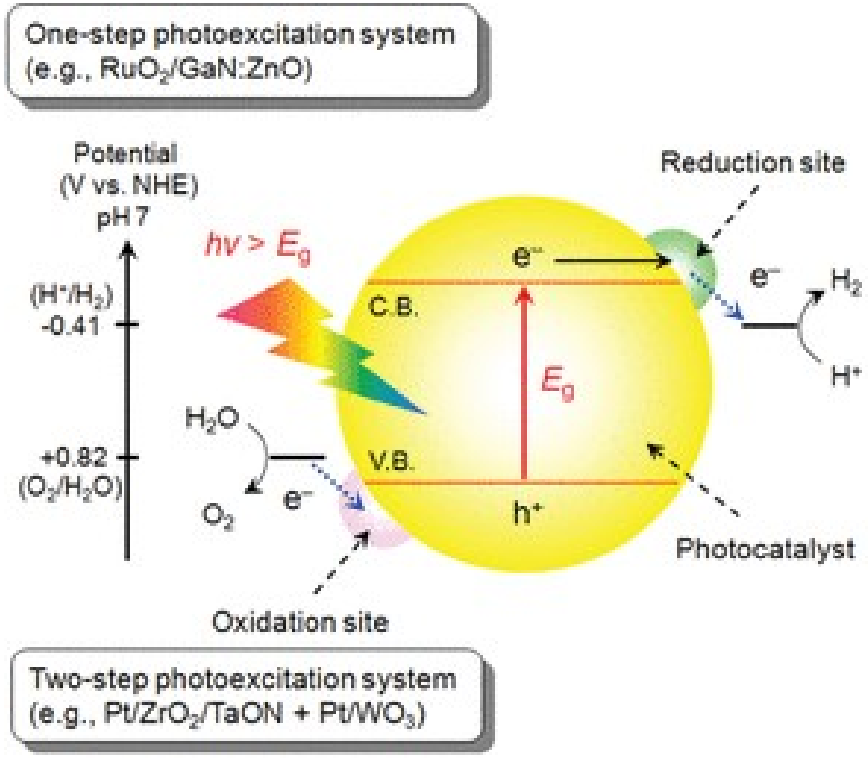


Step 1: Il fotone viene assorbito dal catalizzatore e si forma un eccitone (buca-elettrone)

Step 2: buca ed elettrone si separano e migrano verso la superficie

Step 3: avvengono le reazioni di ossidazione e di riduzione di H2O e dei prodotti della sua decomposizione, con rilascio di H2 e O2

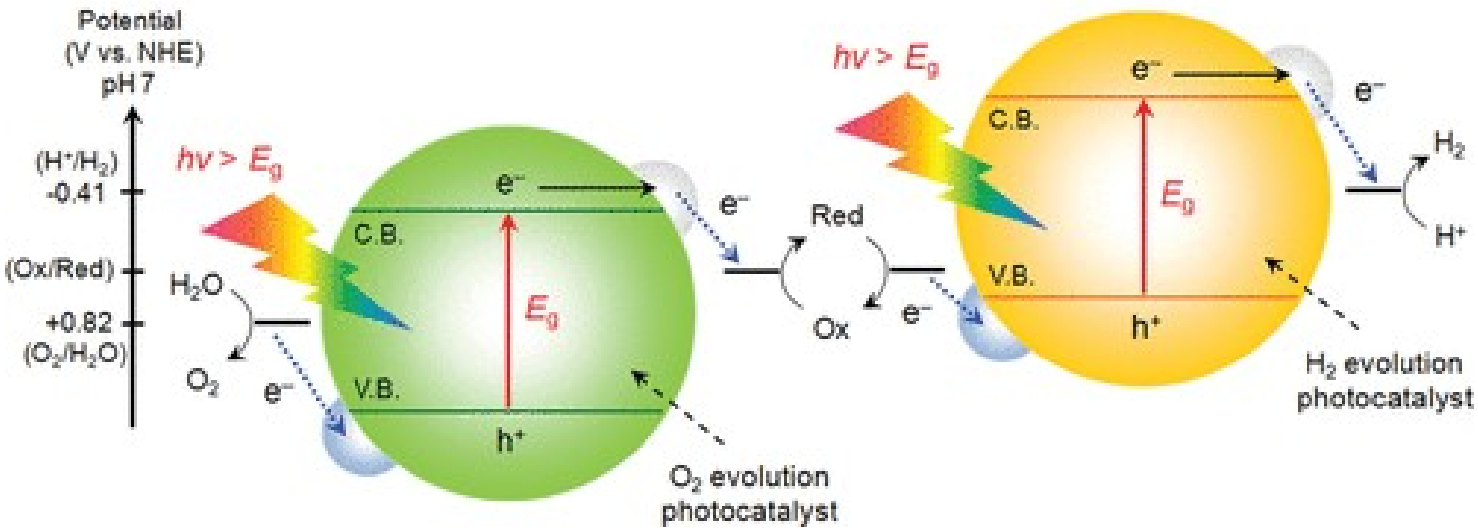
J. Phys. Chem. C 2007, 111, 22, 7851–7861



Il tutto può avvenire su un unico catalizzatore (pochi sistemi ad oggi noti) o con la giunzione di due catalizzatori, che favorisce la separazione e-h^+

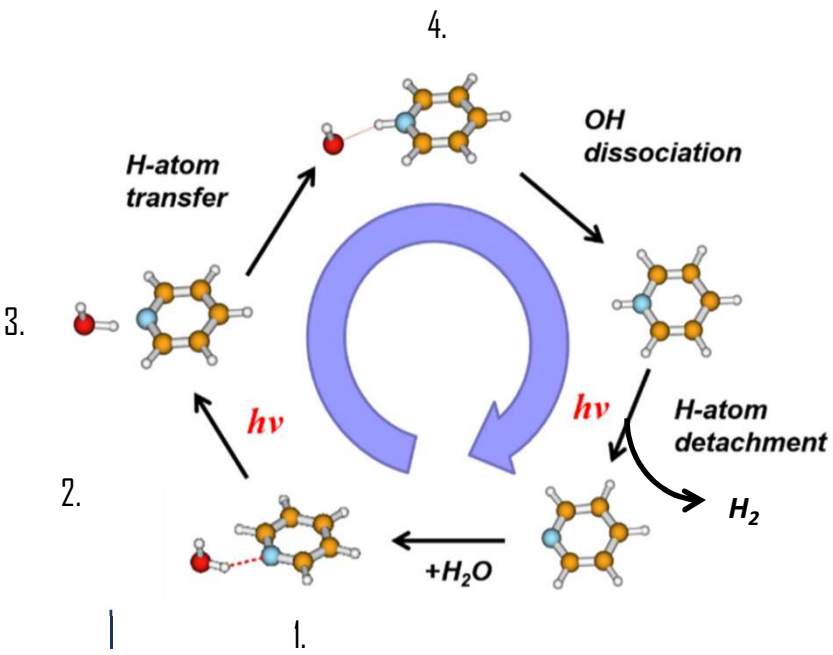
In genere dei co-catalizzatori in superficie facilitano le reazioni HER e OER

HER: hydrogen evolution reaction
OER: oxygen evolution reaction



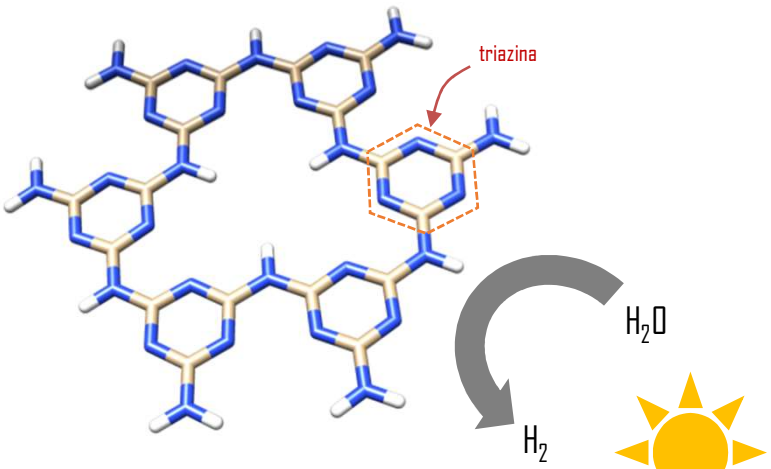
Molecole organiche possono agire da catalizzatori in un processo fotocatalitico di water splitting

Meccanismo “Proton-Coupled Electron Transfer” (W. Domcke)

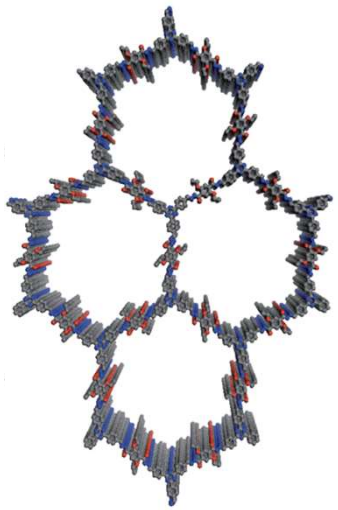


1. Formazione di un legame idrogeno tra la molecola di acqua e l’eterociclo
2. Fotoeccitazione del complesso eterociclo–H_2O
3. Trasferimento di elettrone
4. Trasferimento di protone

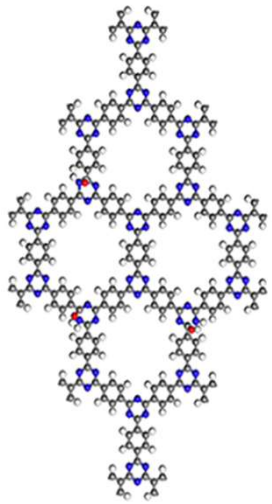
Carbon Nitrides e Covalent Organic Frameworks (COFs)



polytriazine-imide

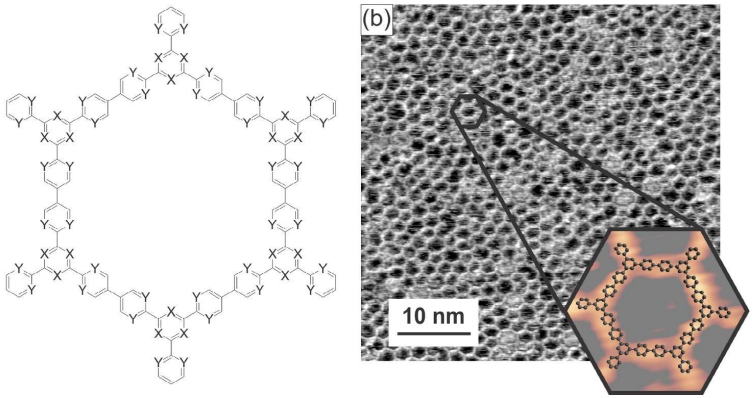


3D COF

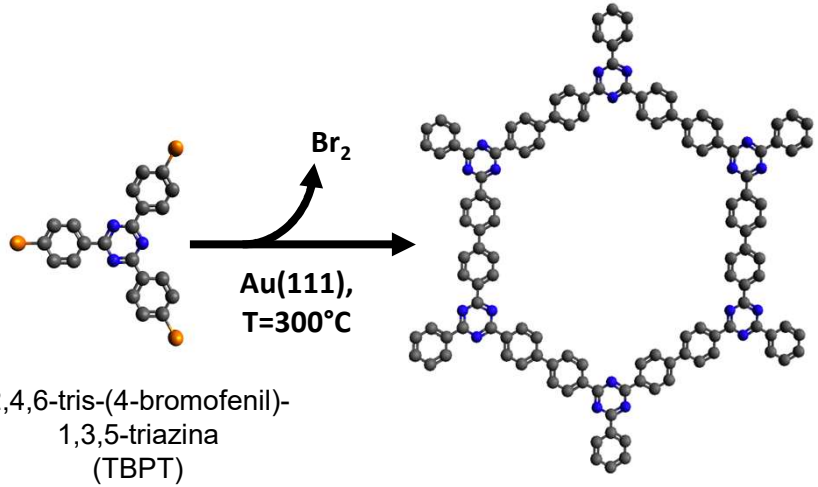


2D COF

Reazione di polimerizzazione di Ullmann



(a)



2,4,6-tris-(4-bromofenil)-
1,3,5-triazina
(TBPT)

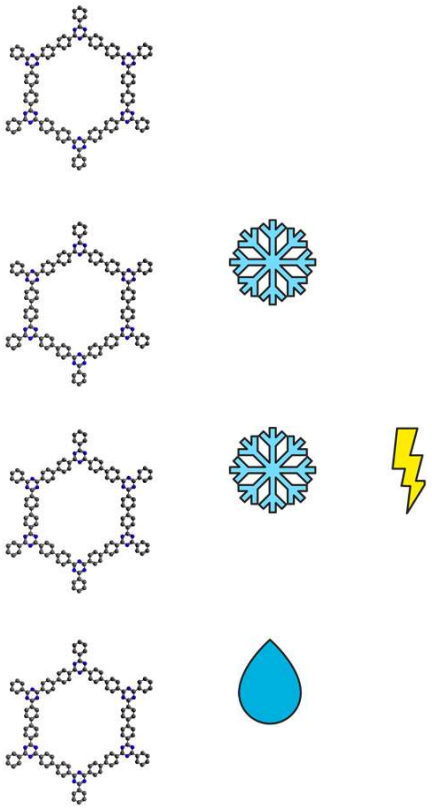
K. Kern *et al.*, Angew. Chem. Int. Ed. 2020, 59, 8411–8415

Sintesi del COF

Interazione tra COF e ghiaccio

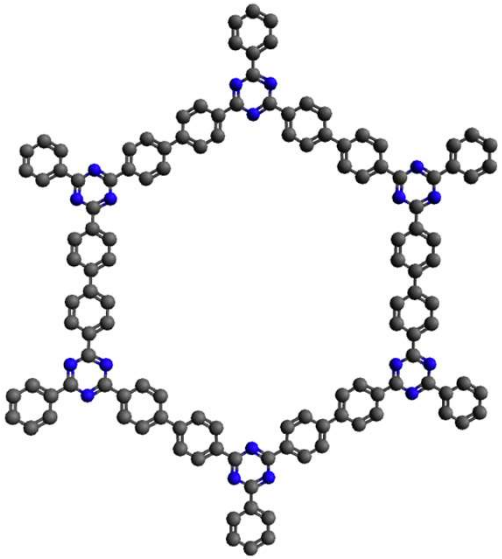
Interazione fotoindotta tra COF e ghiaccio

Interazione tra COF e acqua

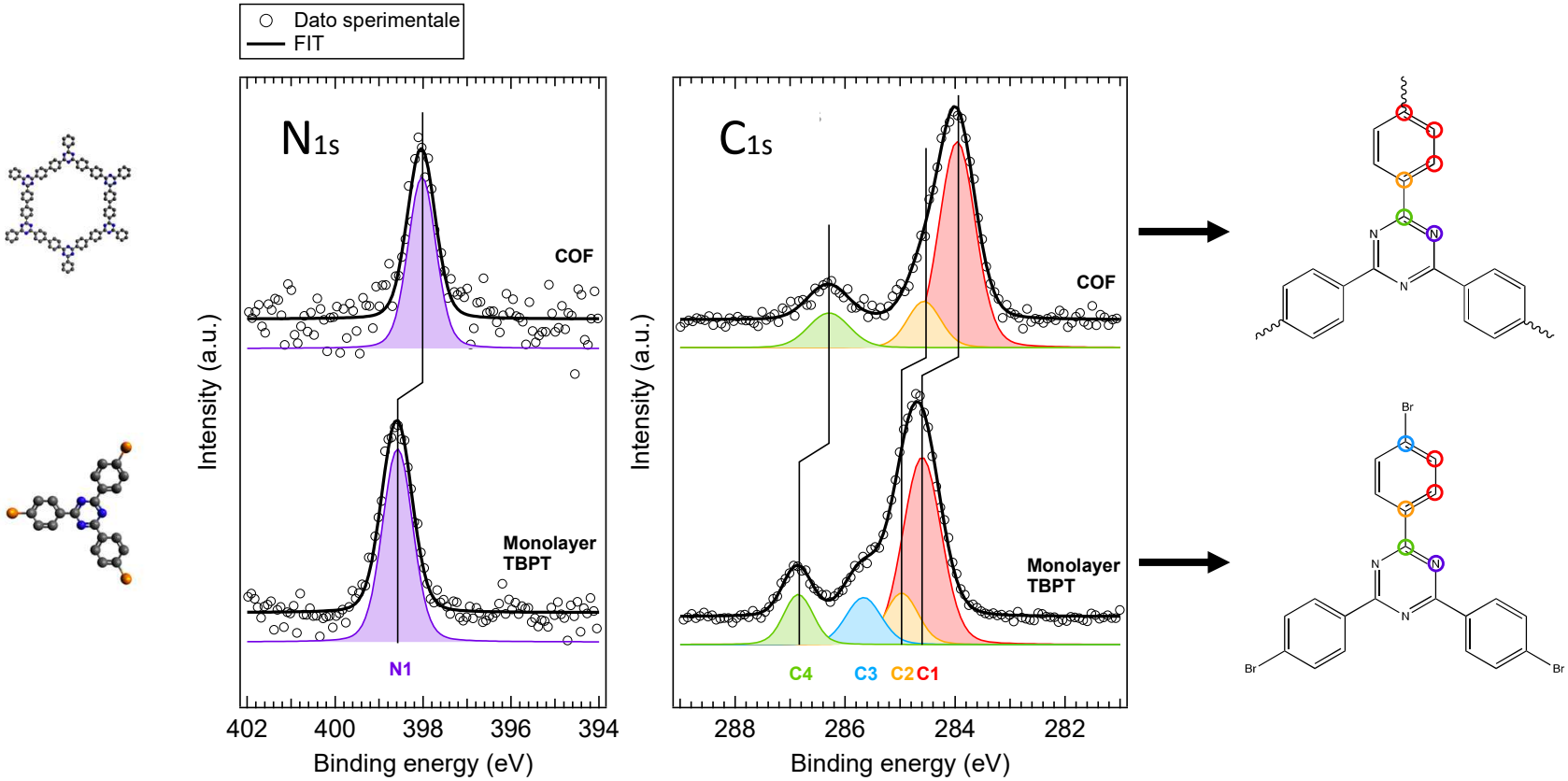


Tesi LM, Davide Piva (2023)

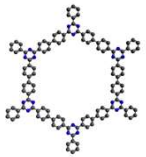
Sintesi del COF

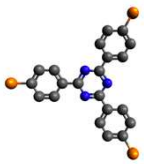


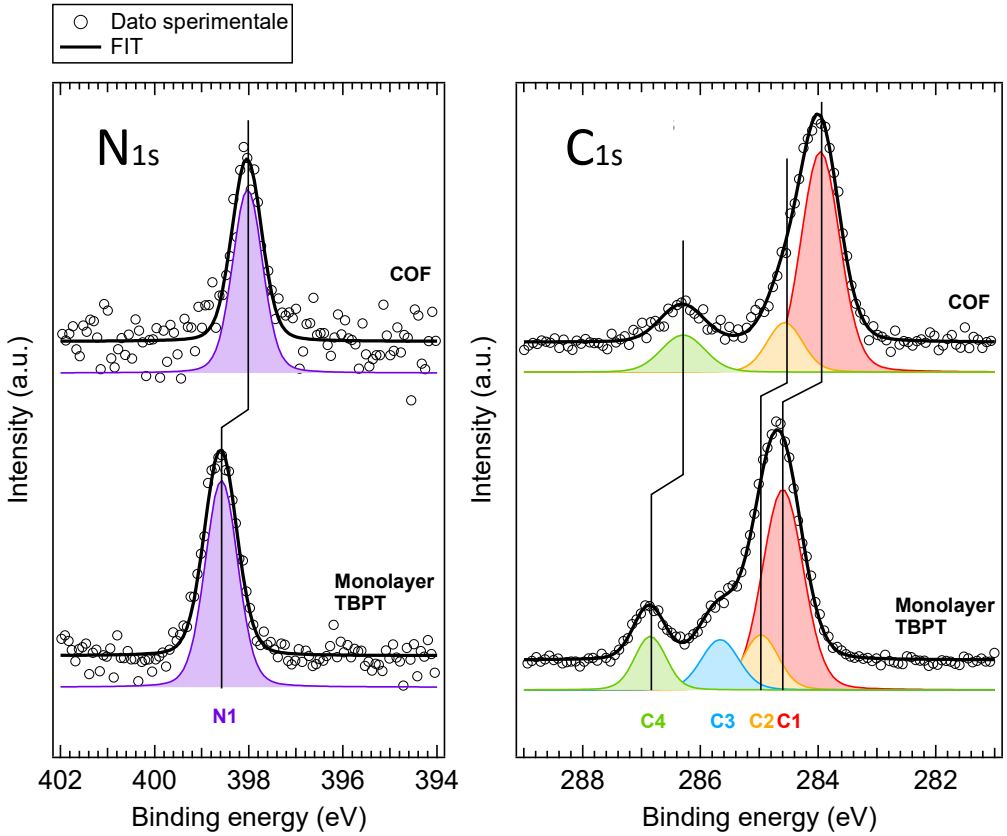
Stechiometria del sistema



Stechiometria del sistema



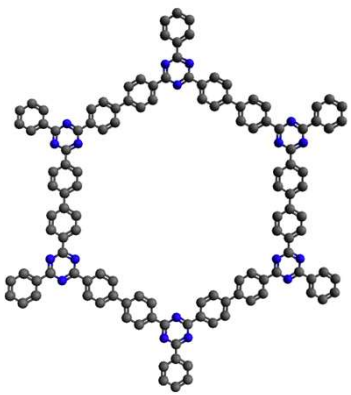


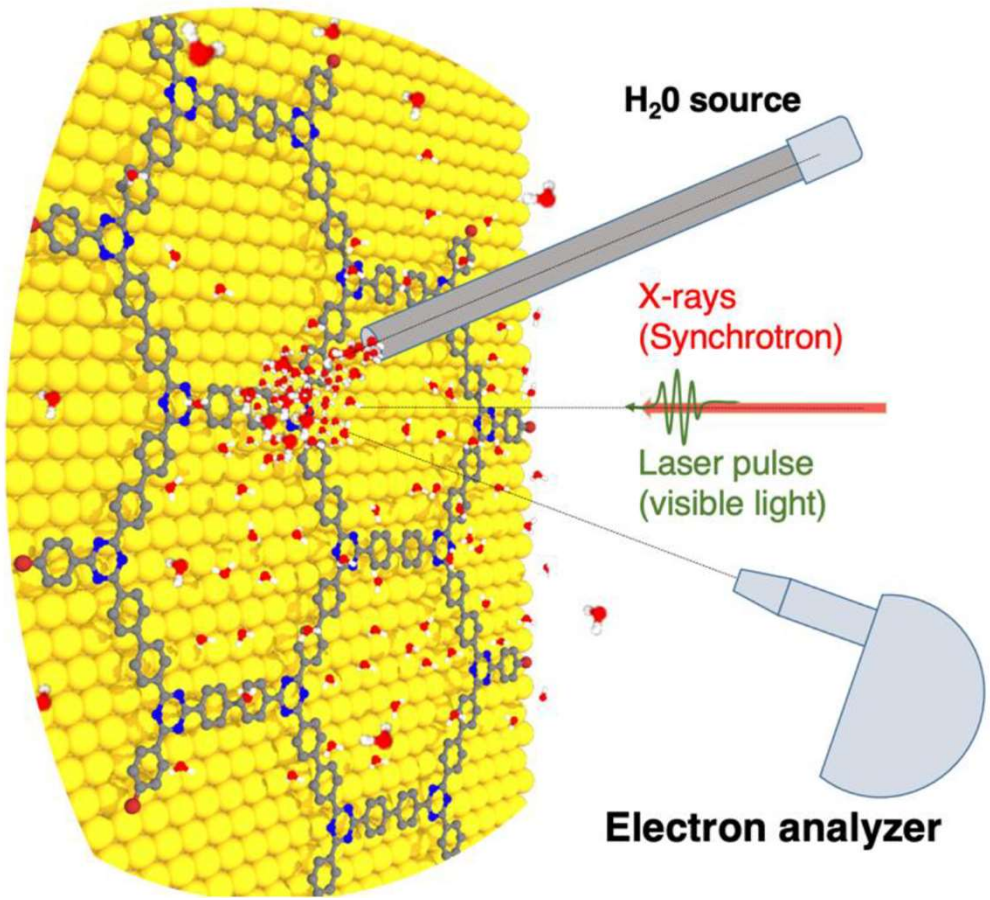


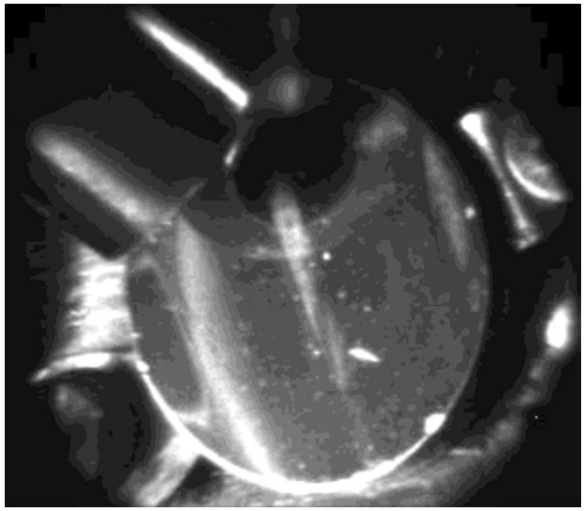
Shift a basse BE:

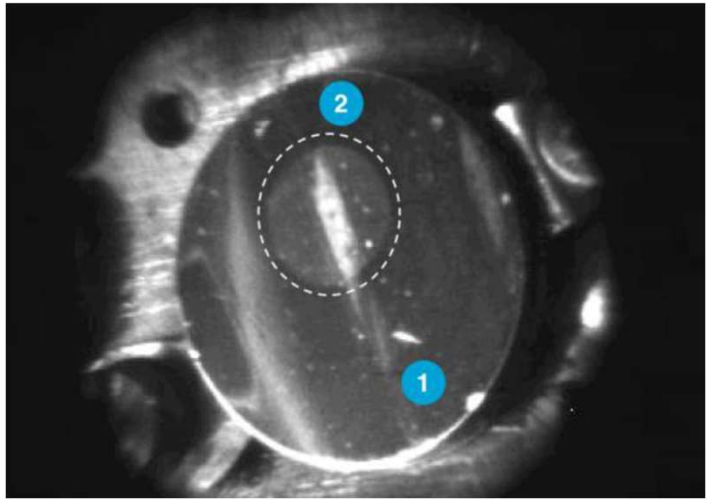
- Effetto di screening
- Delocalizzazione elettronica

Interazione tra COF e ghiaccio

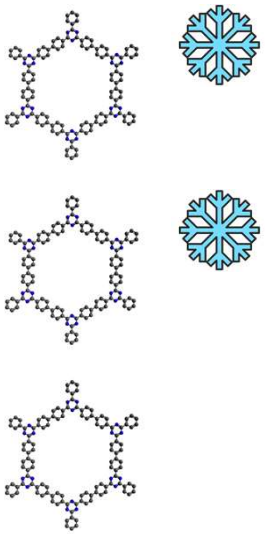


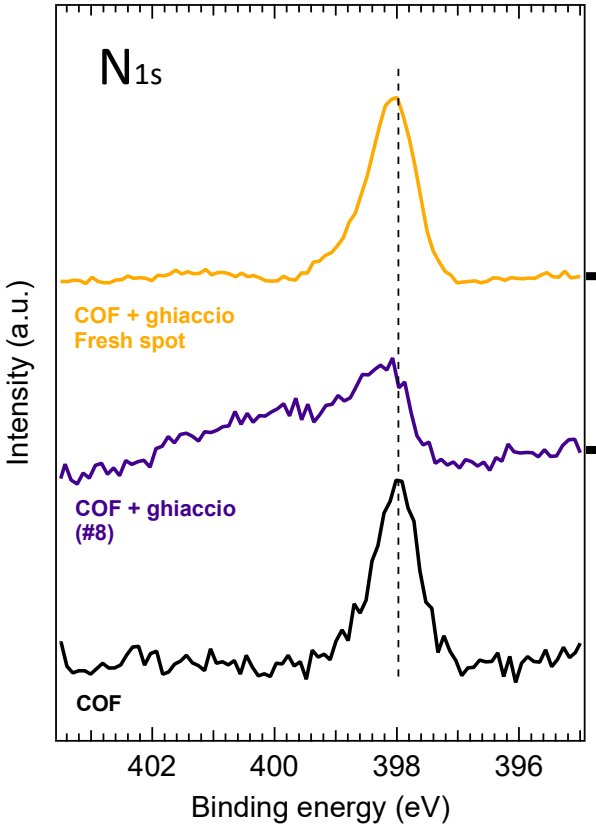

H_20 source
X-rays
(Synchrotron)
Laser pulse
(visible light)
Electron analyzer




2
1

Interazione COF–ghiaccio

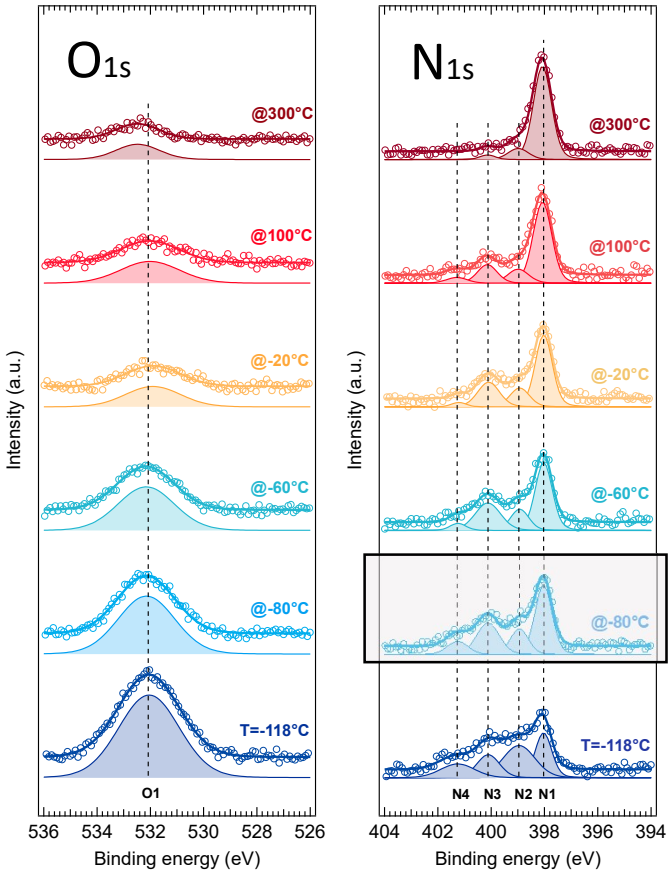




Bassa conversione senza irraggiamento X

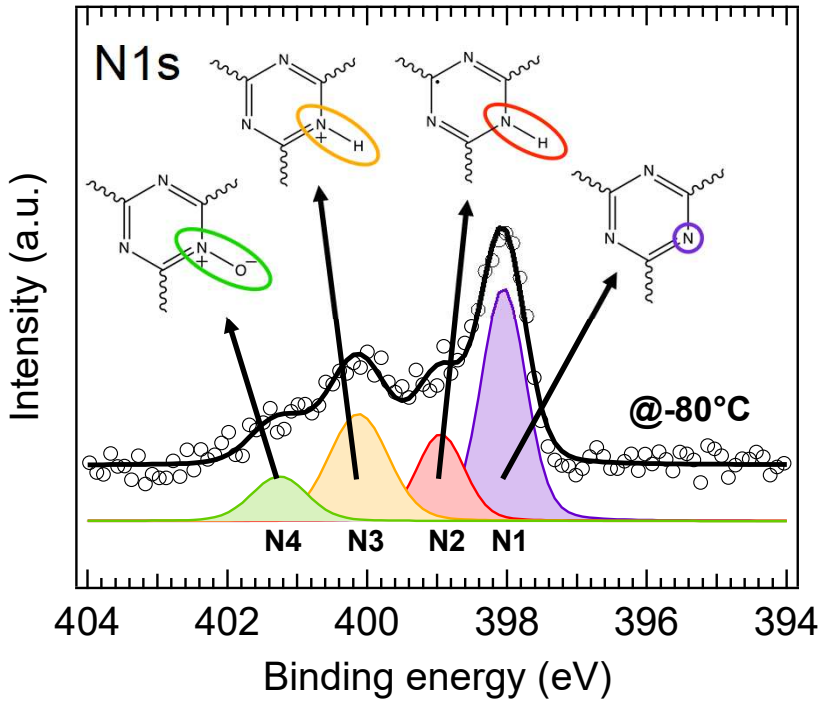
Effetto indotto dalla radiazione

Annealing del sistema «COF + ghiaccio»



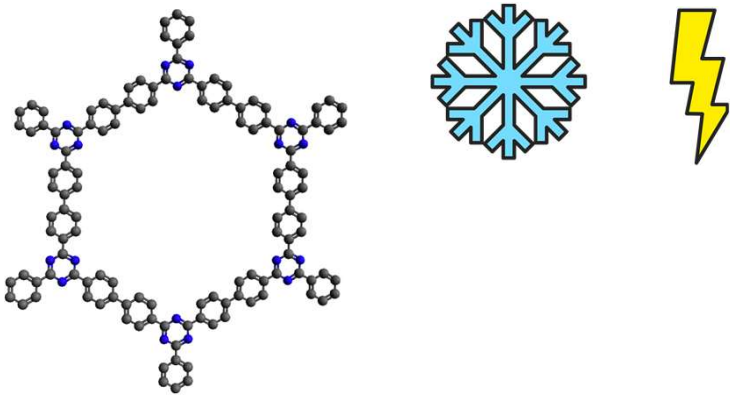
- Azoto multicomponente (almeno quattro)
- Ossigeno singola componente (FWHM~2.5 eV)
- Ossigeno presente a T>-110°C
- ~Ripristino del COF

Identificazione di nuove specie chimiche

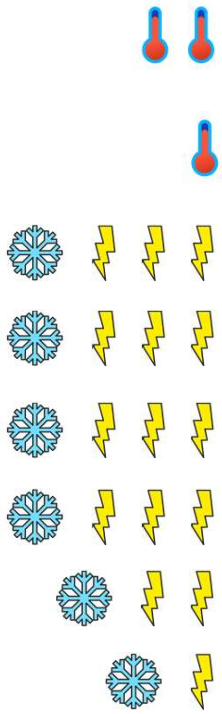


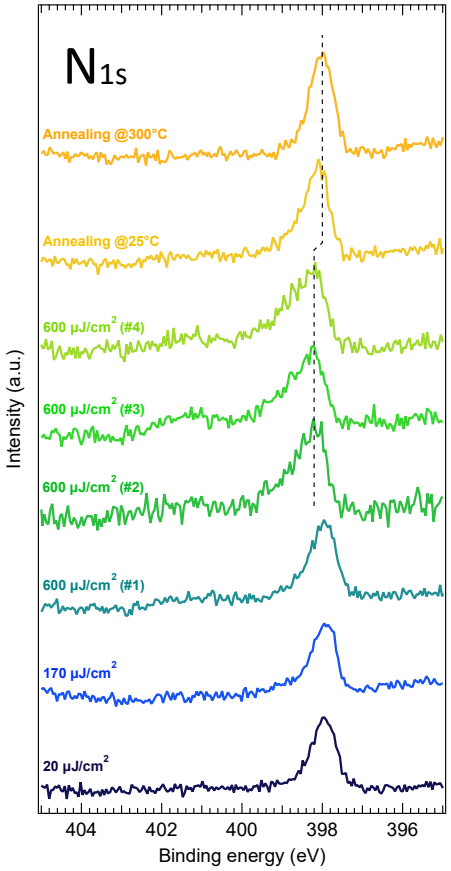
- N1: azoto triazinico
- N2: azoto idrogenato
- N3: azoto protonato
- N4: azoto «piridina N-ossido»

Interazione fotoindotta tra COF e ghiaccio

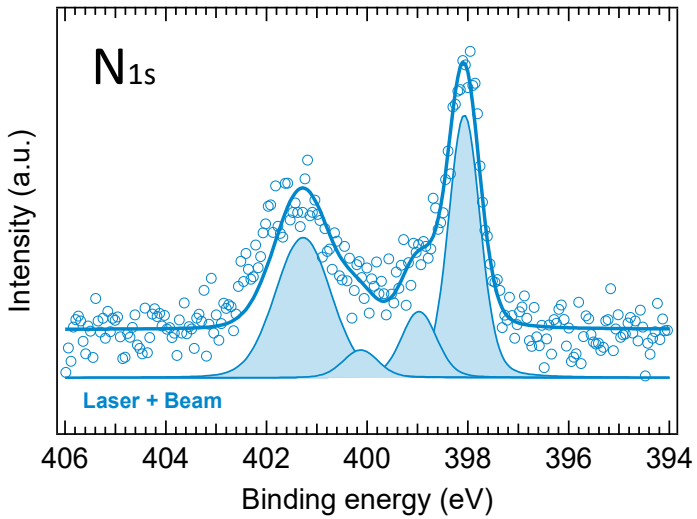


Conversione COF fotoindotta da laser (343 nm)

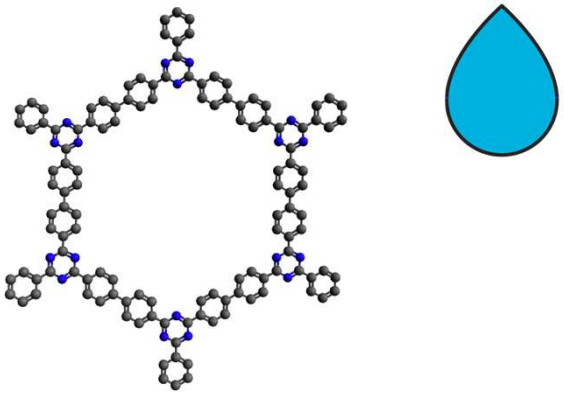




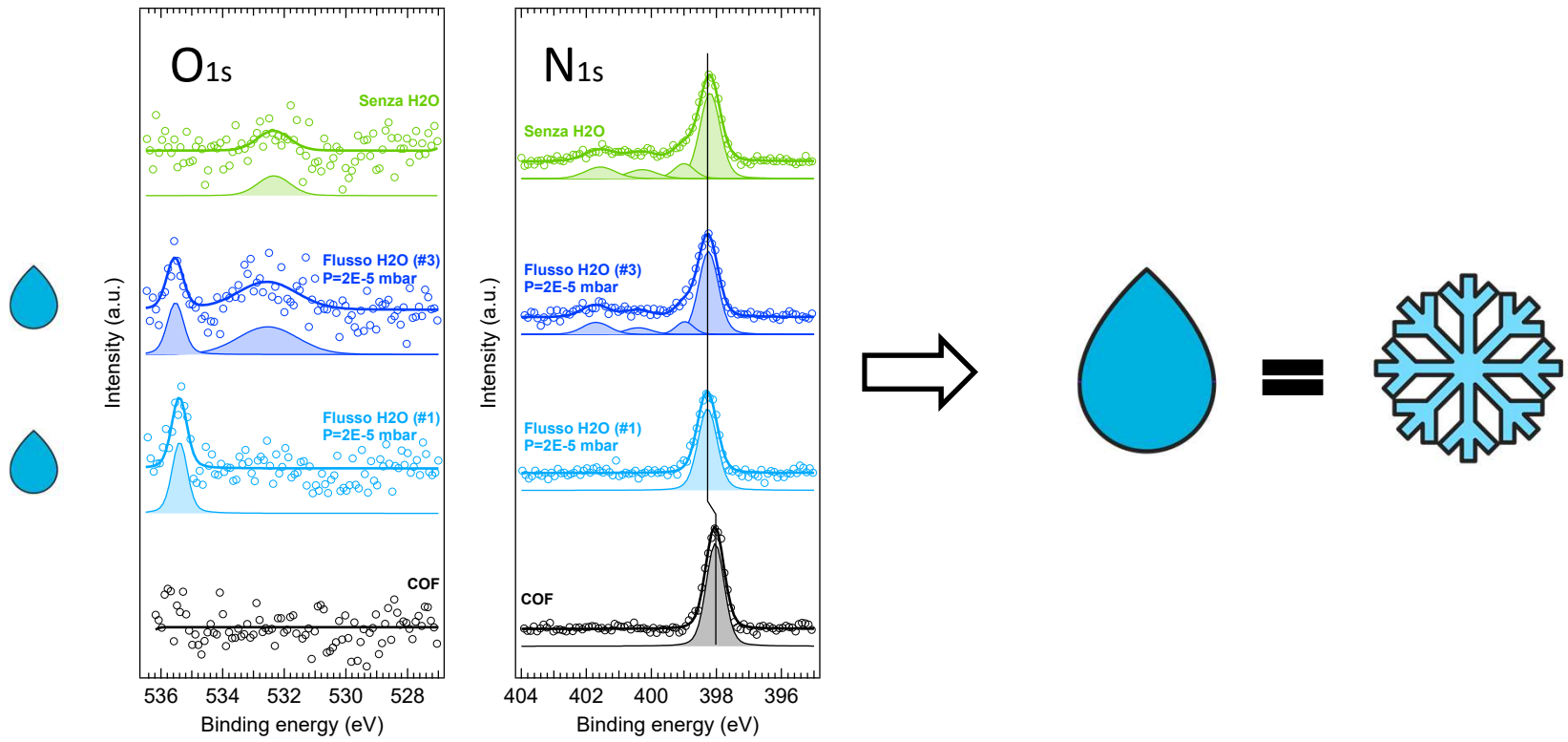
Qual è la conversione massima che si può raggiungere?



Interazione tra COF e acqua



Dosaggio di acqua sul COF



Monolayer di TBPT con ghiaccio