Institut Matériaux Microélectronique Nanosciences Provence

Controlling a Chemical Coupling Reaction on a Surface: Tools and Strategies for On-Surface Synthesis

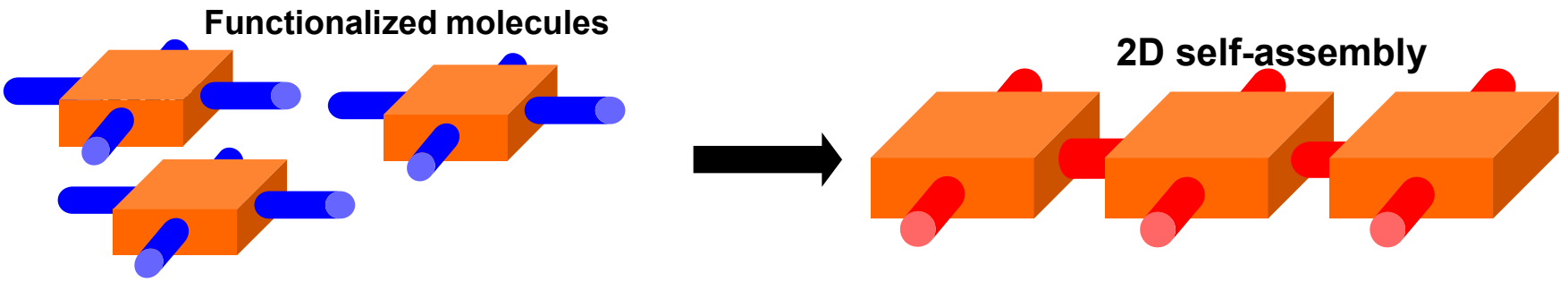
Sylvain Clair

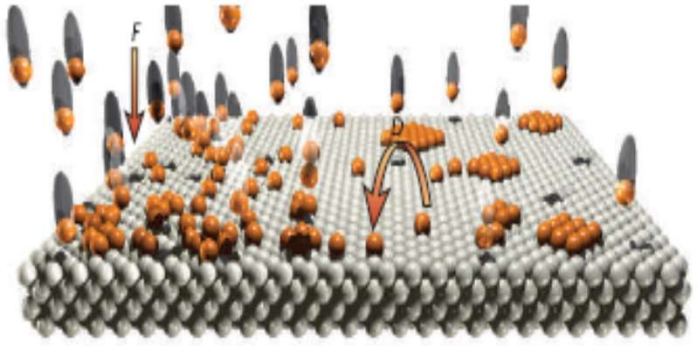
CNRS, Aix Marseille University, IM2NP, Marseille, France

NW2SD Conference
Marseille, July 18th 2019

Supramolecular self-assembly on surfaces

General experimental strategy





- Adsorption
- Diffusion
- Activation

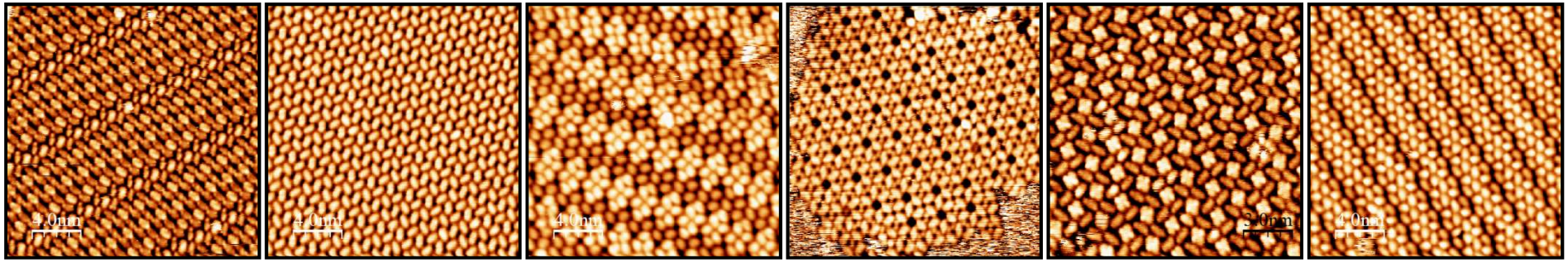
Evaporated species: aromatic molecules, metal atoms (in UHV)

Monolayer or sub-monolayer regime

Surfaces : oriented surfaces of noble metal single crystals

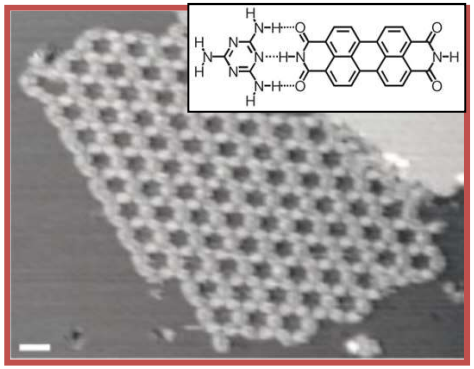
Characterization: STM/AFM, spectroscopy (XPS, NEXAFS, HREELS)

Supramolecular self-assembly on surfaces



van der Waals

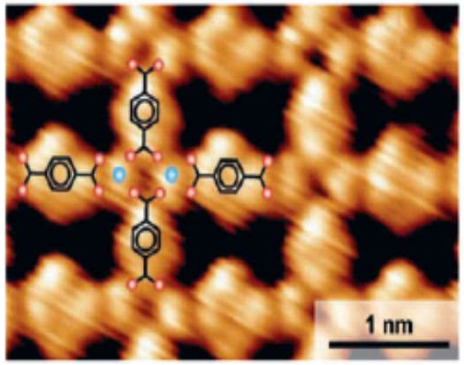
H-bonding



PTCDI+melamine / Ag/Si(111)

Theobald et al., *Nature* **404** (2003)

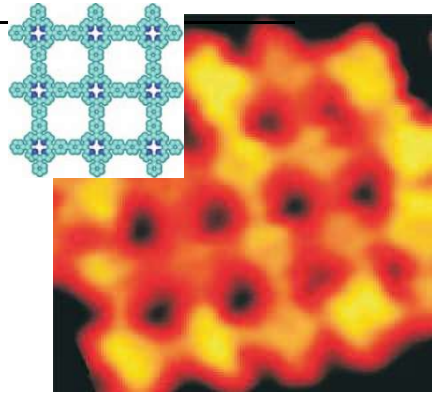
Metal-ligand



Fe-carboxylate / Cu(100)

Stepanow *et al*.,
Nature Materials **3**, 229 (2004)

Covalent



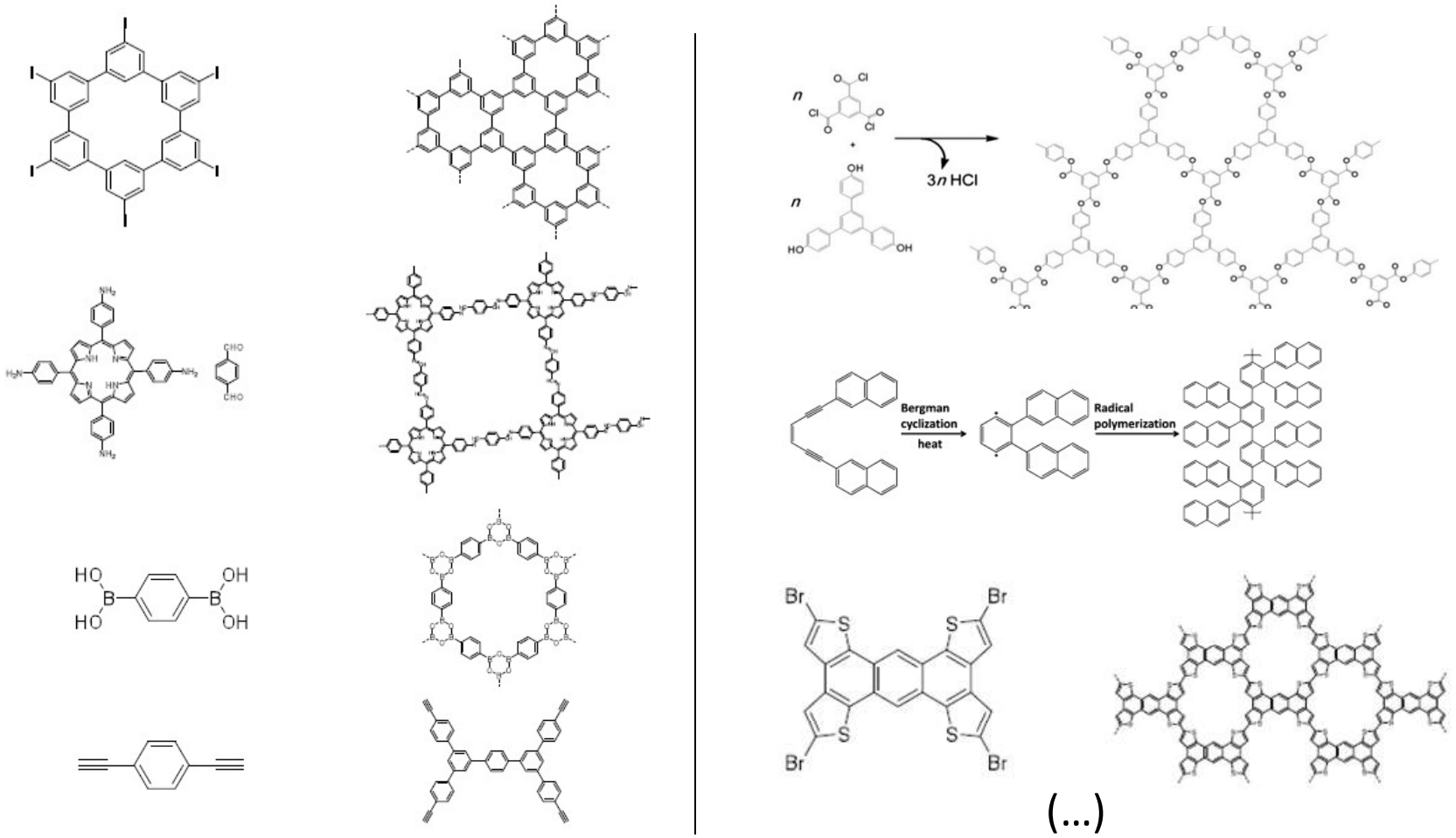
BrTPP polymer / Au(111)

Grill et al., *Nature Nano*. **2**, 687 (2007)

[0.05-0.7ev] **[0.5-2ev]** **[>1ev]**

Interaction Energy

2D polymers and *on-surface synthesis*

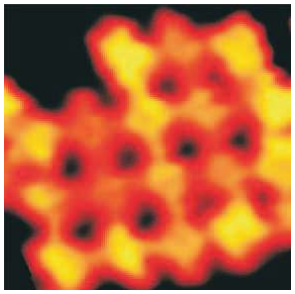


(...)

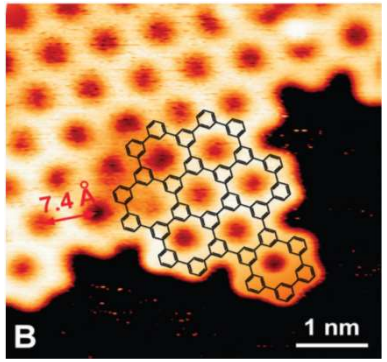
Review articles:

- Franc, G., A. Gourdon (2011). Phys. Chem. Chem. Phys. **13(32): 14283**
- Mendez, J., et al. (2011). Chem. Soc. Rev. **40(9): 4578**
- Zhang, X. M., et al. (2013). Nanoscale **5(18): 8269-8287**
- Björk, J., F. Hanke (2014). Chem. Eur. J. **20(4): 928-934**
- Fan, Q., et al. (2015). Acc. Chem. Res. **48(8): 2484–2494**
- Klappenberger, F., et al. (2015). Acc. Chem. Res. **48(7): 2140-2150**
- Lackinger, M. (2015). Polym. Int. **64(9): 1073-1078**
- Dong, L., et al. (2015). Acc. Chem. Res. **48(10): 2765-2774**
- Shen, Q., Gao, H. Y., Fuchs, H. (2017). Nano Today ***13: 77-96***
- Held, P.A., Fuchs, H., Studer, A. (2017). Chem. Eur. J. **23: 5874-5892**
- Jacobse, P. H., et al. (2017). Synlett **28(19): 2509-2516**
- Di Giovannantonio, M. and G. Contini (2018). J. Phys.-Cond. Mat. **30: 093001**
- Sun, Q., et al. (2018). Advanced Materials **30(17): 1705630**
- Wang, T. and J. F. Zhu (2019). Surface Science Reports **74(2): 97-140**

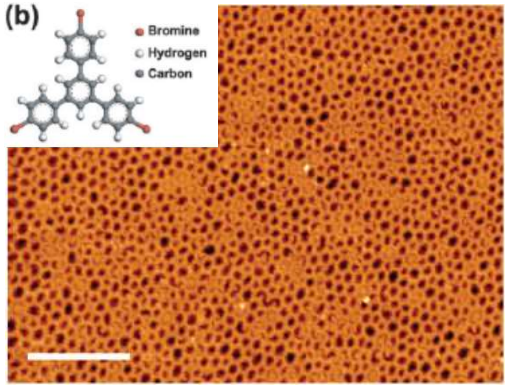
2D polymers and *on-surface synthesis*



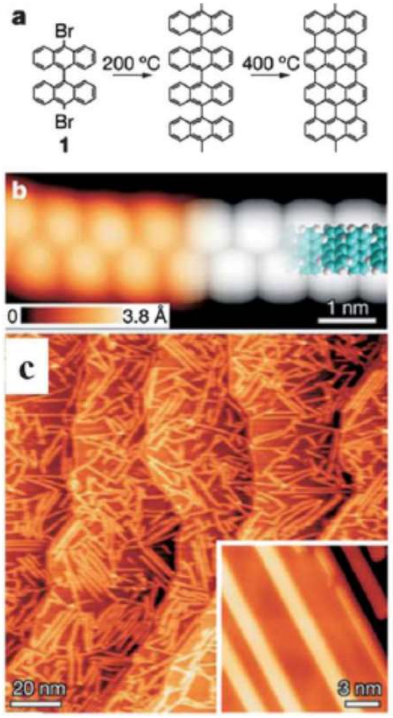
Grill, *Nat. Nano*. **2**, 687 (2007)



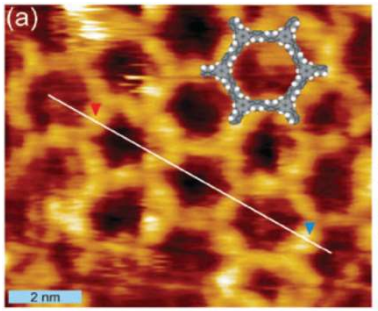
Bieri, *ChemComm* **45,** 6919 (2009)



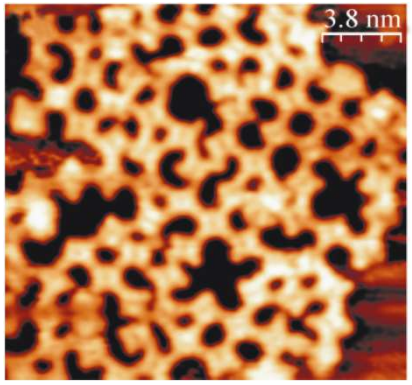
Blunt, *ChemComm.* **46**, 7157 (2010)



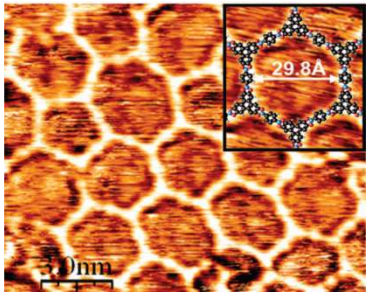
Cai, *Nature* **466**, 470 (2010)



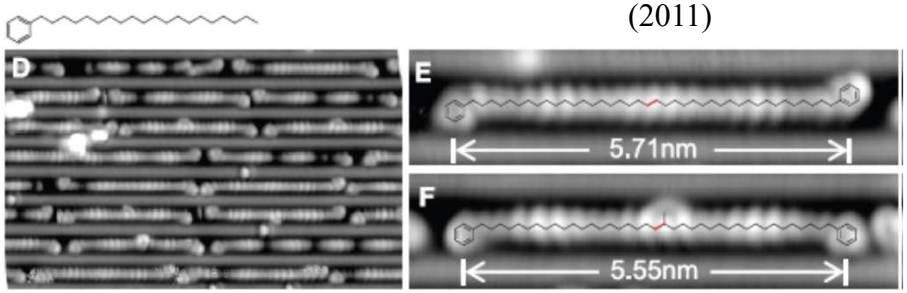
Gutzler, *ChemComm* **45,** 4456 (2009)



Krasnikov, *Nano. Res.* **4,** 376 (2011)



Zwaneveld, *JACS* **130,** 6678 (2008)



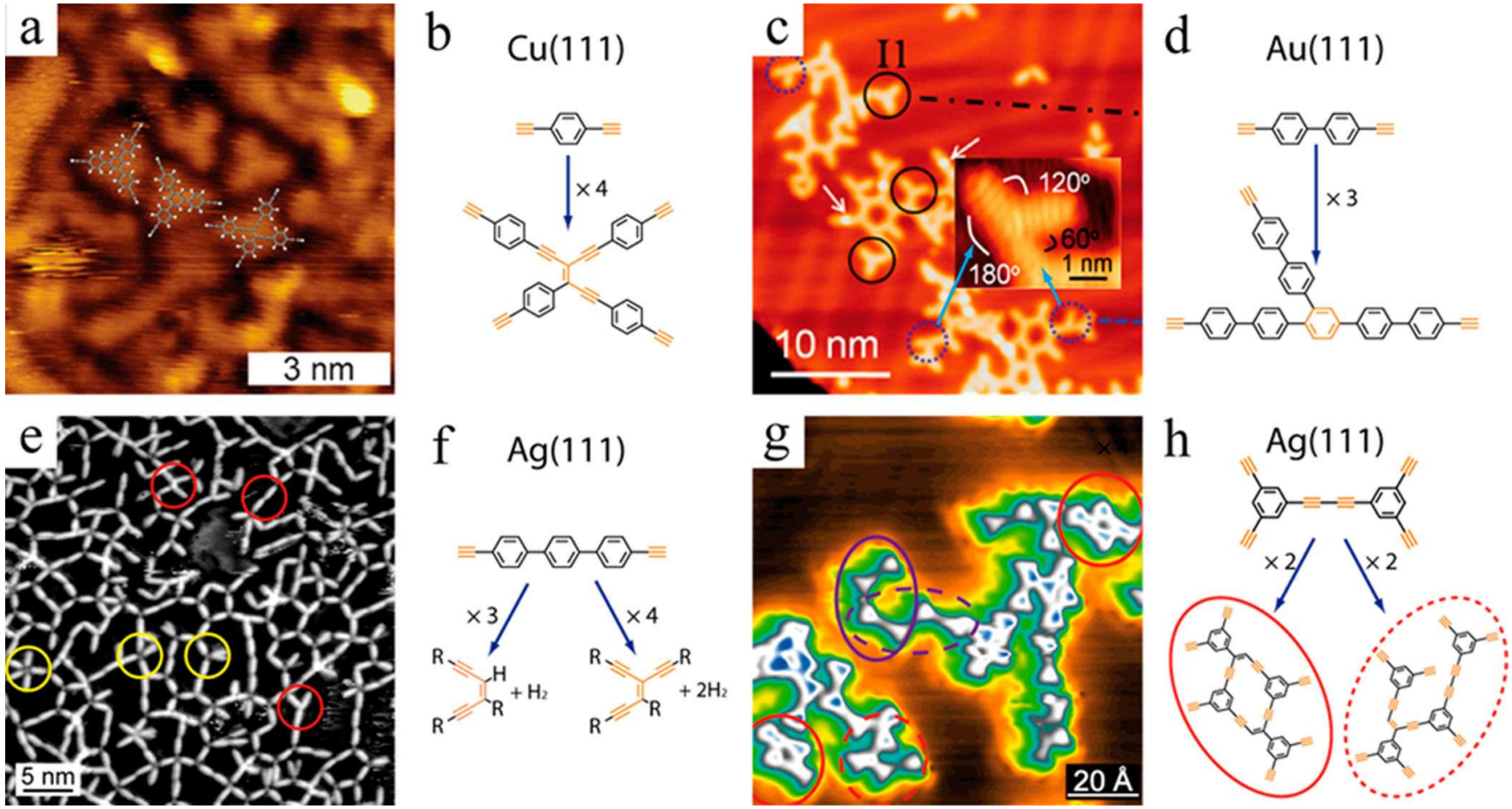
Zhong, *Science* **334**, 213 (2011)

Original reaction mechanisms:

- 2D confinement
- catalytic activity of the substrate

Reaction (non-)selectivity

Homocoupling reactions of terminal alkynes



Klappenberger, *Acc. Chem. Res.* **48**, 2140 (2015)

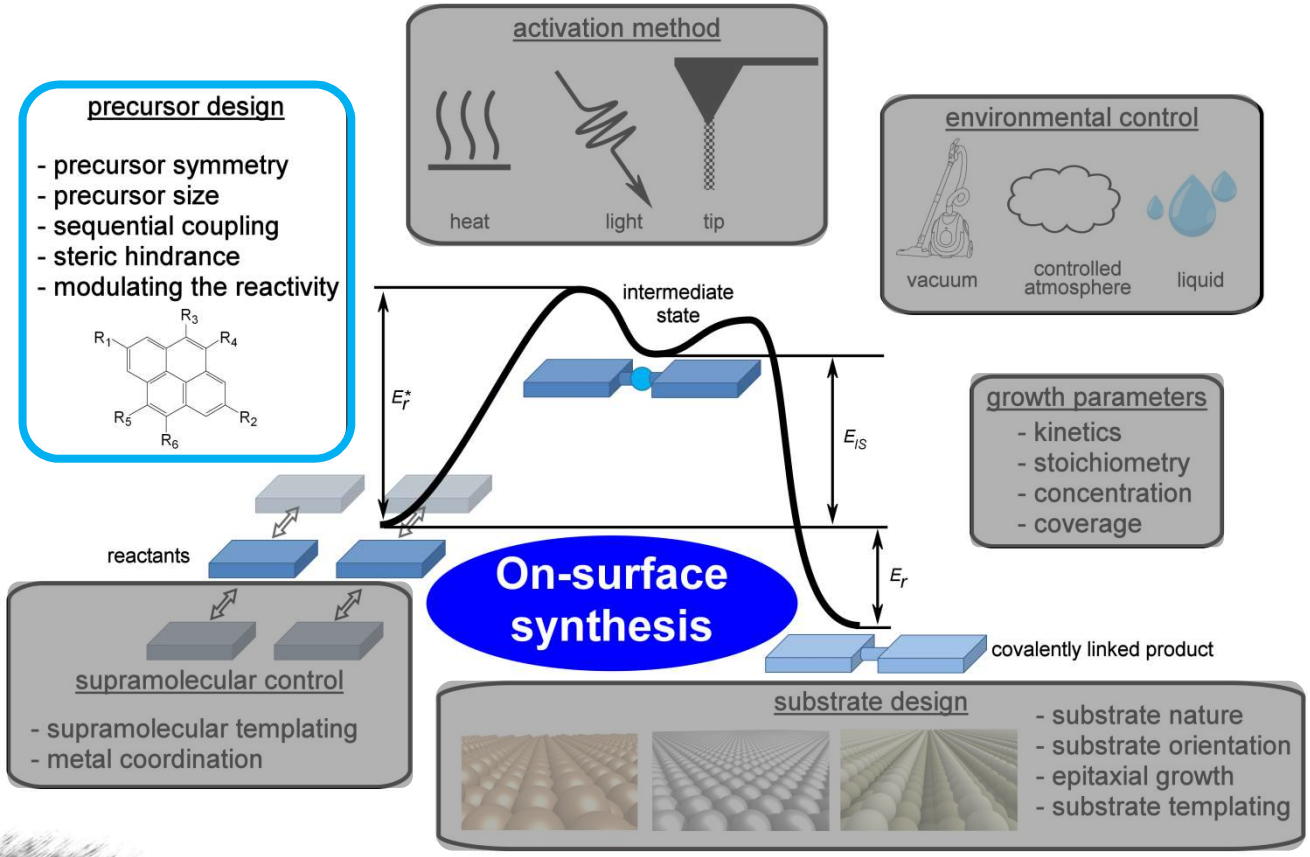
Reaction (non-)selectivity

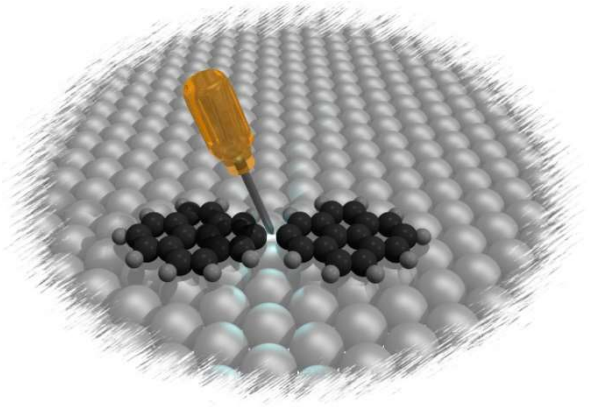
Homocoupling reactions of terminal alkynes

Control is required:

- The initiation step of the reaction and its degree of advancement (kinetics / reaction yield)
- The chemical selectivity
- The structure, position and alignment of the products
- The quality and extension of covalent networks

2D polymers and *on-surface synthesis*



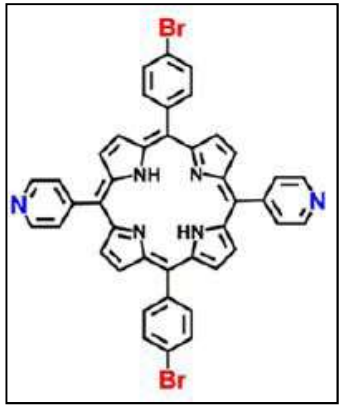


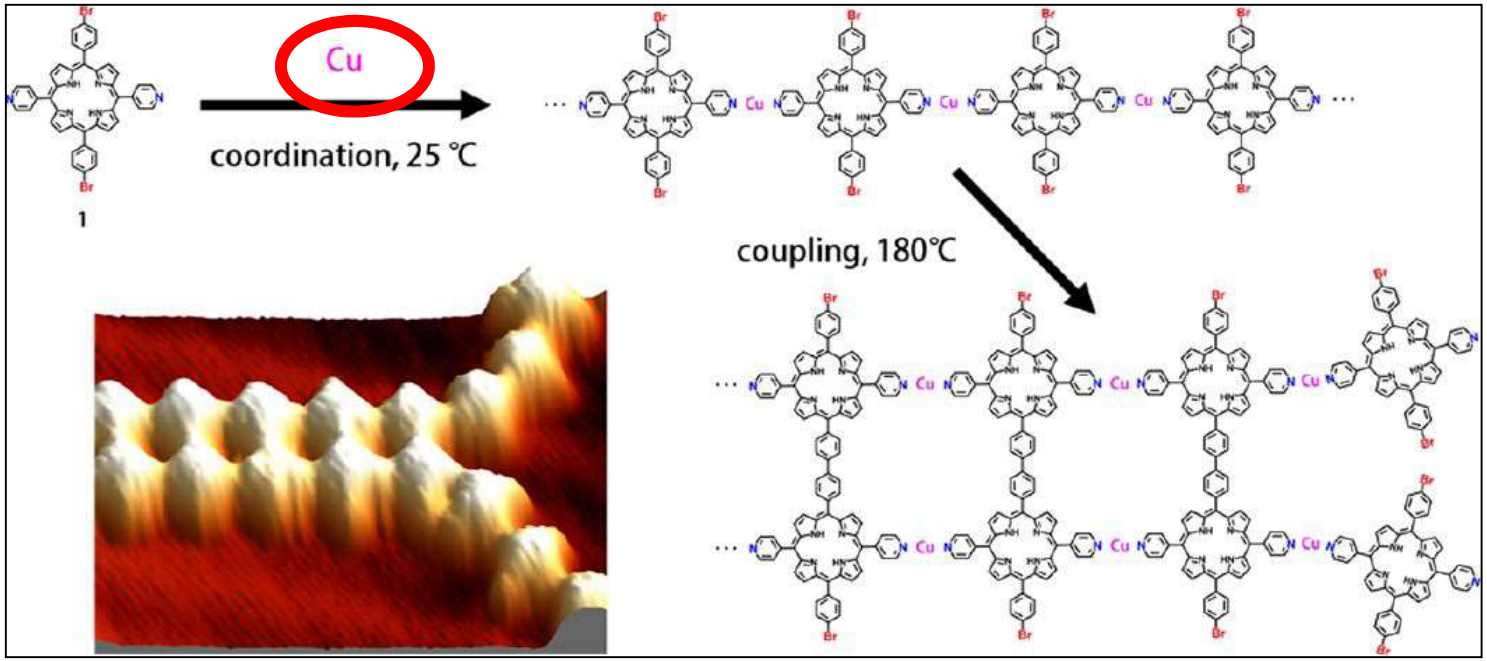
Several tools and strategies are available to achieve effective control on the reaction products

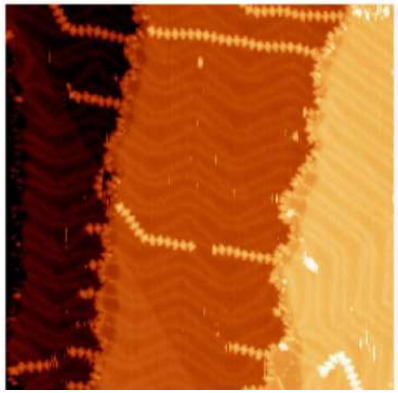
Clair & de Oteyza, *Chem. Rev.* **119**, 4717 (2019)

Precursor design: metal-directed templating

Au(111)
+
Cu adatoms

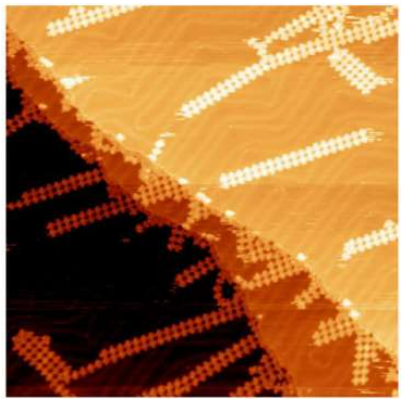


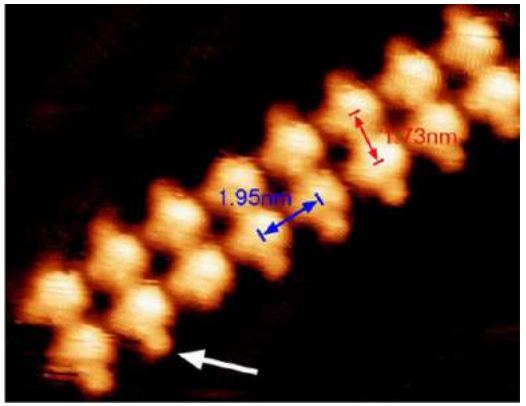




RT deposition

Annealing
180°C

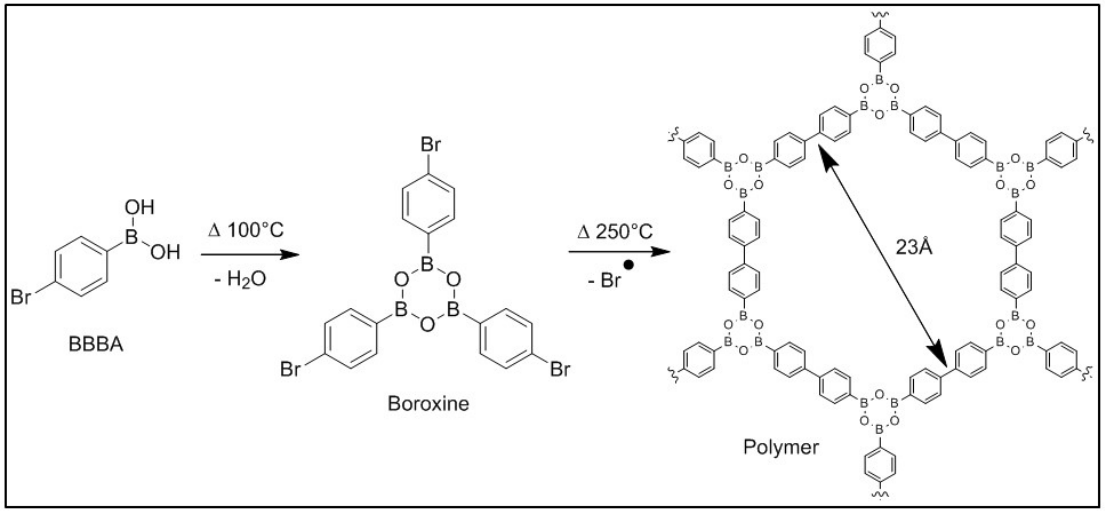




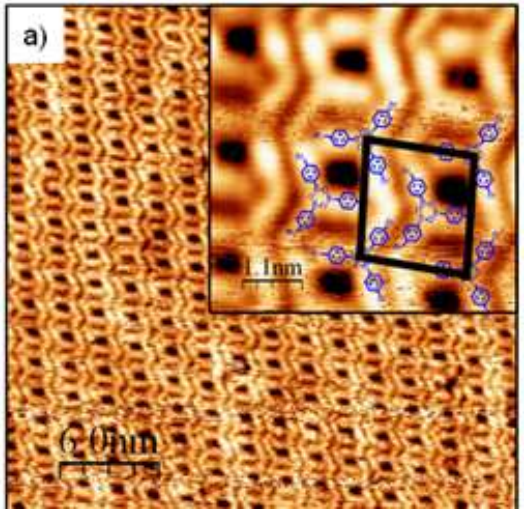
Lin, *JACS* **135**, 3576 (2013)

Precursor design: Sequential reactions

Ullmann coupling
+
boronic acid
condensation

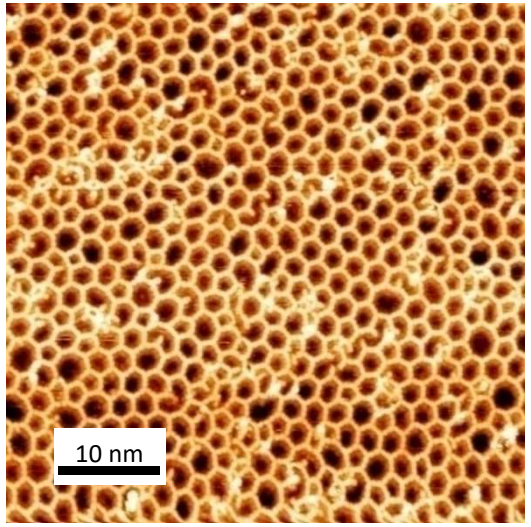


RT deposition



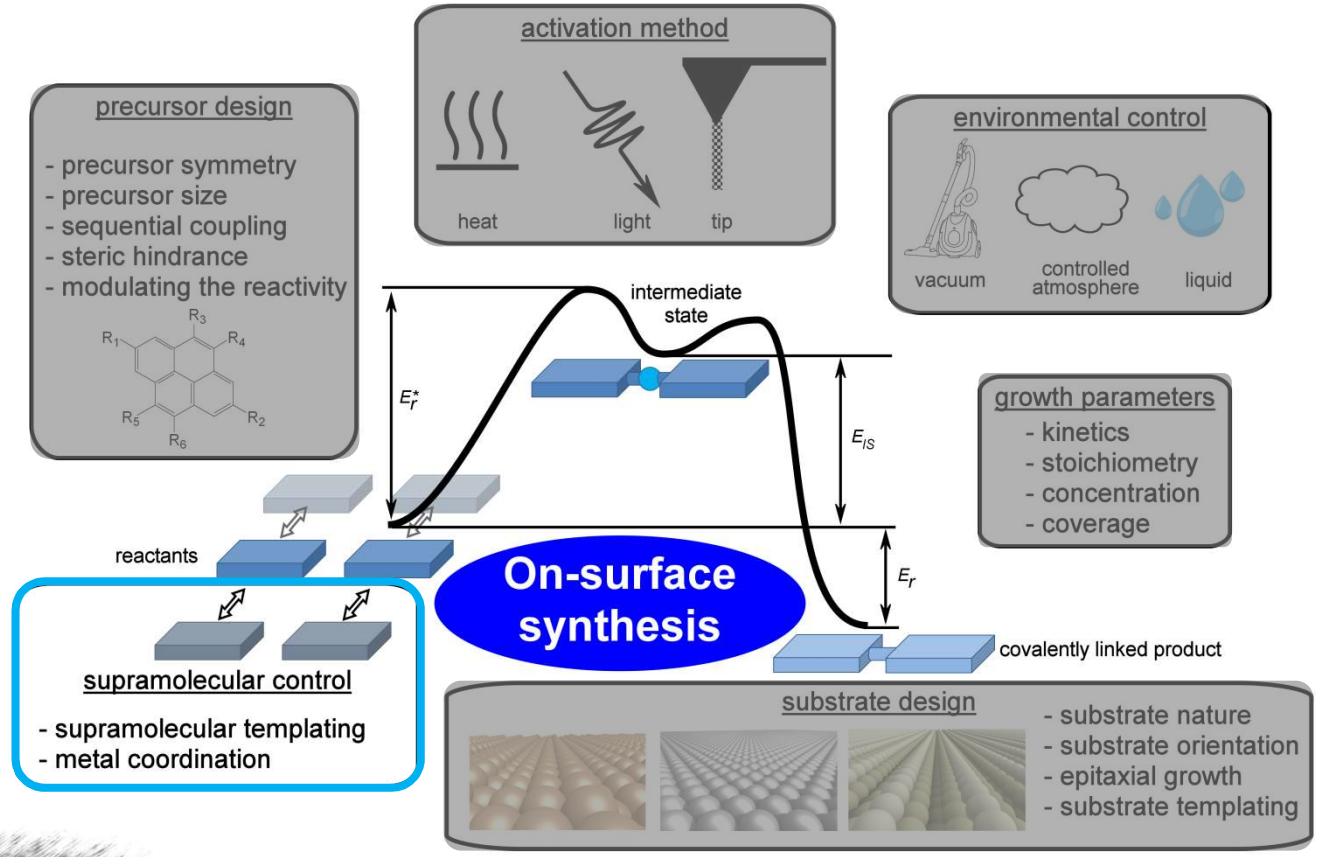
Au(111)

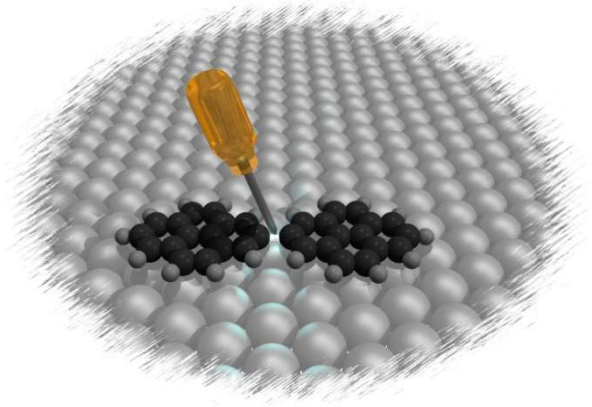
Deposition @ 250°C



Faury, *J. Phys. Chem. C* **116**, 4819 (2012)
Schlögl, *Chem. Comm.* **47**, 12355 (2011)

2D polymers and *on-surface synthesis*

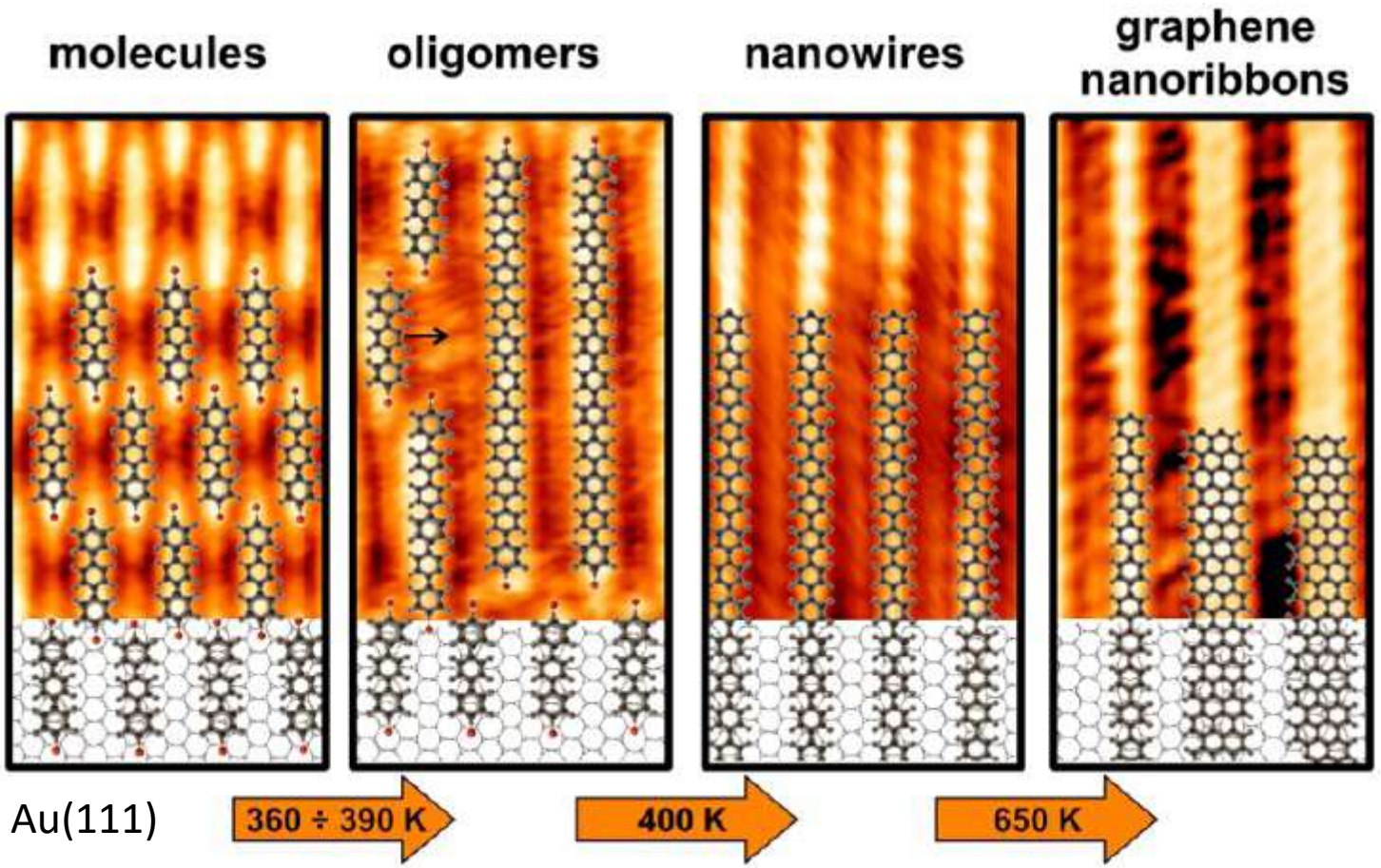




Several tools and strategies are available to achieve effective control on the reaction products

Clair & de Oteyza, *Chem. Rev.* **119**, 4717 (2019)

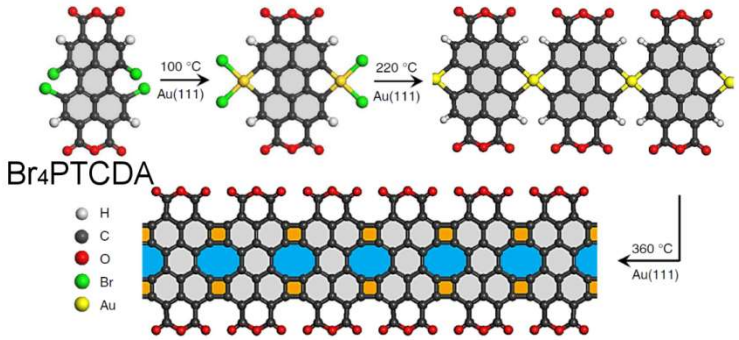
Supramolecular templating

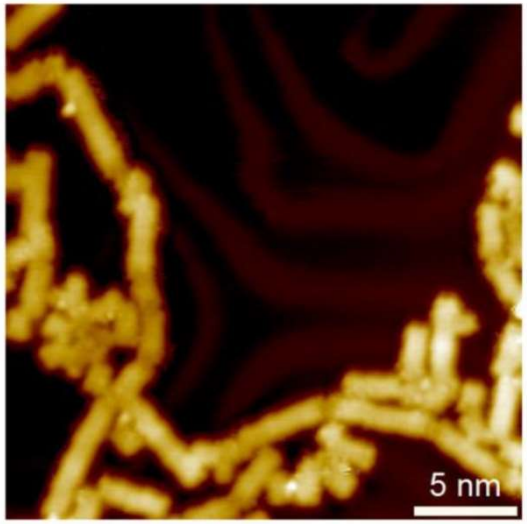


Basagni, *JACS* **137**, 1802 (2015)

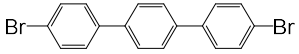
Supramolecular templating

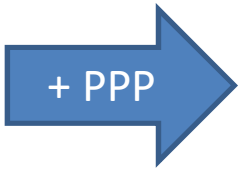
Graphene-like nanoribbons

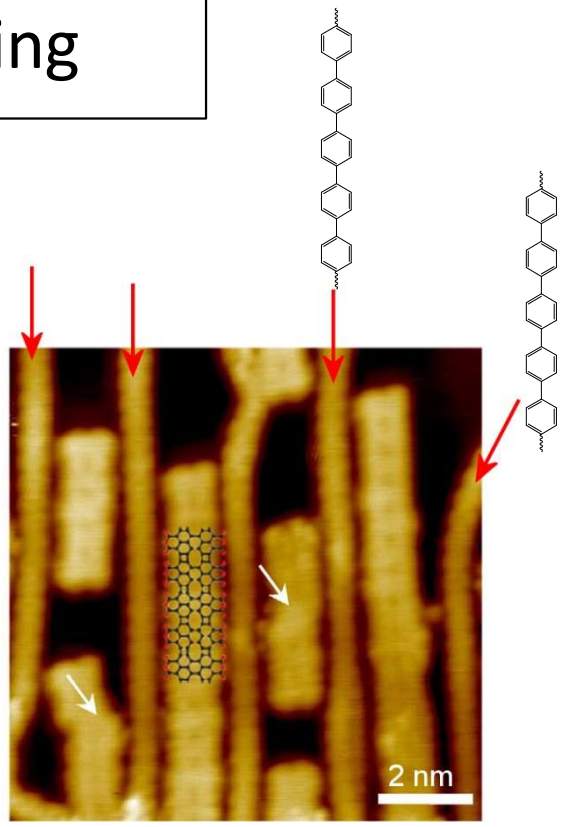


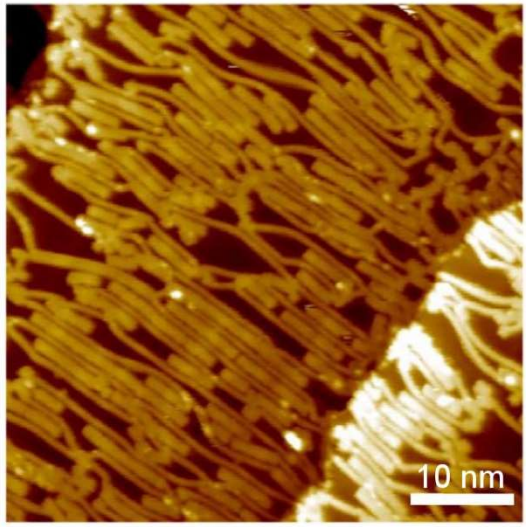


Au(111)



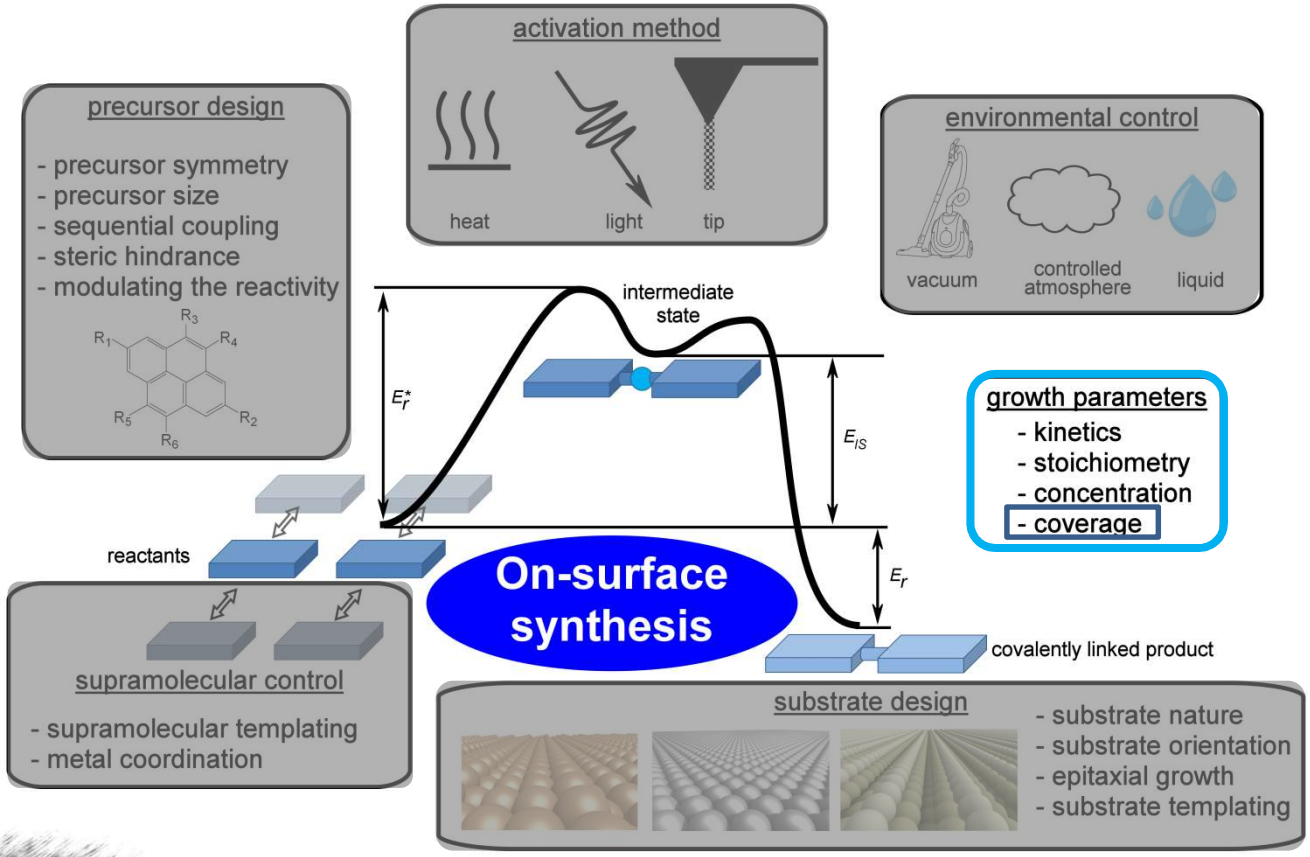


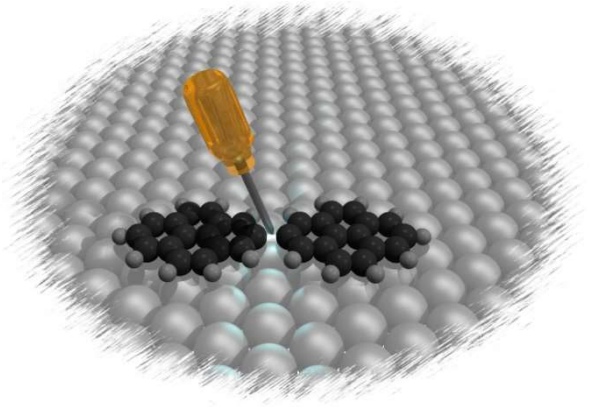




Liu, *Nat. Commun*. **8**, 14924 (2017)

2D polymers and *on-surface synthesis*





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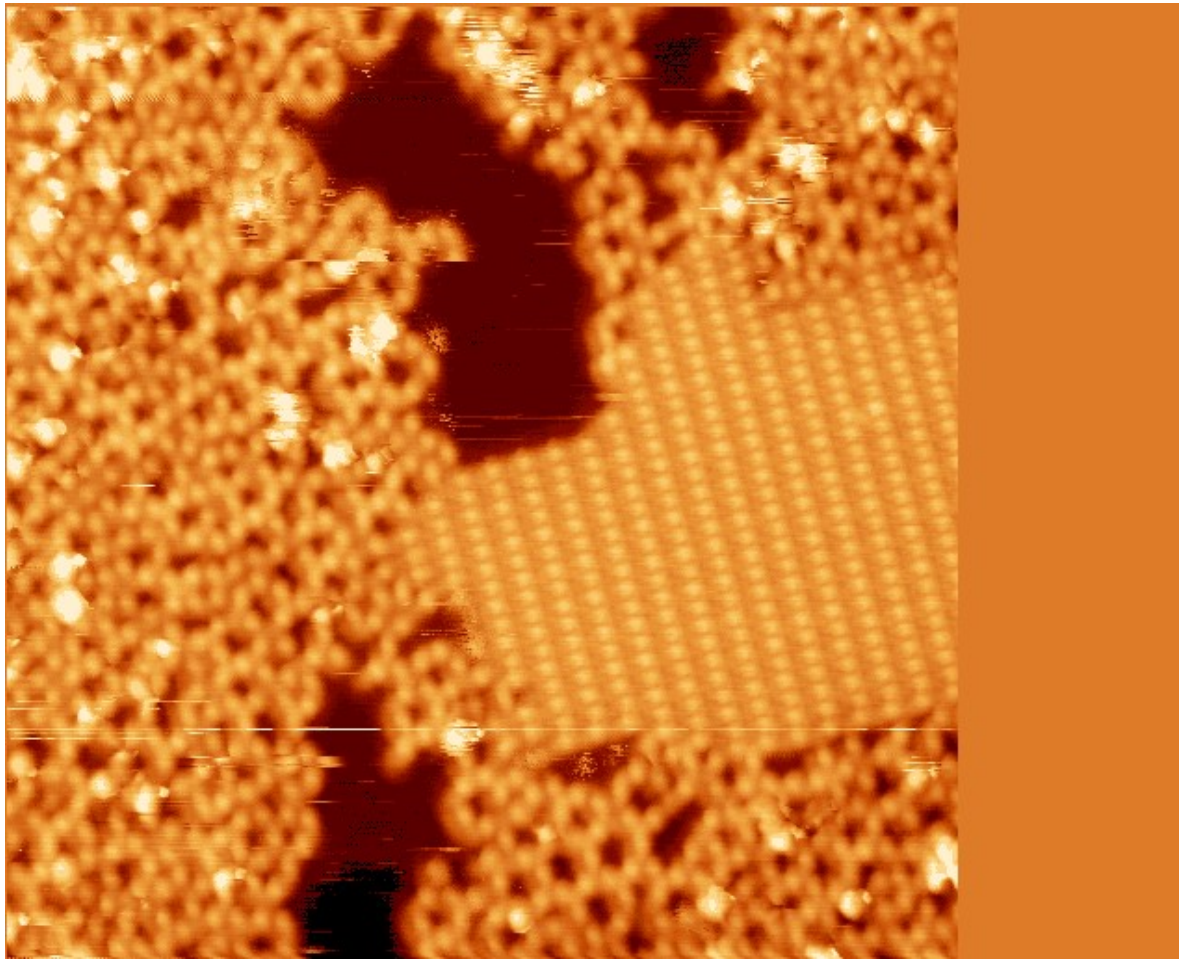
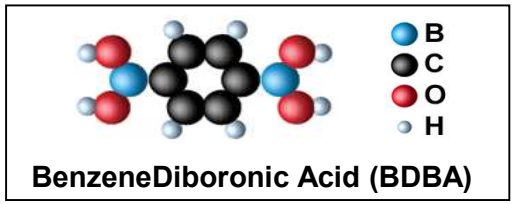
Clair & de Oteyza, *Chem. Rev.* **119**, 4717 (2019)

Kinetic quenching due to surface confinement

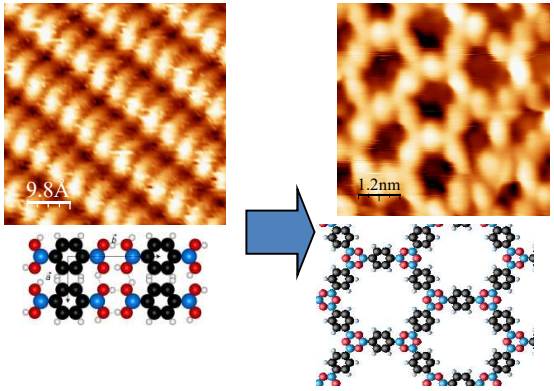


Total movie time: 90 minutes

BDBA / Ag(100)



BenzeneDiboronic Acid (BDBA)



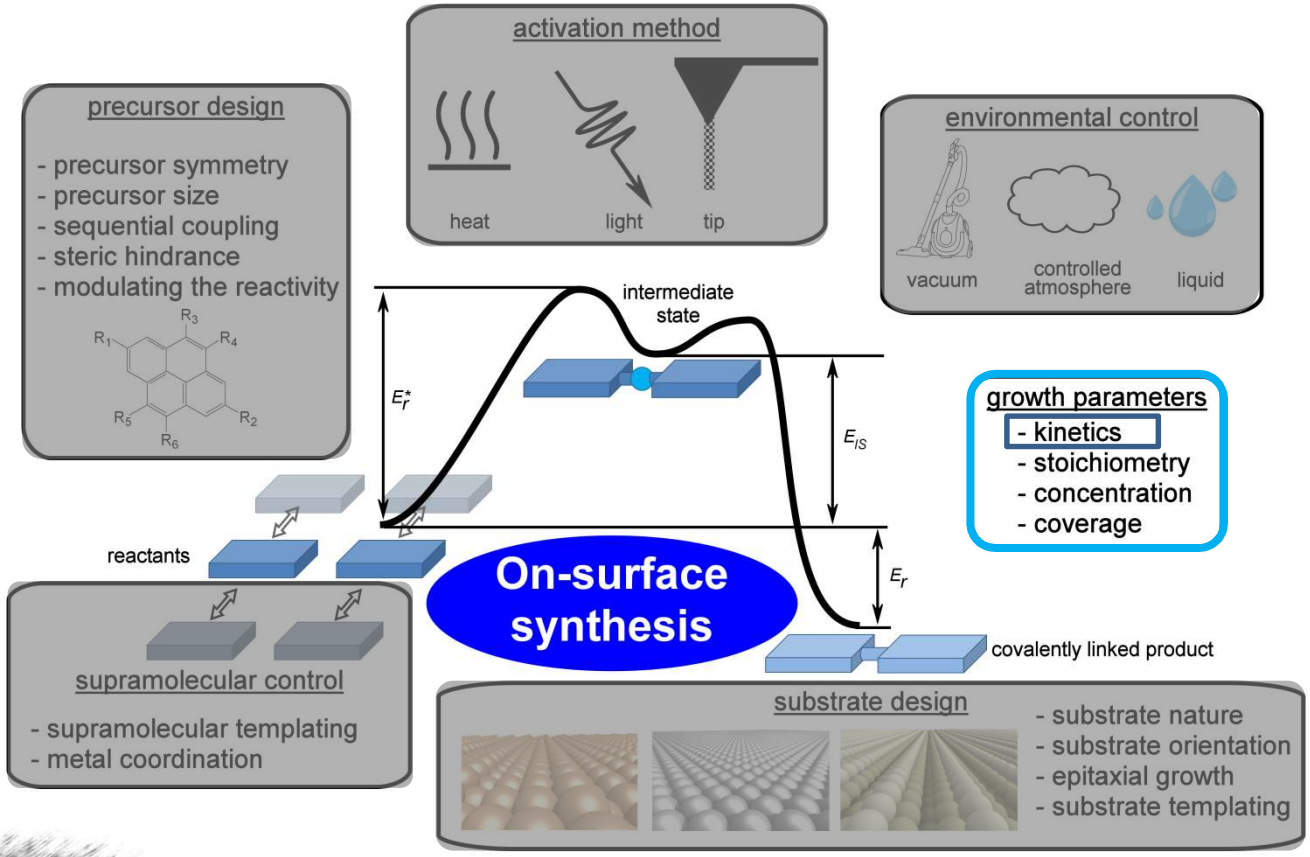
2.0 molecule/nm^2

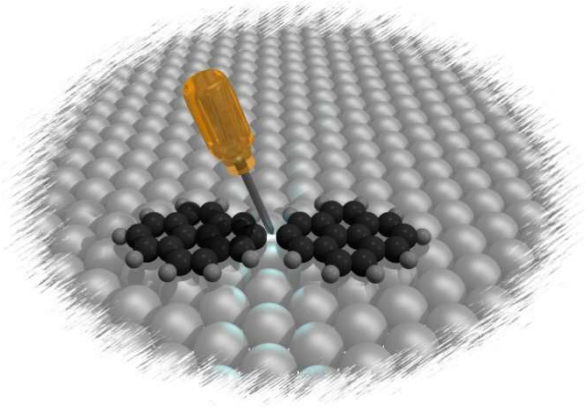
1.5 molecule/nm^2

Small density decrease

Clair et al., *Chem. Commun.* **50**, 9627 (2014)

2D polymers and *on-surface synthesis*



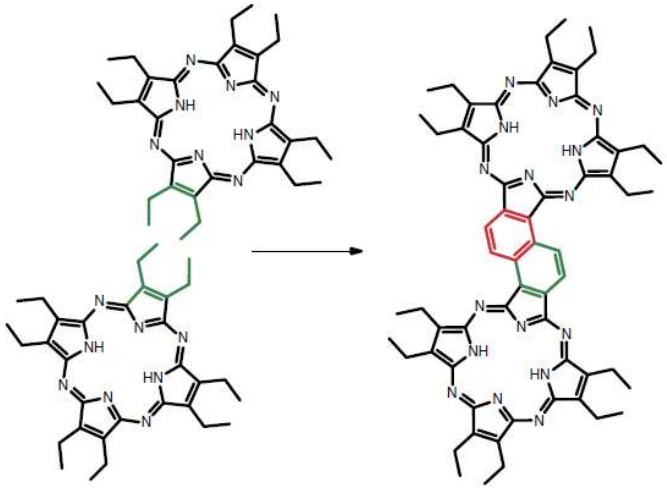


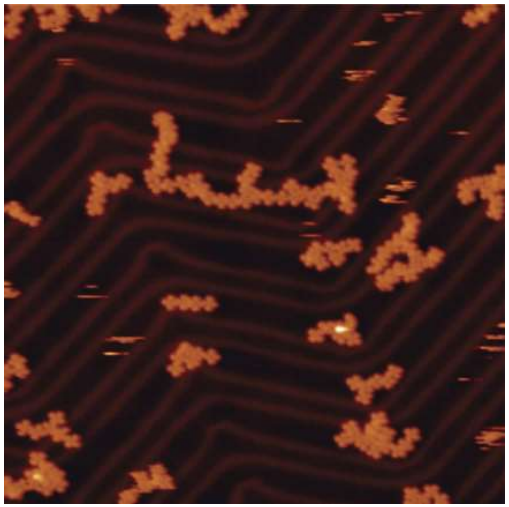
Several tools and strategies are available to achieve effective control on the reaction products

Clair & de Oteyza, *Chem. Rev.* **119**, 4717 (2019)

Kinetic control

Energetically favored

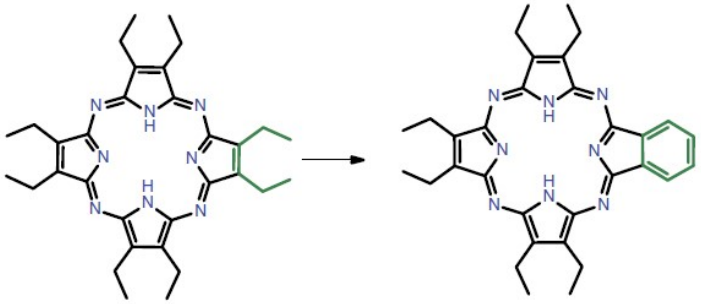


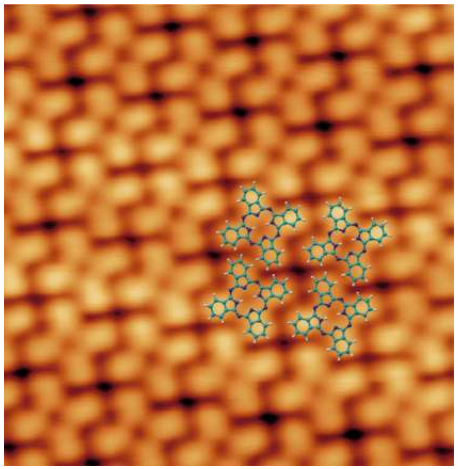


RT deposition
+
Annealing
275 °C

Intermolecular versus intramolecular reaction

Kinetically favored

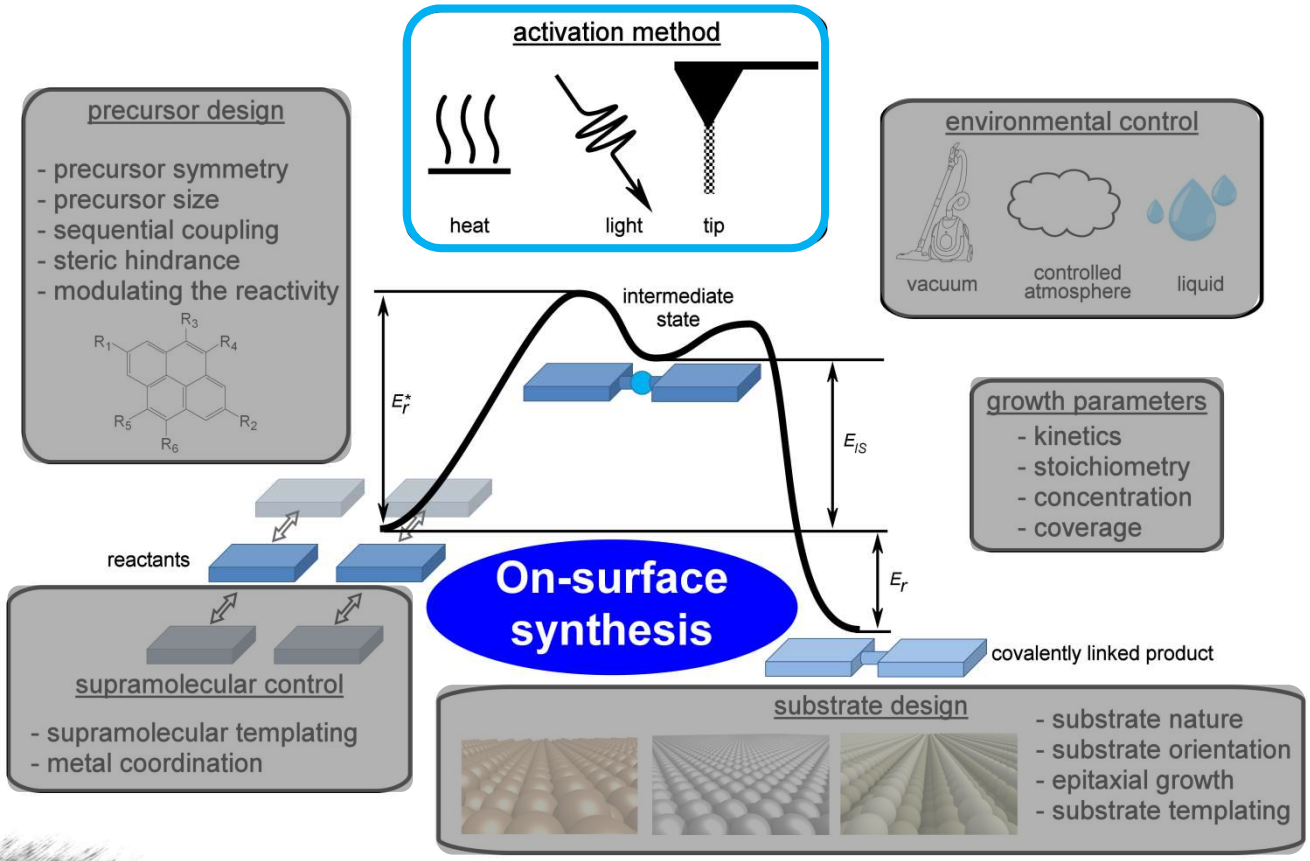


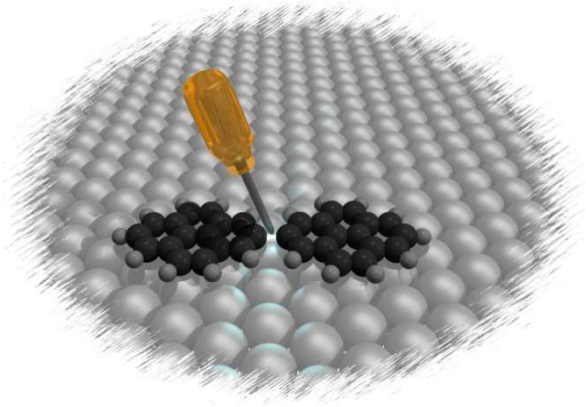


Deposition
300 °C

Cirera, *Nat. Commun.* **7**, 11002 (2016)

2D polymers and *on-surface synthesis*



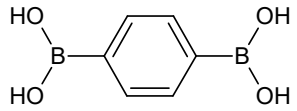


Several tools and strategies are available to achieve effective control on the reaction products

Clair & de Oteyza, *Chem. Rev.* **119**, 4717 (2019)

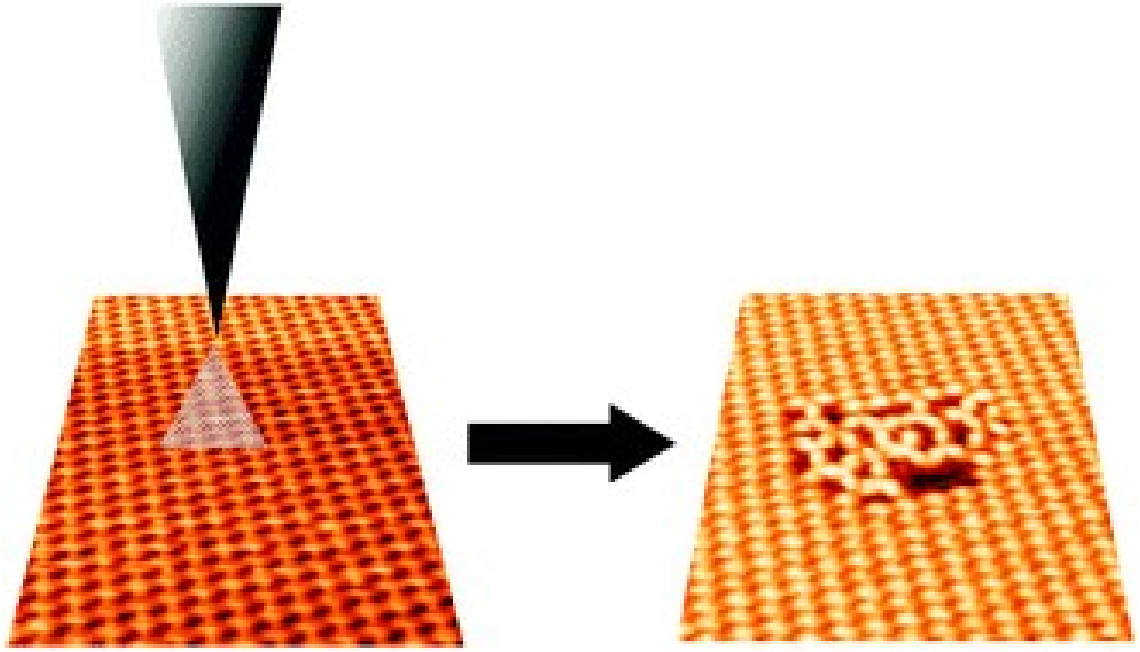
Tip-induced polymerization

Boronic acid condensation



BDBA

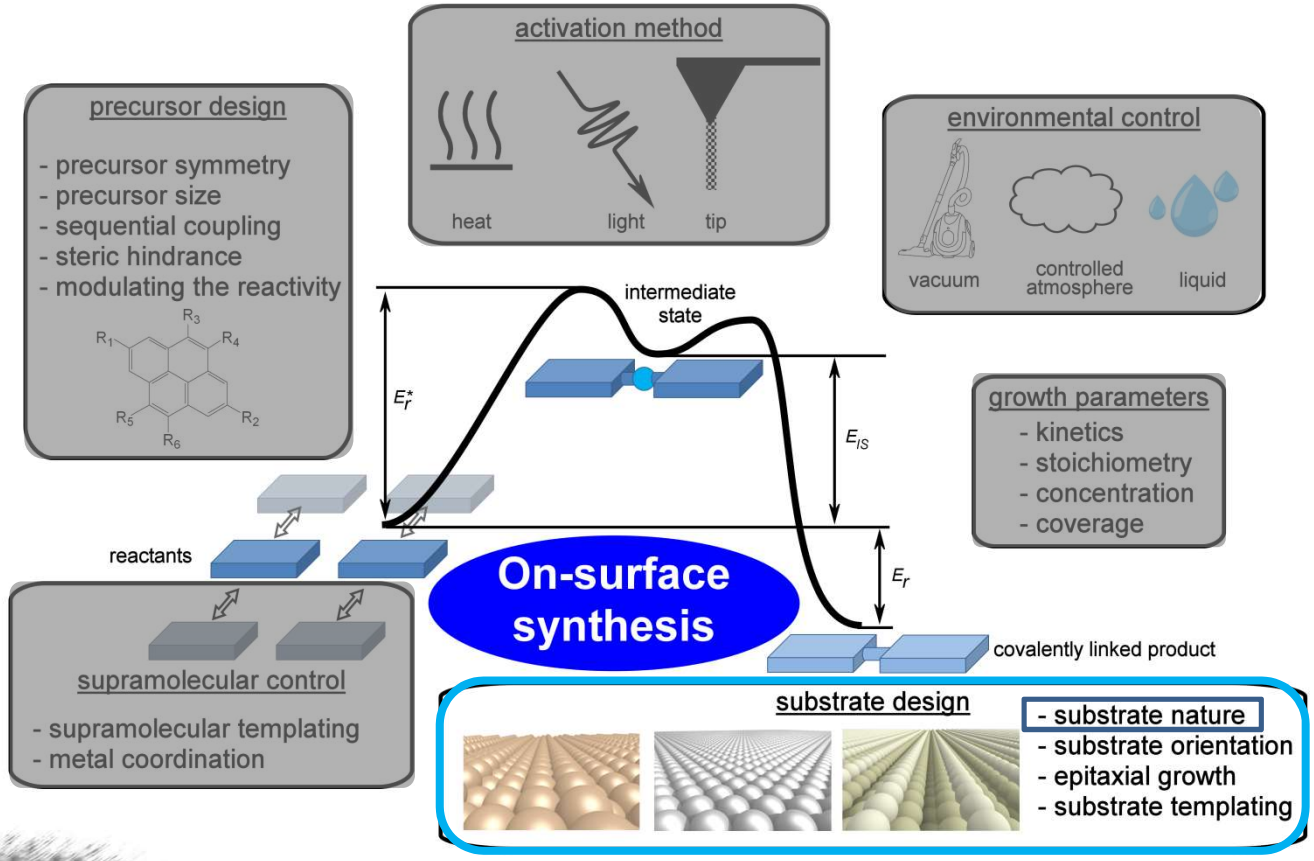
Reducing the tip-surface distance to remove some molecules

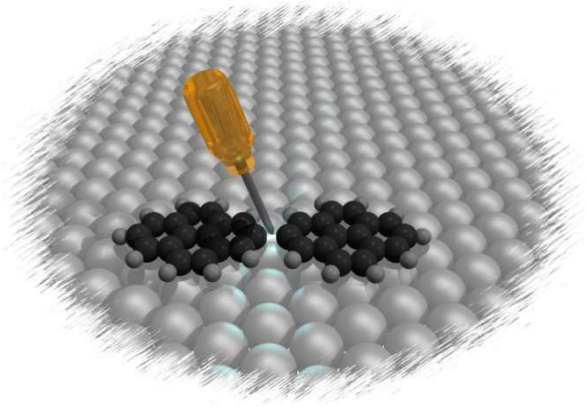


Ag(100)

Clair, *Chem. Commun.* **47**, 8028 (2011)

2D polymers and *on-surface synthesis*



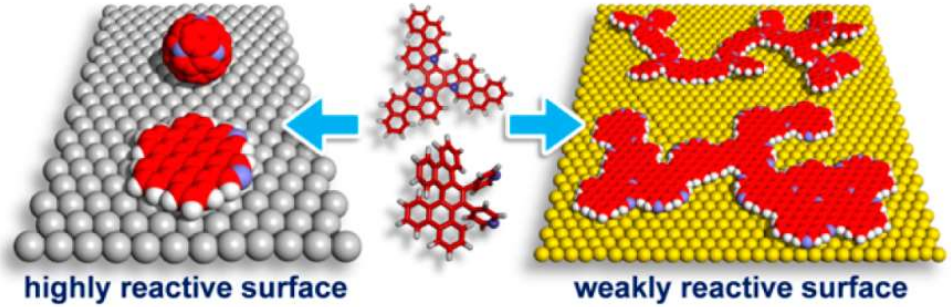


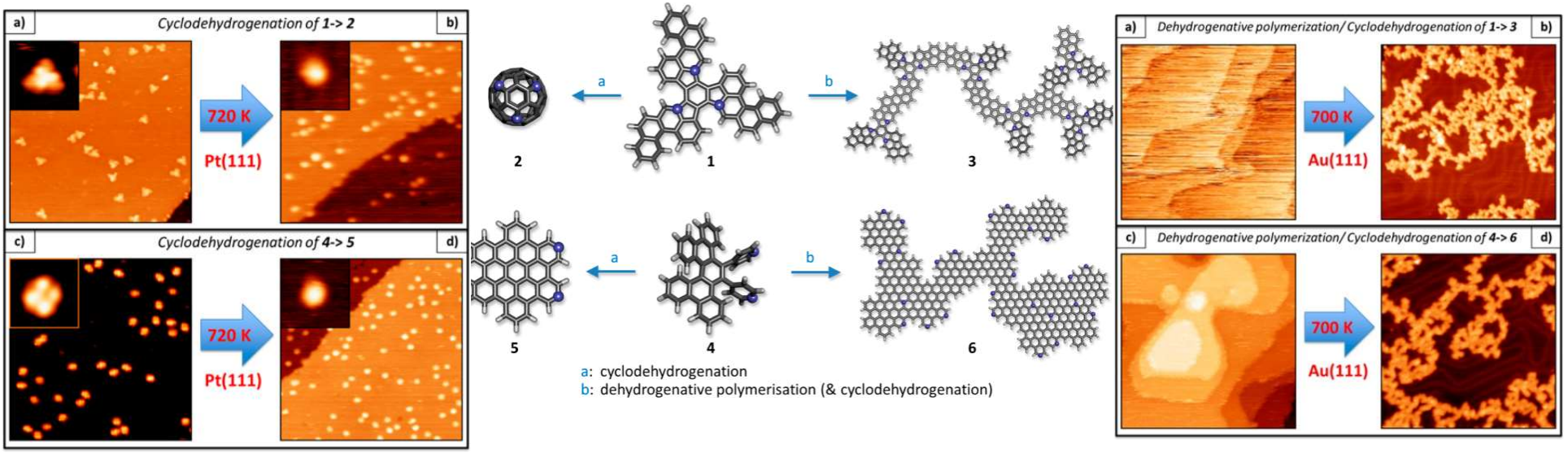
Several tools and strategies are available to achieve effective control on the reaction products

Clair & de Oteyza, *Chem. Rev.* **119**, 4717 (2019)

Intermolecular versus intramolecular reaction

Dehydrogenative coupling





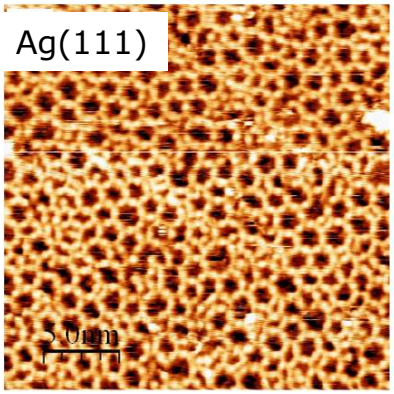
Pt(111)

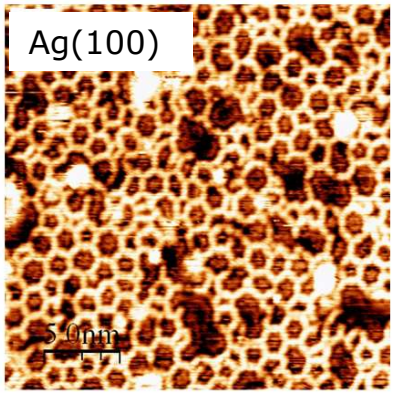
Au(111)

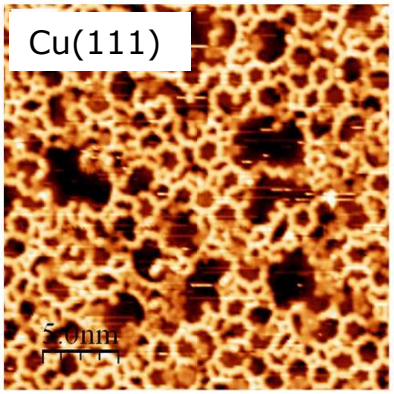
Pinardi, *ACS Nano* **7**, 3676 (2013)

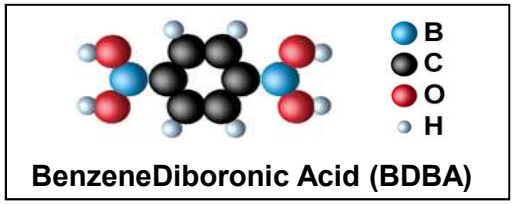
Influence of substrate nature in polymer quality

Boronic acid condensation



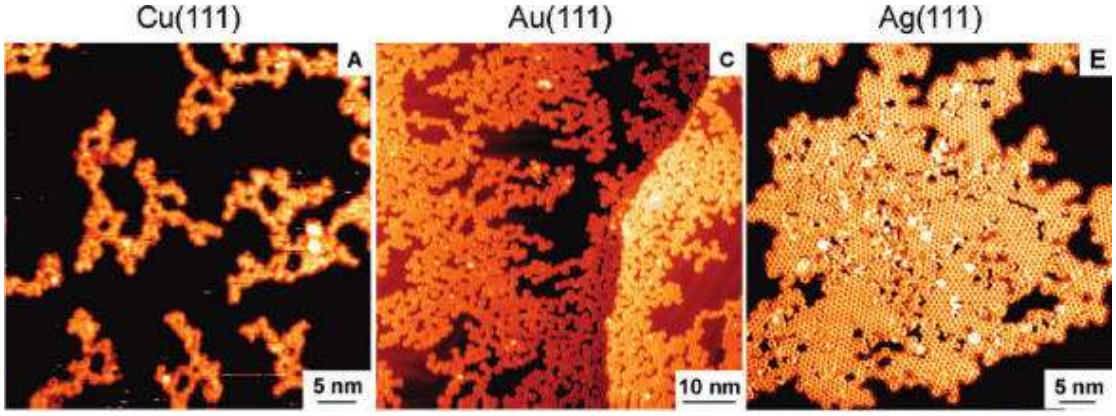


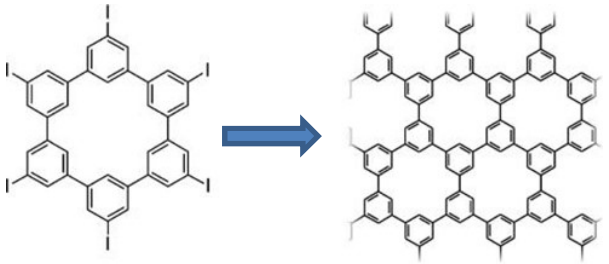




Ourdjini, *PRB* **84** 125421 (2011)

Ullmann coupling

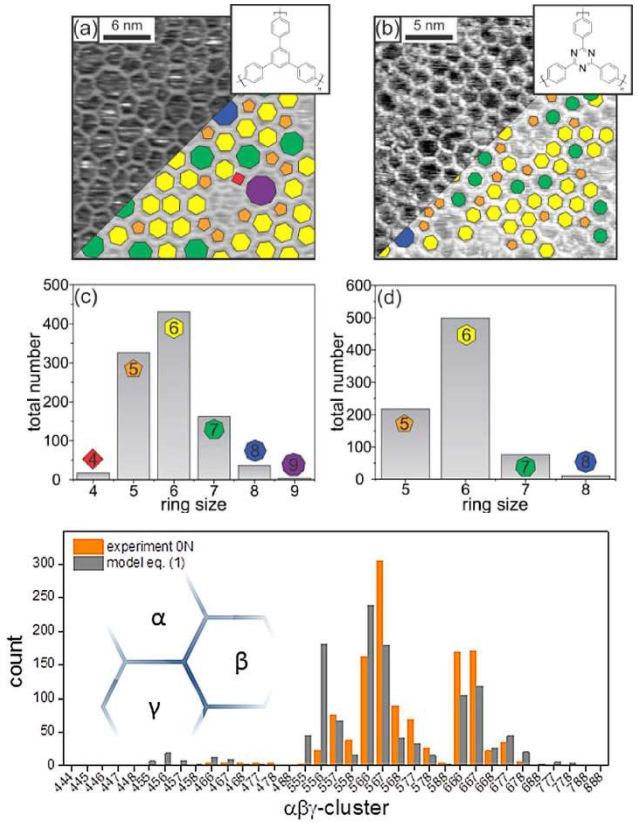




Bieri, *JACS* **132**, 16669 (2010)

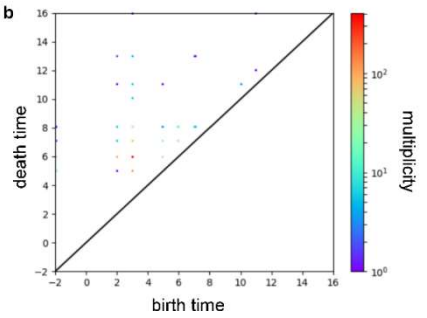
Quantification of polymer quality

Pore distribution and $\alpha\beta\chi$-clusters



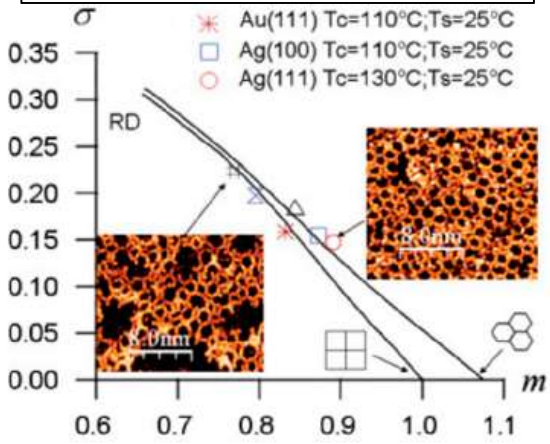
Alexa, *ChemPhysChem* (2019)

Topological analysis Persistent homology

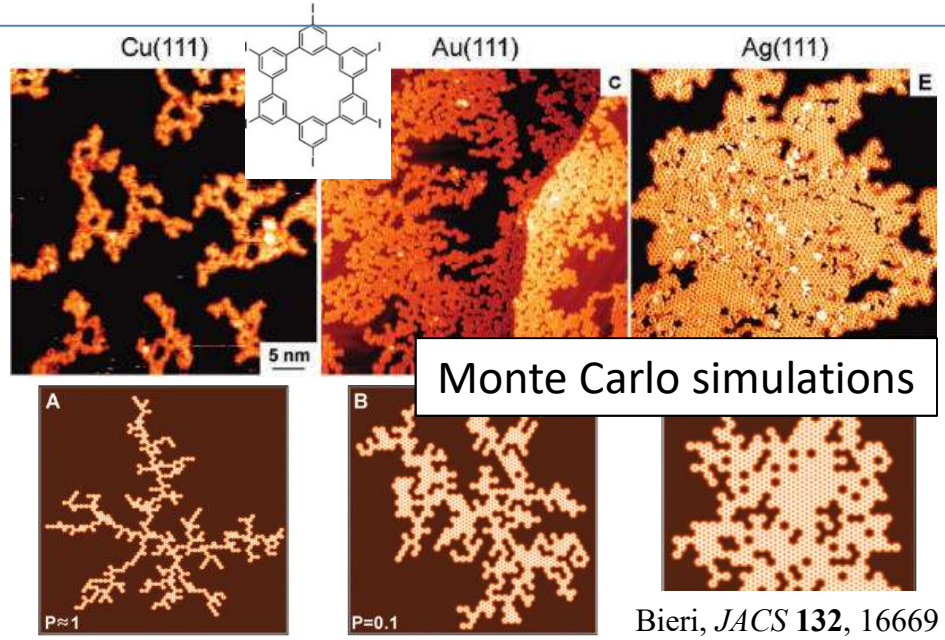


Gutierrez, *ChemPhysChem* (2019)

Minimum spanning tree analysis



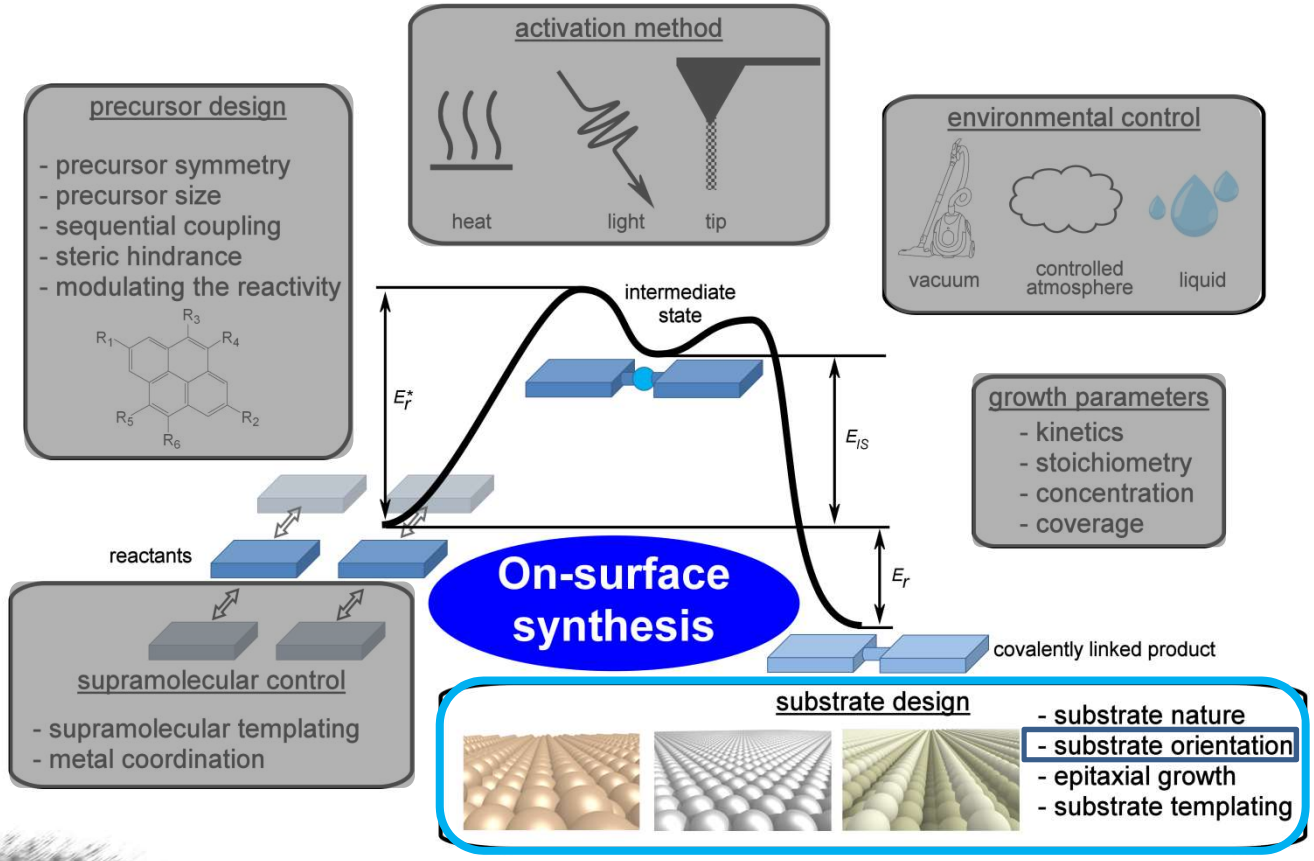
Ourdjini, *PRB* **84**, 125421 (2011)

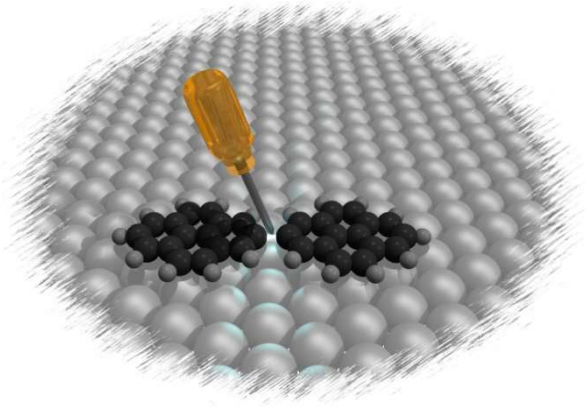


Monte Carlo simulations

Bieri, *JACS* **132**, 16669 (2010)

2D polymers and *on-surface synthesis*

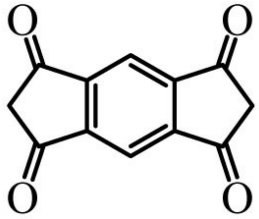




Several tools and strategies are available to achieve effective control on the reaction products

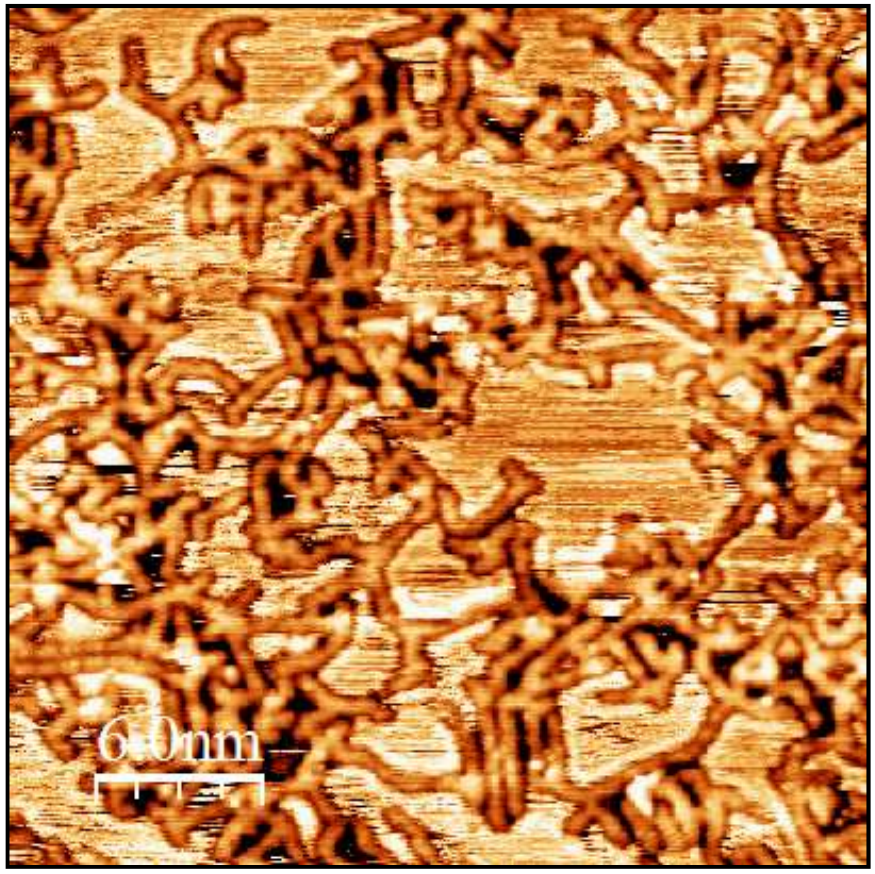
Clair & de Oteyza, *Chem. Rev.* **119**, 4717 (2019)

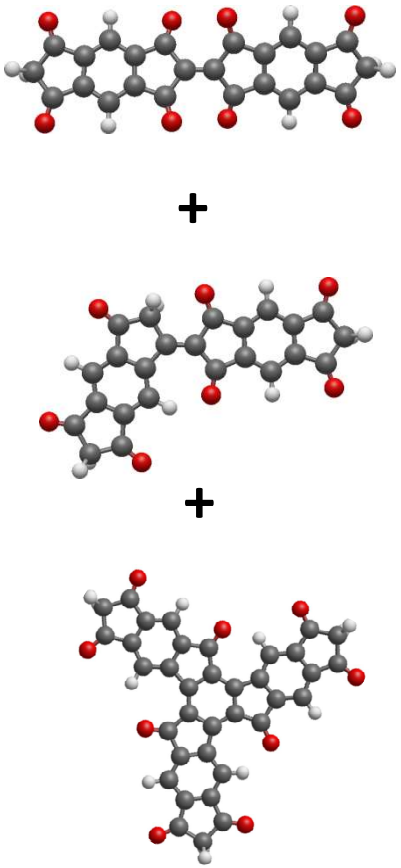
On-surface covalent coupling on Ag(100)

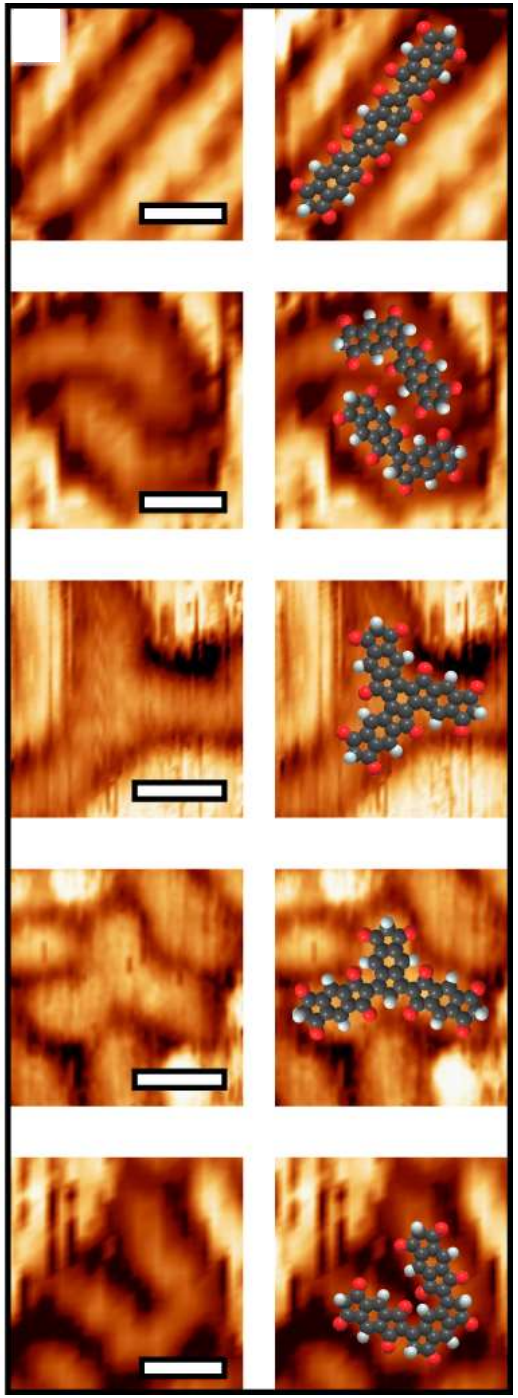


Indacene tetrone
$INDO_4$

High temperature annealing (350 °C)

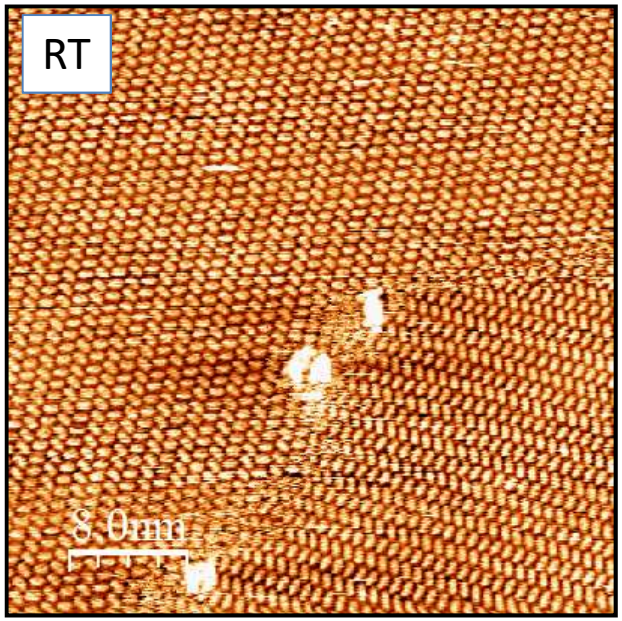






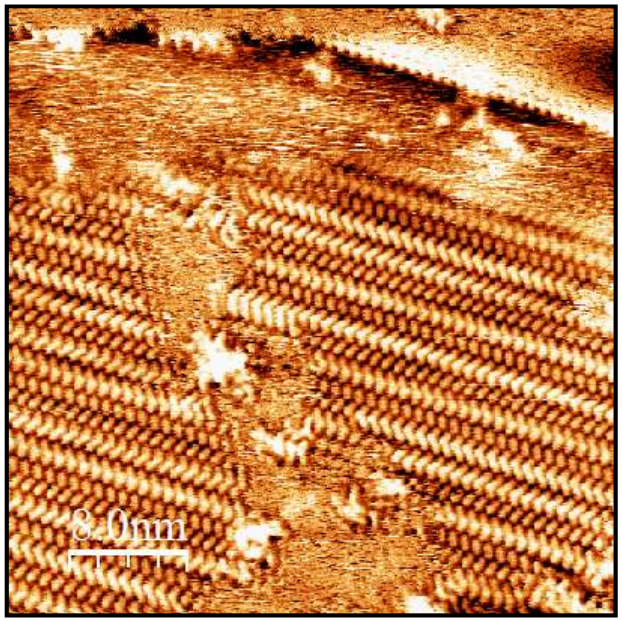
Kalashnyk, *ChemPhysChem* **19**, 1802 (2018)

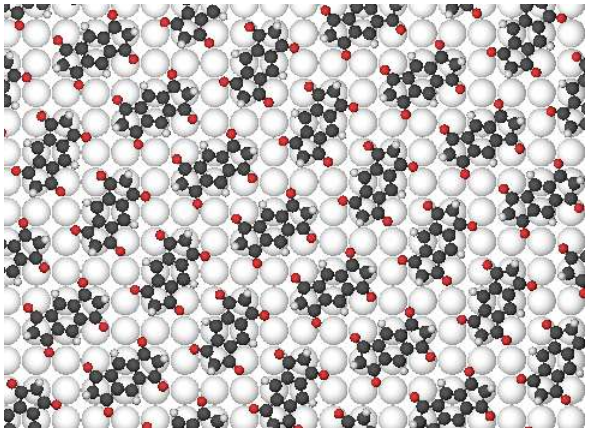
Supramolecular phase on Ag(100)

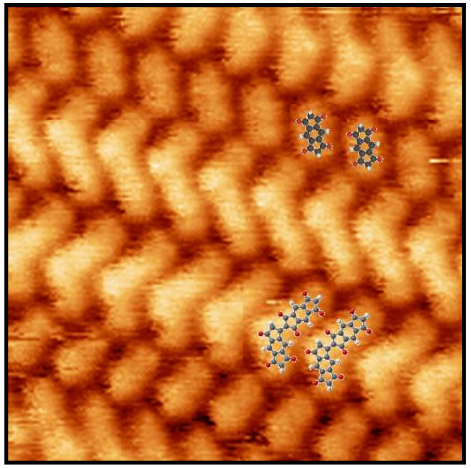


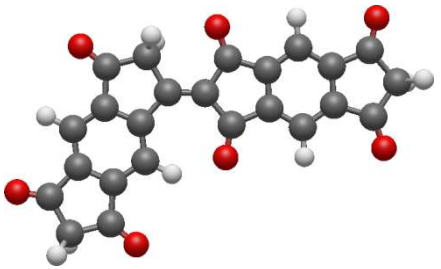
~~350°C~~

300°C





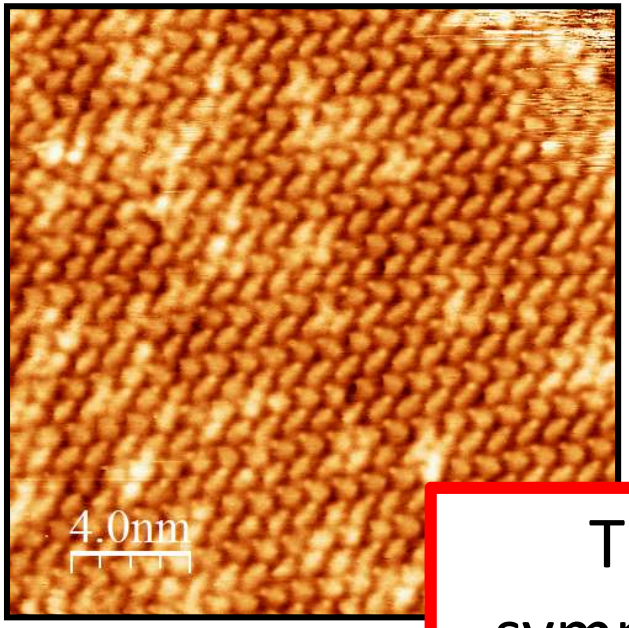




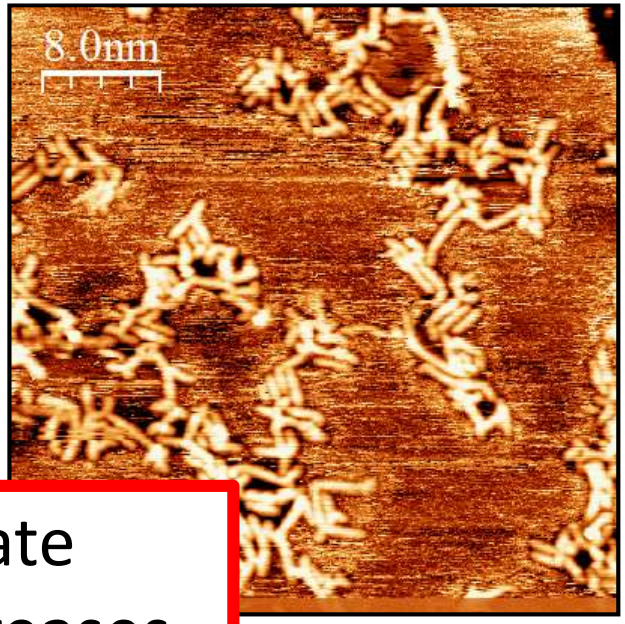
The temperature controls the reaction type

Kalashnyk, *ChemPhysChem* **19**, 1802 (2018)

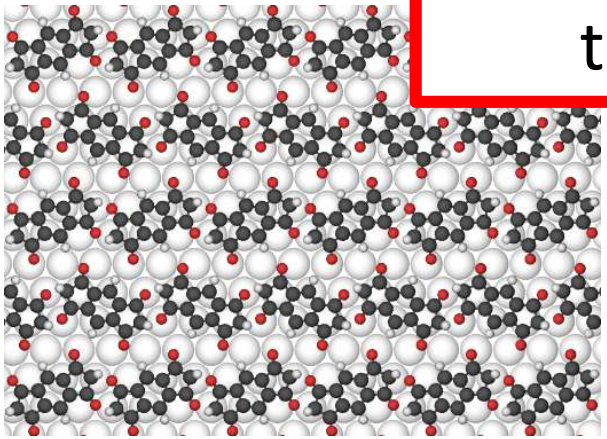
On-surface covalent coupling on Ag(111)



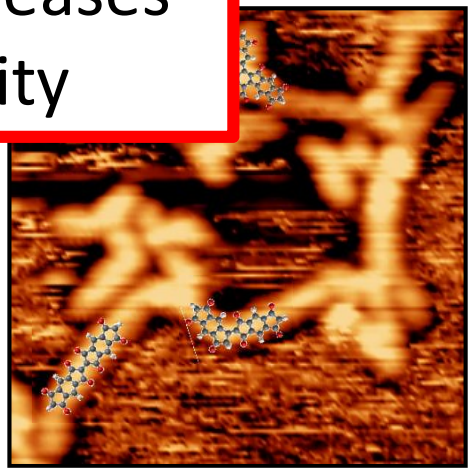
180°C

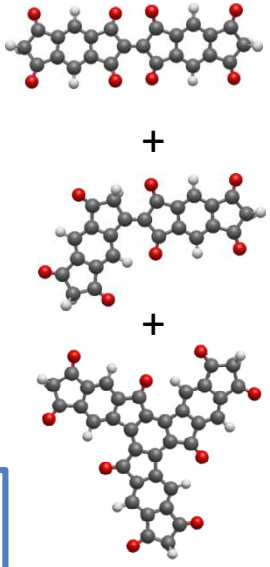


The substrate symmetry increases the reactivity



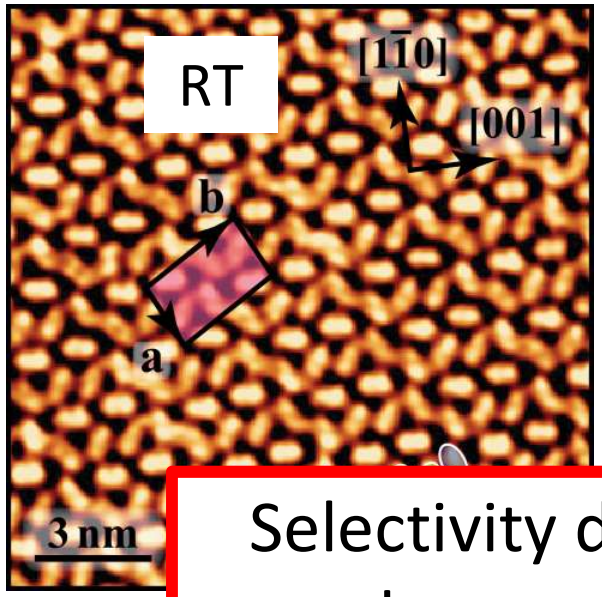
Herringbone phase

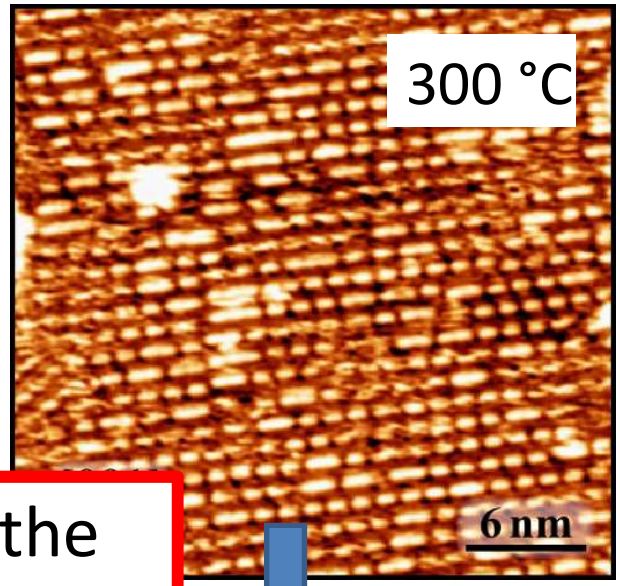




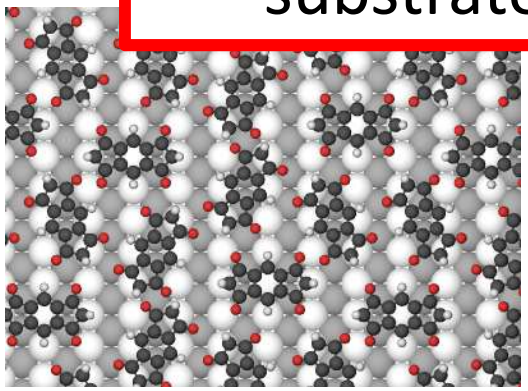
Similar to Ag(100) but with activation temperature ~ 100 - 150°C lower

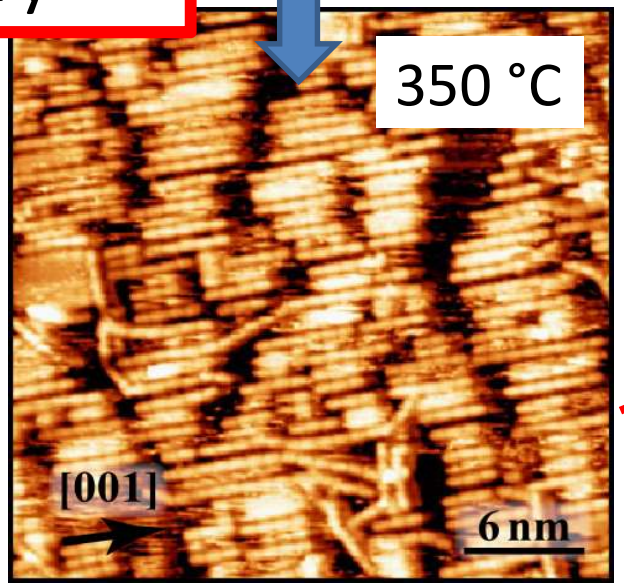
On-surface covalent coupling on Ag(110)

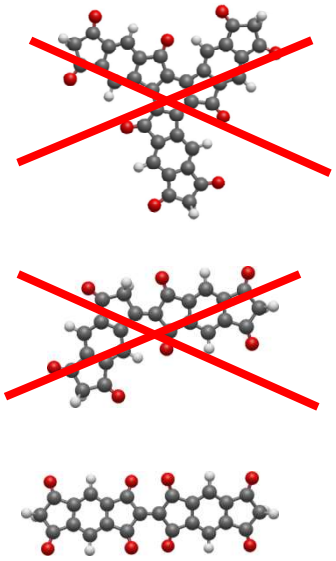




Selectivity driven by the substrate symmetry

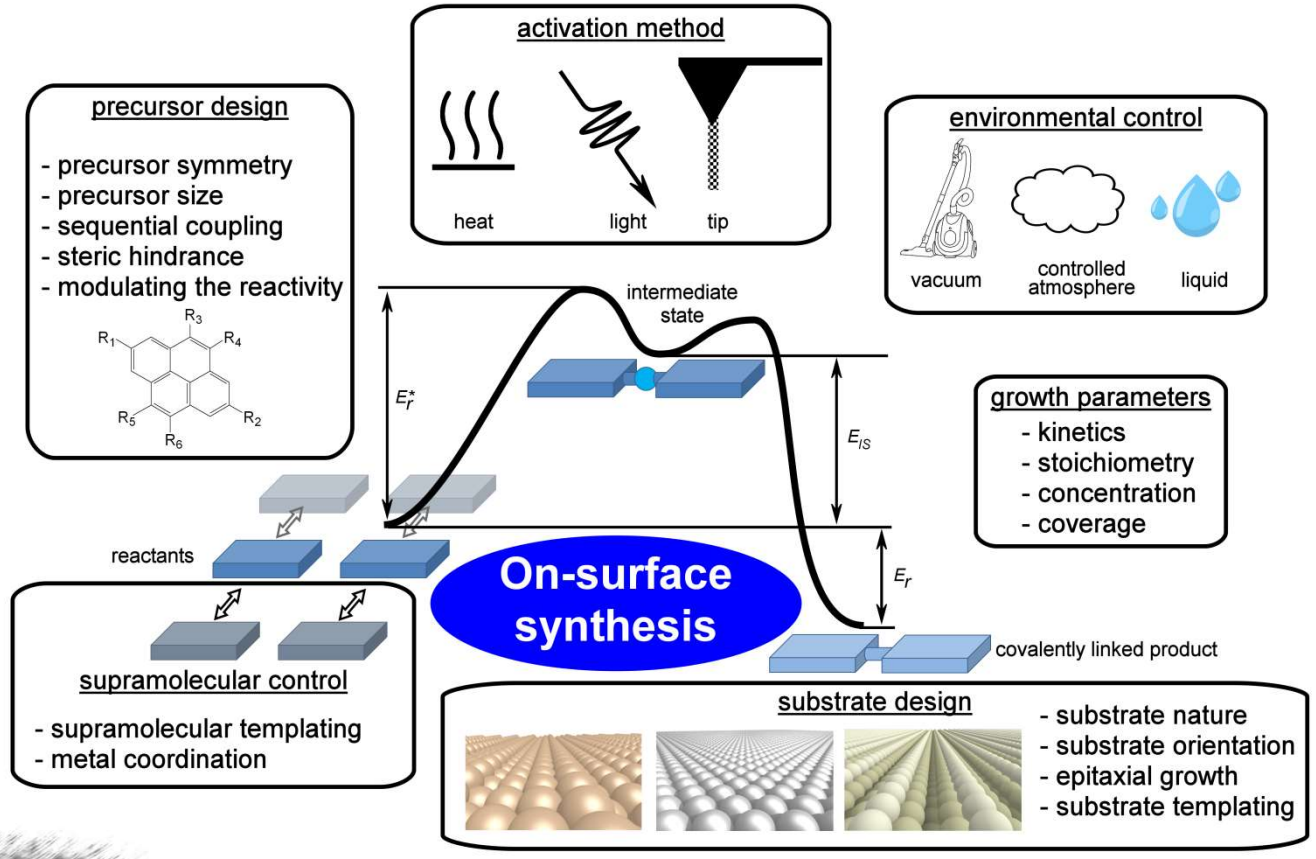


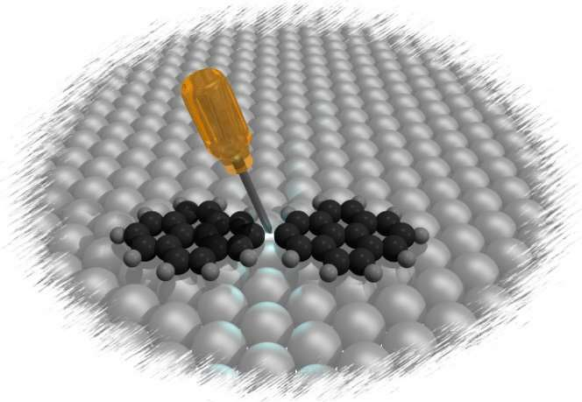




The temperature controls the advancement

2D polymers and *on-surface synthesis*

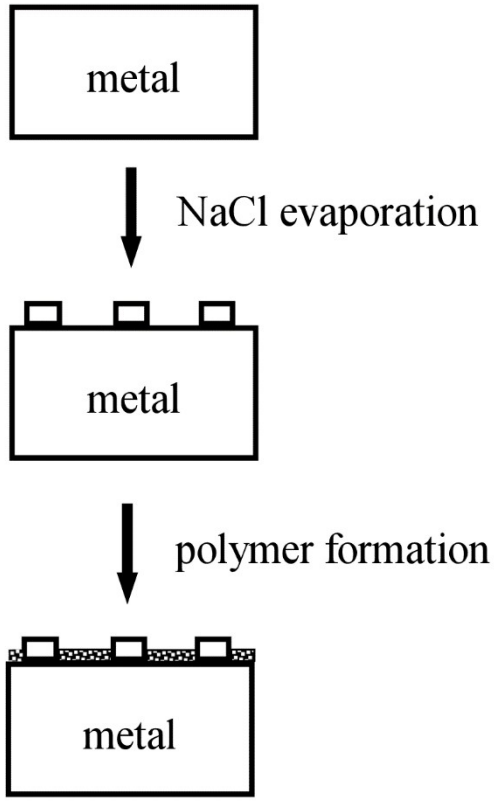




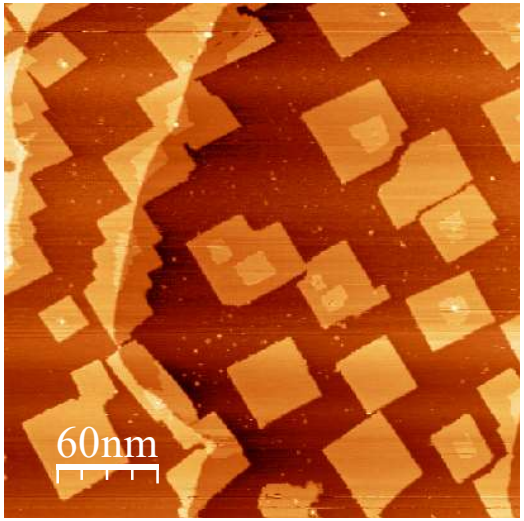
Advanced strategies

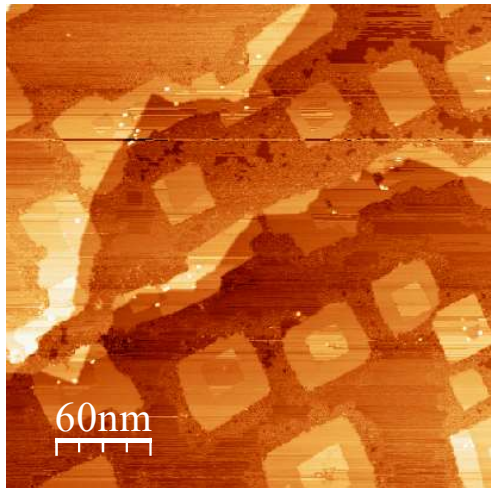
Clair & de Oteyza, *Chem. Rev.* **119**, 4717 (2019)

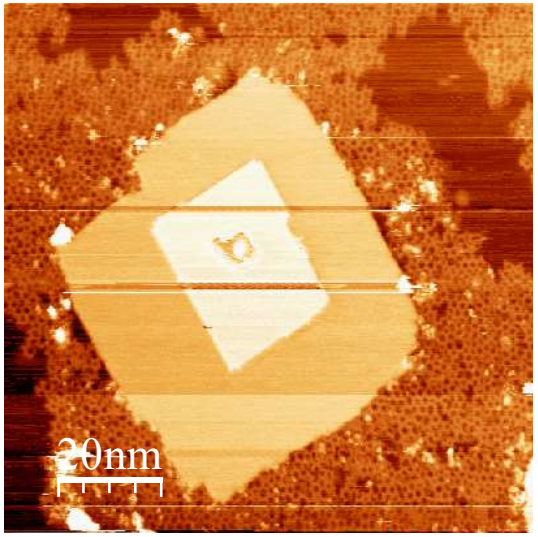
Surface nanopatterning



Ag(100)

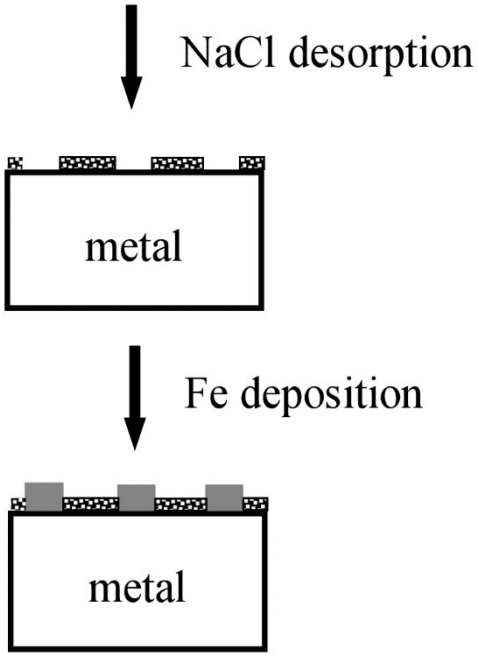


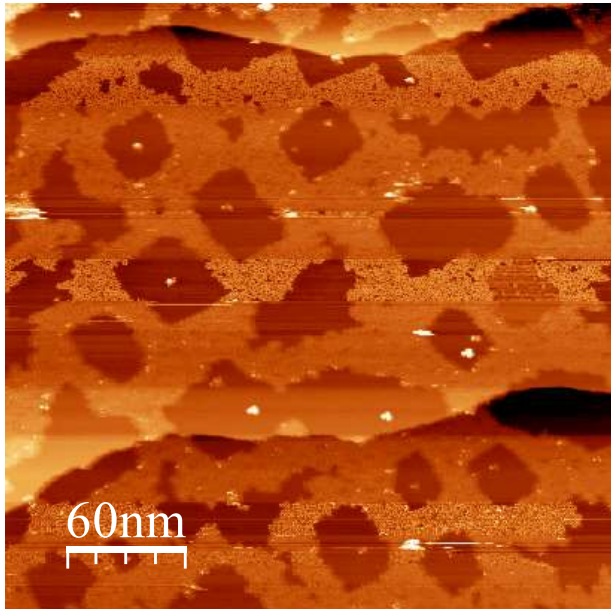


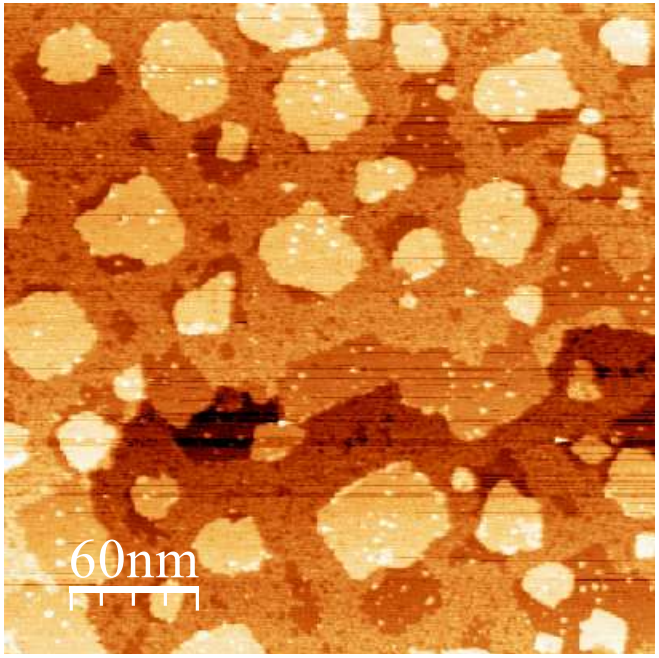


Clair, *Adv. Mater.* **24**, 1252 (2012)

Surface nanopatterning

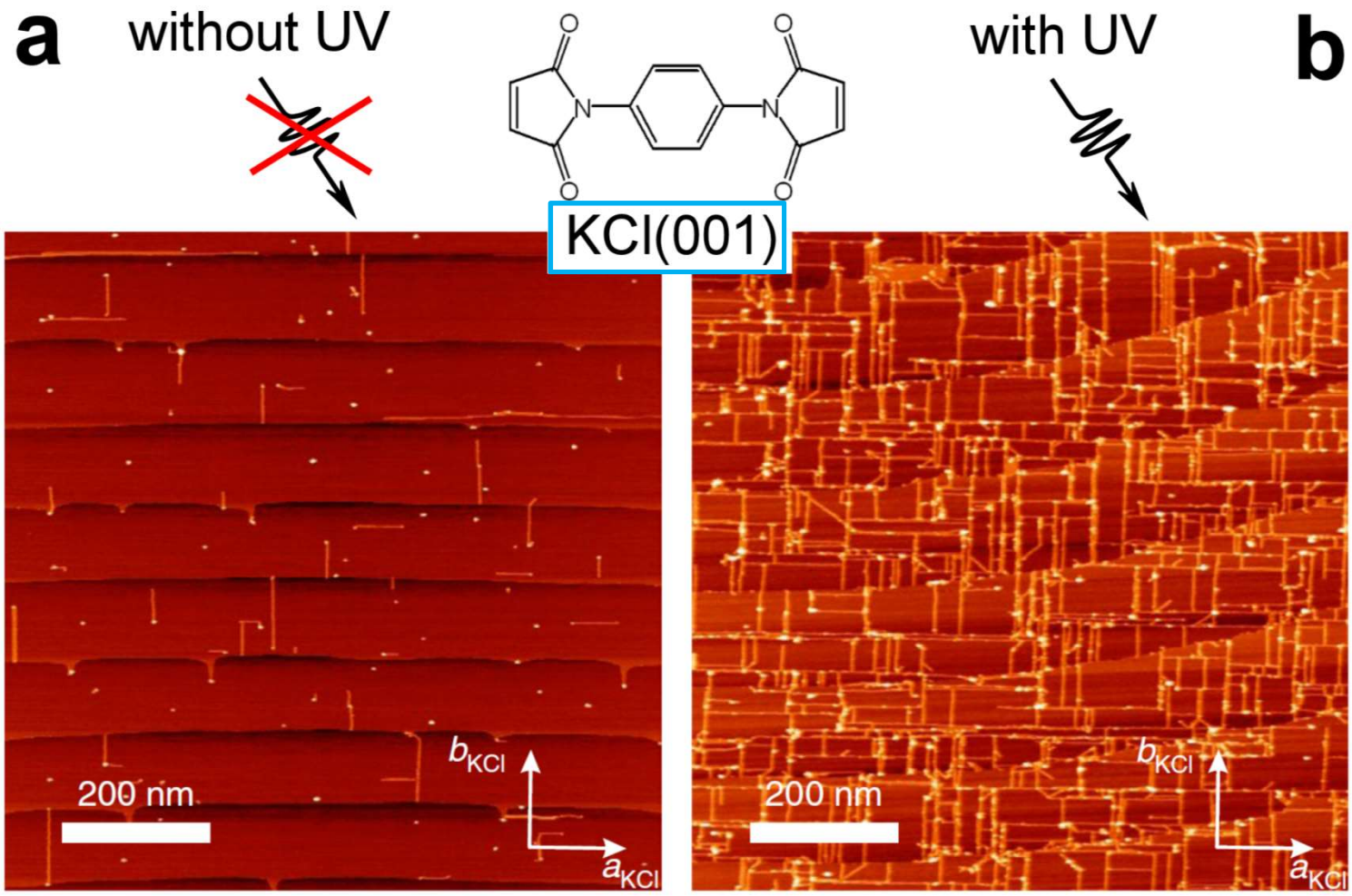






Clair, *Adv. Mater.* **24**, 1252 (2012)

On-surface synthesis on insulating substrates



Para, *Nat. Chem.* **10**, 1112 (2018)

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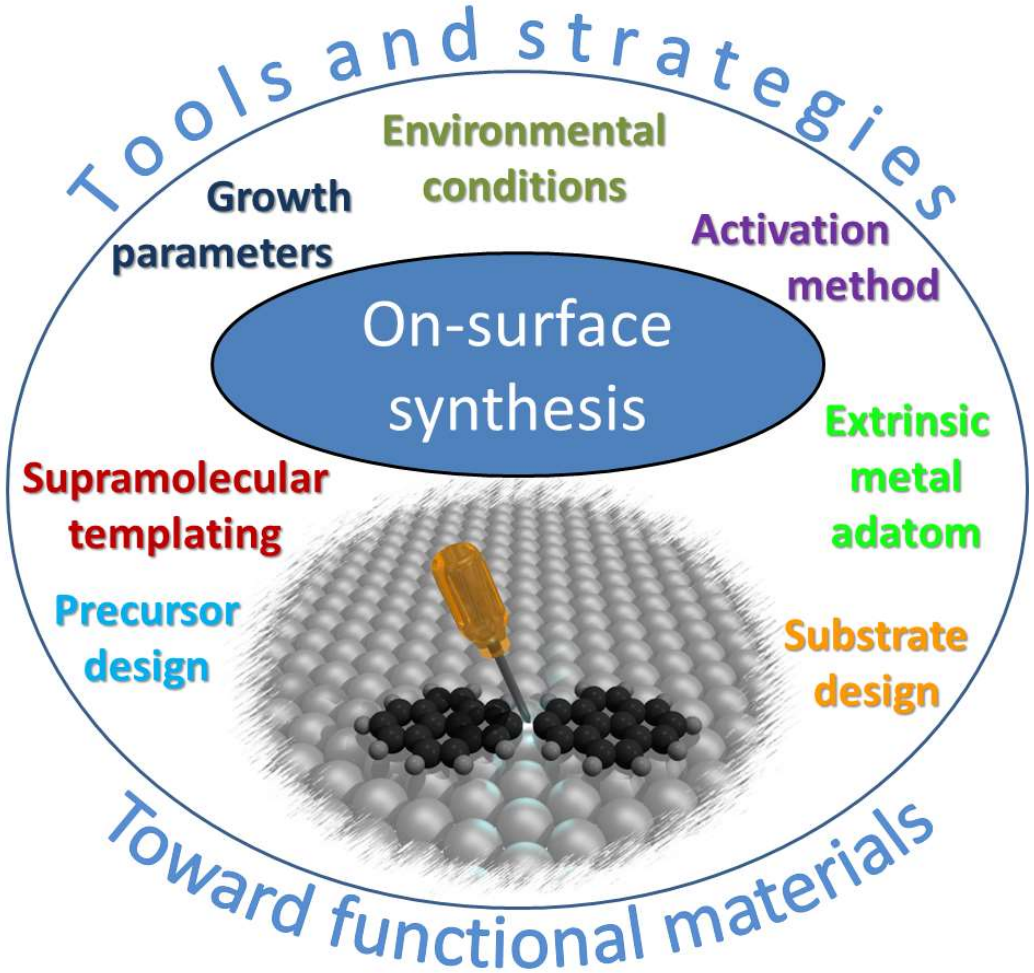
Kawtar Mouhat

Eric Salomon
Thierry Angot

Jaehoon Jung
Jihun Oh

Dimas de Oteyza

Controlling a Chemical Coupling Reaction on a Surface: Tools and Strategies for On-Surface Synthesis



Clair & de Oteyza, *Chemical Reviews* **119**, 4717 (2019)