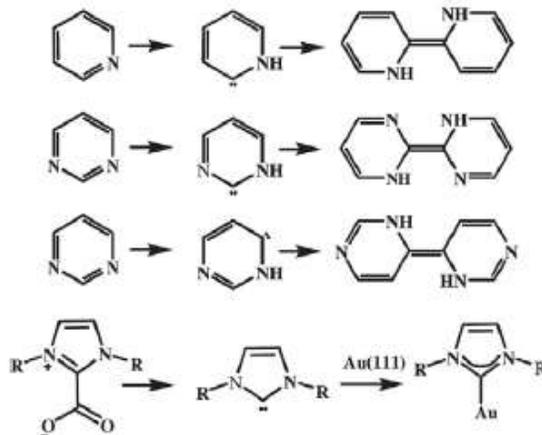


On-surface synthesis

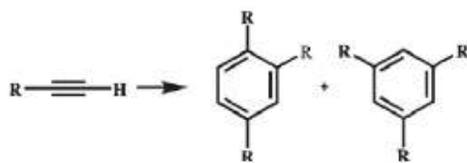
N-heterocyclic carbenes formation and dimerization



Glaser coupling



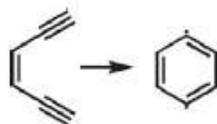
Alkyne cyclotrimerization



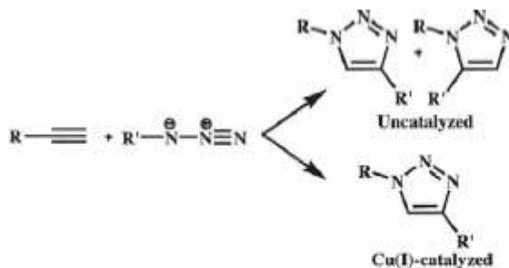
Metalated carbyne



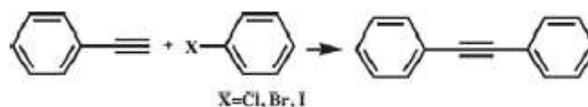
Bergman reaction



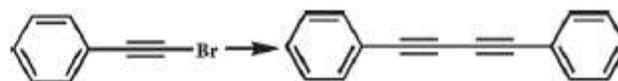
Azide-alkyne cycloaddition



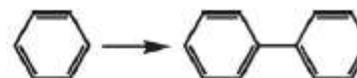
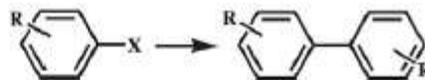
Sonogashira coupling



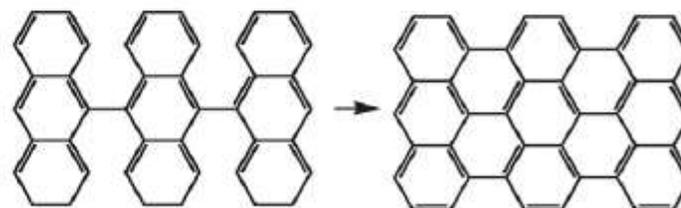
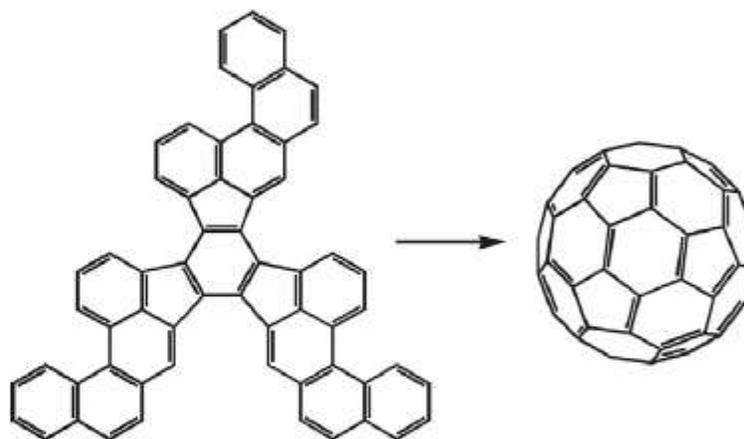
Dehalogenative homocoupling of terminal alkynyl bromides



Ullmann coupling



Aryl-aryl dehydrogenation coupling



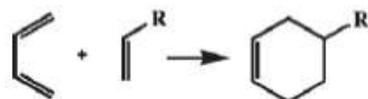
Dehydrogenative homocoupling of terminal alkene



Dehalogenative homocoupling
of terminal alkenyl bromides



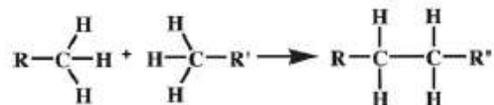
Diels-Alder reaction



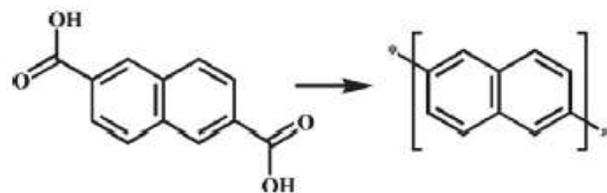
Wurtz coupling



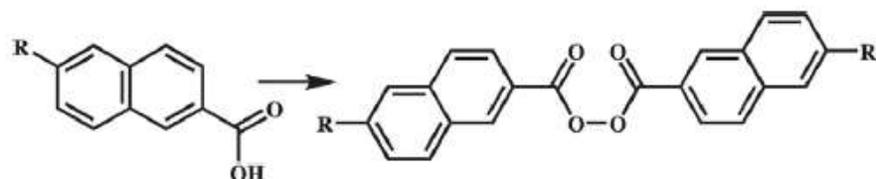
Linear alkane polymerization



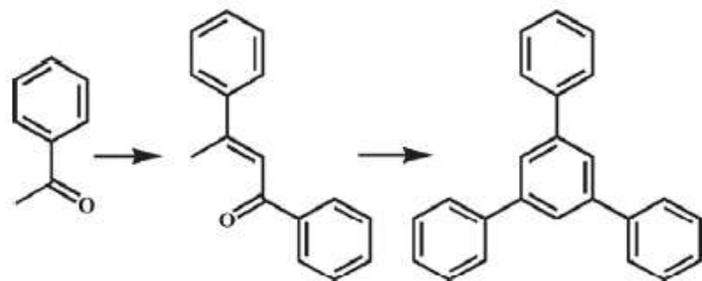
Decarboxylative
polymerization



Dehydrogenative coupling



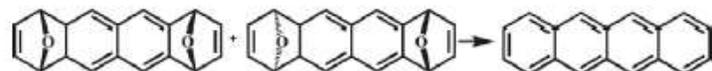
Dimerization and
cyclotrimerization of acetyls



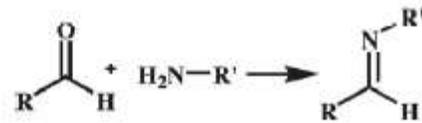
Dealkylation of ethers to
alcohols



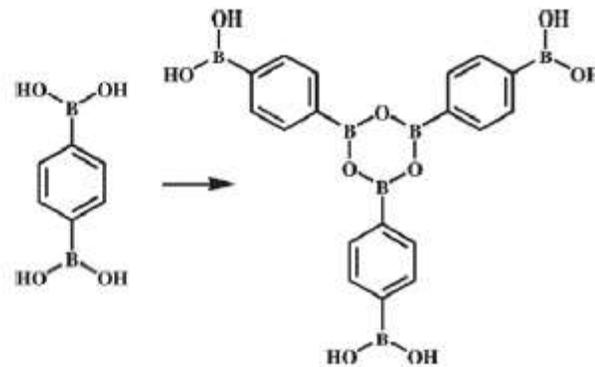
Reduction



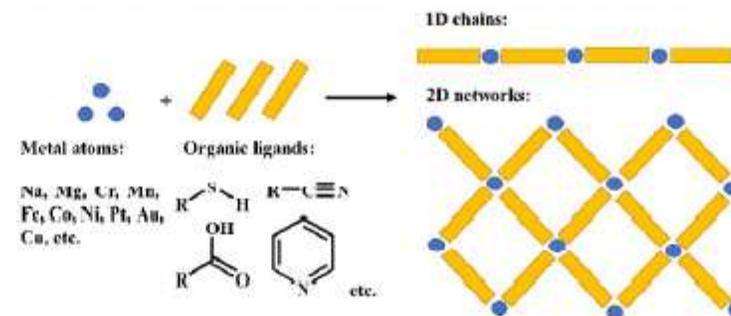
Schiff-base reaction (imine formation)



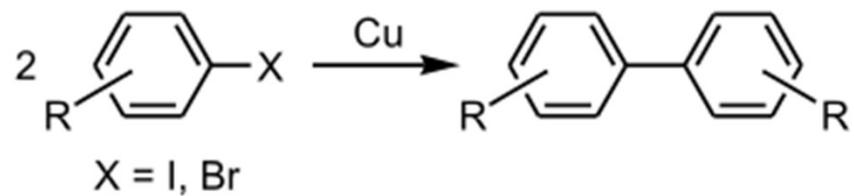
Boronic acid condensation



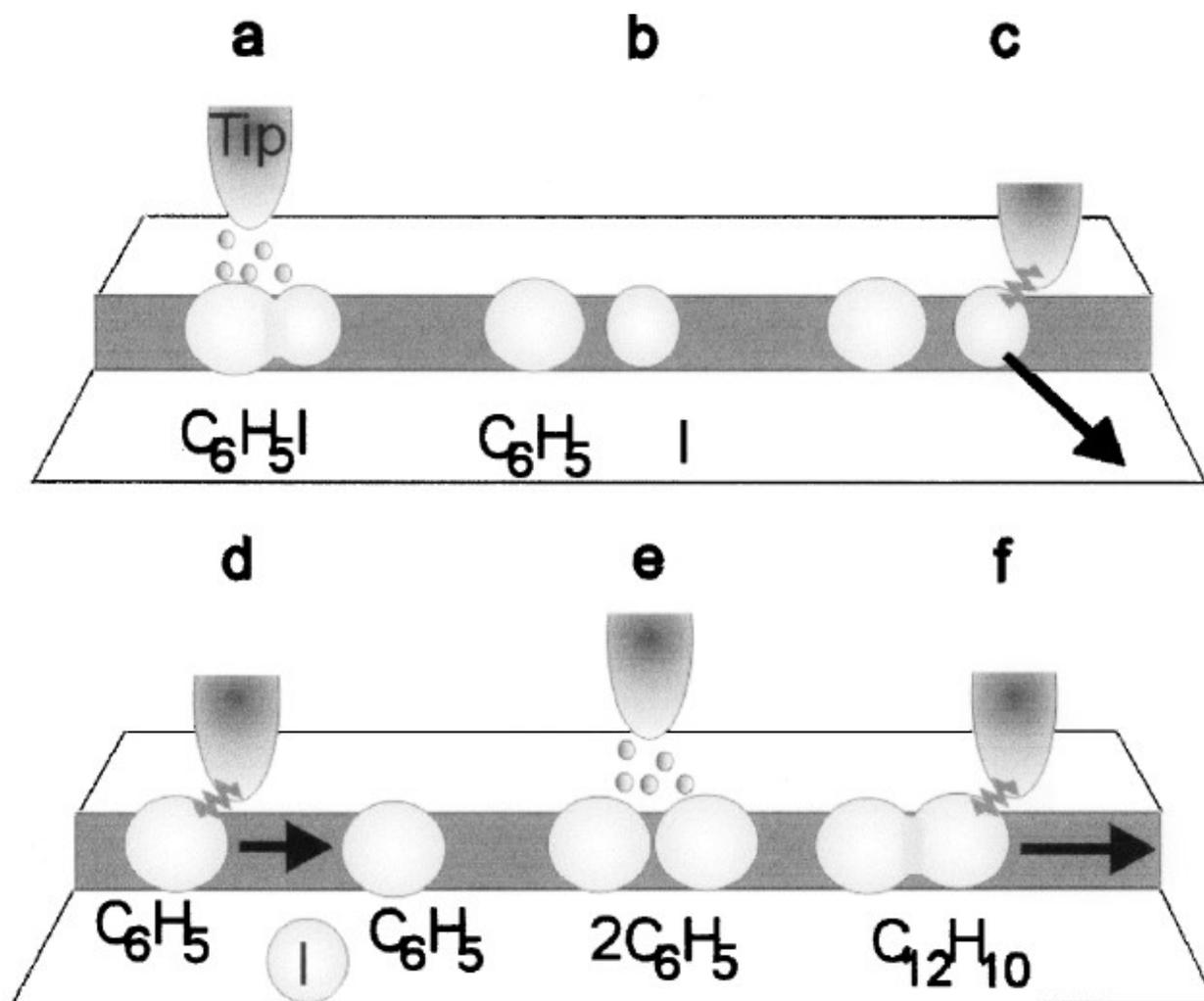
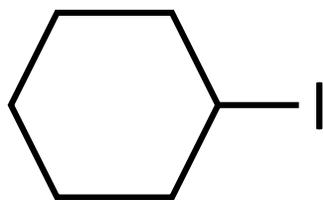
Surface confined
Metal-organic coordination



Reazione di Ullmann o Ullmann coupling

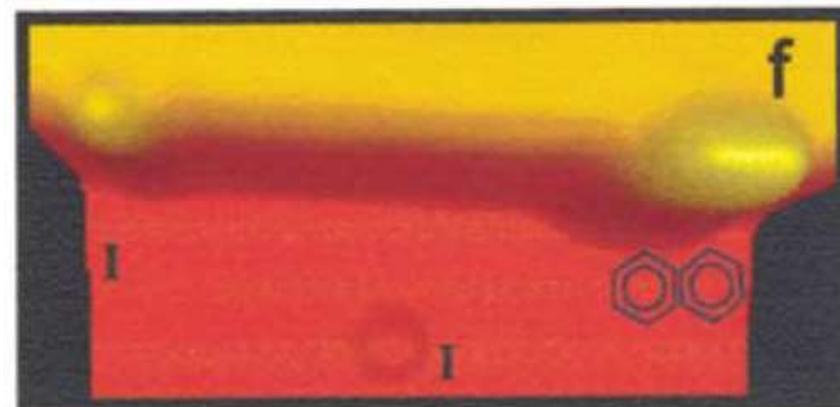
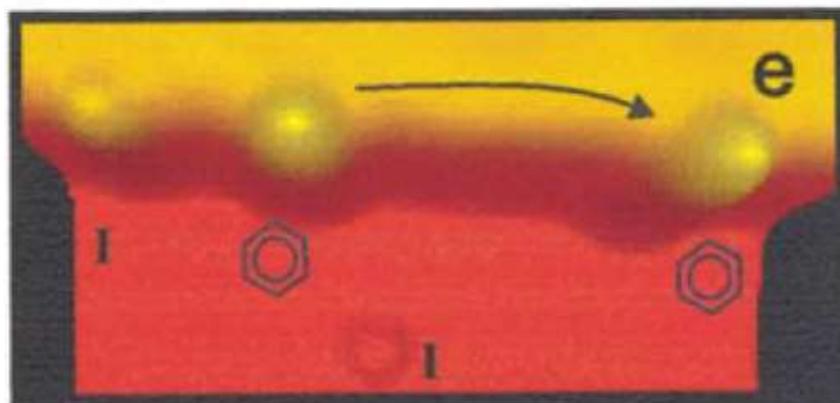
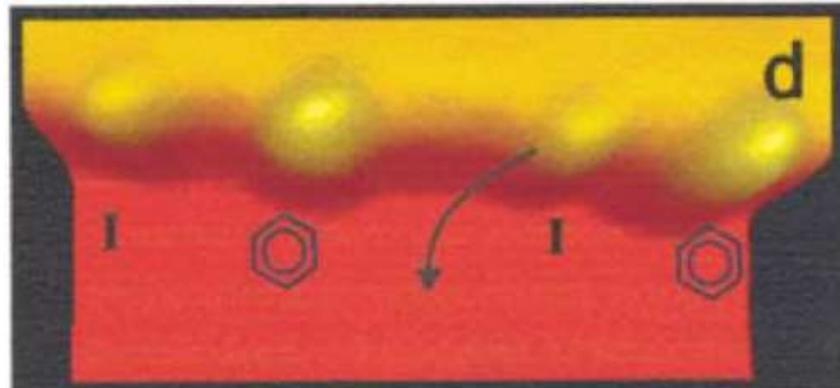
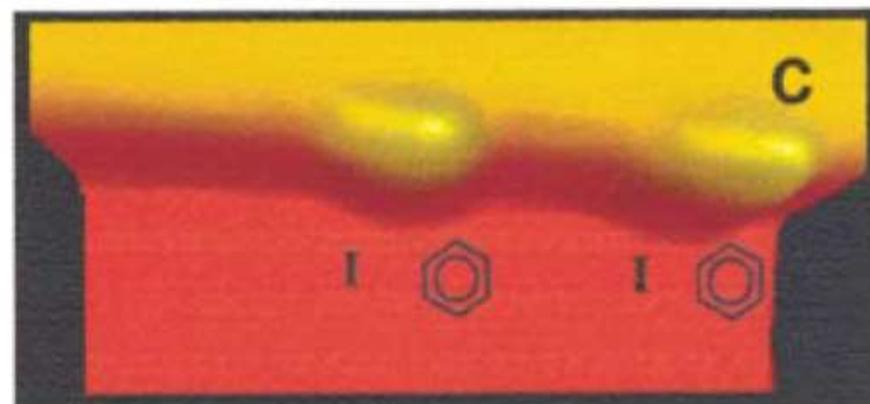
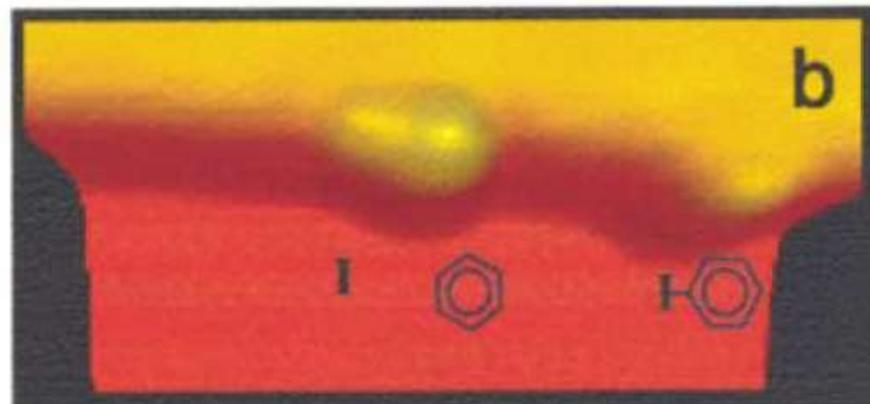
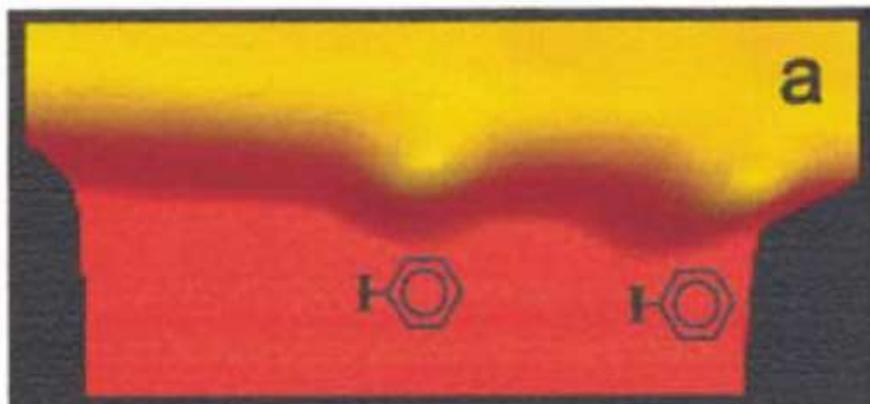


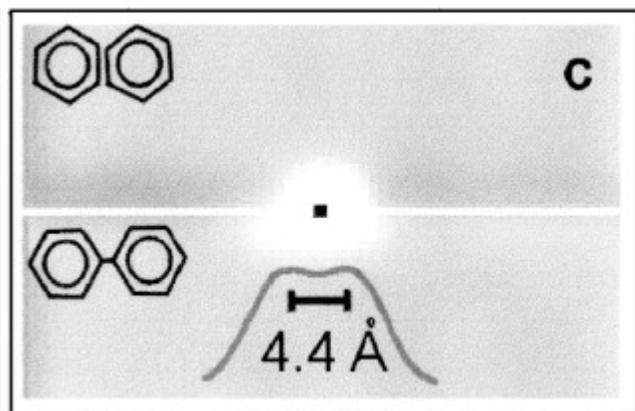
X alogeni, tipicamente Br

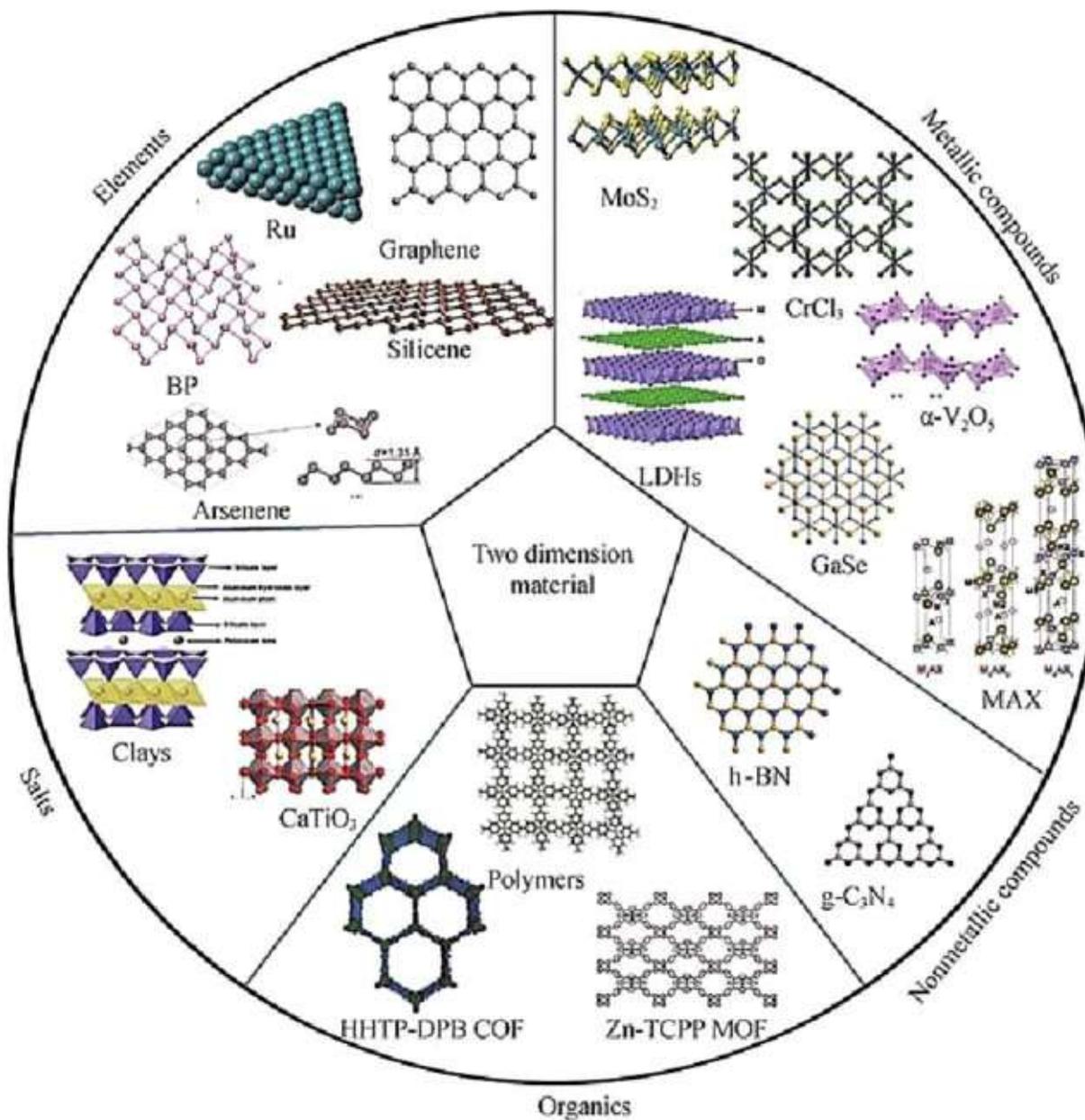


**Inducing All Steps of a Chemical Reaction with the Scanning Tunneling Microscope Tip:
Towards Single Molecule Engineering**

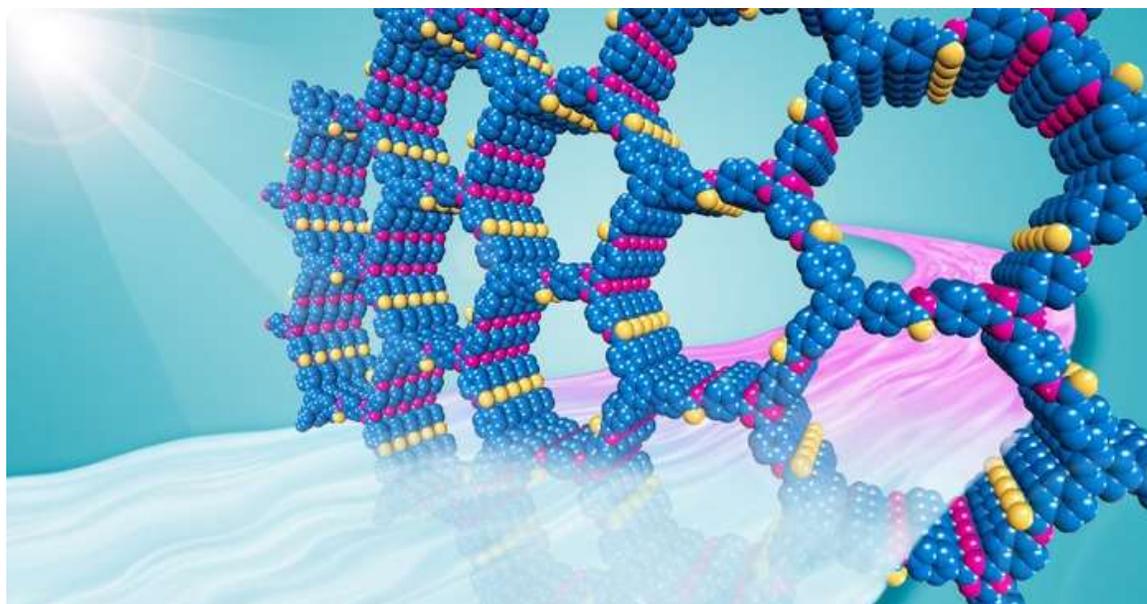
Saw-Wai Hla,^{1,2,*} Ludwig Bartels,^{1,†} Gerhard Meyer,¹ and Karl-Heinz Rieder¹



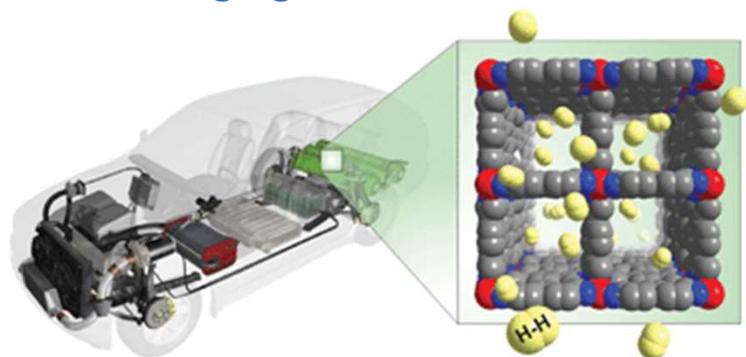




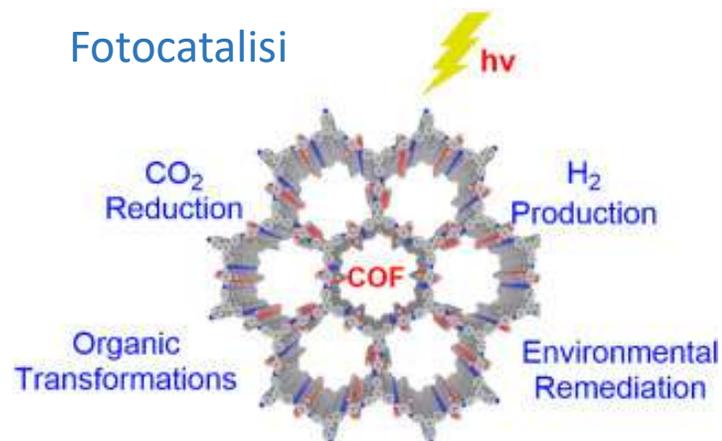
Covalent Organic Frameworks



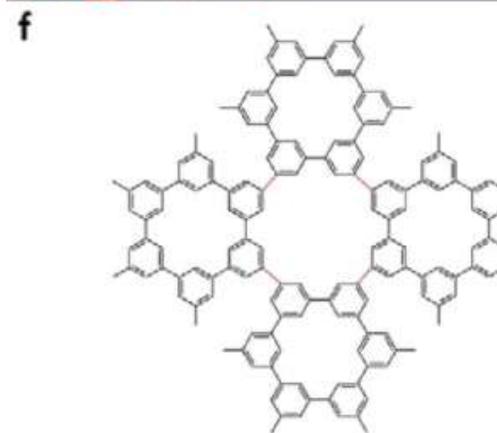
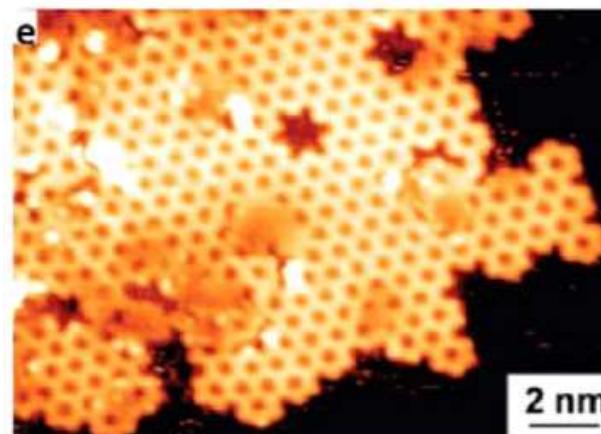
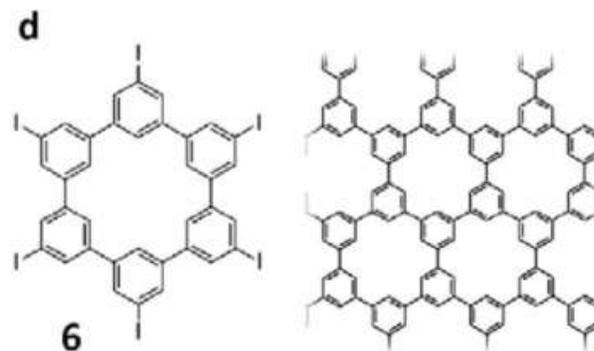
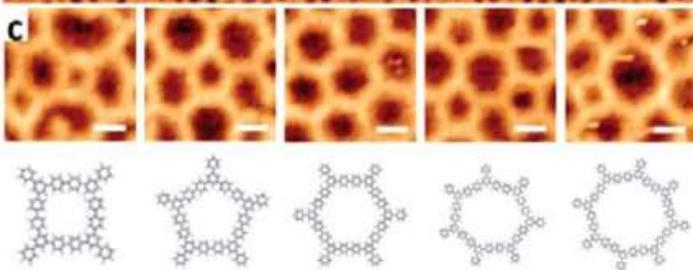
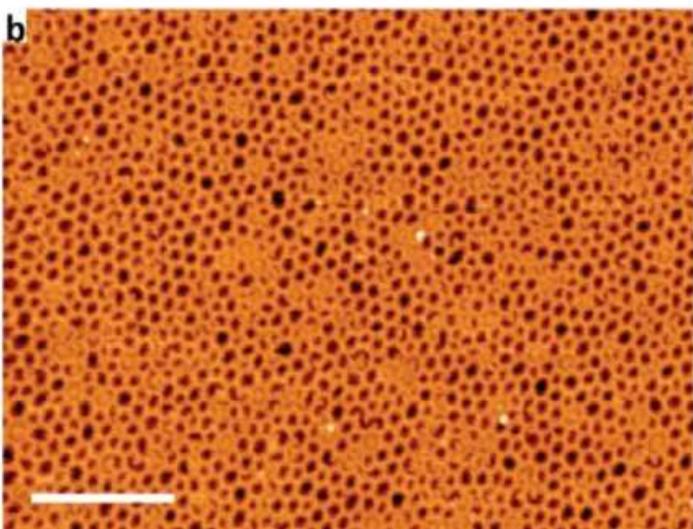
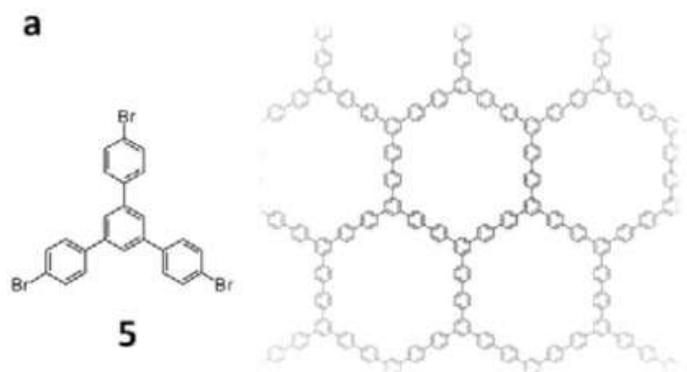
Storaging



Fotocatalisi



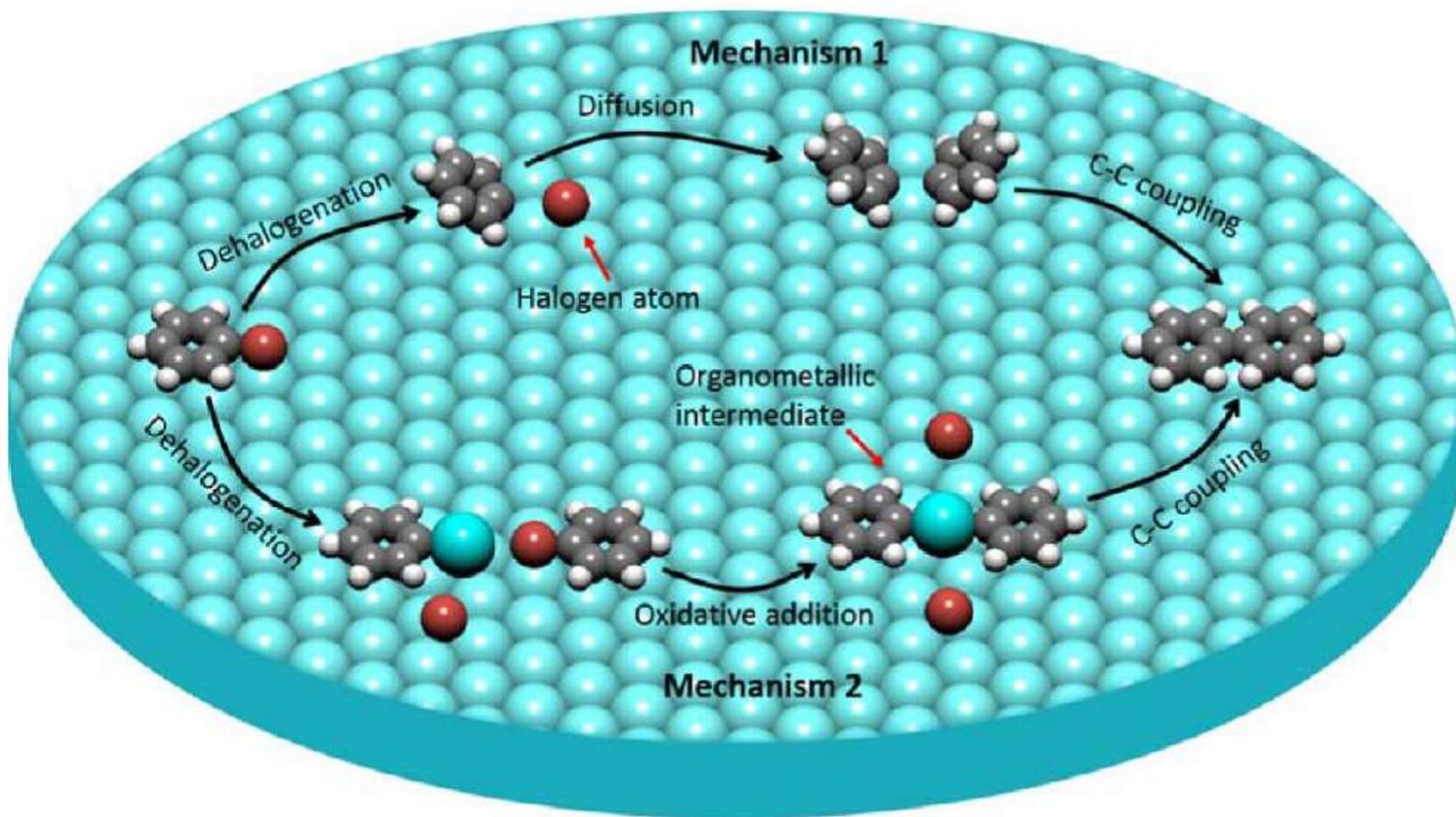
La struttura del precursore determina la morfologia del 2D e la concentrazione di difetti

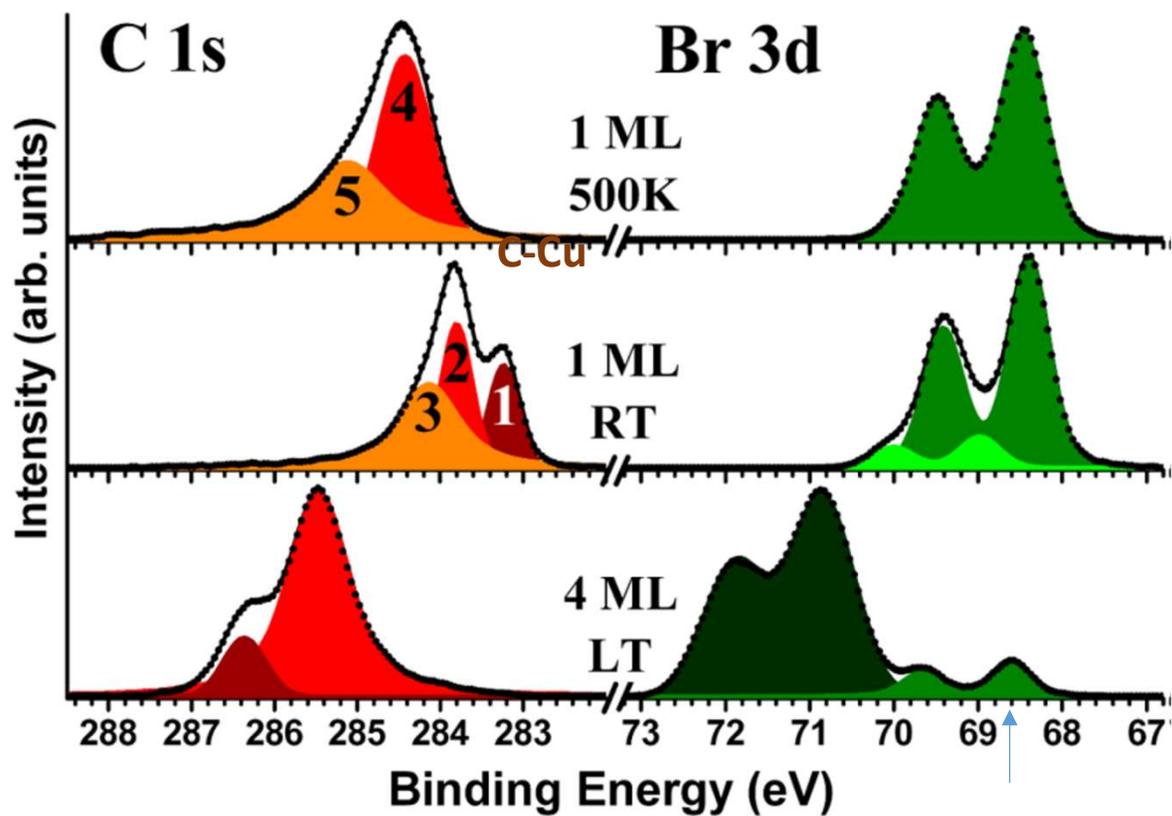
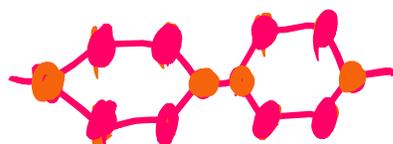


2D -
COVALENT
ORGANIC
FRAMEWORK

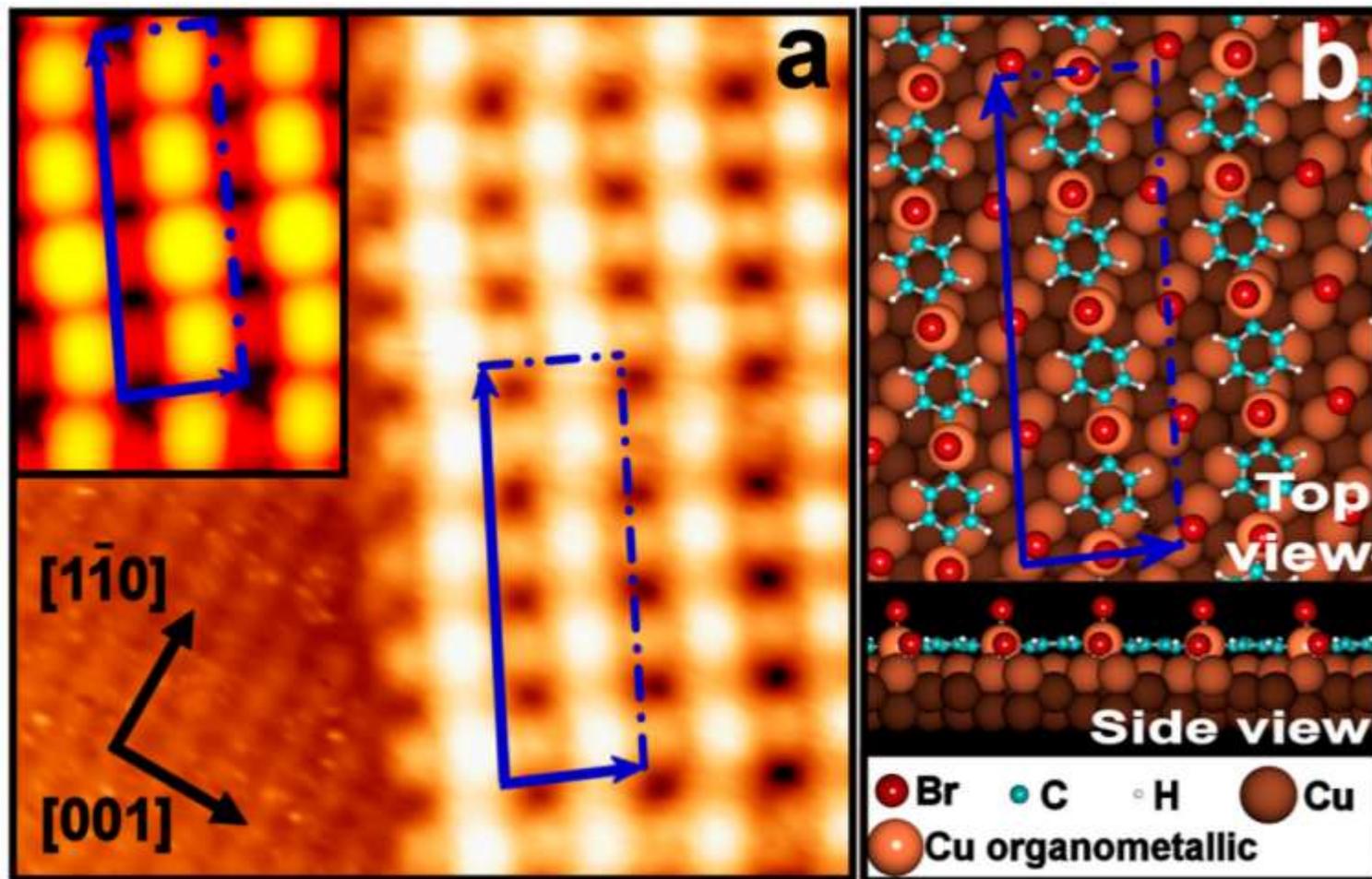
ACS Nano 2014, 8, 7880–7889.

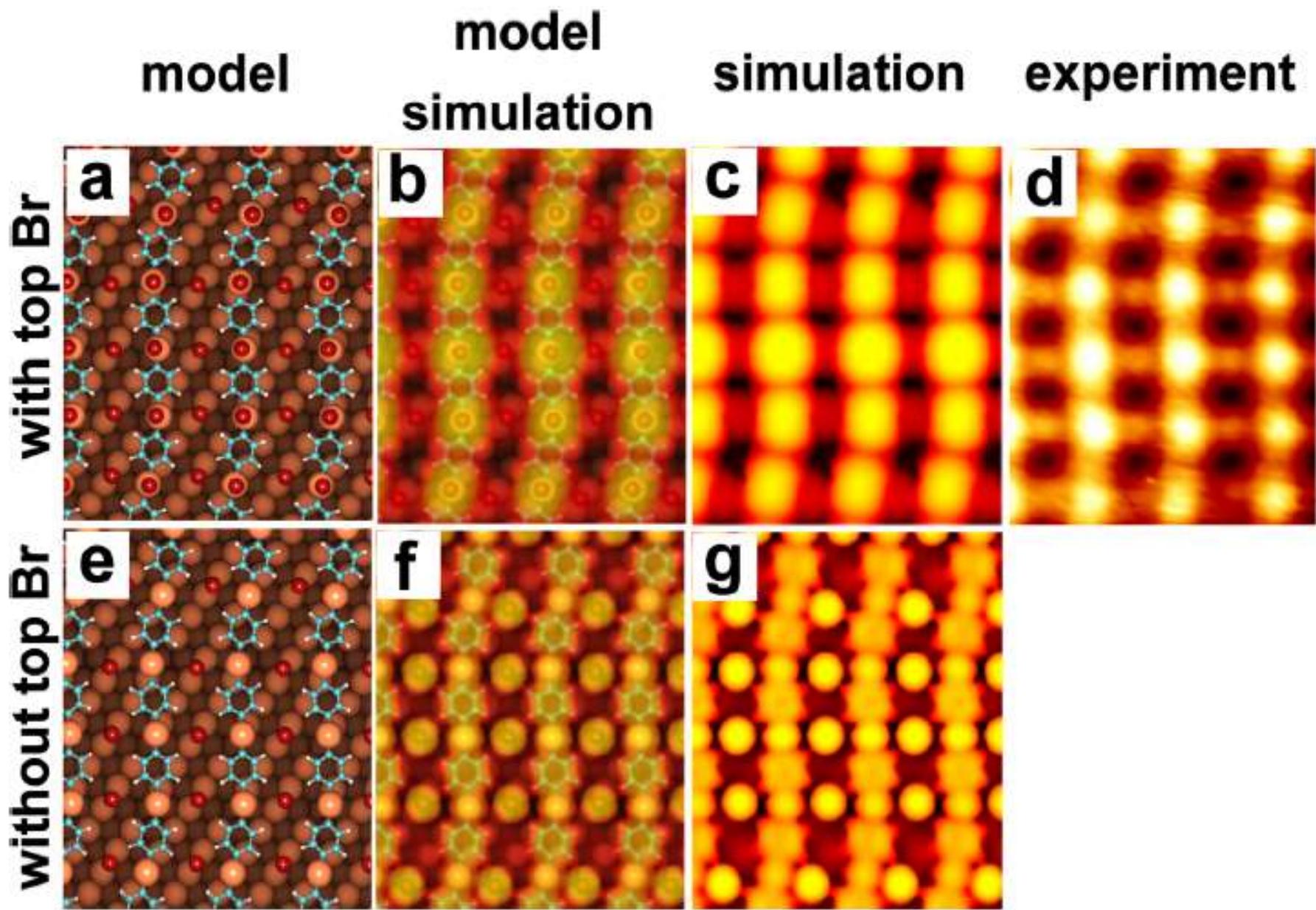
Chem. Commun. 2010, 46, 7157–7159.



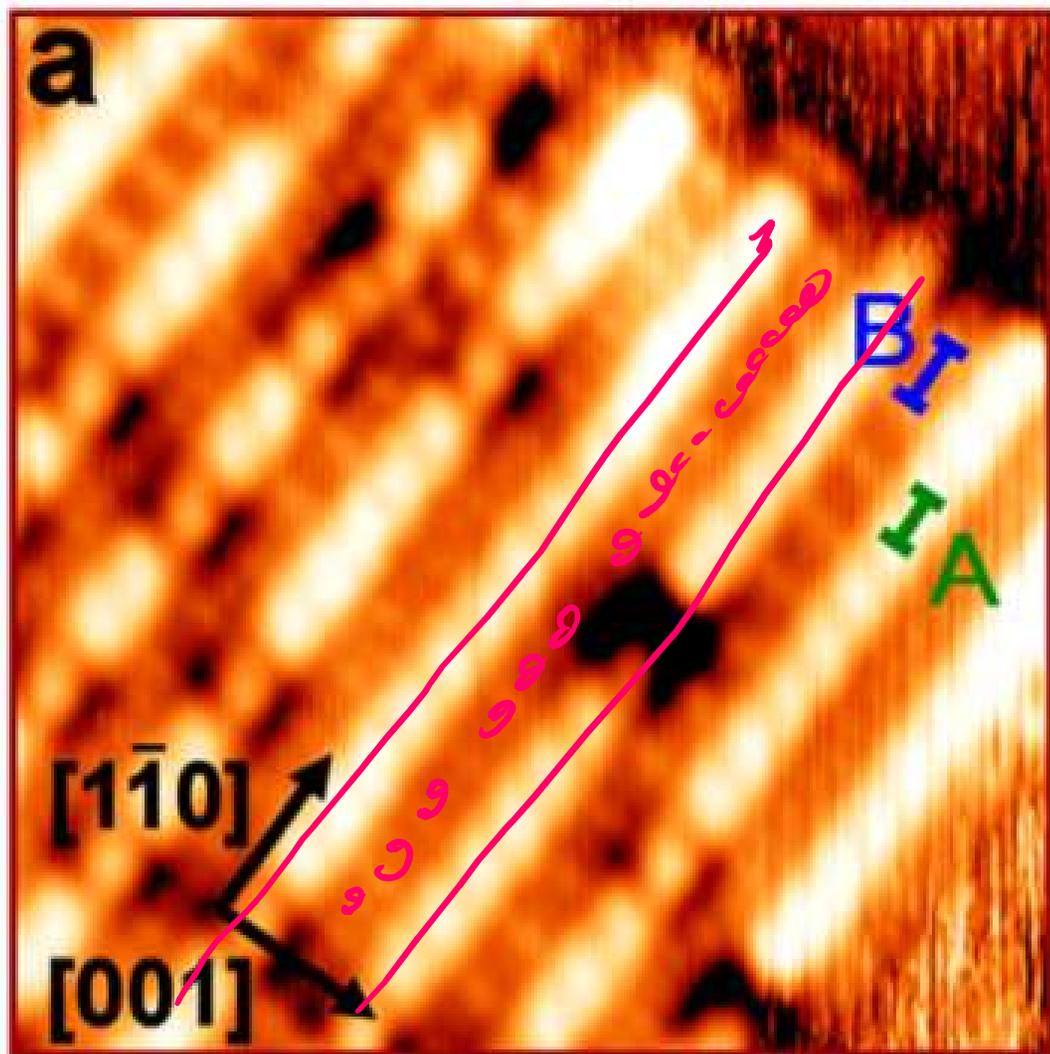


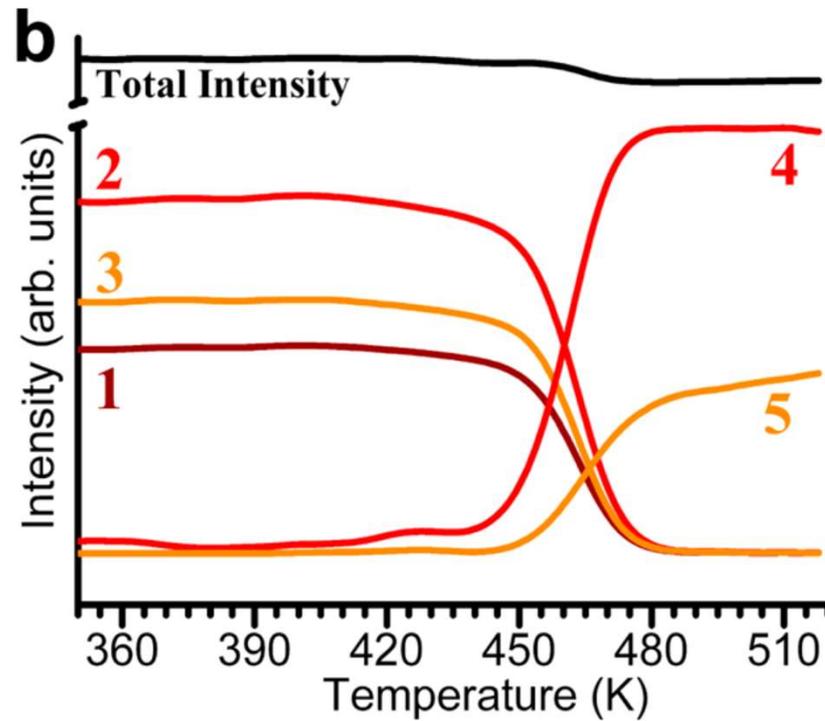
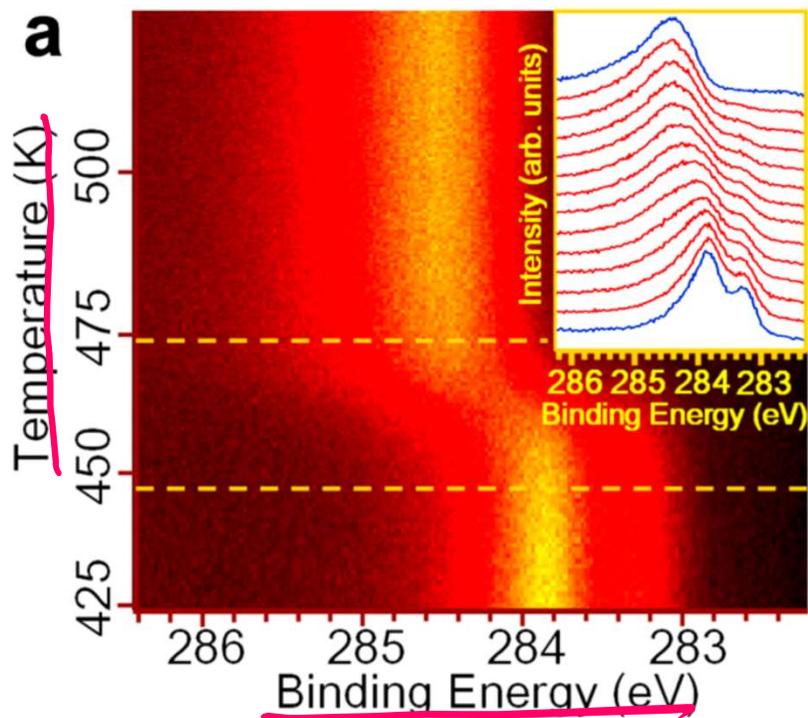
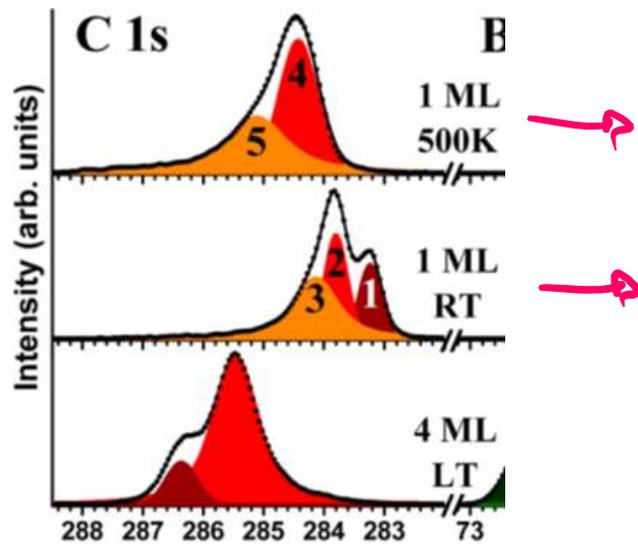
Br atomico

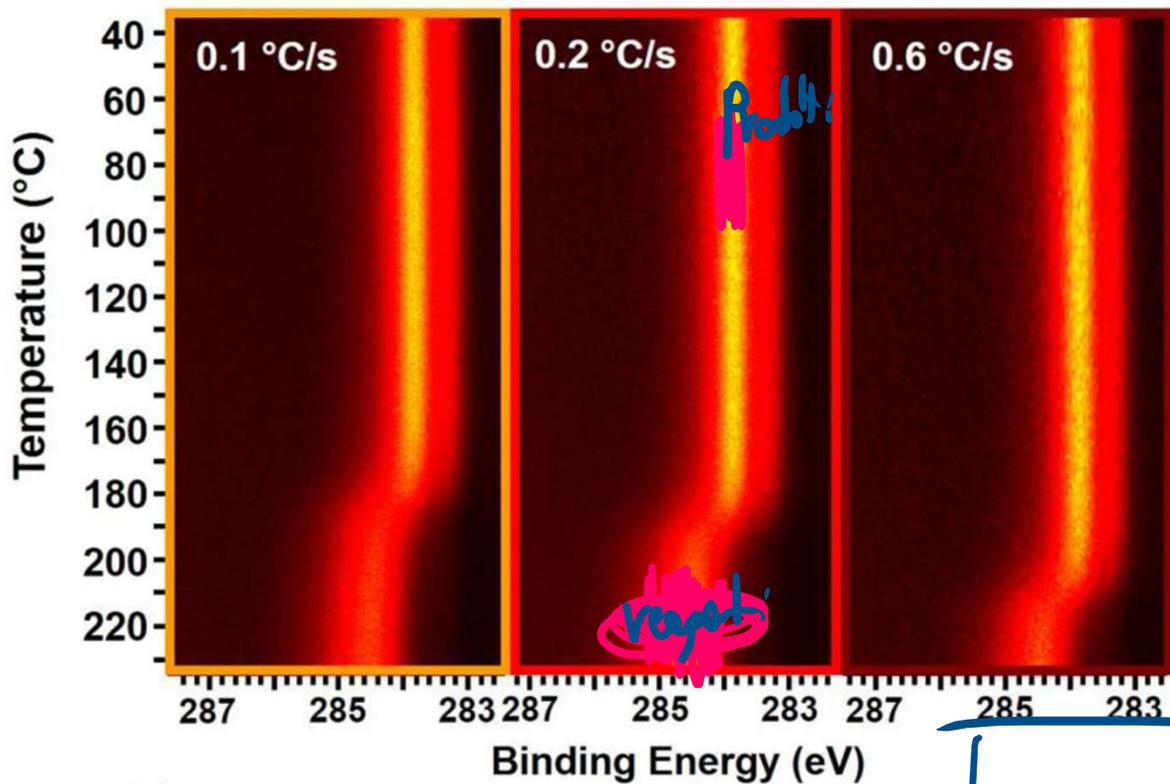




Annealing @ 500°C





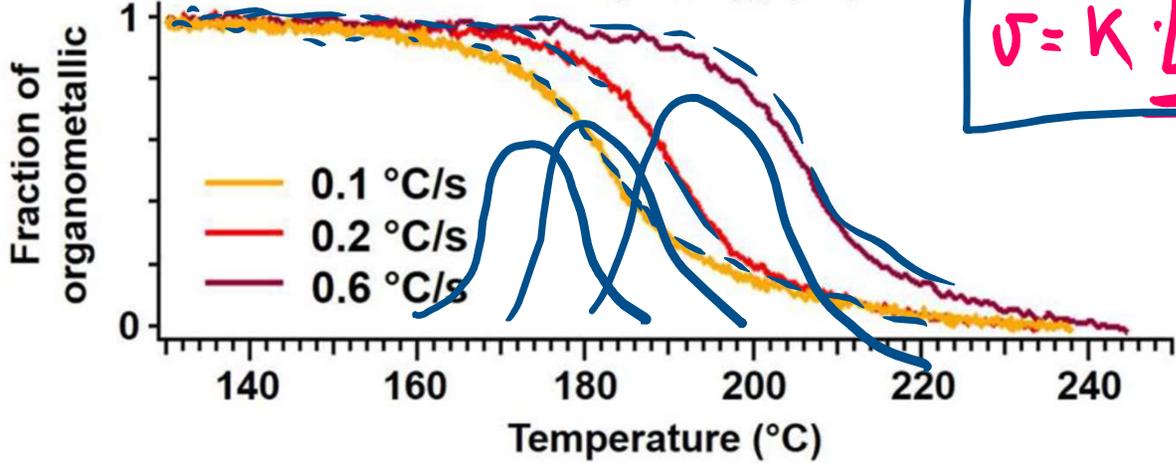


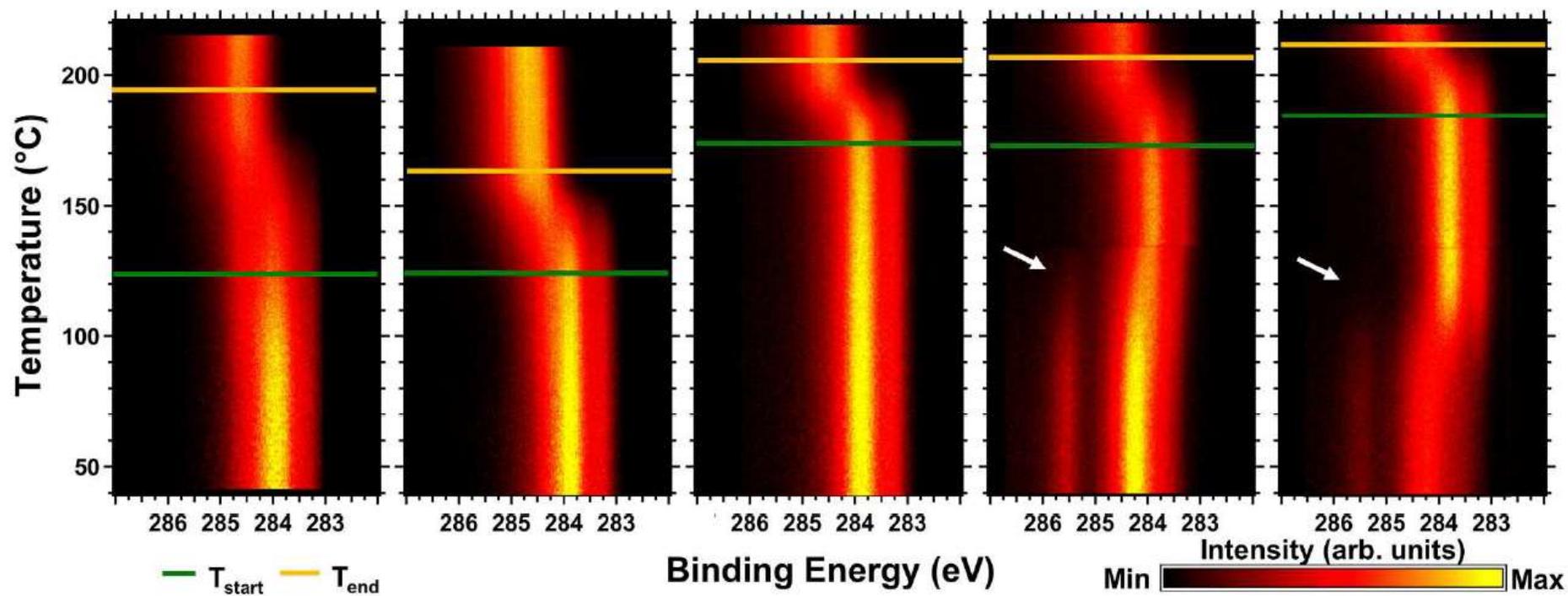
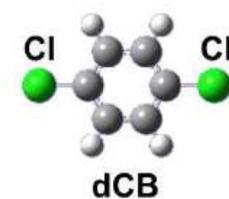
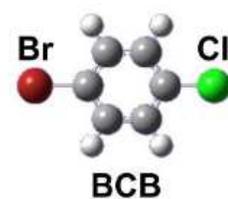
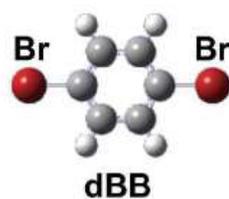
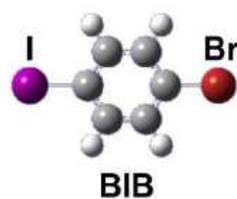
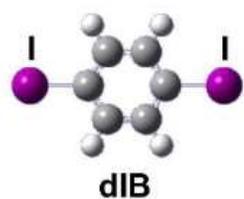
diversi rate di riscaldamento

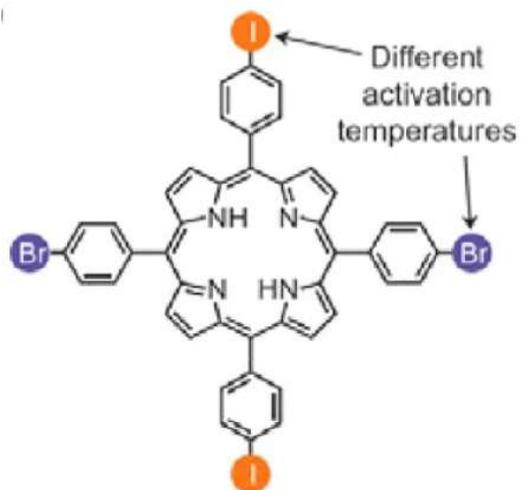
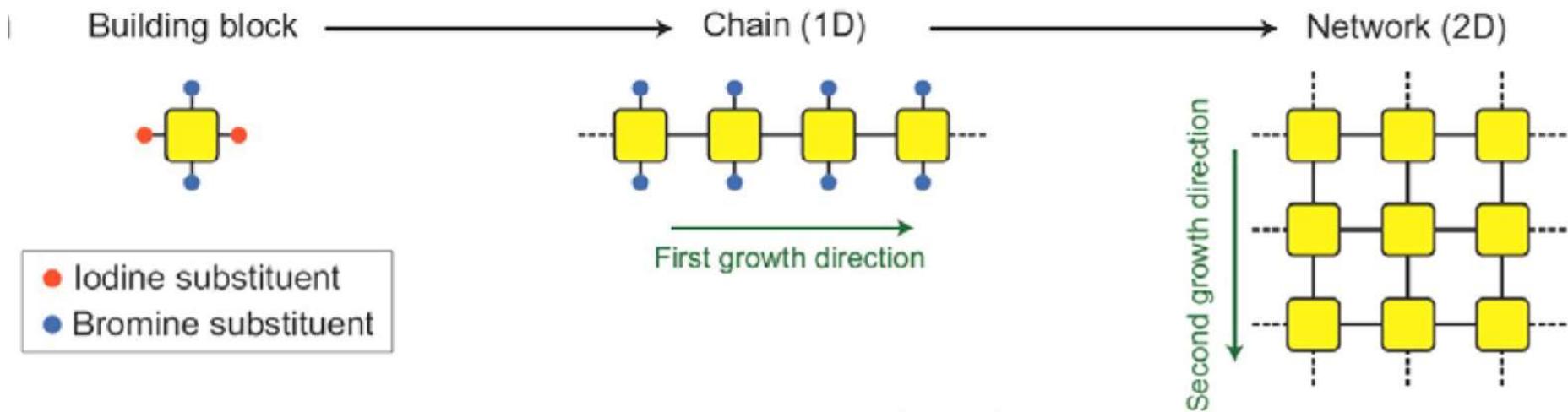
studio delle velocità di reazione

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

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

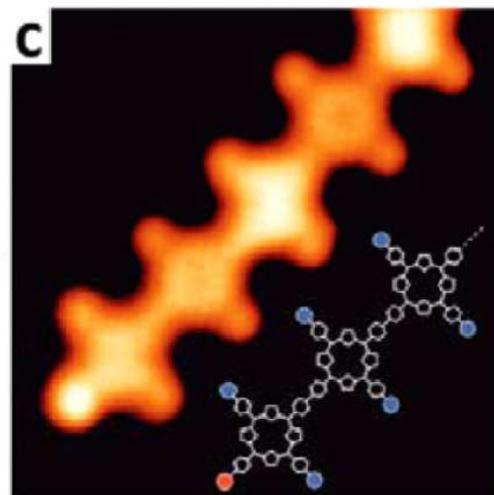






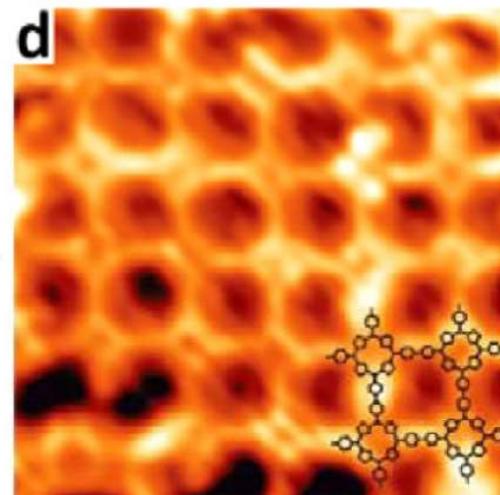
Step 1

393 K



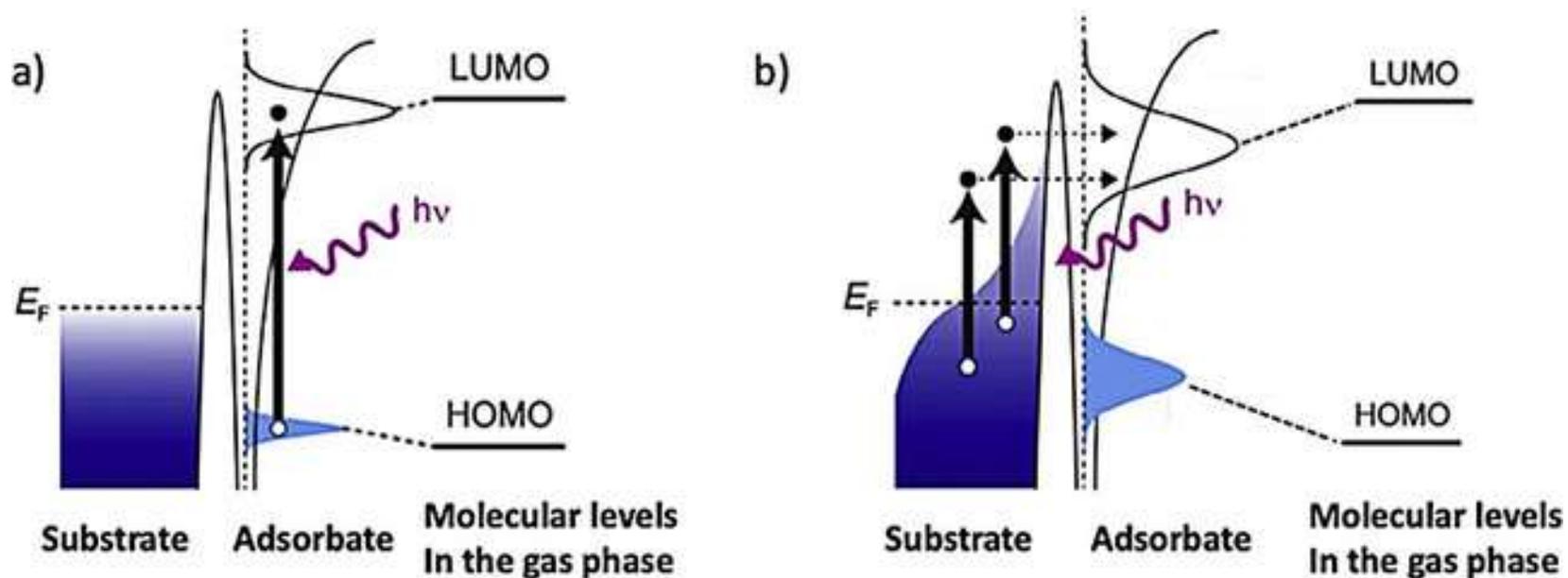
Step 2

523 K

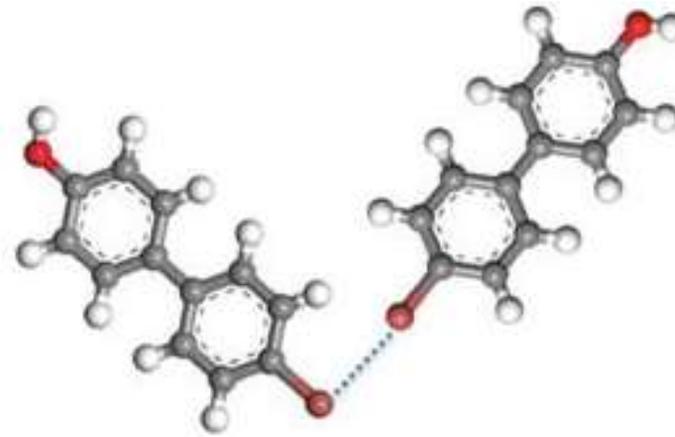
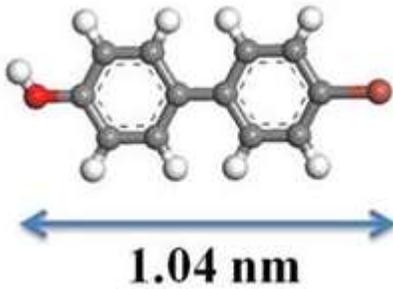


Sintesi foto-indotta

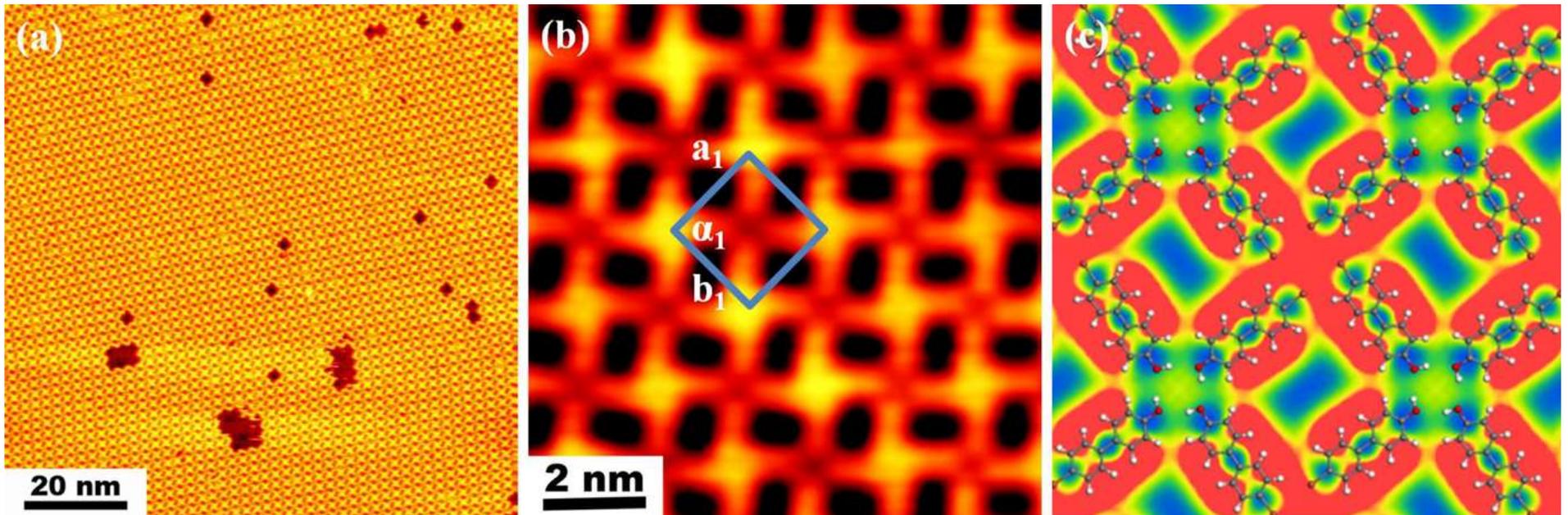
Molecole sulla superficie possono modificare la loro struttura elettronica se illuminate (UV o visibile), a seguito di due possibili processi: eccitazione interna (ADS, adsorbate excitation) o popolazione del LUMO con elettroni del substrato (HEA Hot Electron Attachment).



4-bromo-4'-hydroxybiphenyl

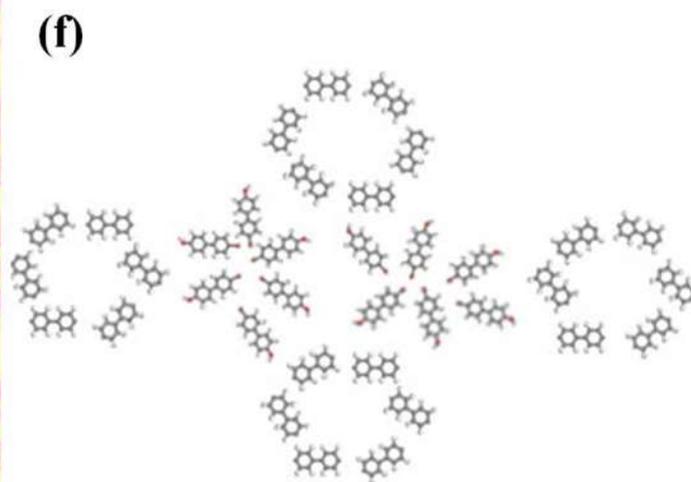
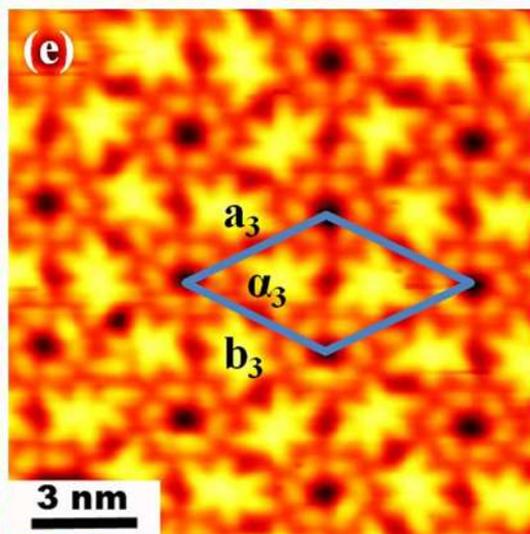
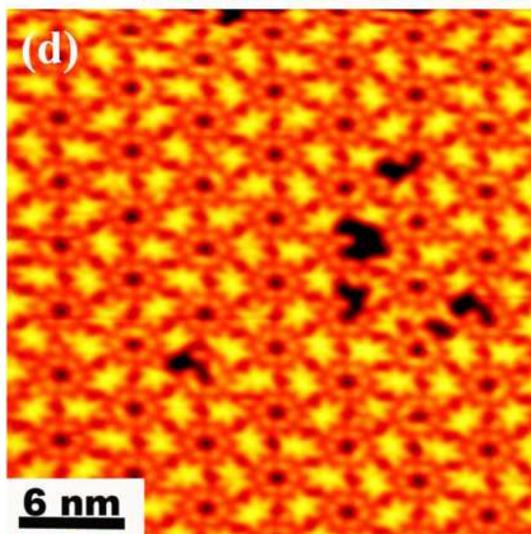
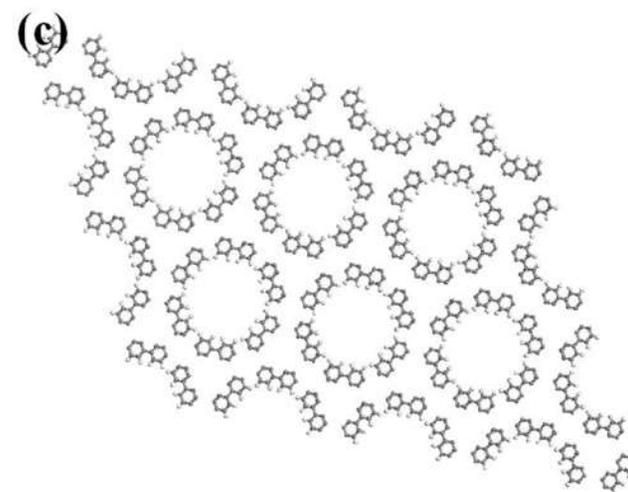
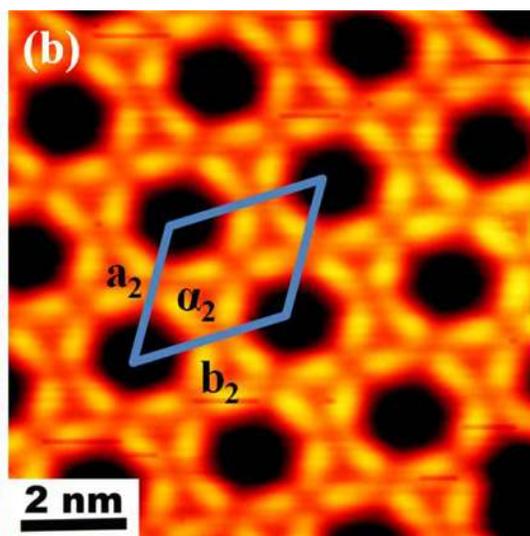
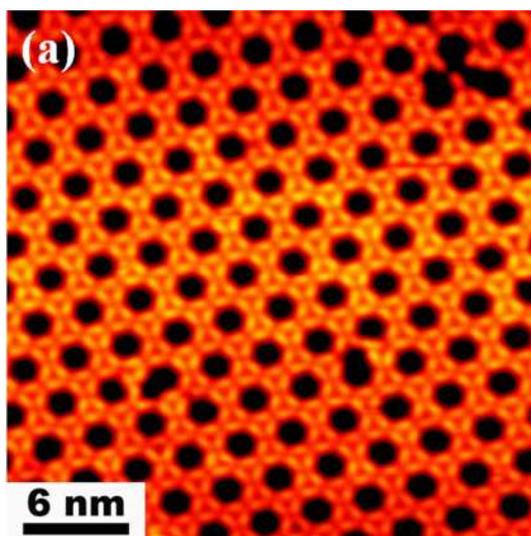


Le molecole dosate su Ag(111), temperatura campione 80K, autoassemblano formando un network basato su legami idrogeno e alogeno

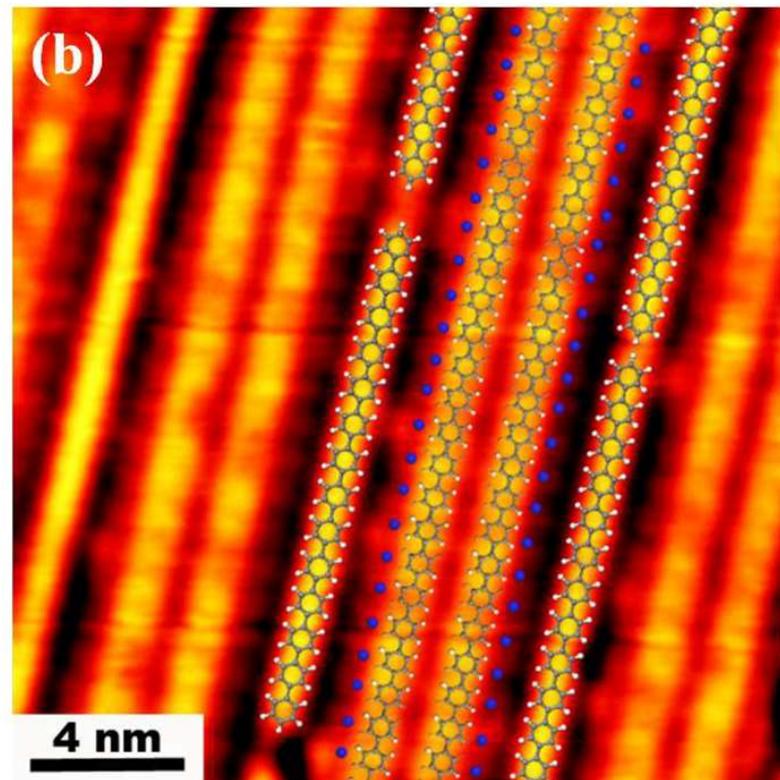
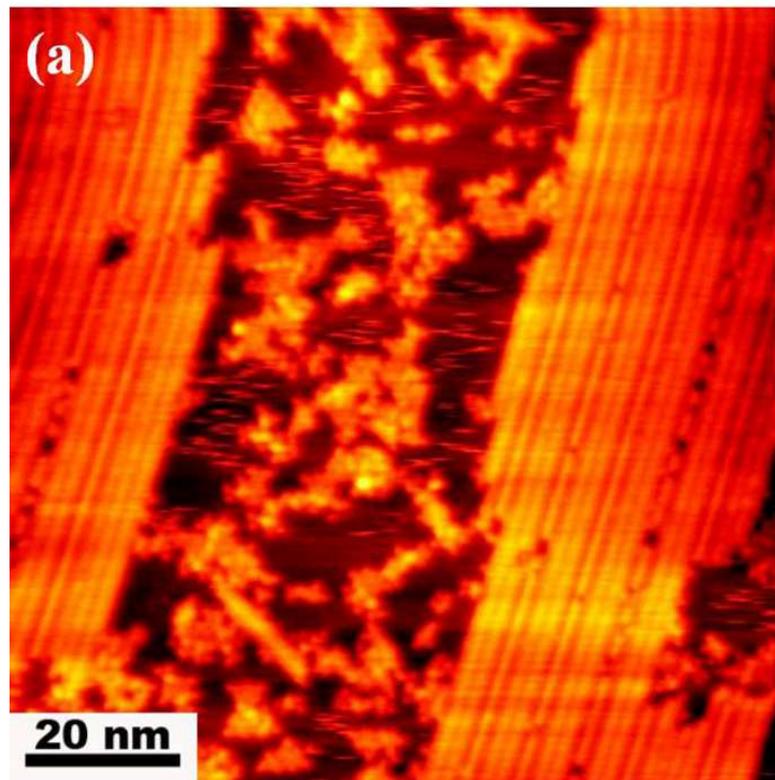




Illuminazione UV (266 nm, 10 min): si rompono i legami con -OH e con -Br, si formano biradicali e ho due fasi diverse sulla superficie



Scaldo a RT: polimerizzazione



Self-Assembly and Photopolymerization of Sub-2 nm One-Dimensional Organic Nanostructures on Graphene

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

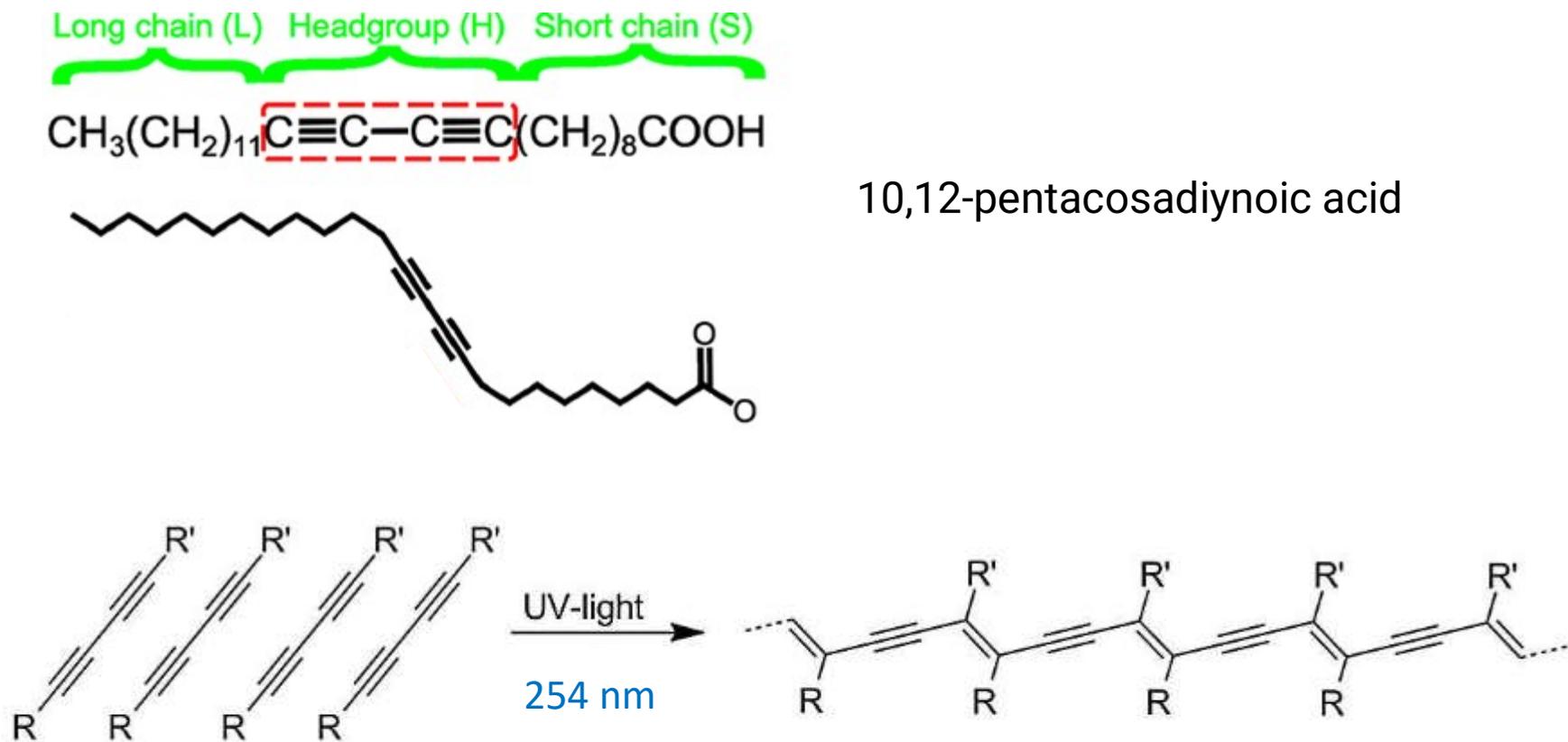
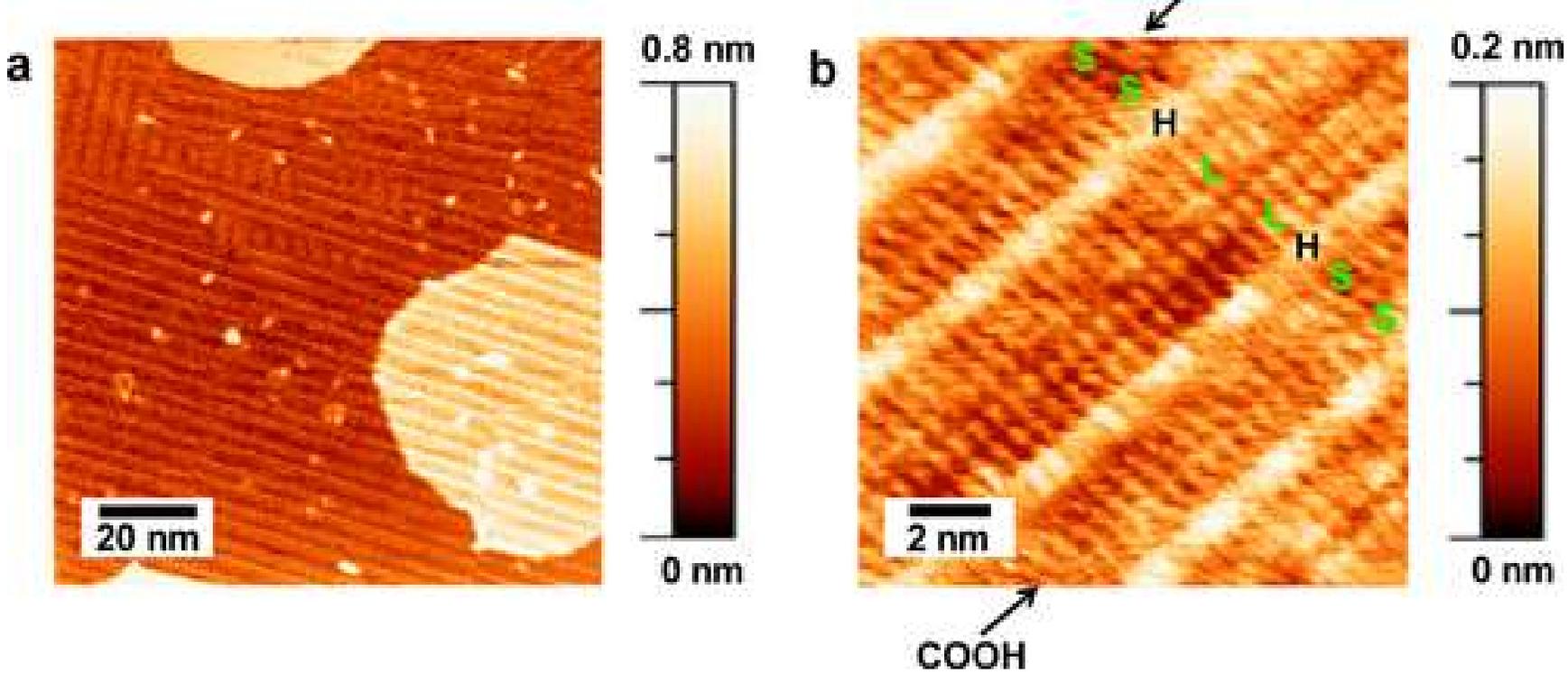
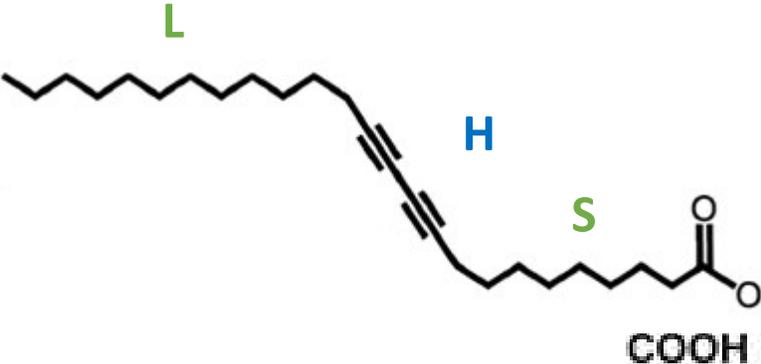
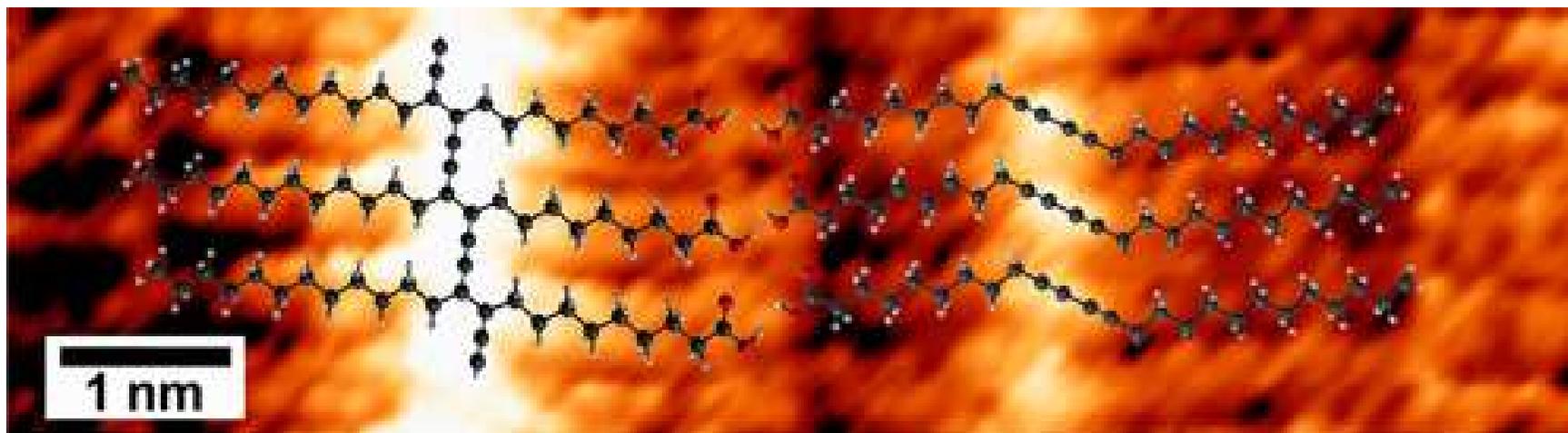
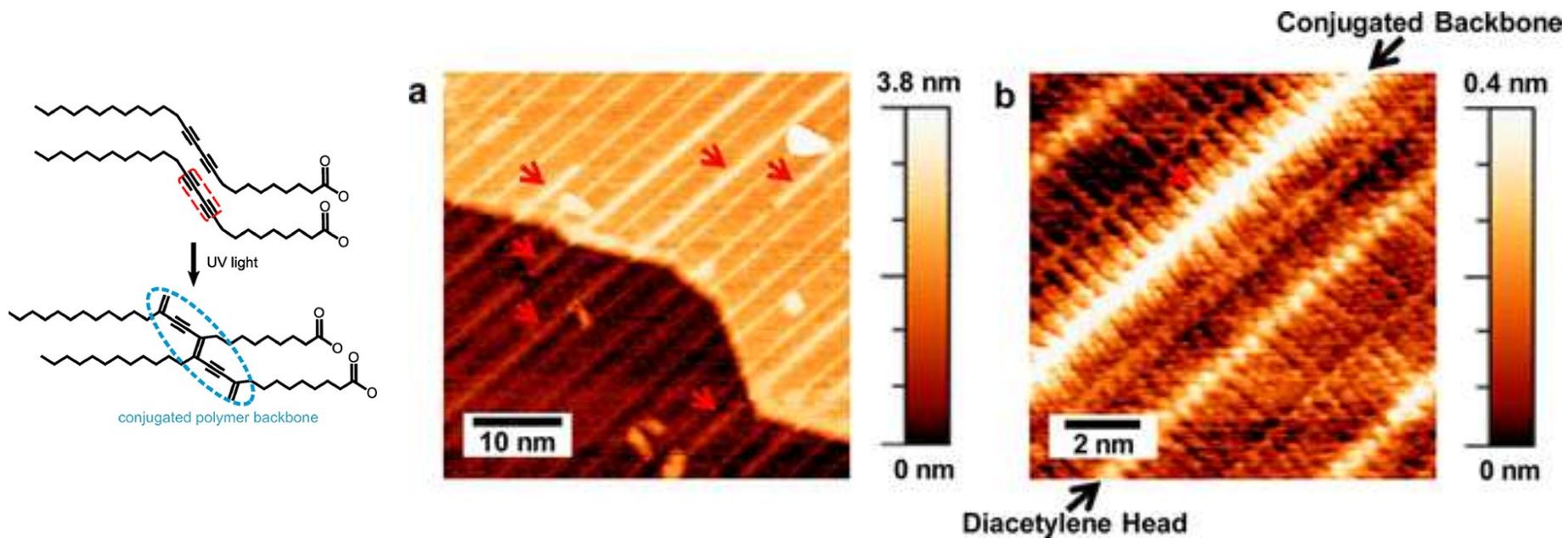


Figure 2. Schematic reaction of diacetylene after UV illumination.

Self-assembly su grafene:





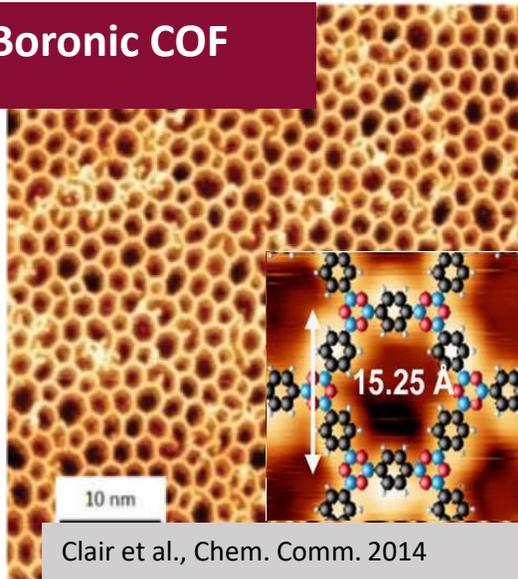
Qui, con la fotochimica, riesco a fare on-surface synthesis anche su un substrato poco reattivo come il grafene

[J. Am. Chem. Soc. 2012, 134, 40, 16759-16764](#)

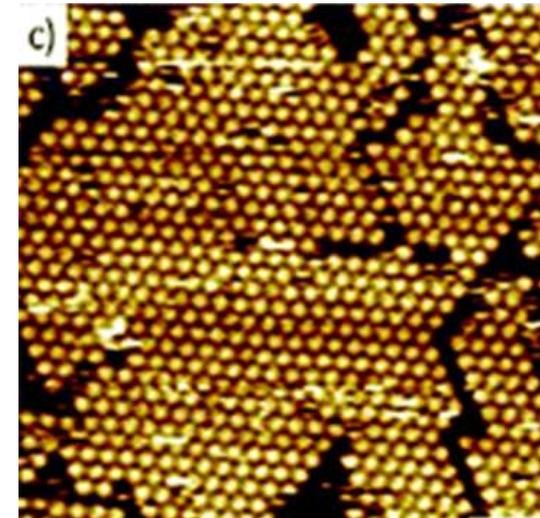
Boronic condensation

2D Covalent Organic Frameworks

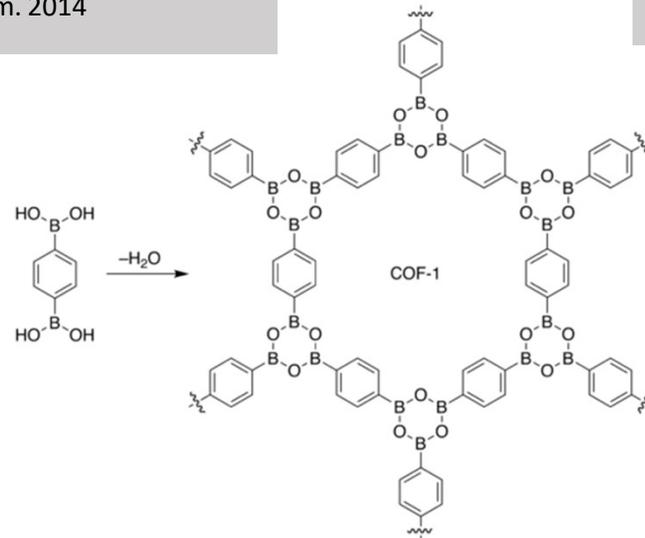
Boronic COF



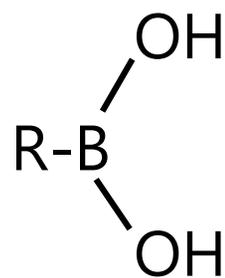
fullerene



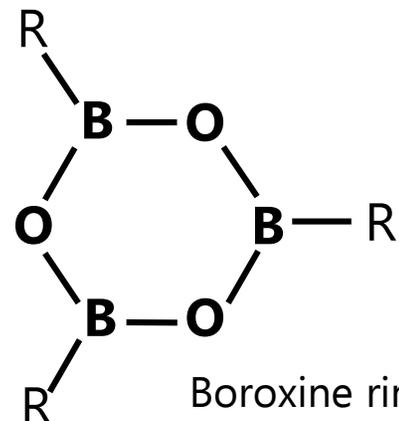
Plas et al., Chem. Comm. 2016



Boronic acid

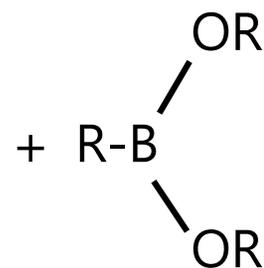
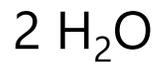


Boroxination

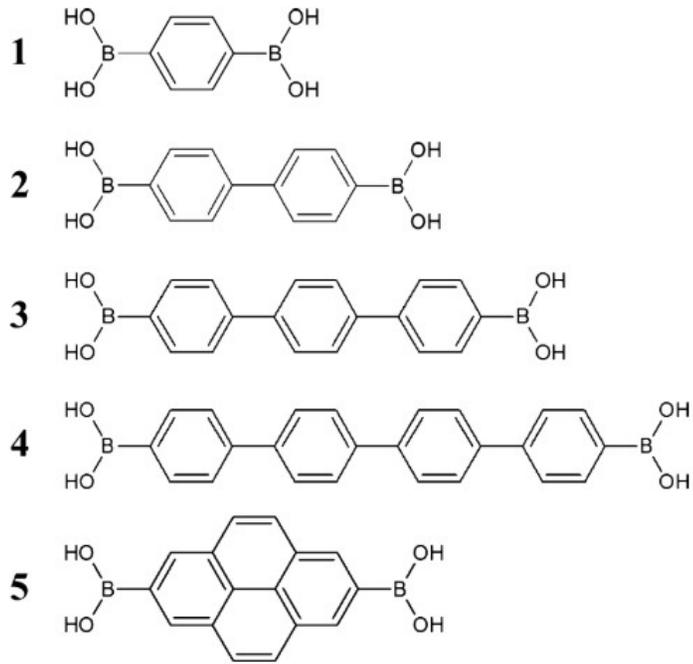


Boroxine ring

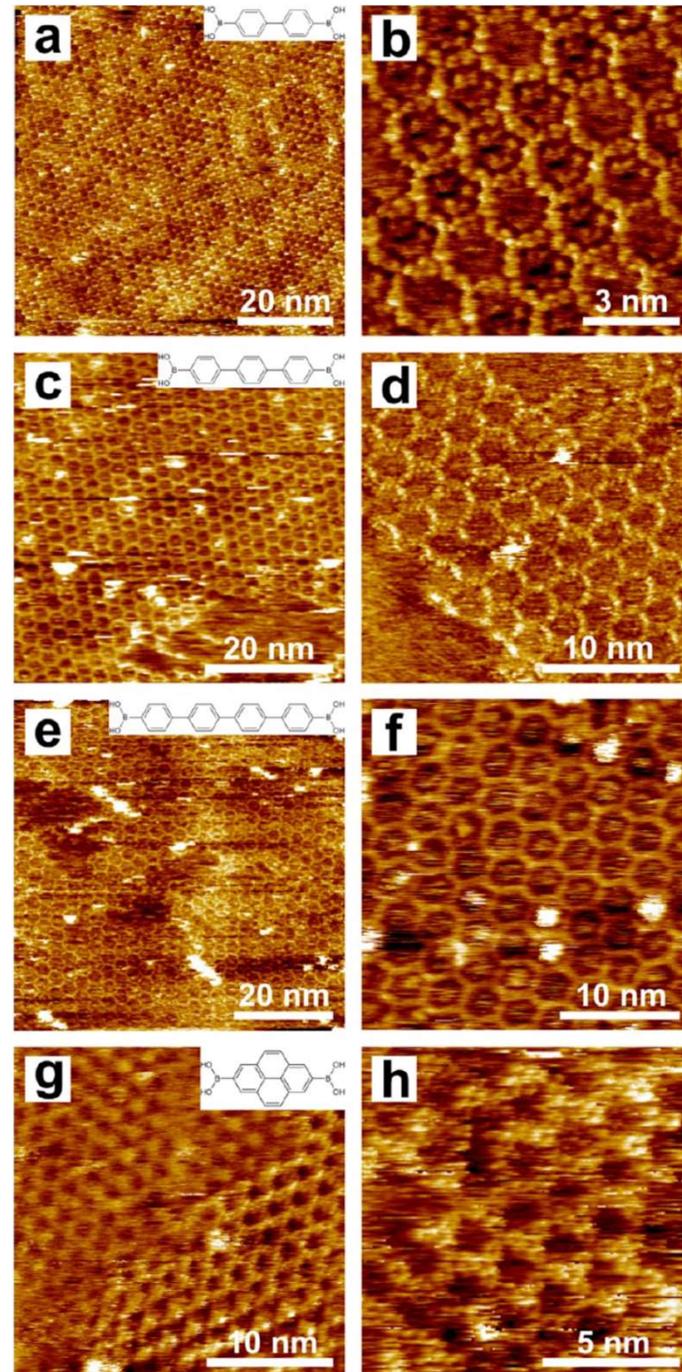
+ 2 R-OH
Esterification



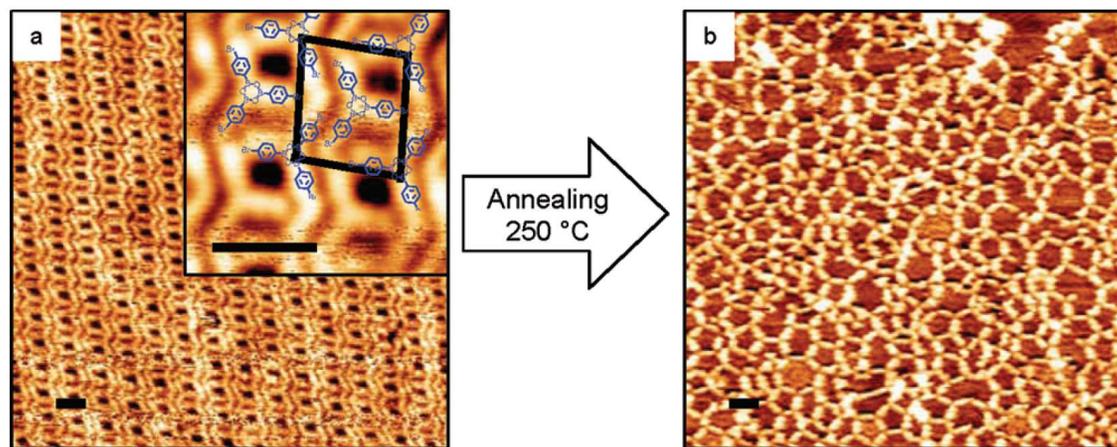
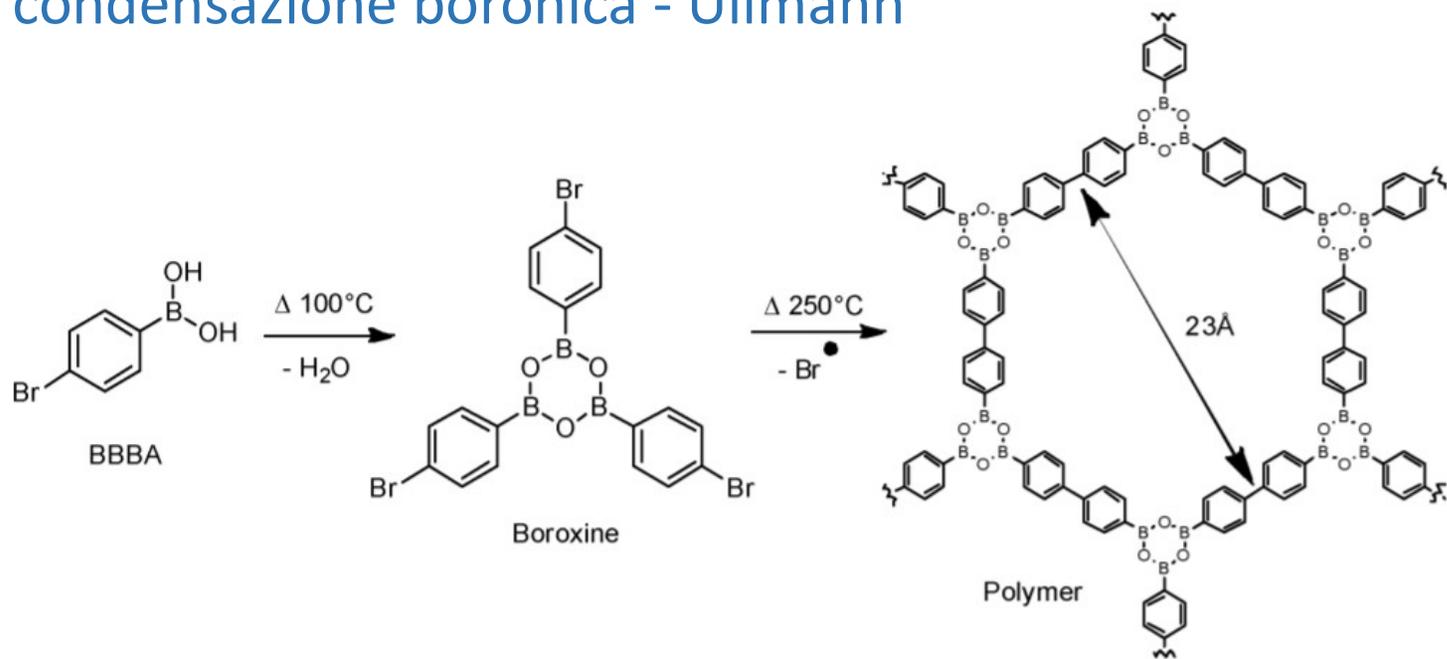
weak Lewis acids
Suzuki-Miyaura reaction
detection of sugars
molecular imprinting



Nota: 1. è sublimabile da crogiolo, gli altri no. Se si prova a farlo la condensazione avviene nel crogiolo stesso. 2-5 vanno depositati da soluzione (*drop casting*)

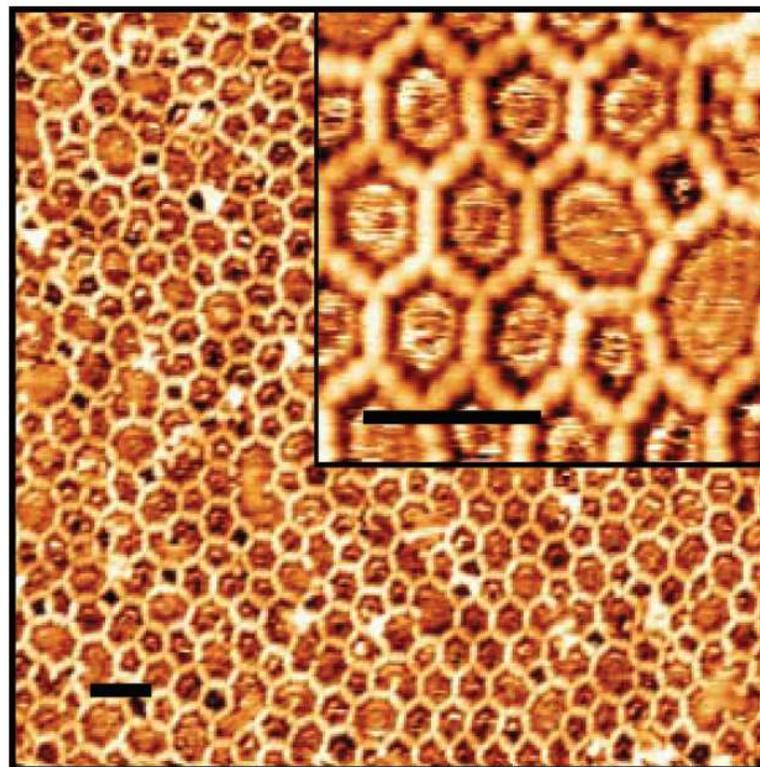


Sequenza condensazione boronica - Ullmann

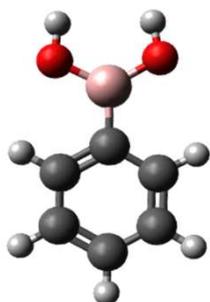




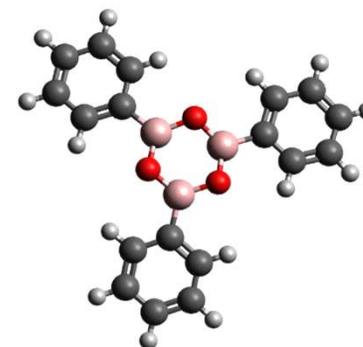
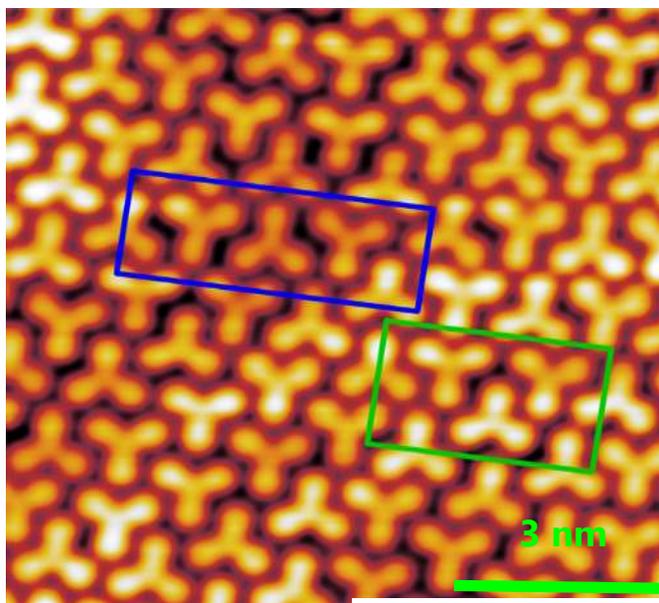
$T_s=250^\circ\text{C}$



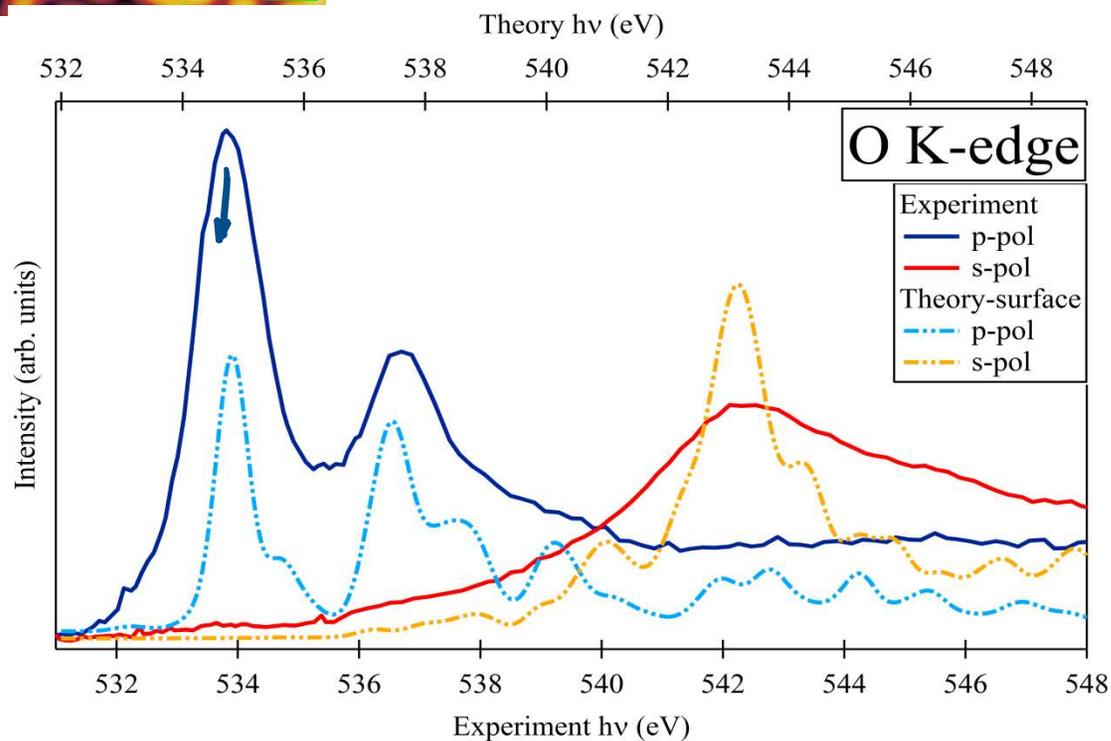
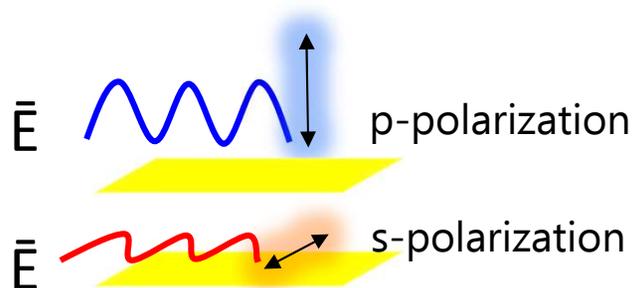
Boroxine macromolecules



Phenylboronic acid
on Au(111)



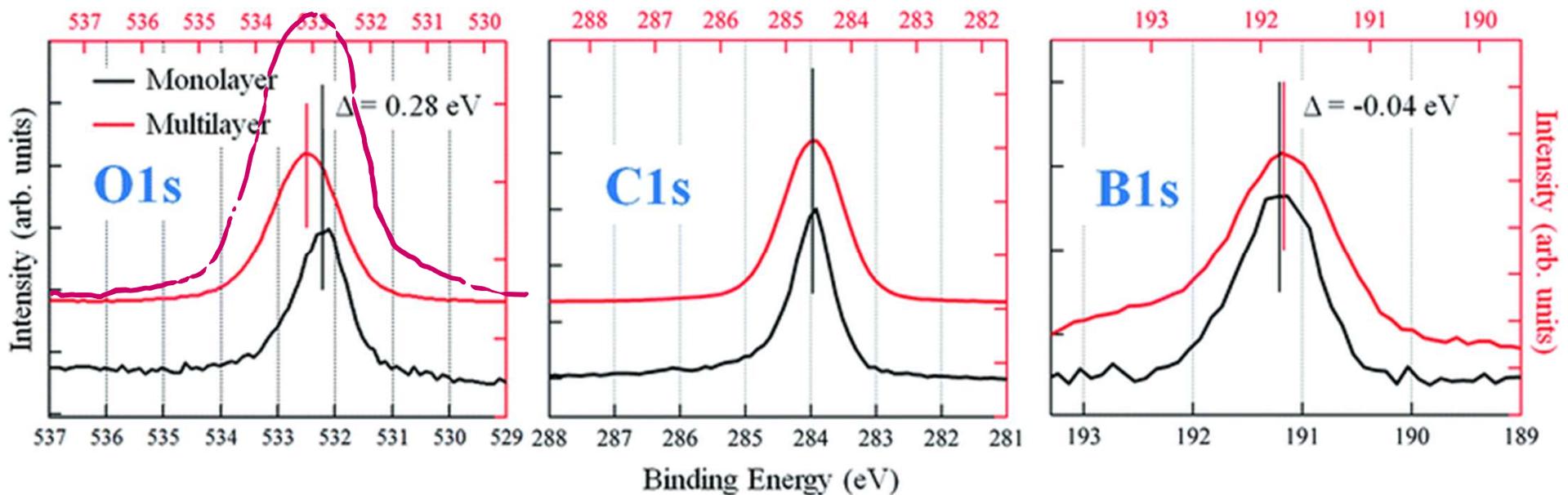
On surface synthesis
Triphenylboroxine

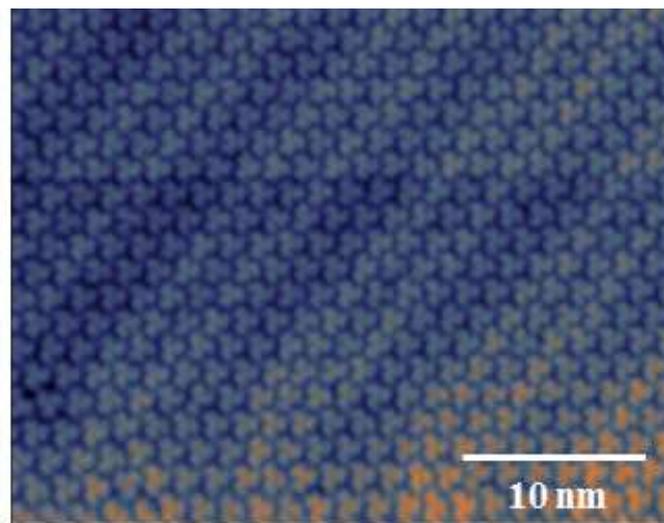
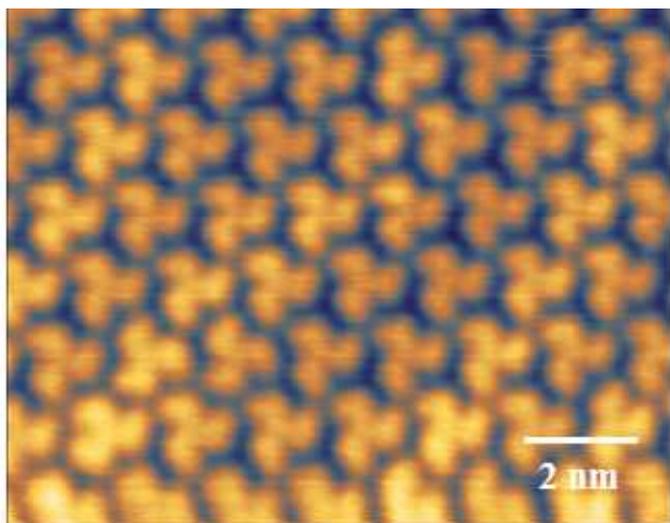
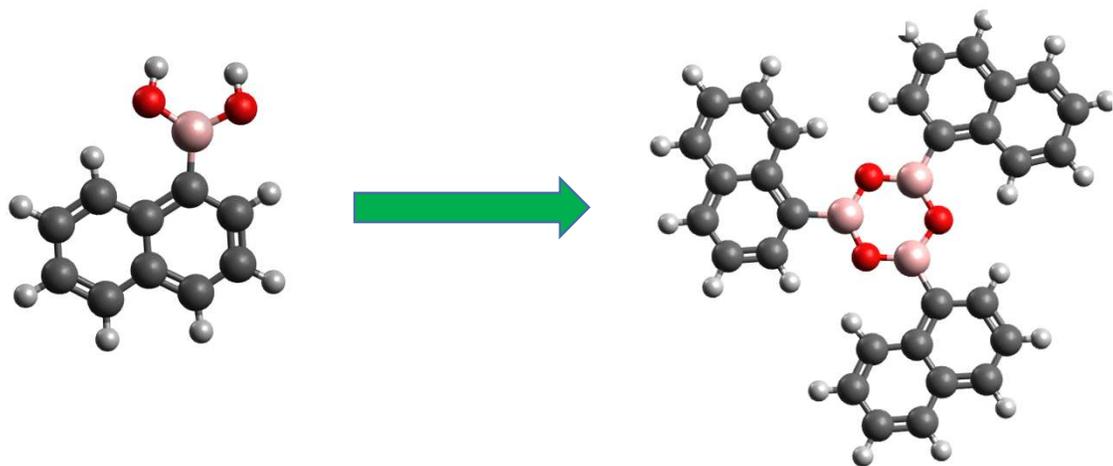


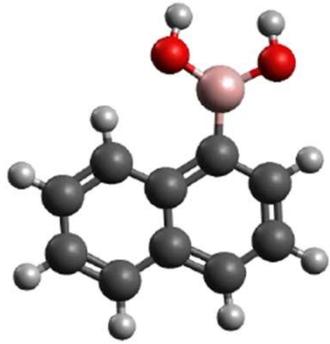
$T < -50^\circ\text{C}$ → caso multilayer del precursor

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

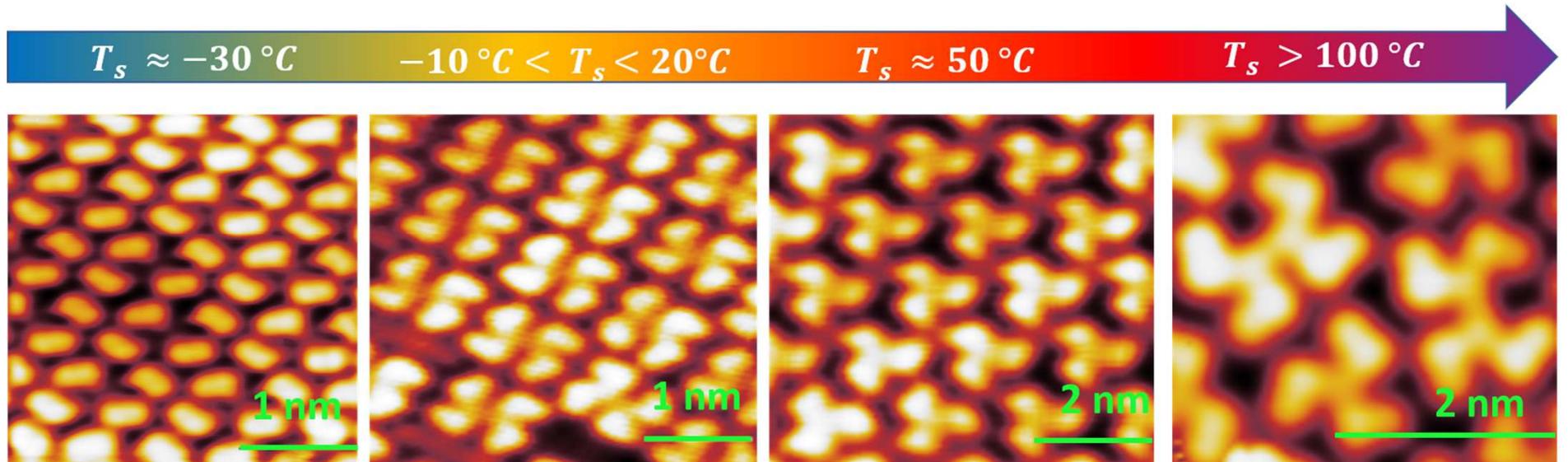
$h\nu$ la probabilità di fotoemissione da un certo livello (O_{1s}, D_{1s}, \dots)
dipende dalla cross section ($\sigma_{O_{1s}}, \sigma_{D_{1s}}$)

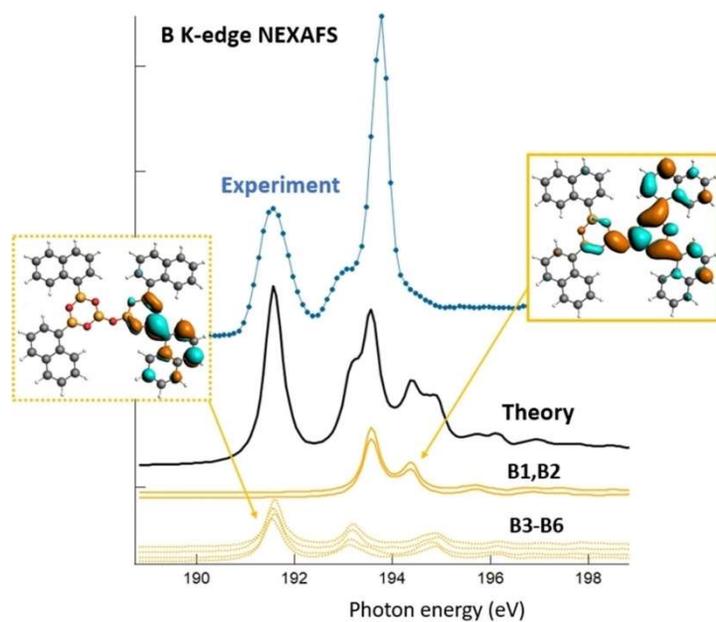
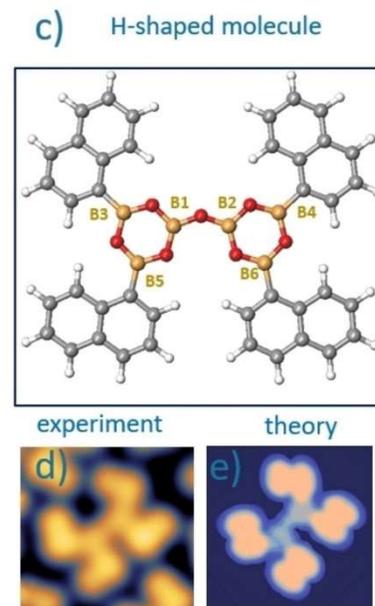
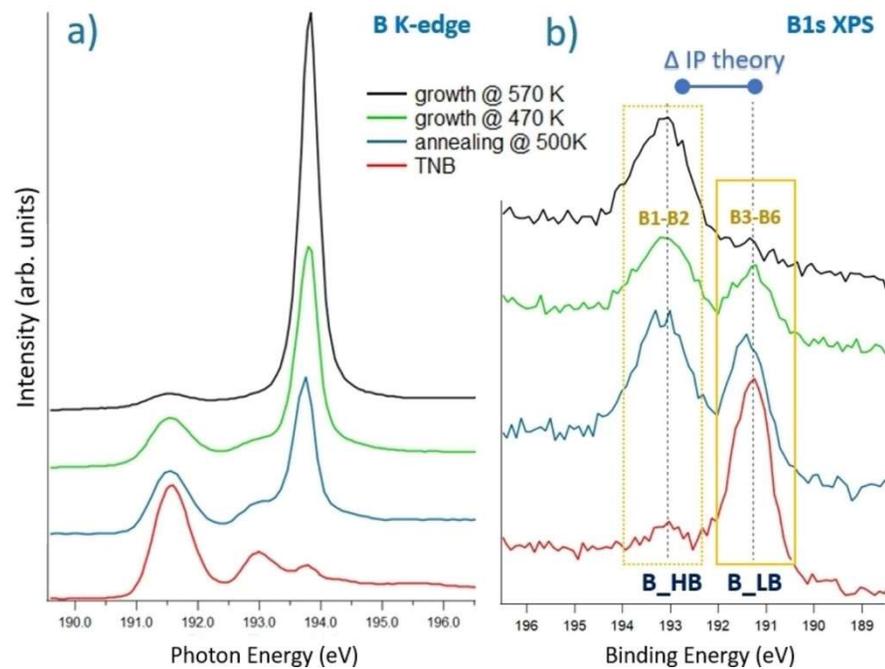




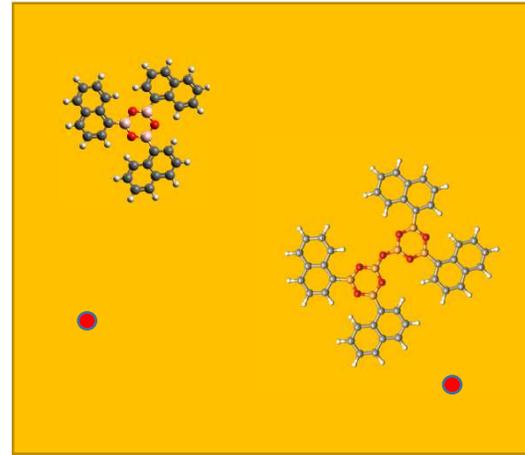
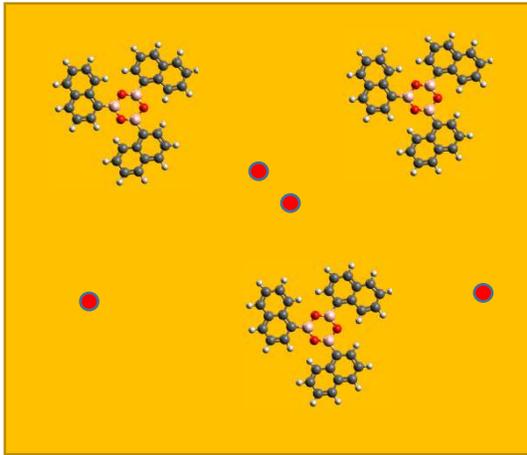


NBA su Au(111)



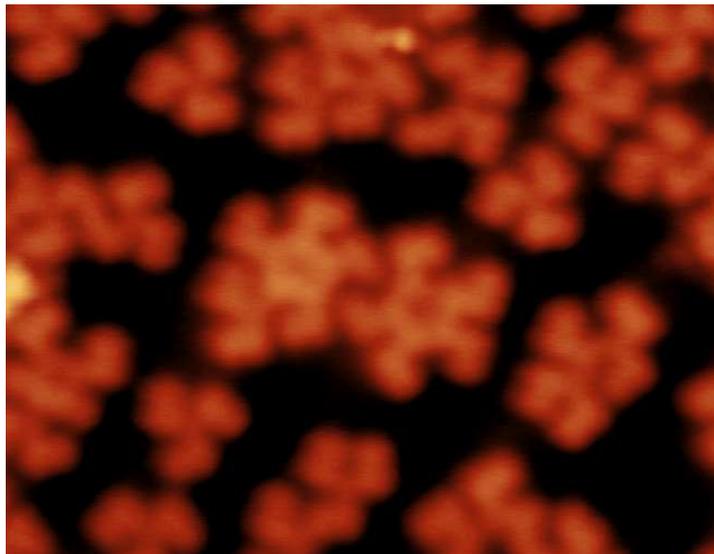


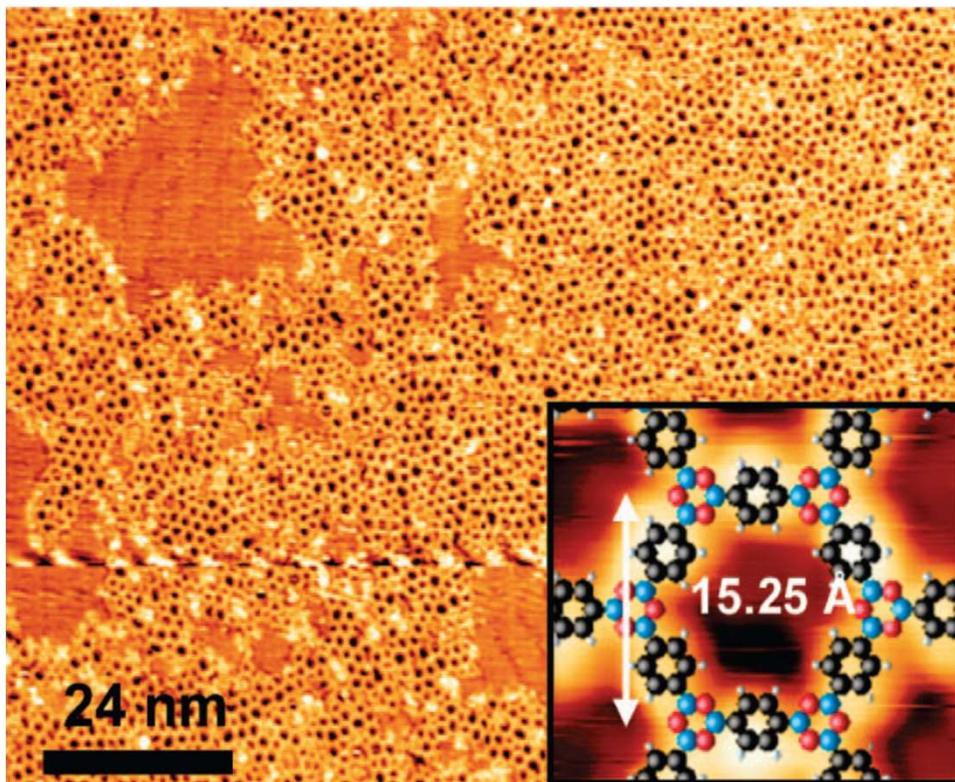
<https://doi.org/10.1002/chem.202401565>



A seguito della condensazione, specie O, OH restano sulla superficie.

Il riscaldamento del campione attiva la reazione di rilascio di gruppi naftalenici, con i siti di ossigeno che agiscono da attivatori e partecipano alla sintesi delle strutture a farfalla.





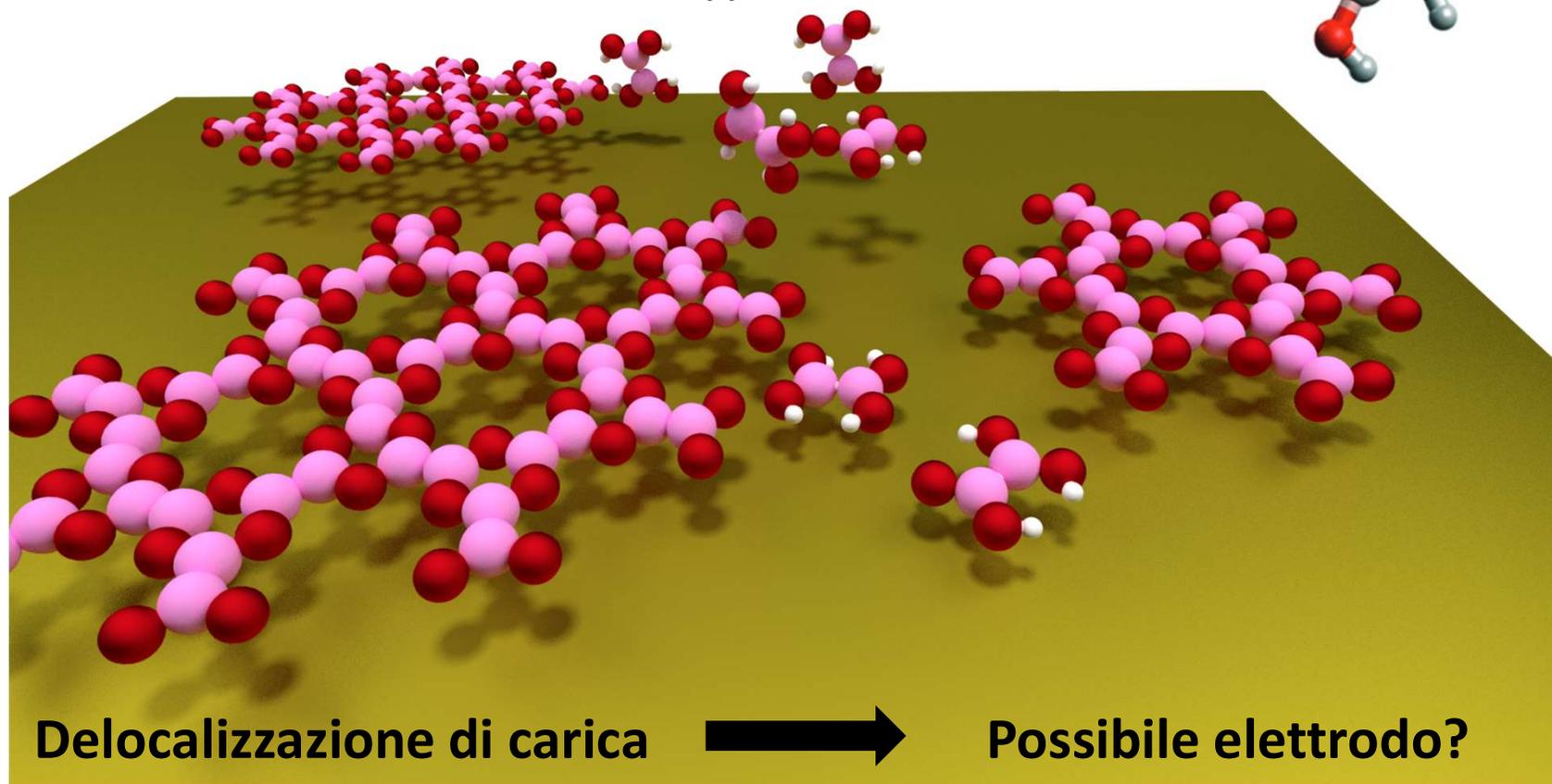
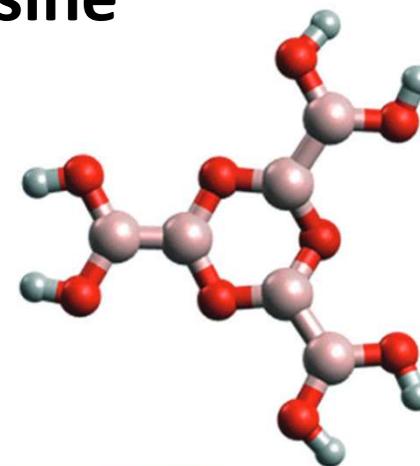
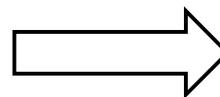
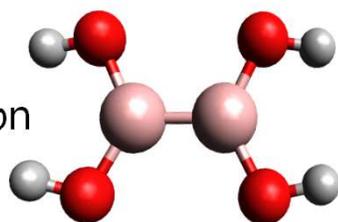
T. Faury et al., J. Phys. Chem. C 2012, 116, 4819–4823

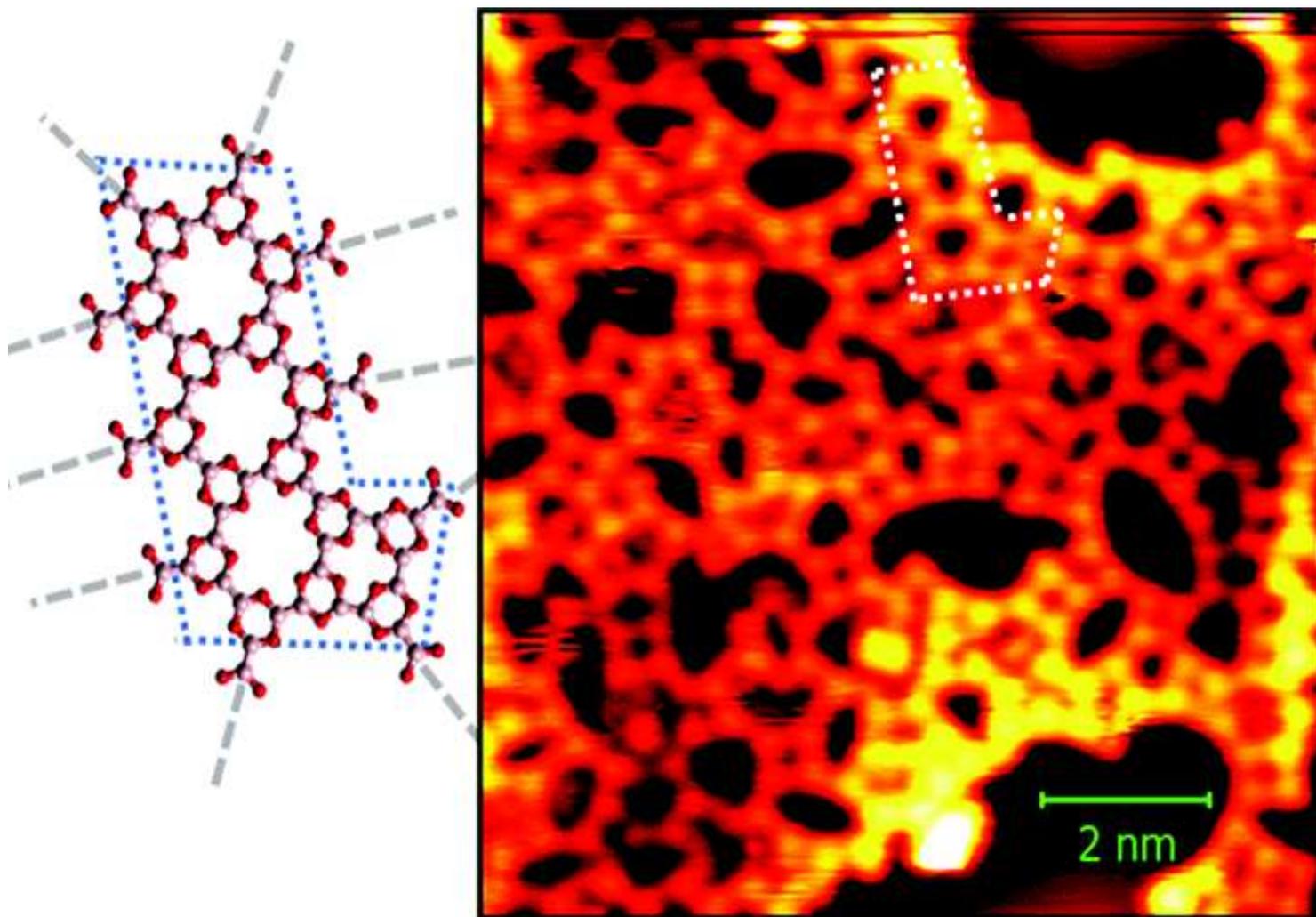
DFT calculations:
Boroxine rings break the aromaticity of phenyl rings

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

Framework di borossine

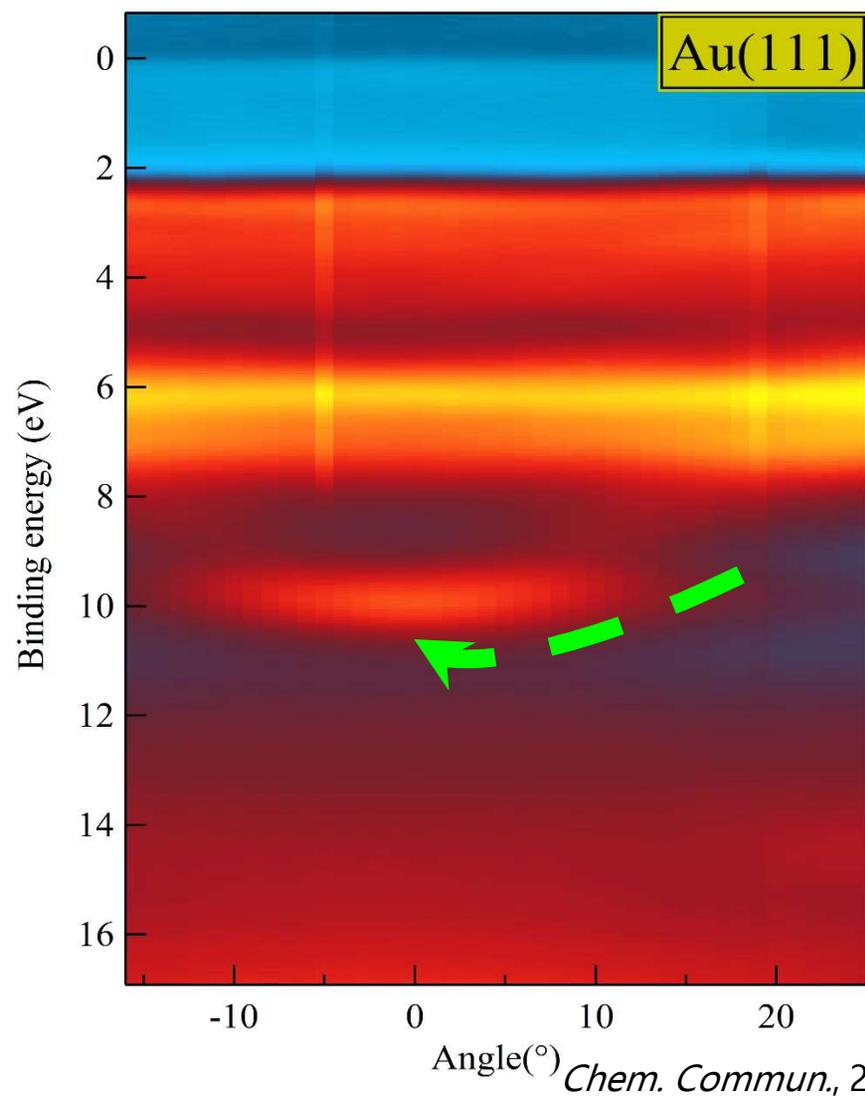
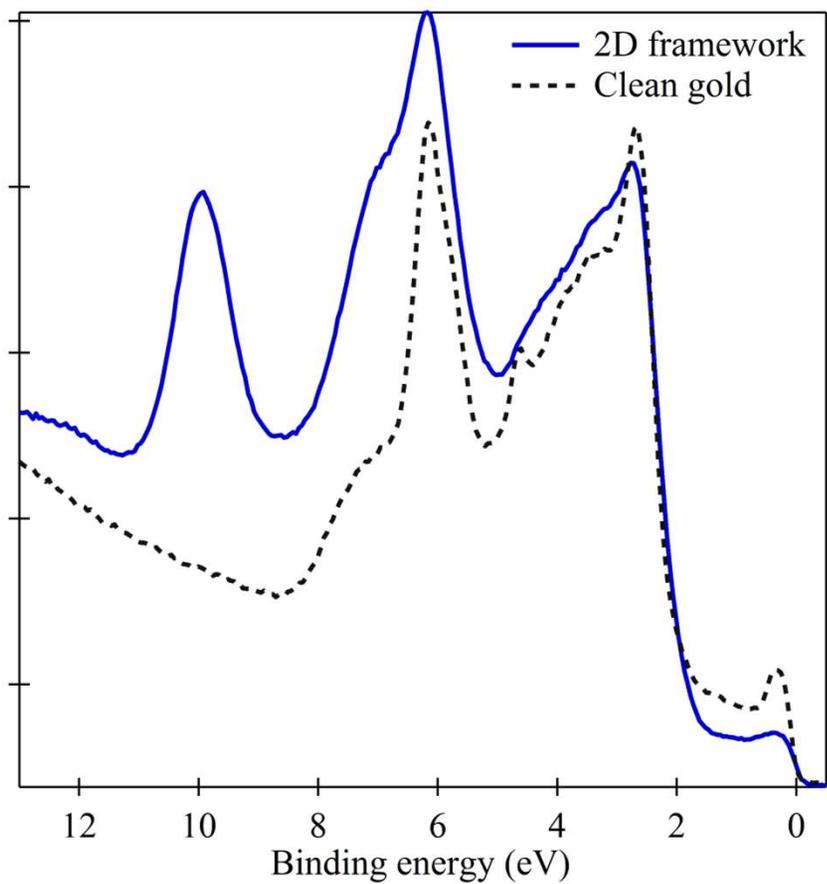
THDB
Tetrahydroxydiboron



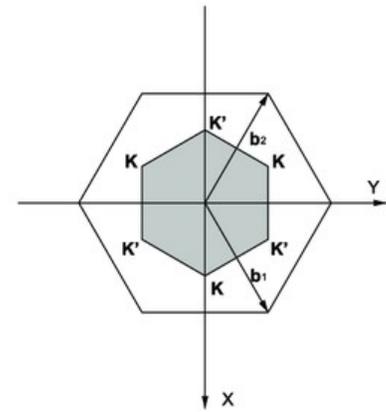
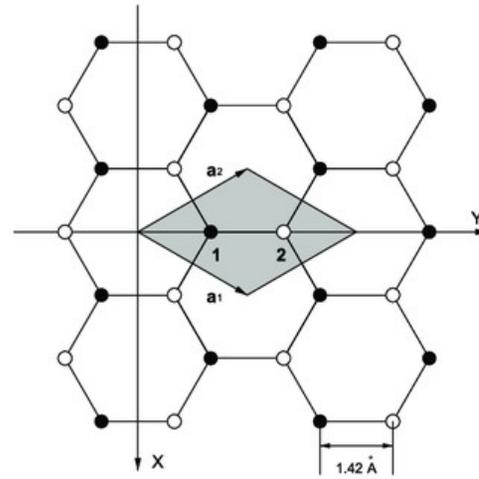
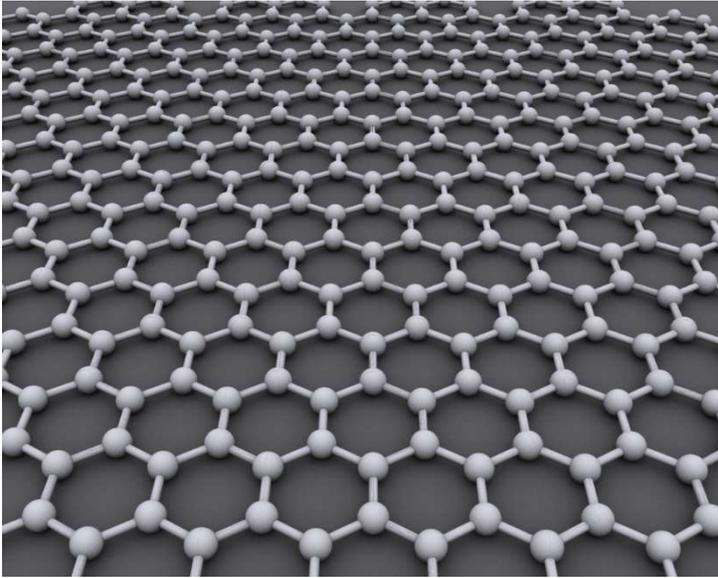


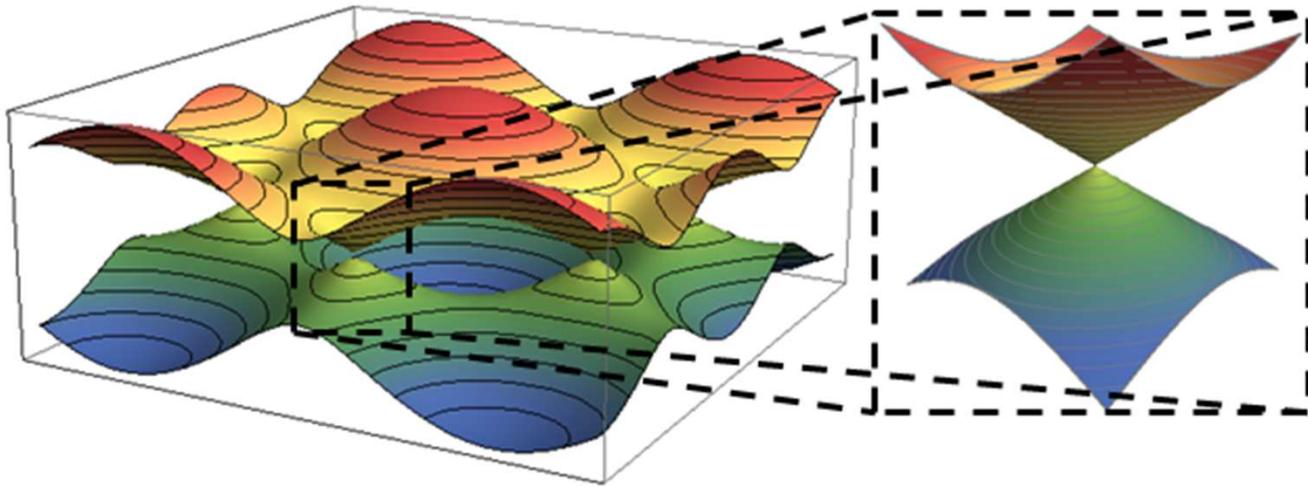
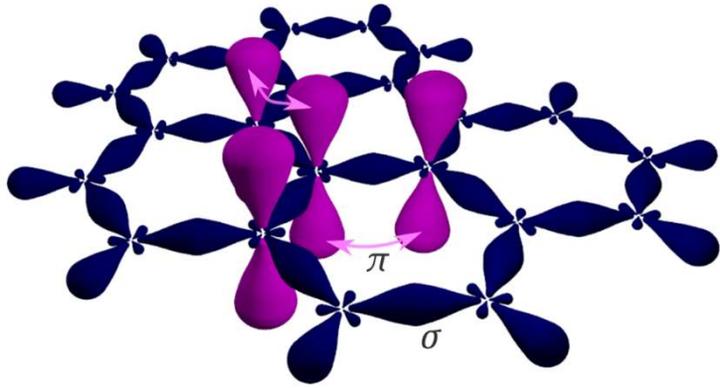
amorphous morphology
Proliferation of defects

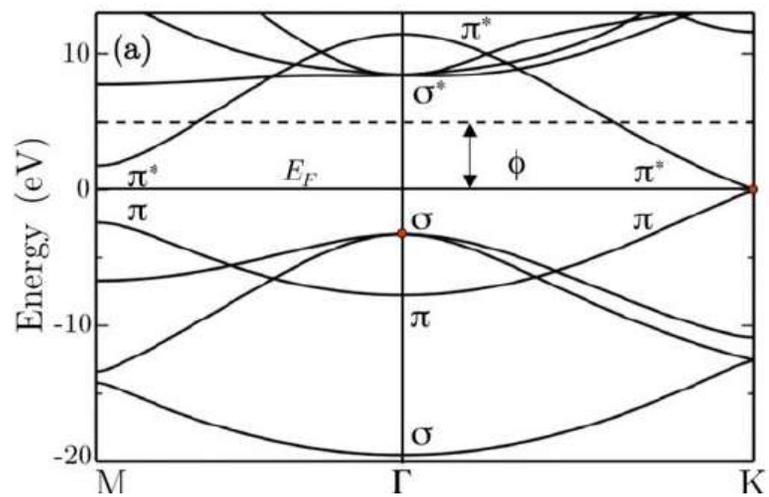
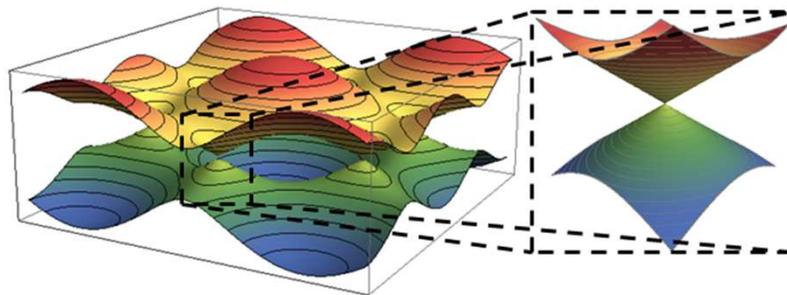
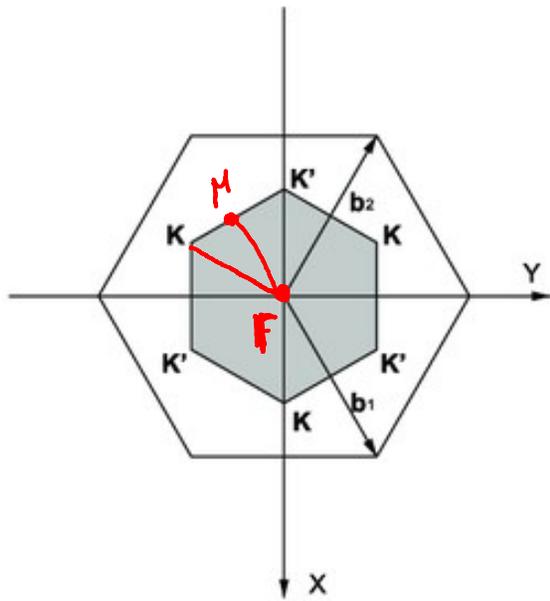
Chem. Commun., 2018

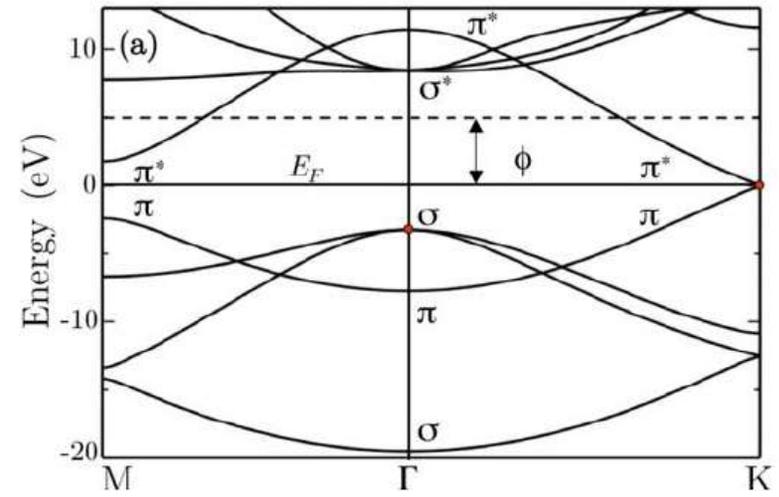
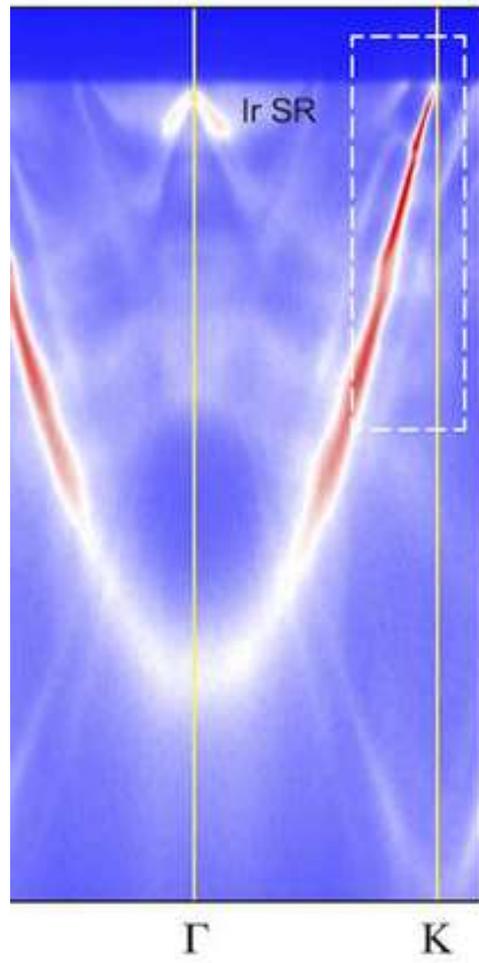


Band dispersion at room temperature – electron delocalization



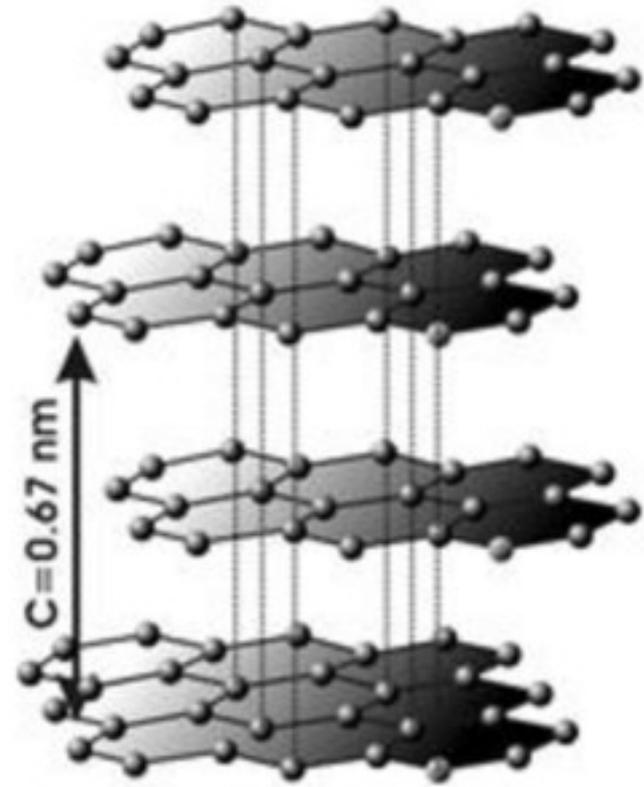


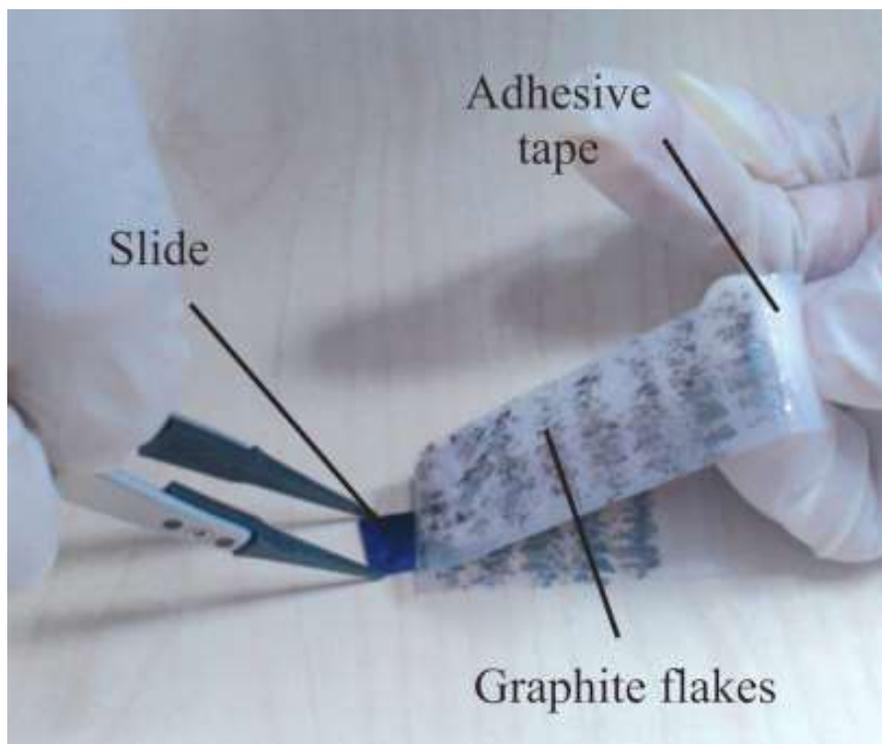




•Journal of Physics Condensed Matter 2015 27(30)

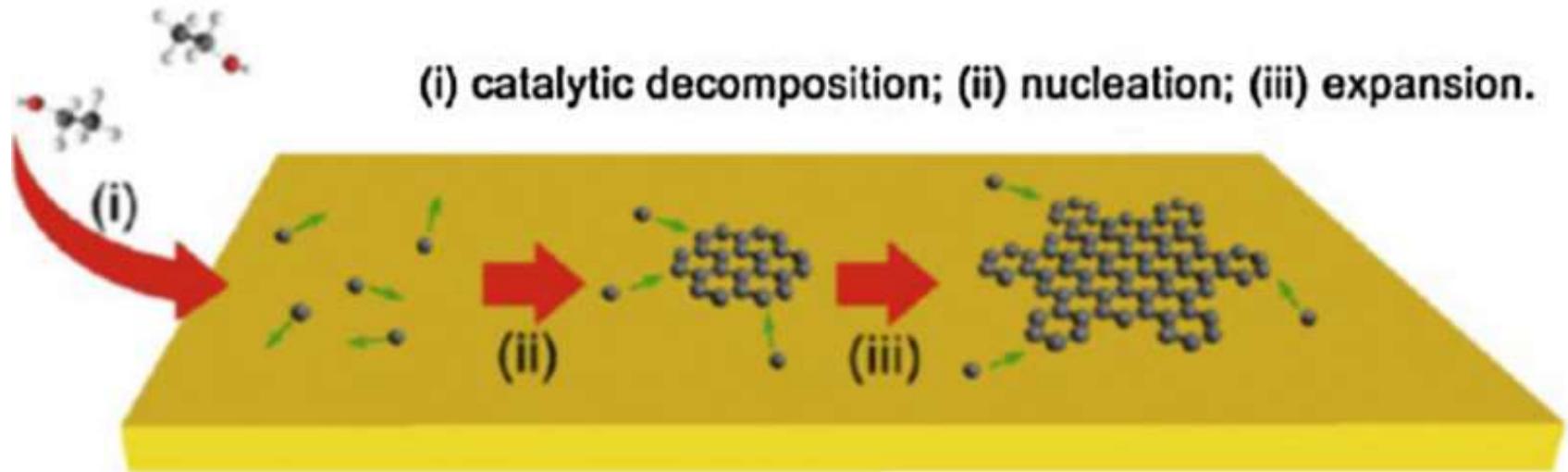
Sintesi di grafene



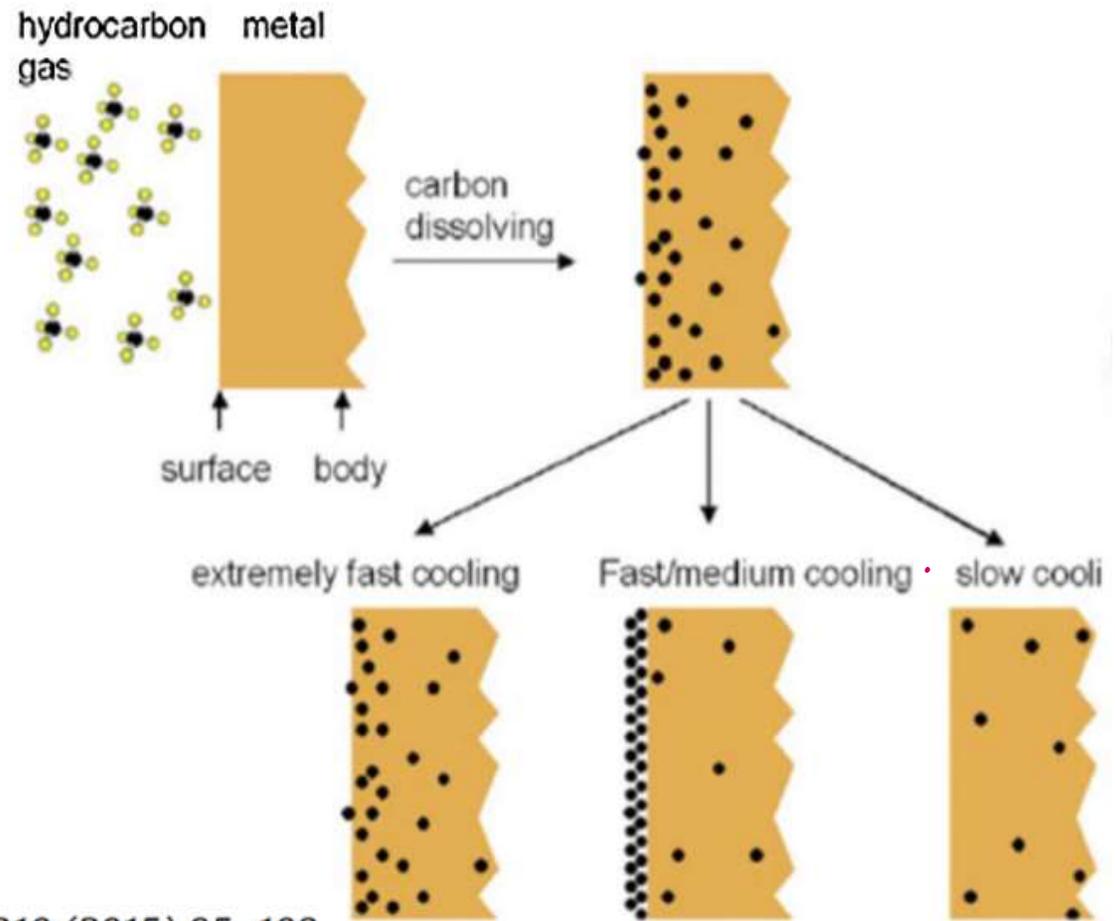


Chemical Vapor Deposition

Cu (111) , 1000°C



Ni(111)

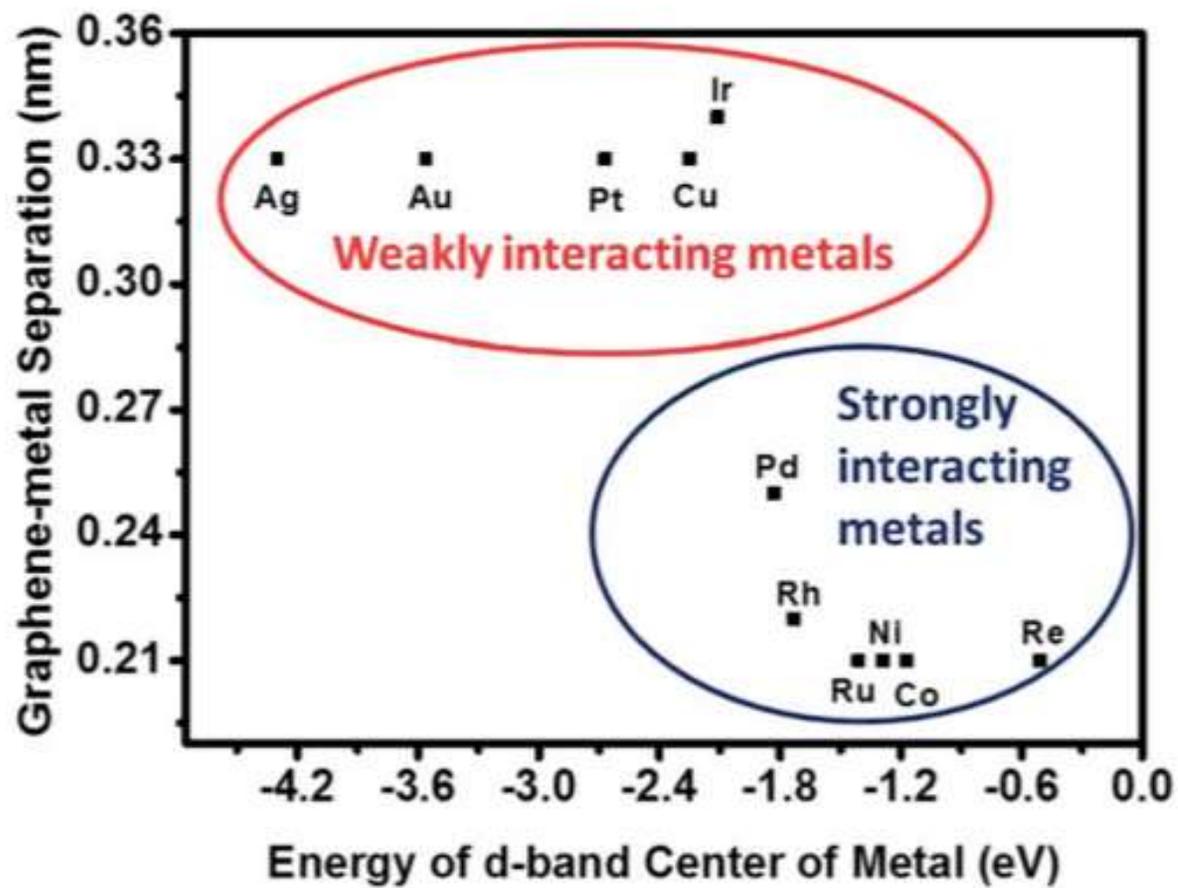


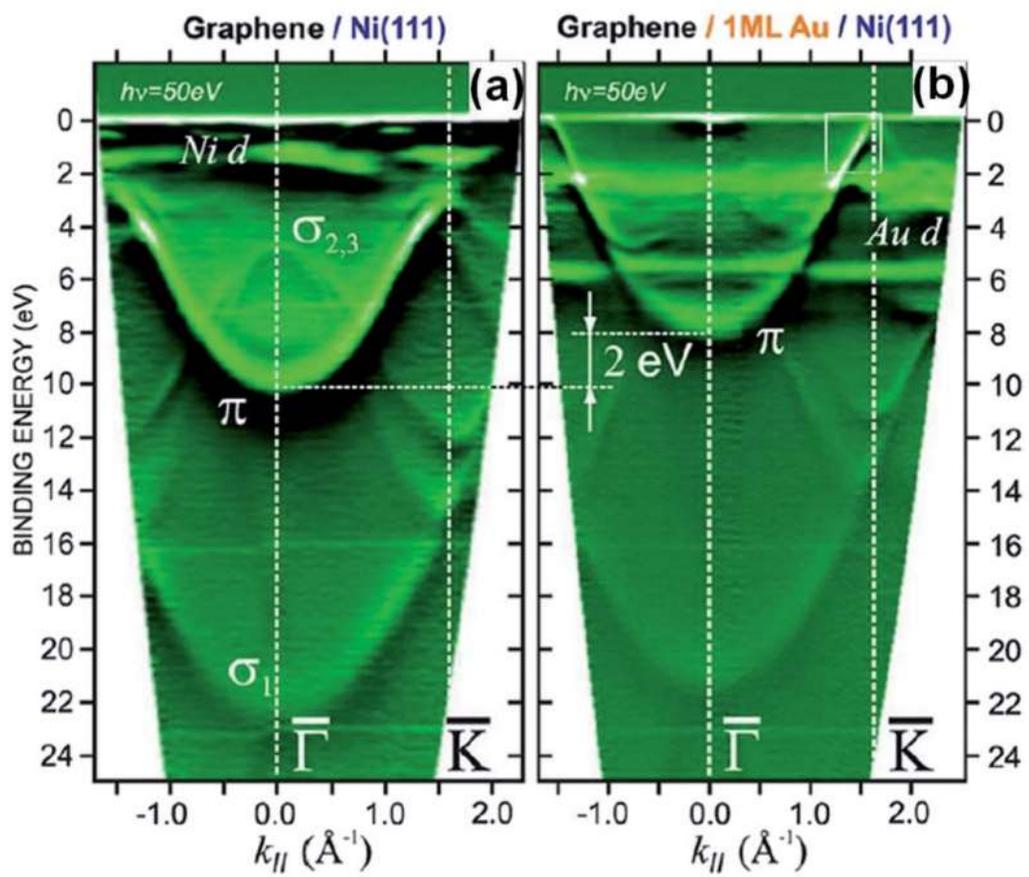
X. Chen et al. / *Synthetic Metals* 210 (2015) 95–108



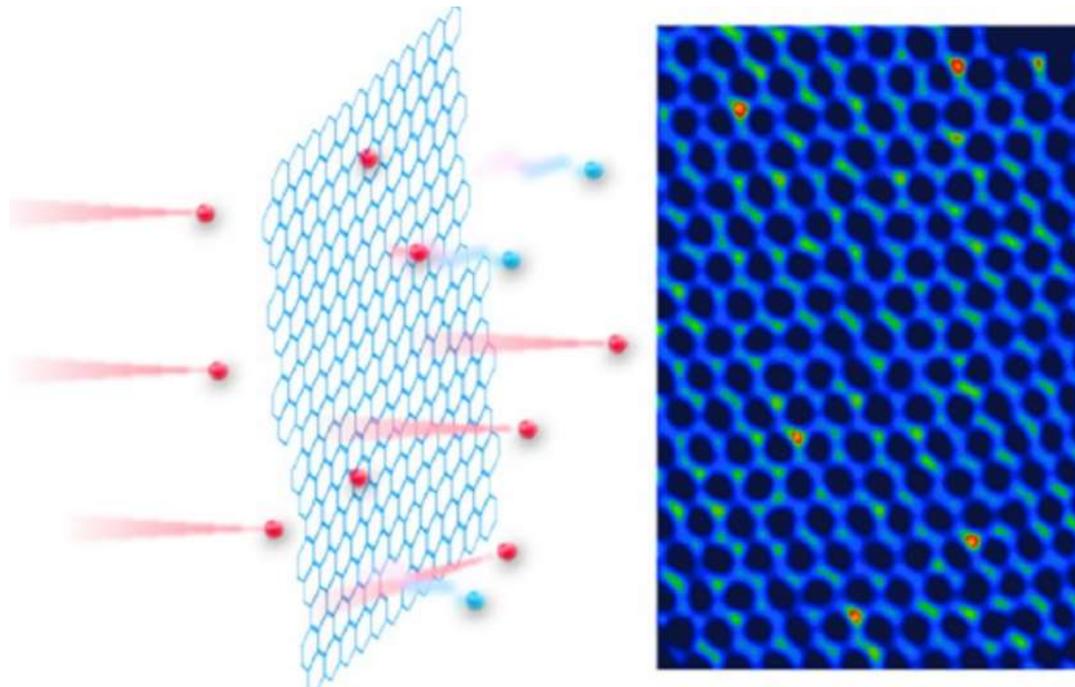
Table 1 Carbon solubilities (atom%) in different transition metals at 1000 °C according to ref. 17

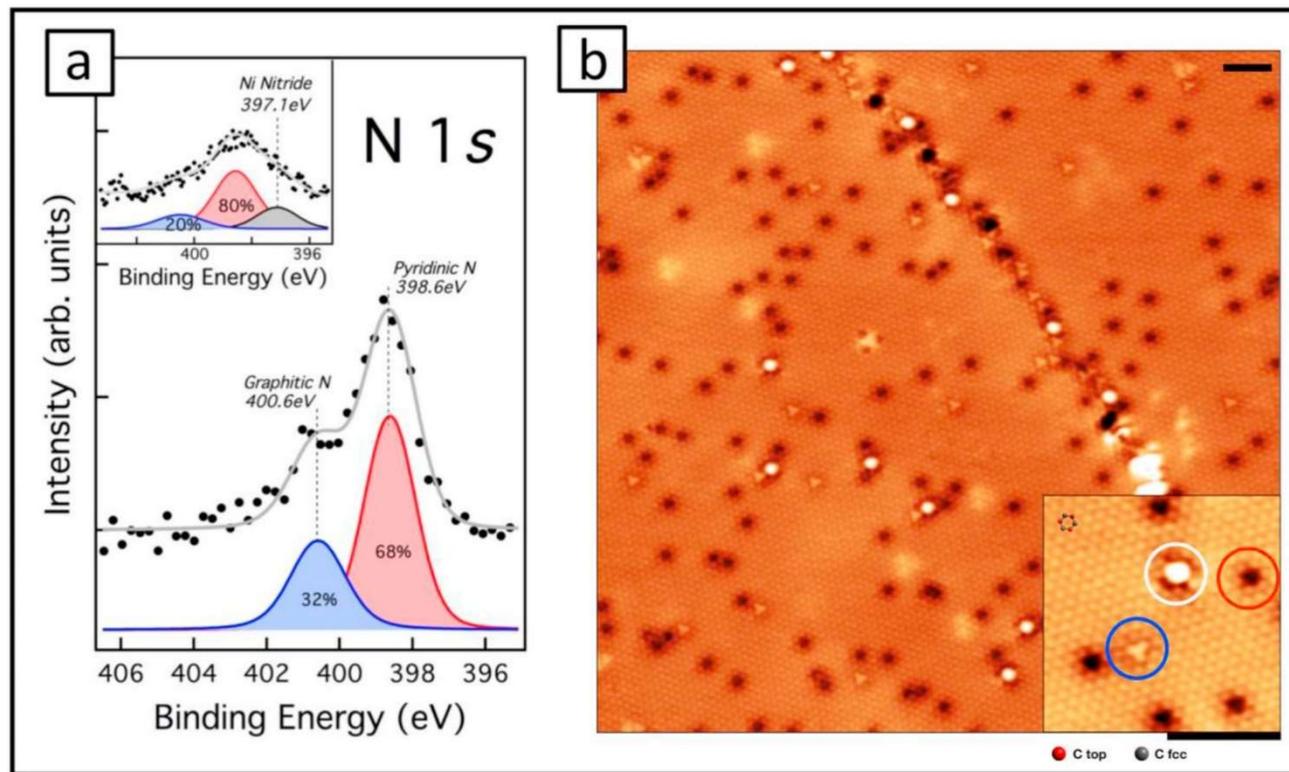
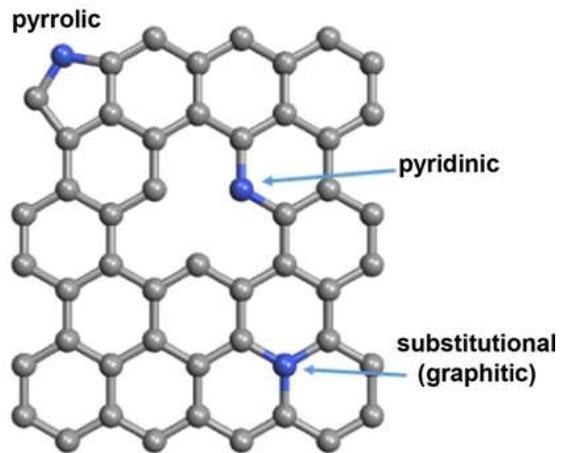
Metal	Carbon solubility (atom%) at 1000 °C
Co	3.41
Ni	<u>2.03</u>
Cu	0.04
Ru	1.56
Rh	0.89
Pd	<u>5.98</u>
Ag	0.01
Re	4.39
Ir	1.35
Pt	1.76
Au	<u>0.01</u>



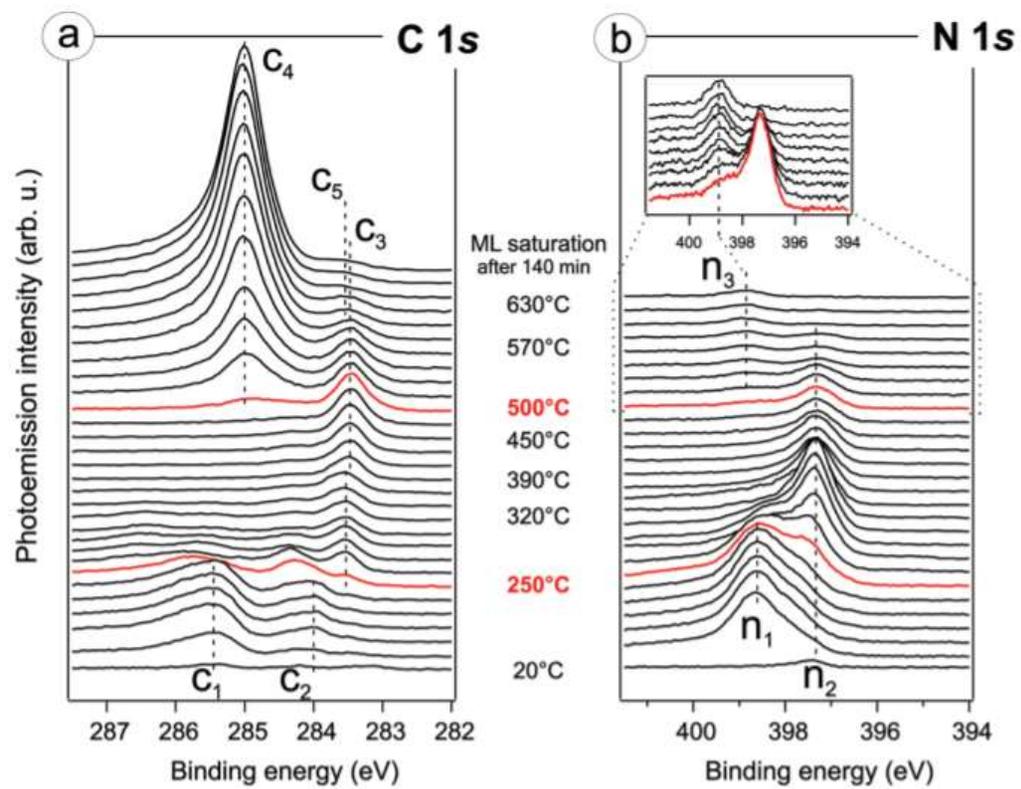
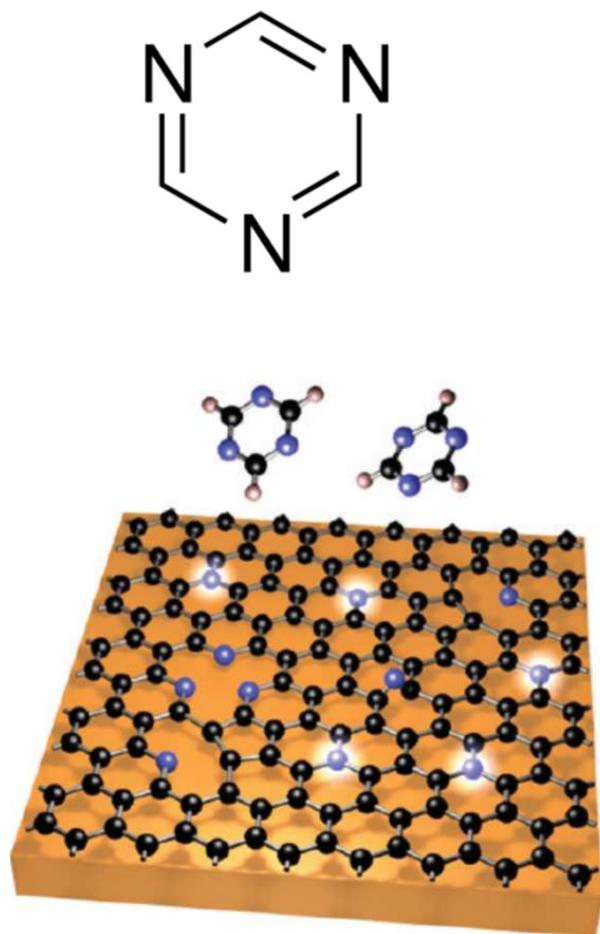


Doping di grafene Sostituire alcuni atomi di carbonio con atomi ad esempio di N o B permette di modificare la struttura elettronica del film.

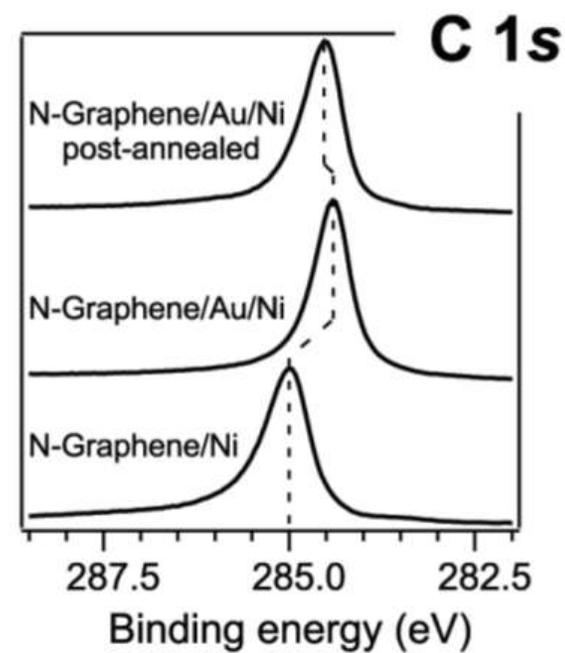
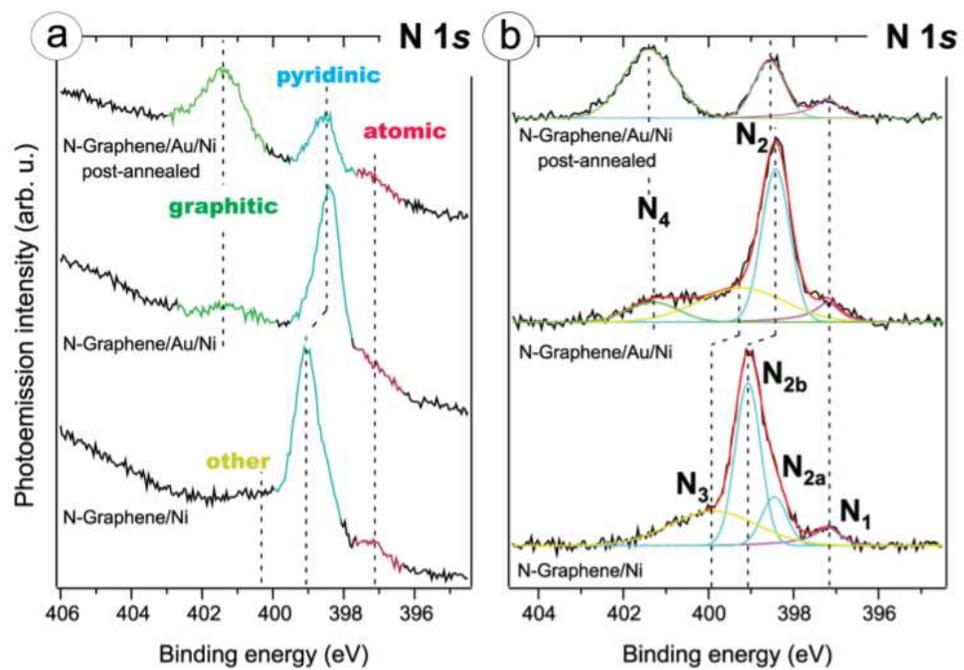




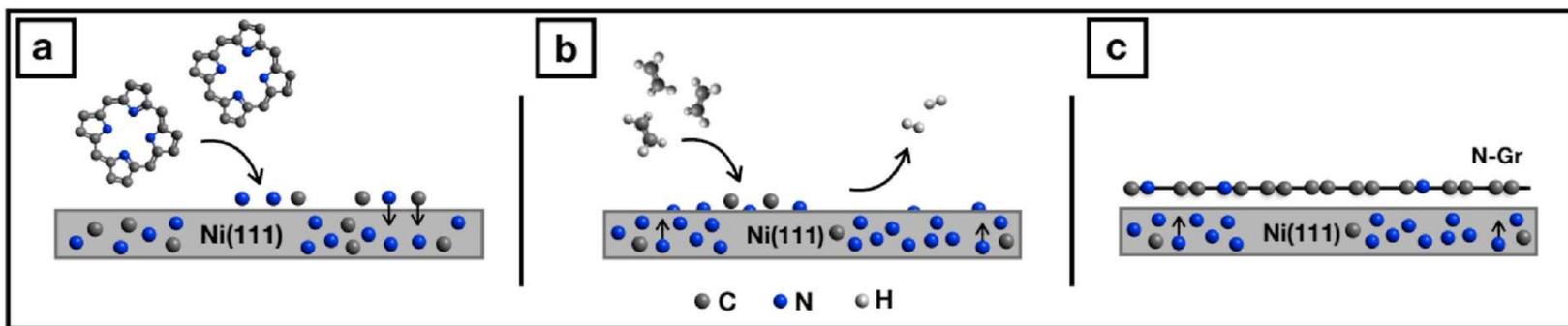
Carbon 171 (2021) 704–710



Nano Lett. 2011, 11, 5401–5407



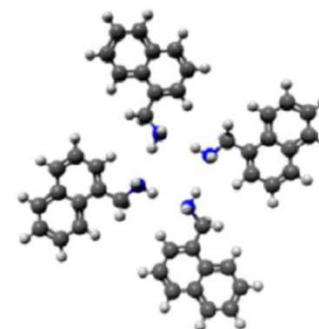
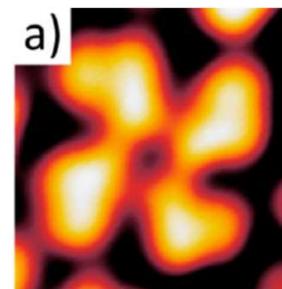
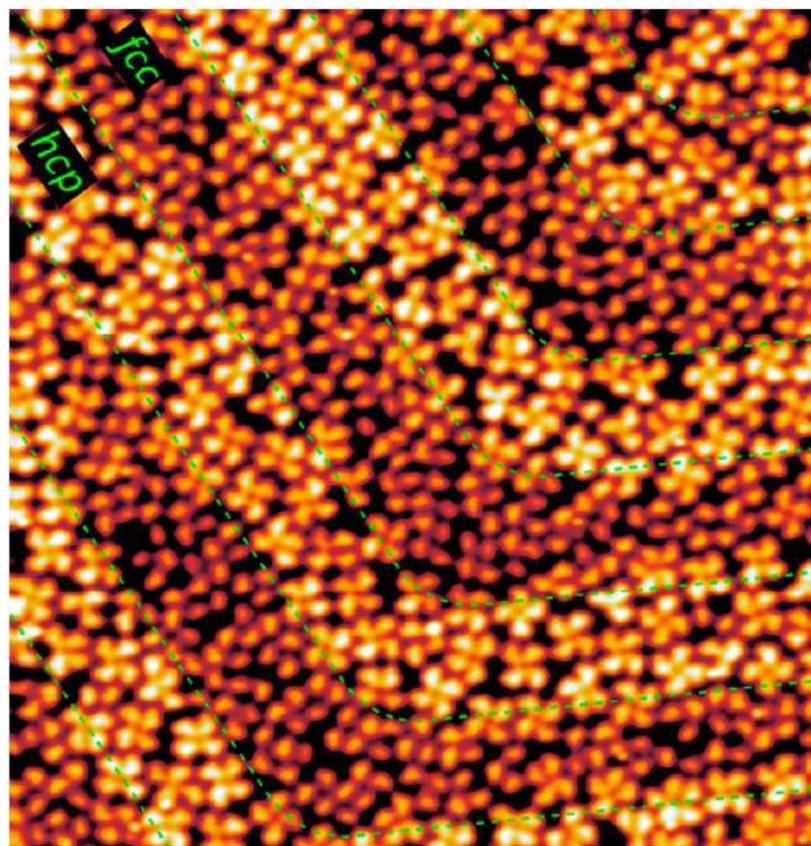
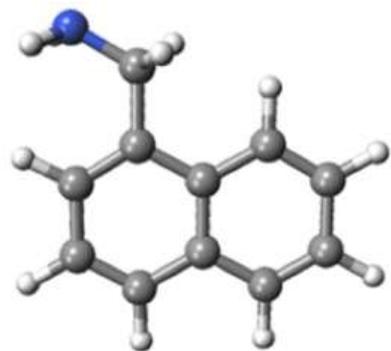
Nano Lett. 2011, 11, 5401–5407



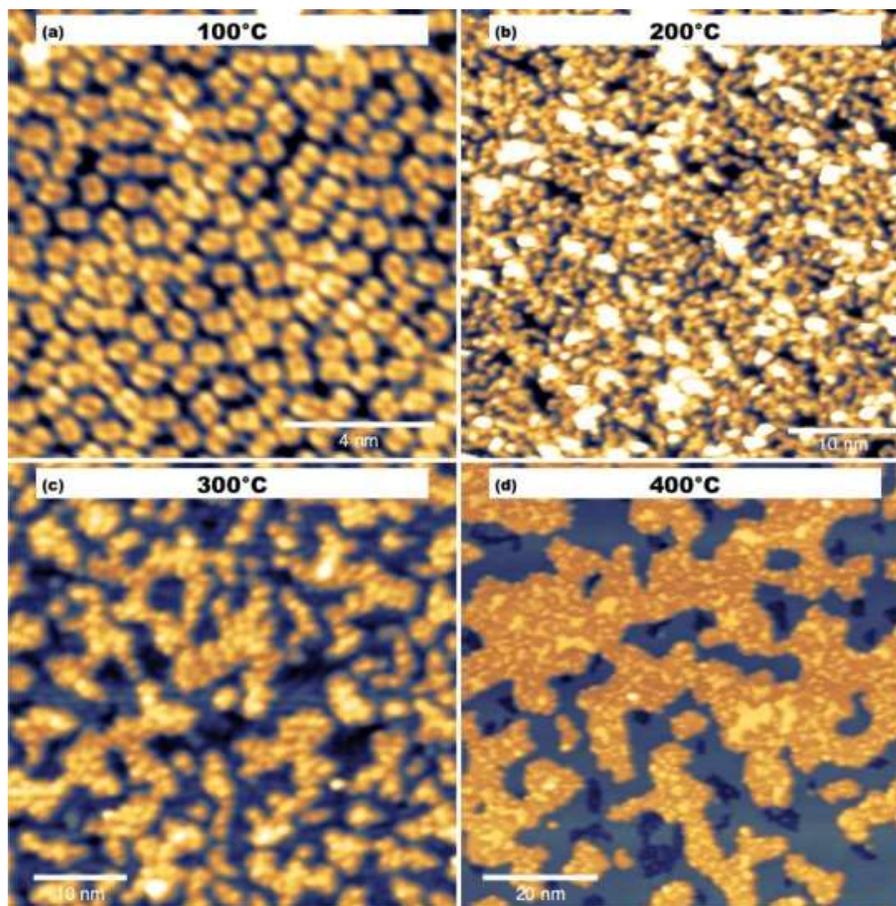
Carbon 171 (2021) 704–710

on Au(111)

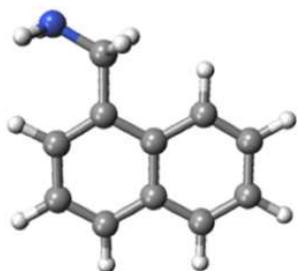
Naphthylmethyl amine (NMA)



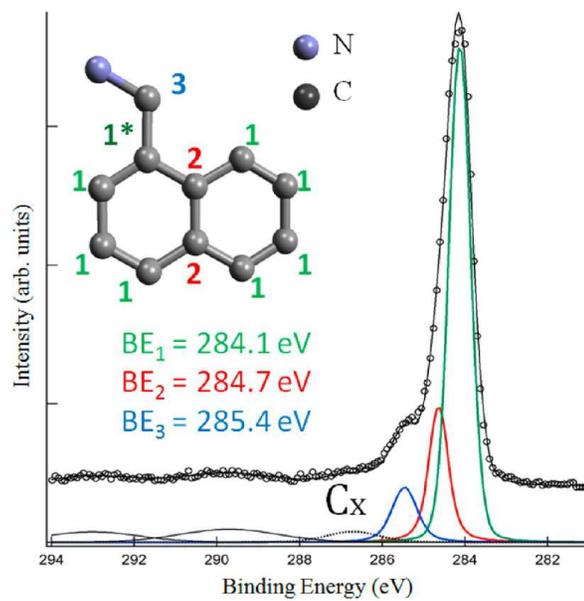
J. Phys. Chem. C 2016, 120, 11, 6104–6115

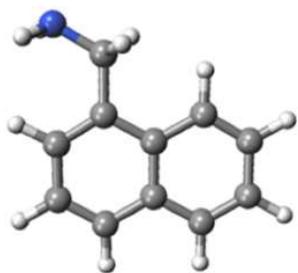


Costantini et al., FlatChem 24 (2020) 100205

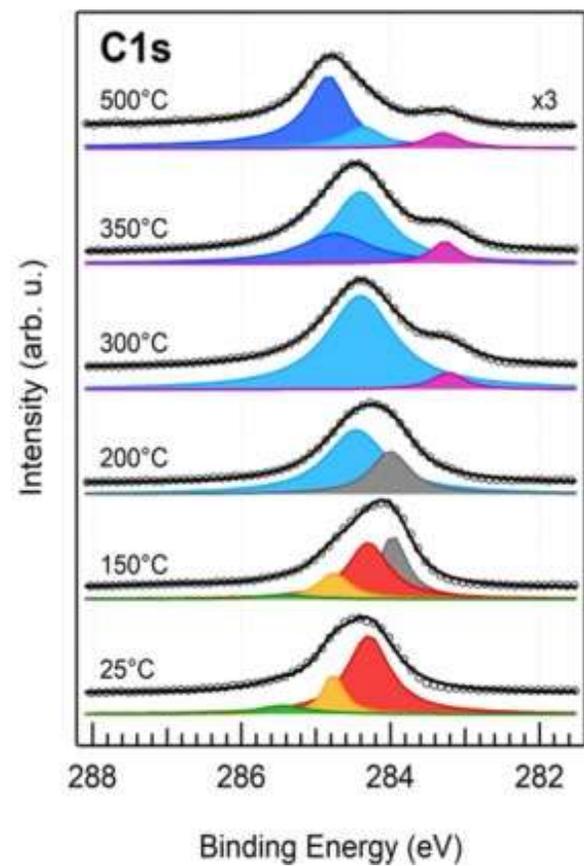
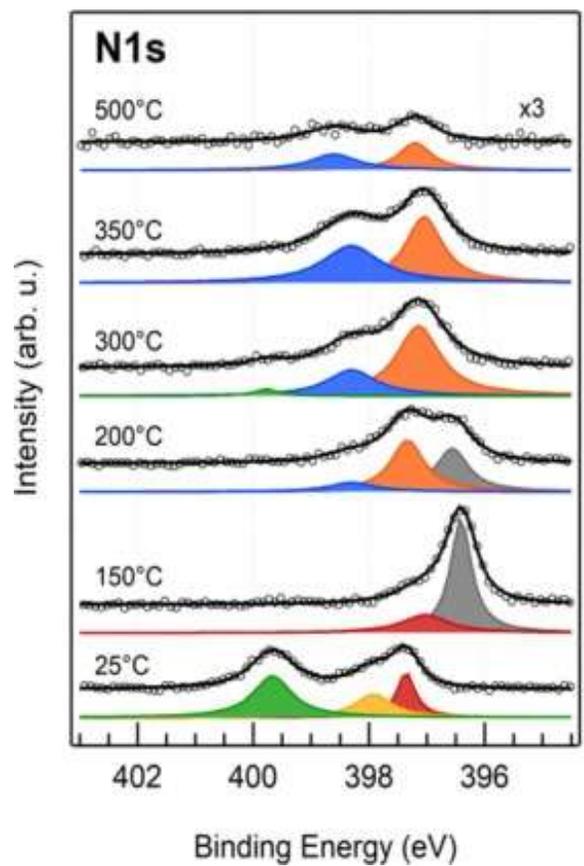


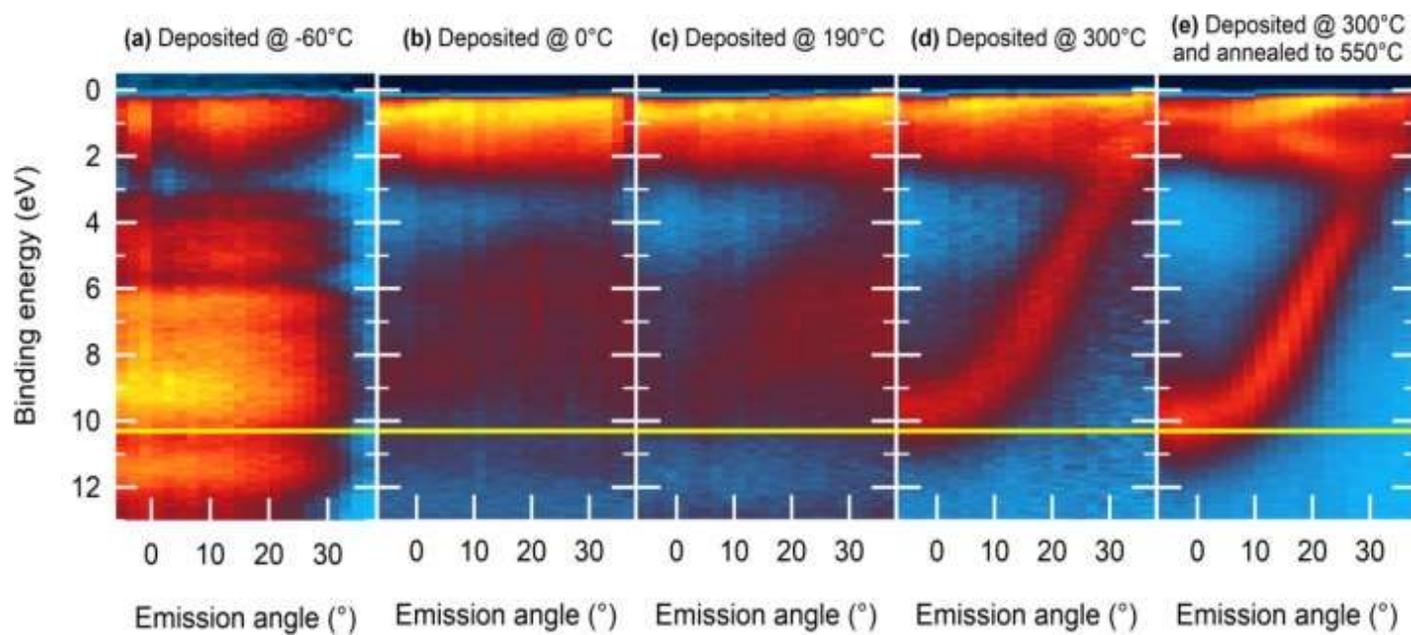
on Au(111)





on Ni(111)

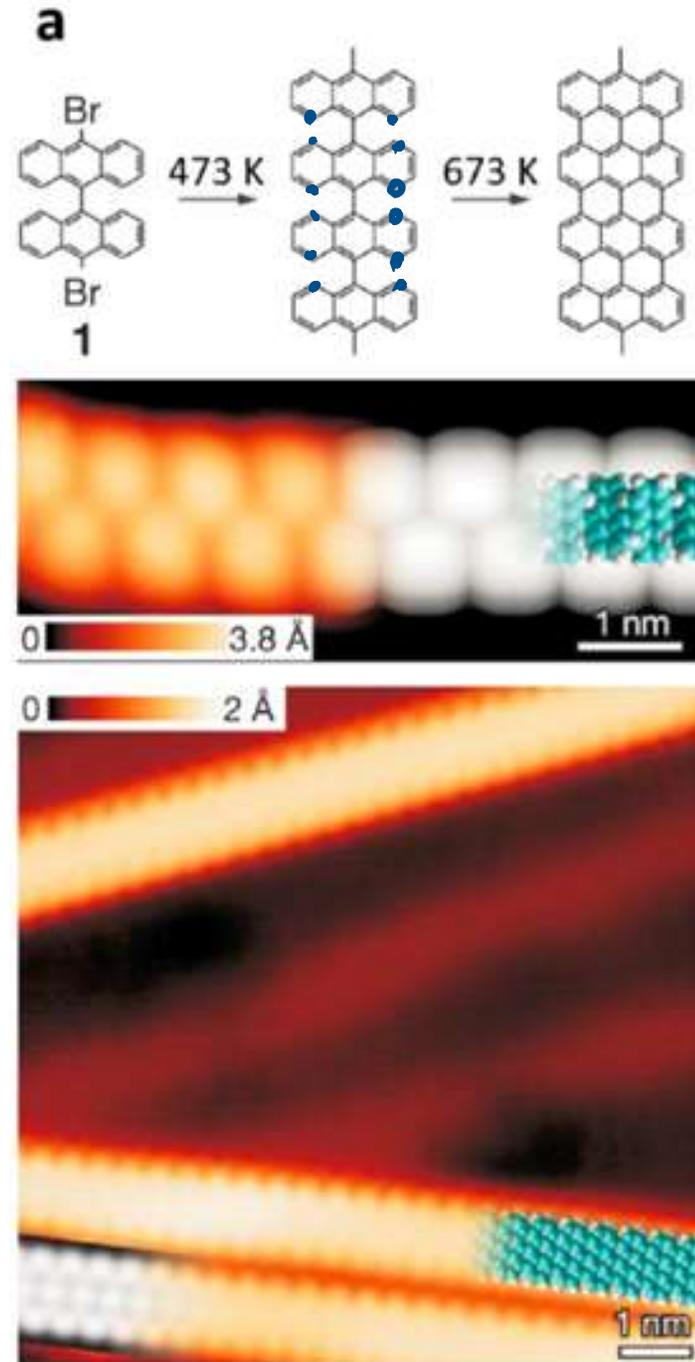




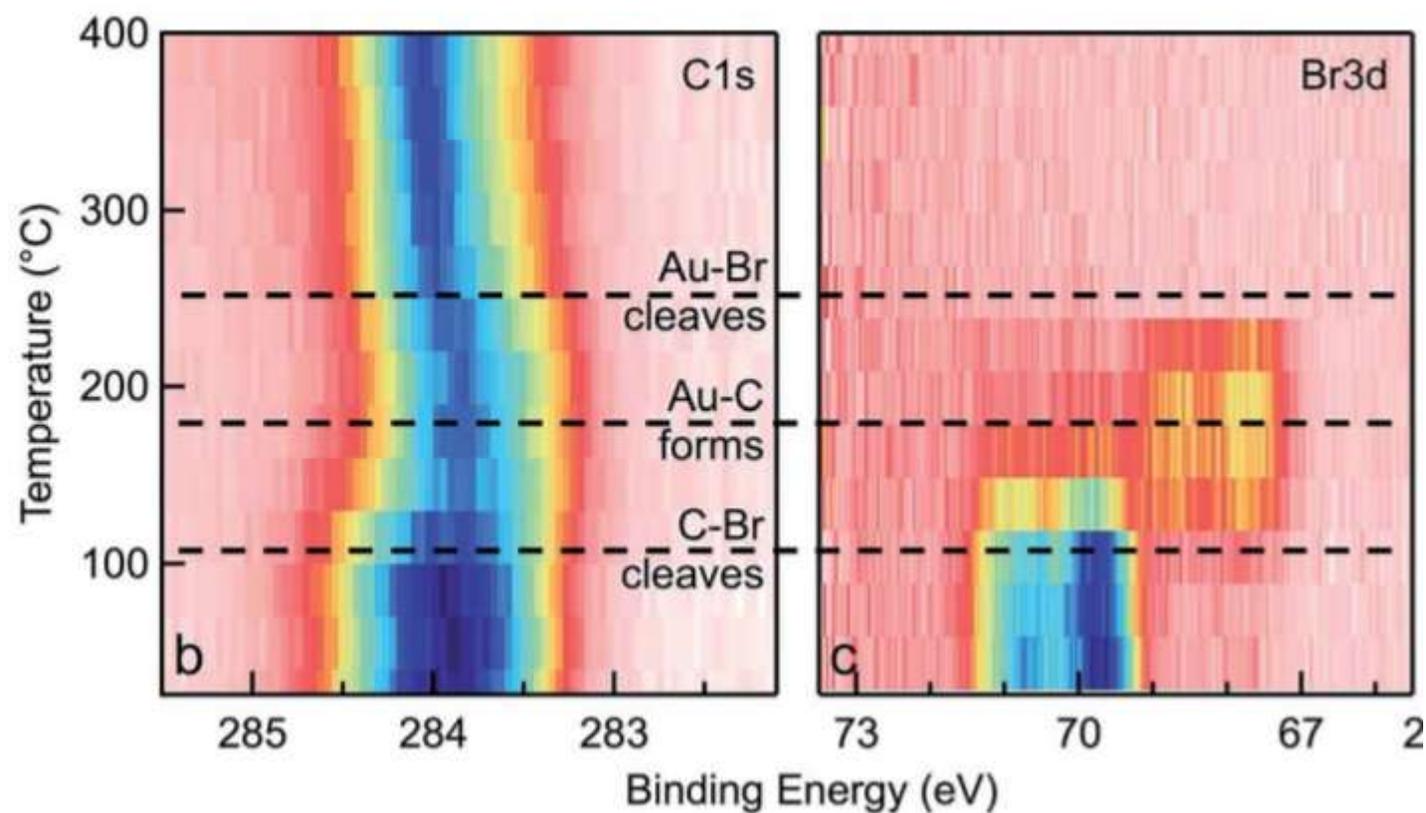
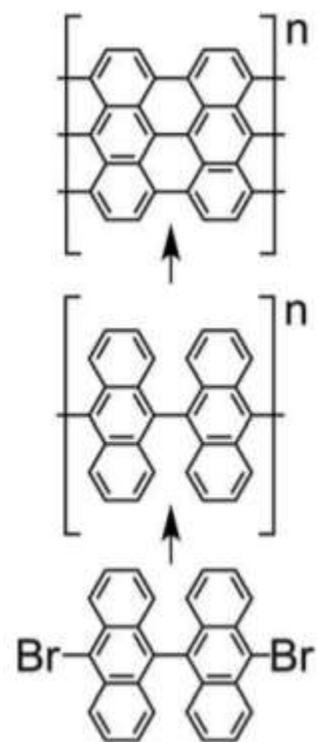
Costantini et al., *FlatChem* 24 (2020) 100205

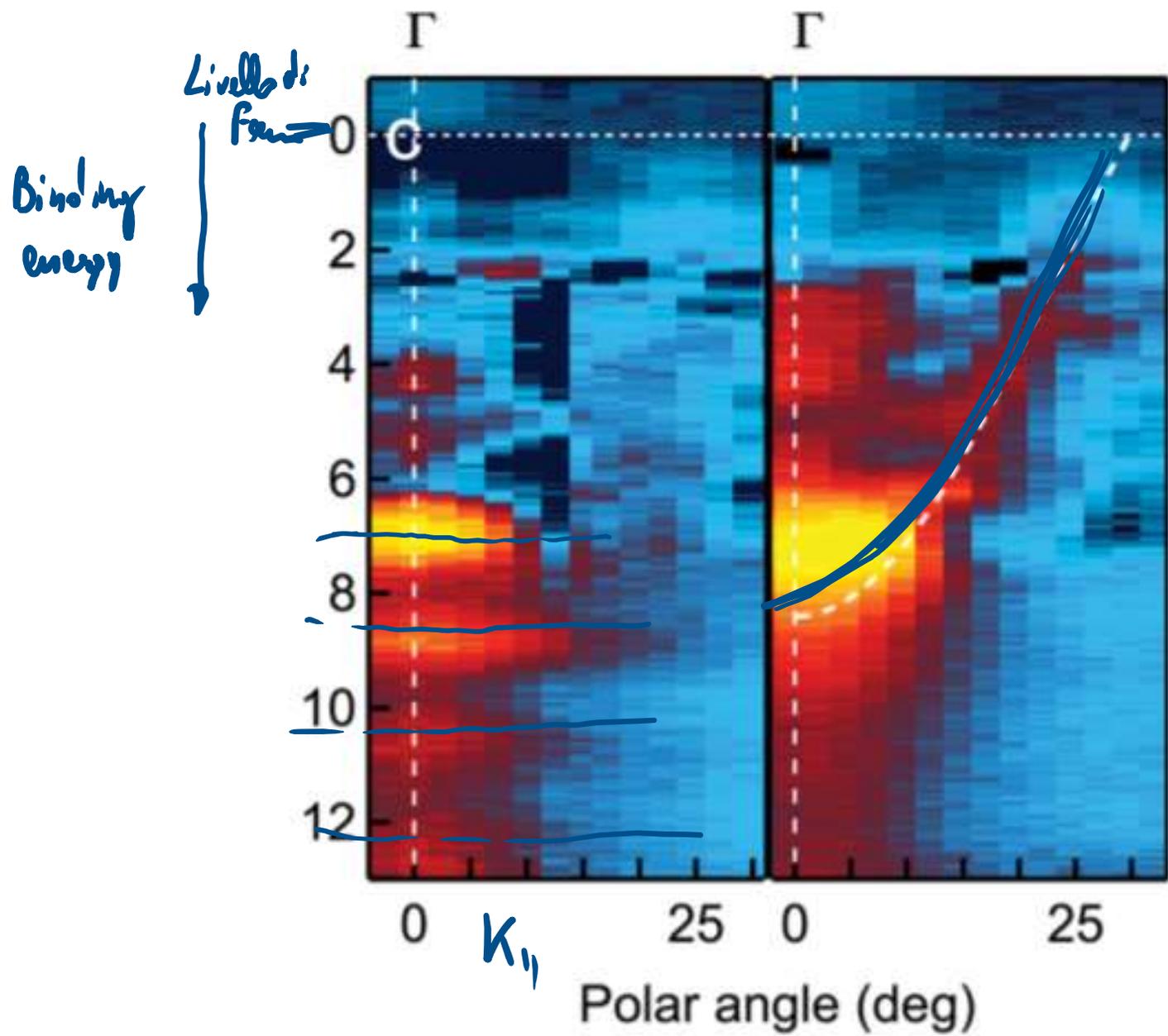
Sintesi in sequenza:

1. Ullmann
2. Cyclodehydrogenation

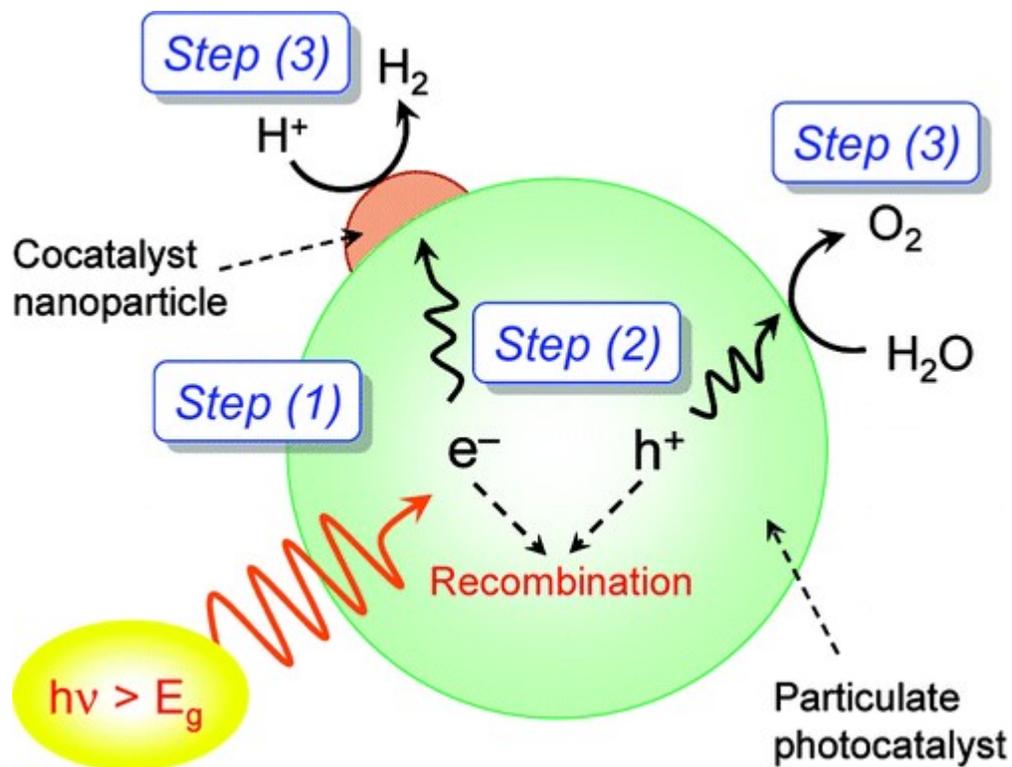


Nature 2010, 466, 470–473





Fotocatalisi per il processo di water-splitting

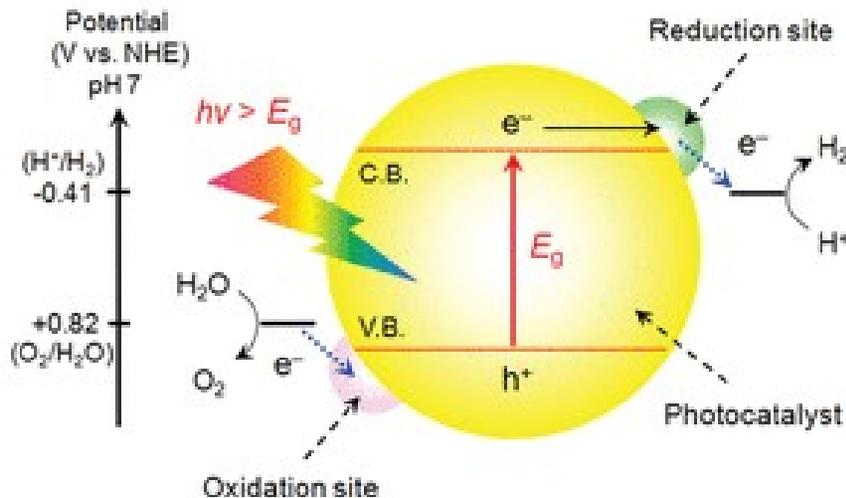


Step 1: Il fotone viene assorbito dal catalizzatore e si forma un eccitone (buca-elettrone)

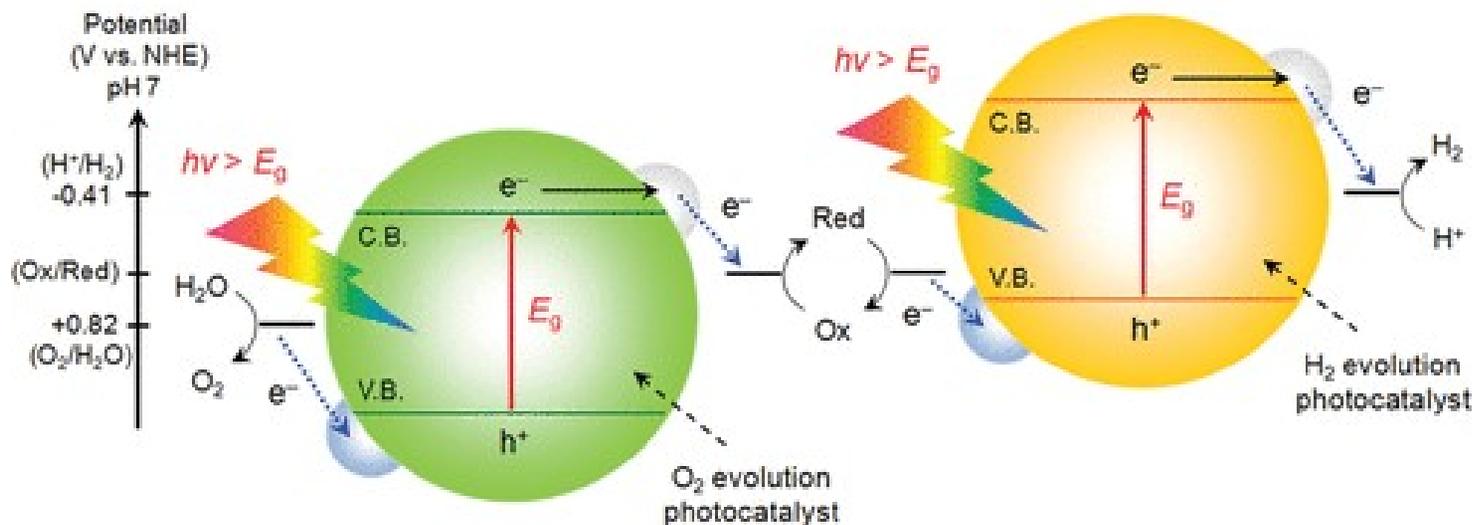
Step 2: buca ed elettrone si separano e migrano verso la superficie

Step 3: avvengono le reazioni di ossidazione e di riduzione di H_2O e dei prodotti della sua decomposizione, con rilascio di H_2 e O_2

One-step photoexcitation system
(e.g., $\text{RuO}_2/\text{GaN}:\text{ZnO}$)



Two-step photoexcitation system
(e.g., $\text{Pt}/\text{ZrO}_2/\text{TaON} + \text{Pt}/\text{WO}_3$)



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^+

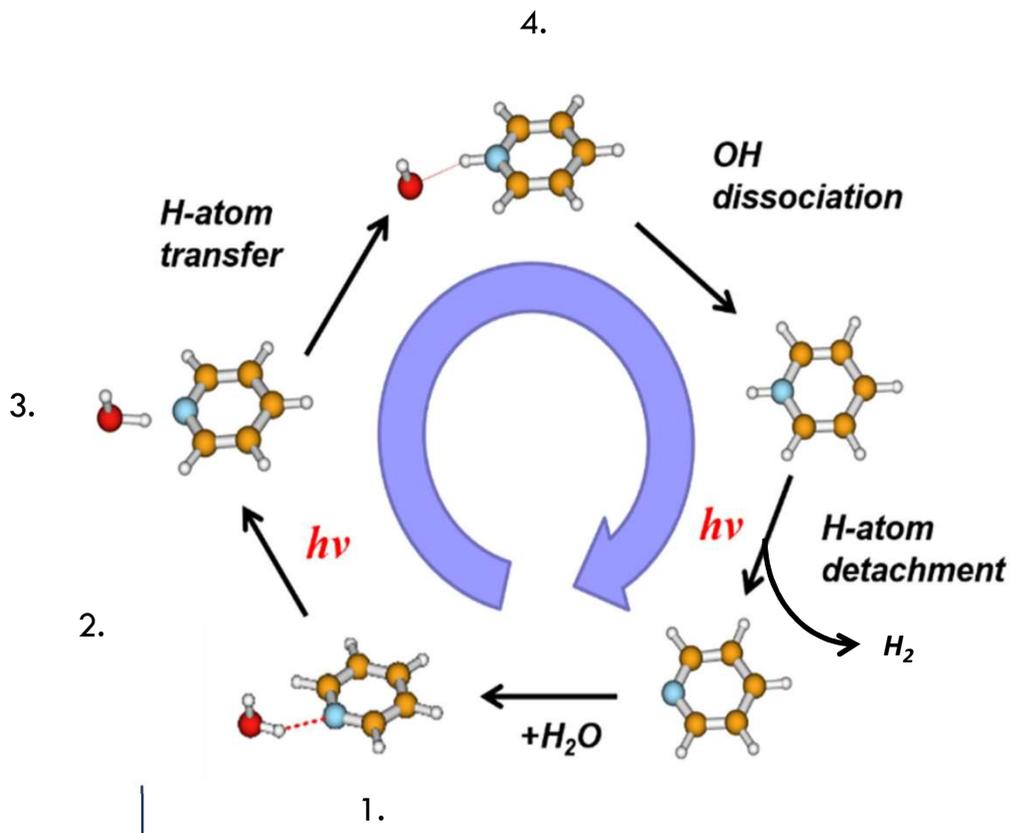
In genere dei co-catalizzatori in superficie facilitano le reazioni HER e OER

HER: hydrogen evolution reaction

OER: oxygen evolution reaction

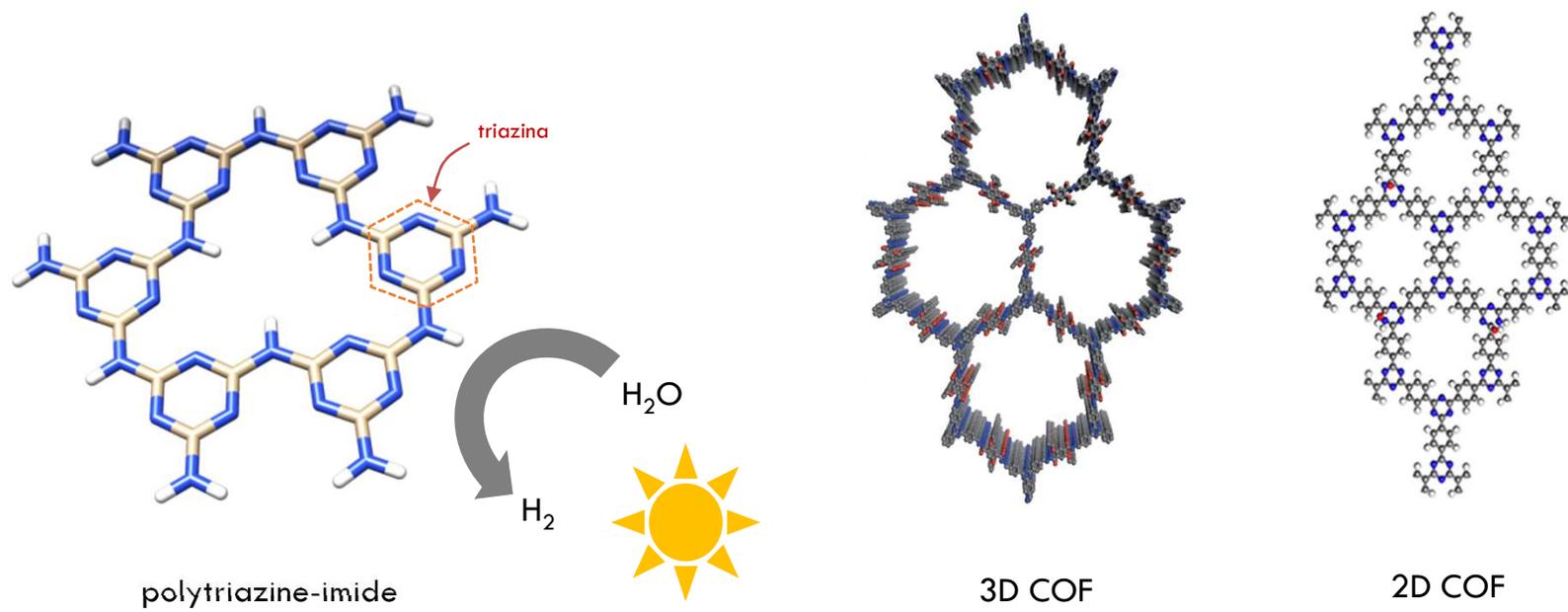
Molecole organiche possono agire da catalizzatori in un processo fotocatalitico di water splitting

Meccanismo "Proton-Coupled Electron Transfer" (W. Domcke)

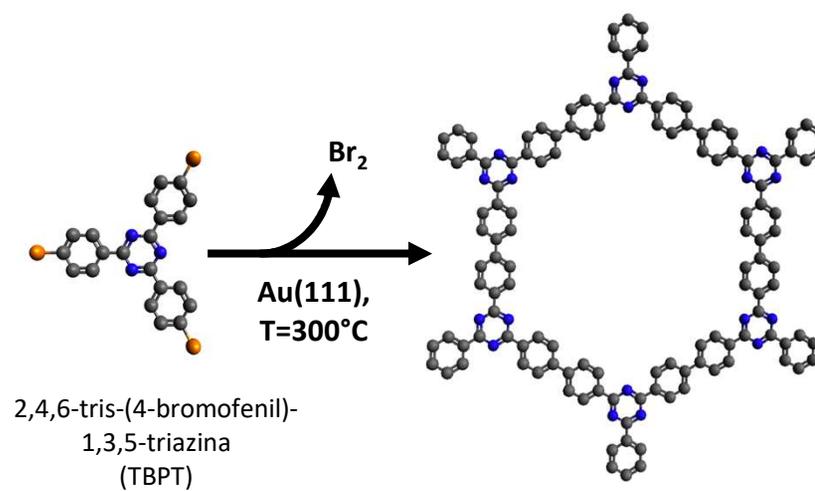
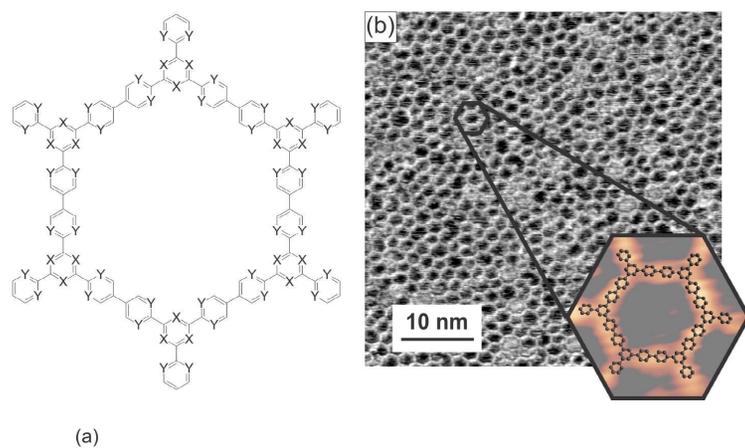


1. Formazione di un legame idrogeno tra la molecola di acqua e l'eterociclo
2. Fotoeccitazione del complesso eterociclo- H_2O
3. Trasferimento di elettrone
4. Trasferimento di protone

Carbon Nitrides e Covalent Organic Frameworks (COFs)

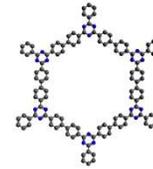


Reazione di polimerizzazione di Ullmann

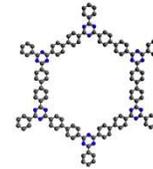


K. Kern *et al.*, *Angew. Chem. Int. Ed.* 2020, 59, 8411–8415

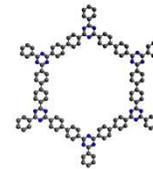
Sintesi del COF



Interazione tra COF e ghiaccio



Interazione fotoindotta tra COF e ghiaccio

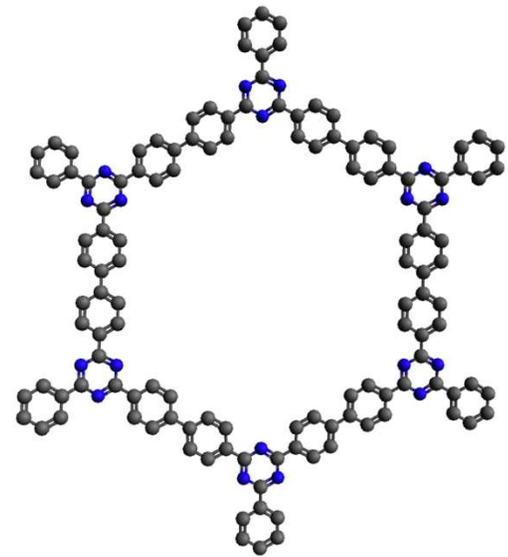


Interazione tra COF e acqua

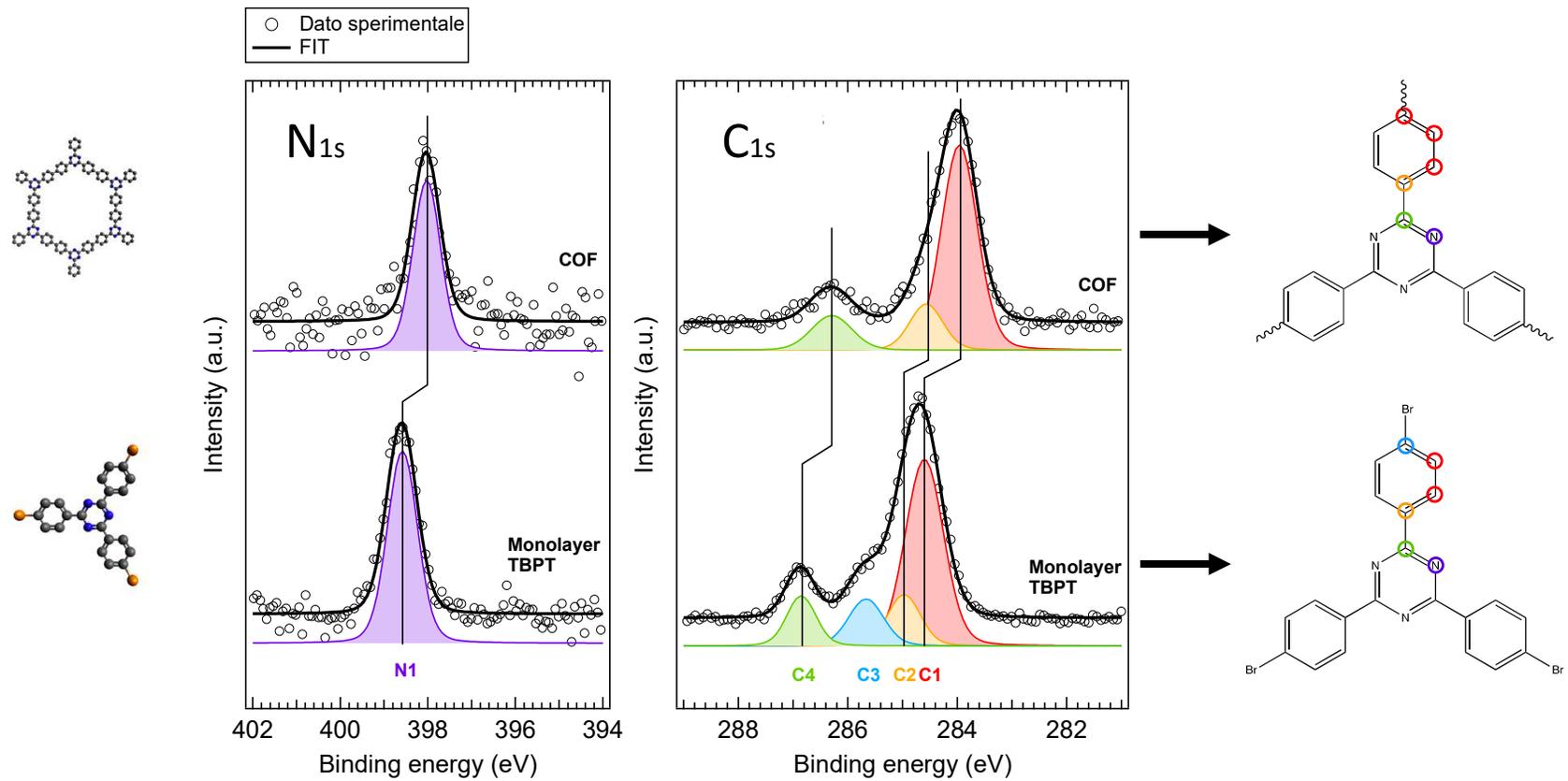


|

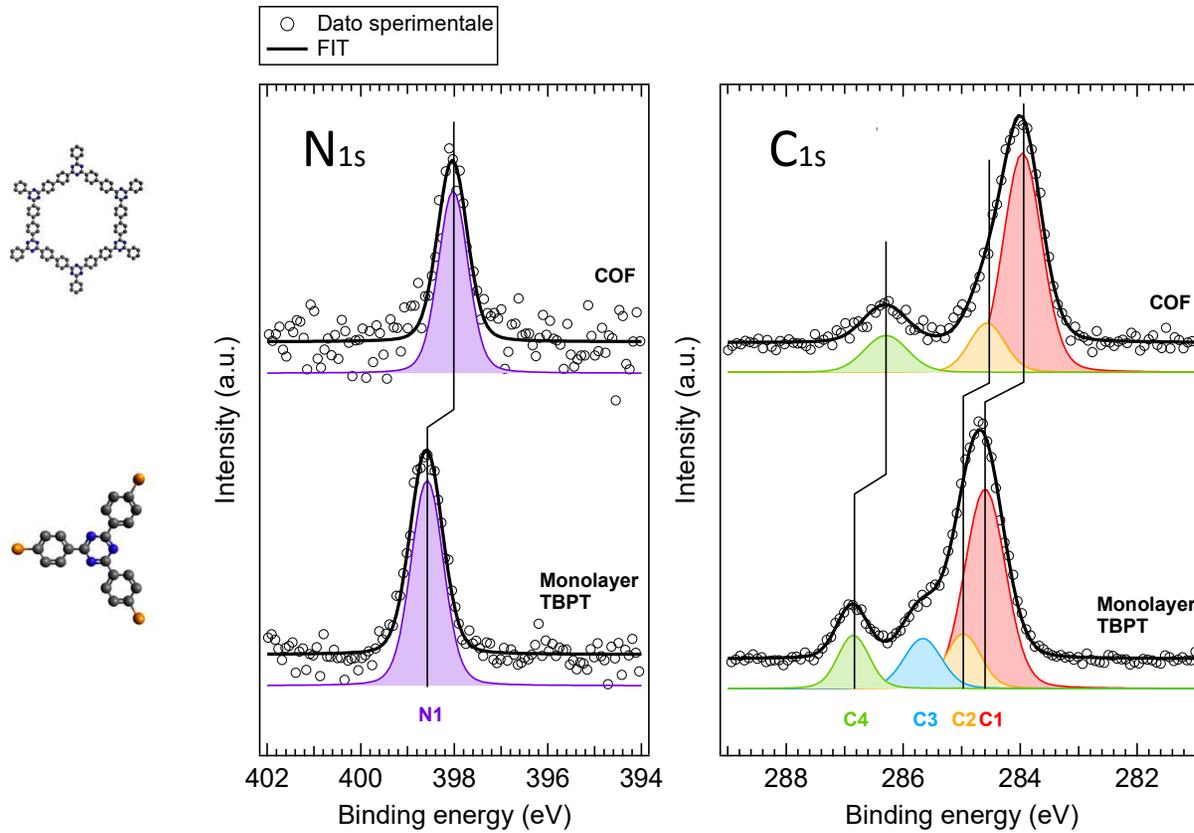
Sintesi del COF



Stechiometria del sistema



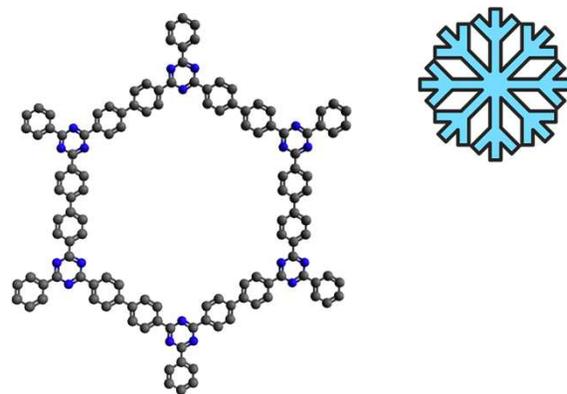
Stechiometria del sistema

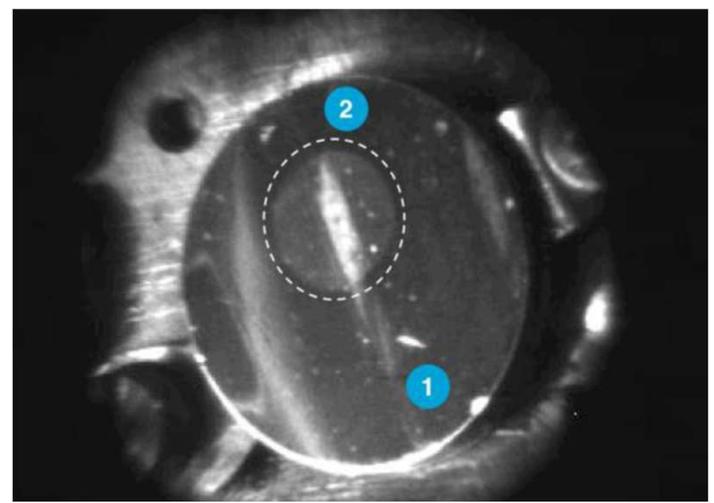
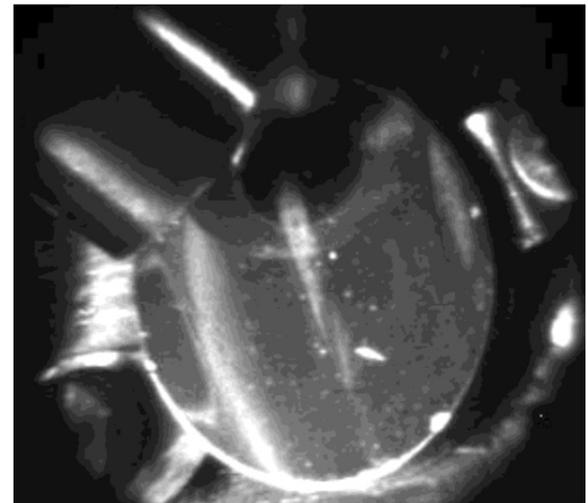
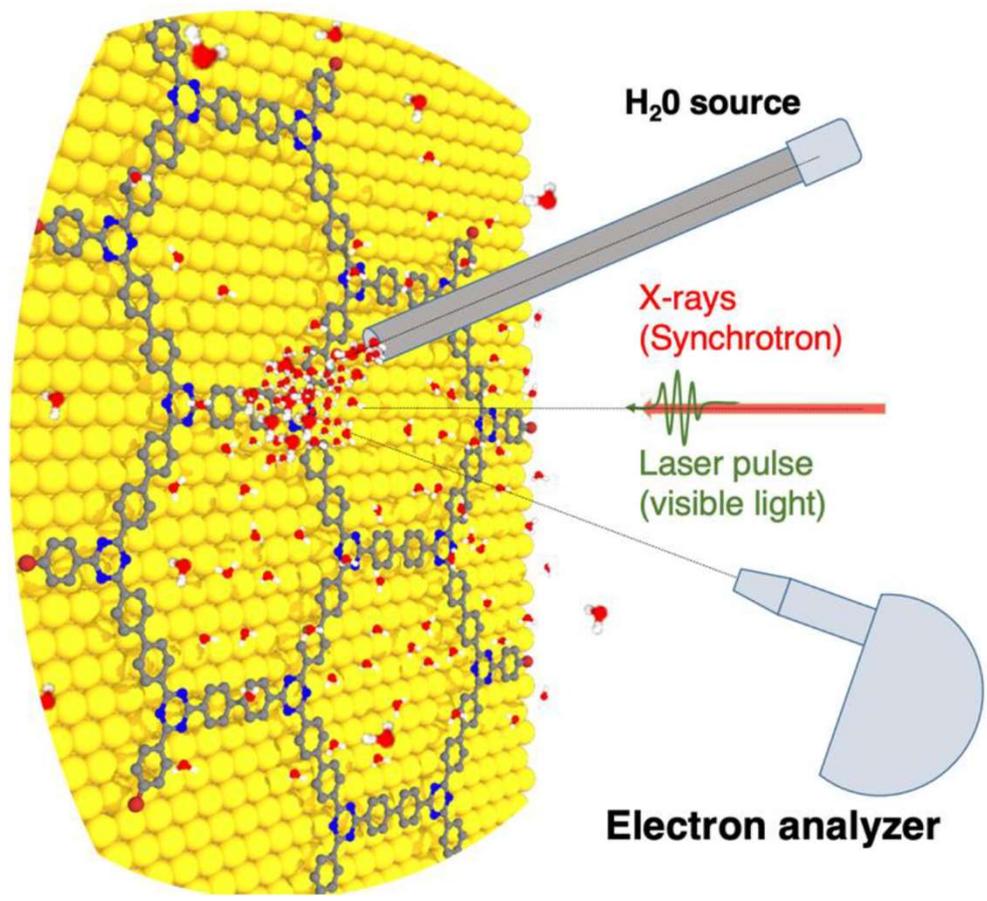


Shift a basse BE:

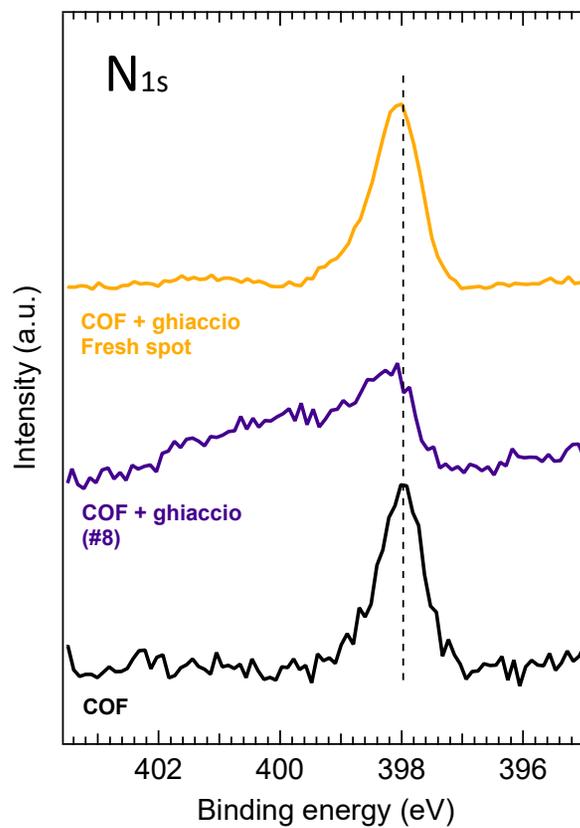
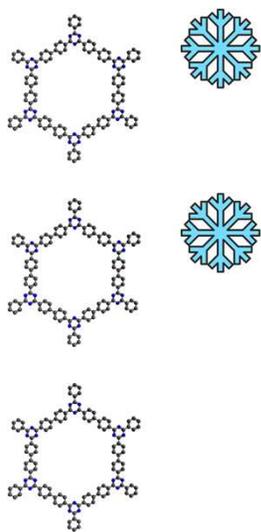
- Effetto di screening
- Delocalizzazione elettronica

Interazione tra COF e ghiaccio





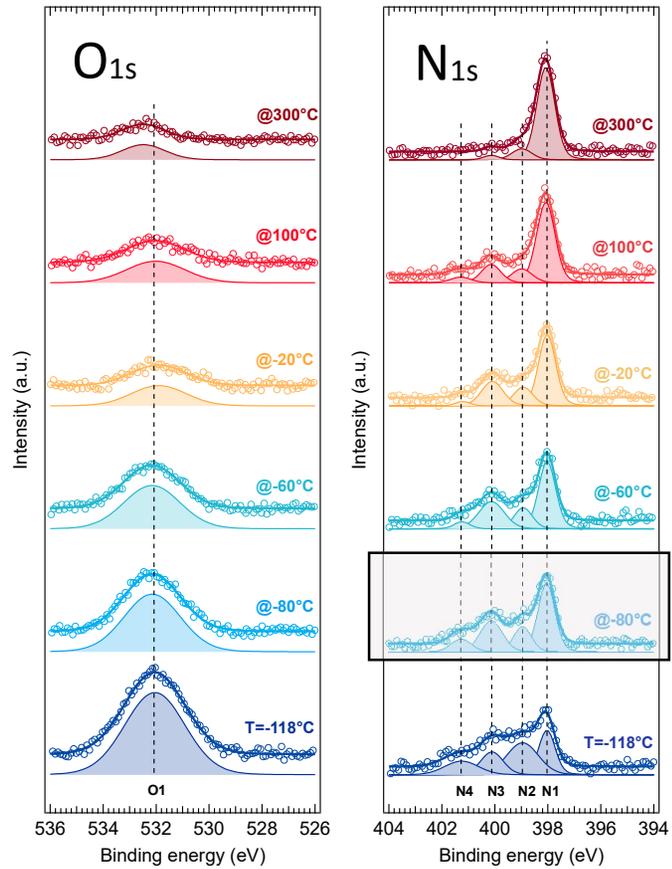
Interazione COF-ghiaccio



Bassa conversione senza irraggiamento X

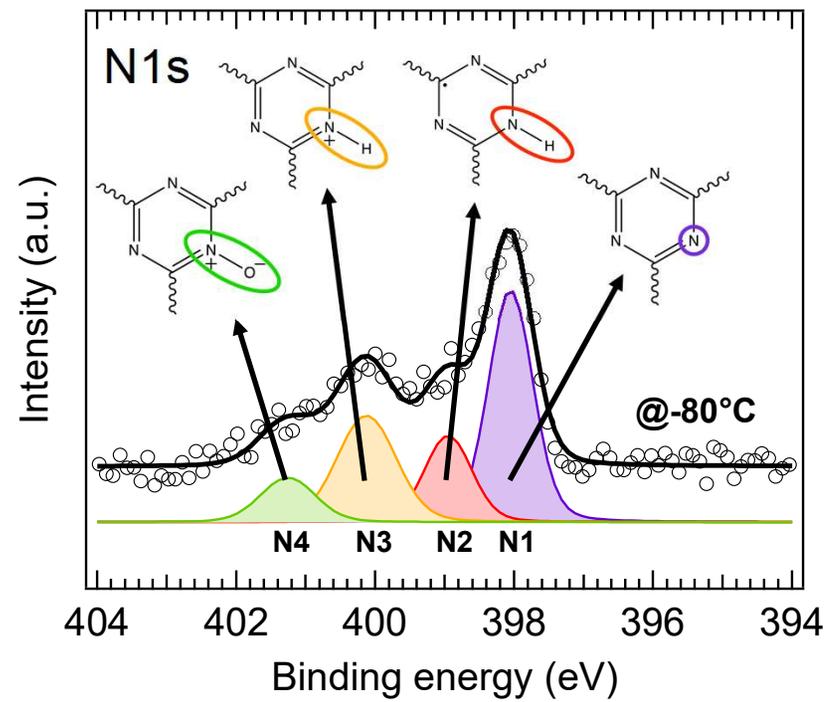
Effetto indotto dalla radiazione

Annealing del sistema «COF + ghiaccio»



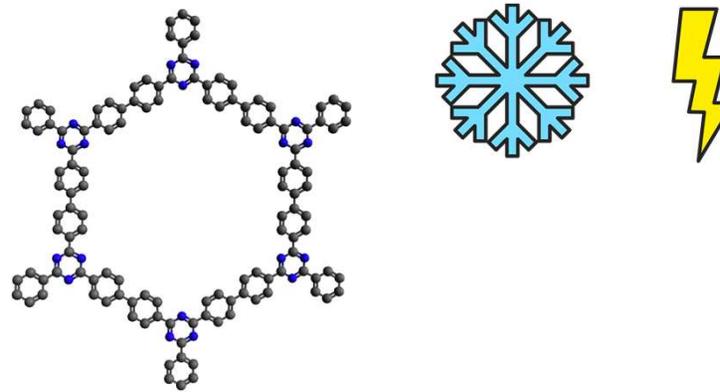
- Azoto multicomponente (almeno quattro)
- Ossigeno singola componente (FWHM~2.5 eV)
- Ossigeno presente a $T > -110^{\circ}\text{C}$
- ~Ripristino del COF

Identificazione di nuove specie chimiche

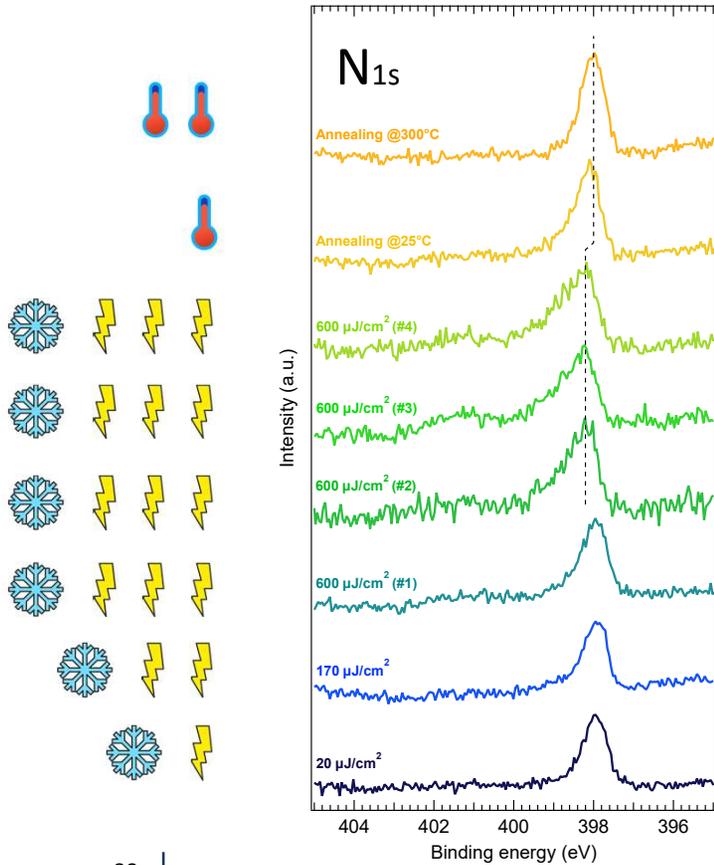


- N1: azoto triazinico
- N2: azoto idrogenato
- N3: azoto protonato
- N4: azoto «piridina N-ossido»

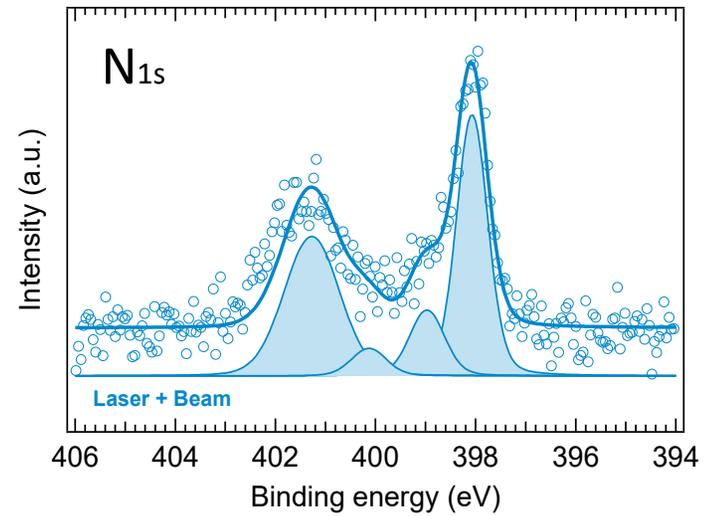
Interazione fotoindotta tra COF e ghiaccio



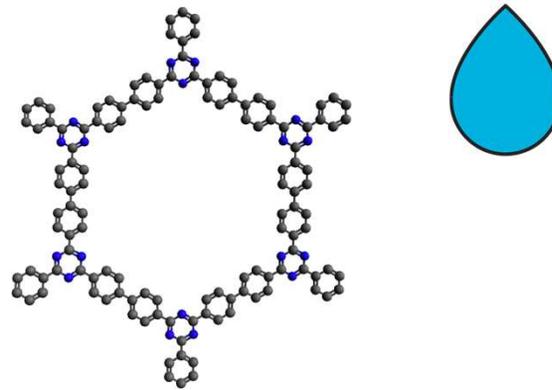
Conversione COF fotoindotta da laser (343 nm)



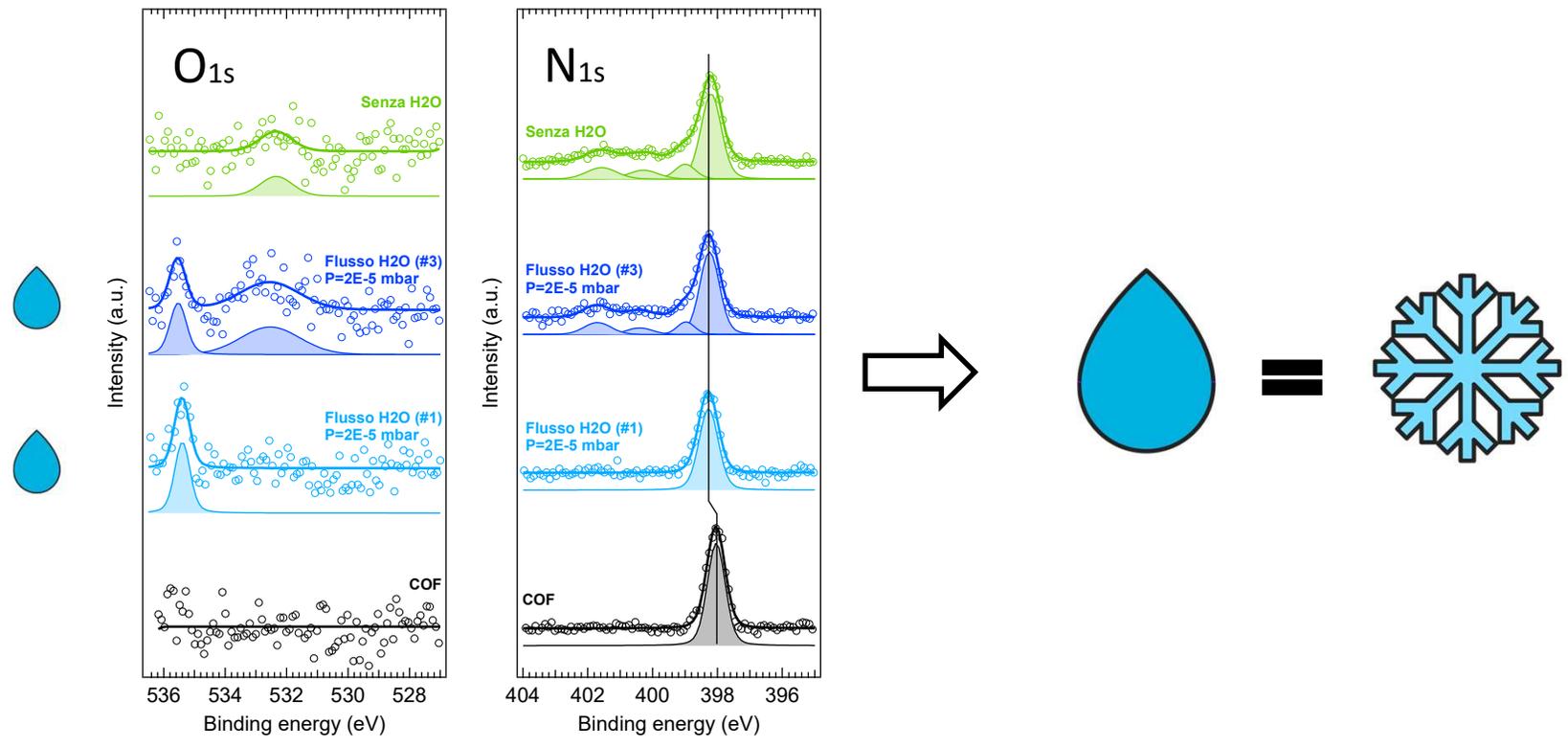
Qual è la conversione massima che si può raggiungere?



Interazione tra COF e acqua



Dosaggio di acqua sul COF



Monolayer di TBPT con ghiaccio

