Adatom-mediated chemical conversions and dynamic heterogeneity at surfaces

- from catalysis to 2D-materials -

JV Barth – Physics Department E20, TUM
www.e20.ph.tum.de

Technical University of Munich

TUM Locations in Bavaria

- **Science and Study Center** since june 2016 in a restaurated monastery

TUM - Selected Nobel Laureates

- Heinrich O. **Wieland**
  1927, Chemistry

- Hans **Fischer**
  1930, Chemistry

- Rudolf L. **Mößbauer**
  1961, Physics

- Ernst Otto **Fischer**
  1973, Chemistry

- Klaus **von Klitzing**
  1985, Physics

- Robert **Huber**
  1988, Chemistry

Campus Garching

MERCI - THANKS – DANKE - GRACIAS

Synthesis
Synchrotron
Modeling

Mario Ruben, Svetlana Klyatskaya & Co Davide Bonifazi et al.
Pietro Gambardella / Sebastian Stepanow - Alberto Morgante - Christoph Wöll
Ari P. Seitsonen Marie-Laure Bocquet Andres Arnau F. Javier Garcia de Abajo

Munich-Centre for Advanced Photonics

EUROPEAN SCIENCE FOUNDATION
SETTING SCIENCE AGENDAS FOR EUROPE

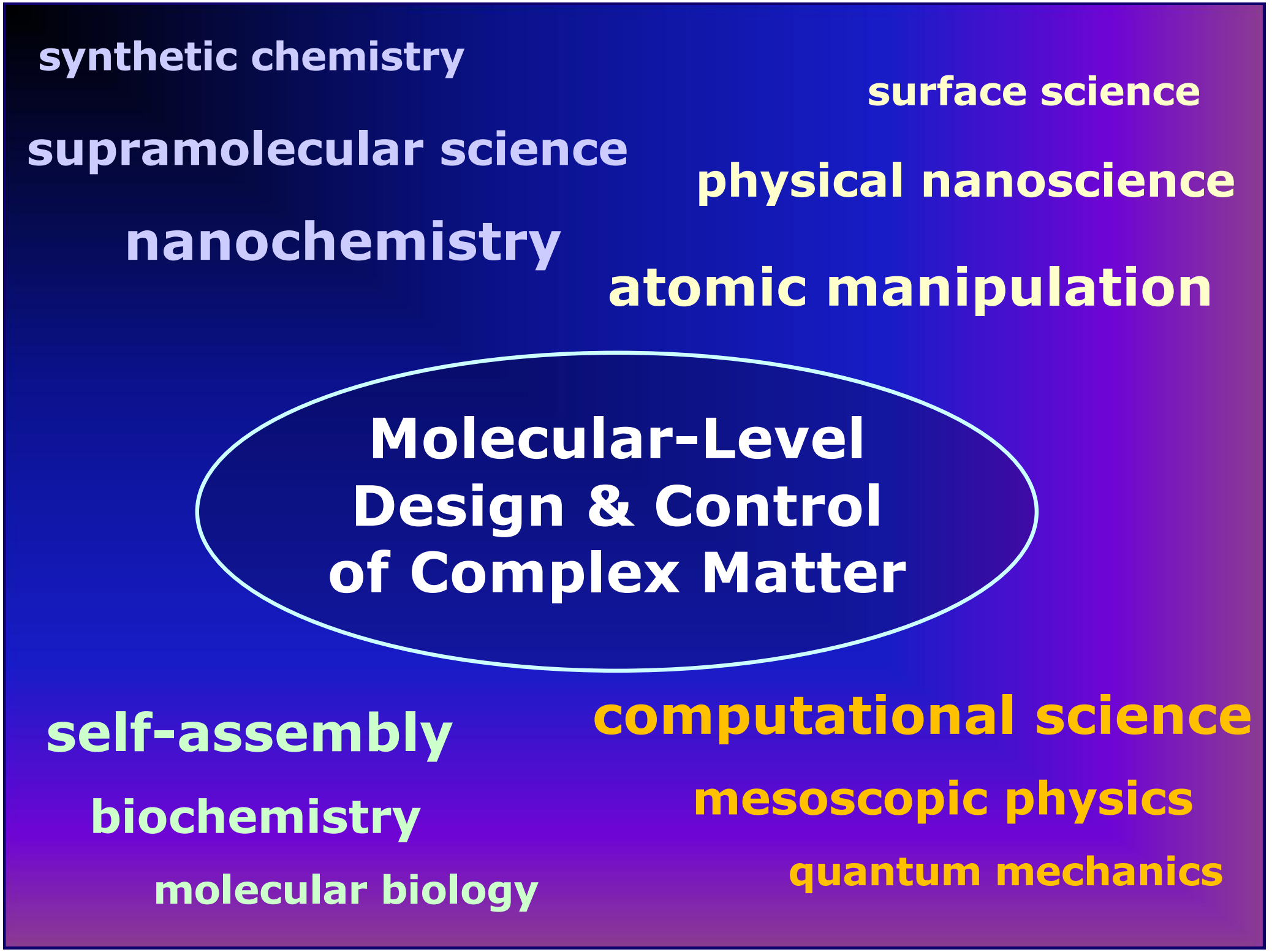
DFG Deutsche Forschungsgemeinschaft

erc

FNSNF
SCHWEIZERISCHER NATIONALFONDS ZUR FÖRDERUNG DER WISSENSCHAFTLICHEN FORSCHUNG
FONDS NATIONAL SUISSE DE LA RECHERCHE SCIENTIFIQUE
SWISS NATIONAL SCIENCE FOUNDATION
FONDO NAZIONALE SVIZZERO PER LA RICERCA SCIENTIFICA

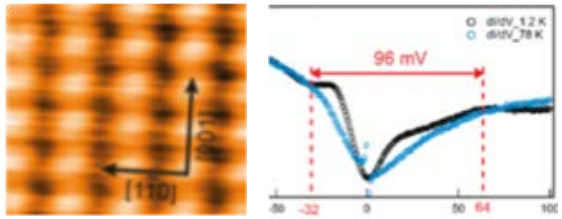
Canada Foundation for Innovation
Fondation canadienne pour l'innovation

CRSNG NSERC

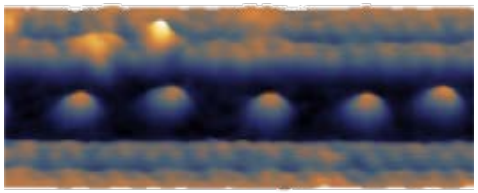

synthetic chemistry
supramolecular science
nanochemistry
surface science
physical nanoscience
atomic manipulation
Molecular-Level
Design & Control
of Complex Matter
self-assembly
biochemistry
molecular biology
computational science
mesoscopic physics
quantum mechanics

Scope of Research Activities

www.e20.ph.tum.de



FeSi(110) band gap at 1.2 K



Fe atom alignment

Nanochemistry

surface-anchored molecules
complex architectures
chemical conversions

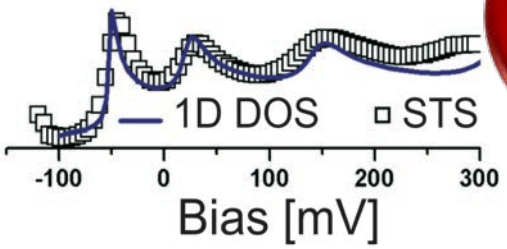
Quantum Materials

high-resolution STS
physical properties
quantum state engineering

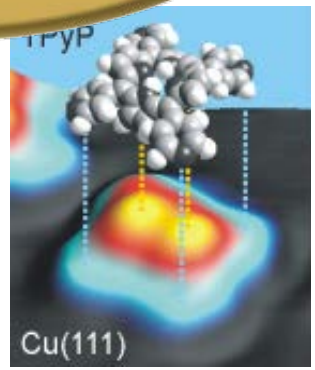
Manipulation of Atoms and Molecules

flexible molecular species
quantum corrals

Nanoscale Control of Matter at Interfaces



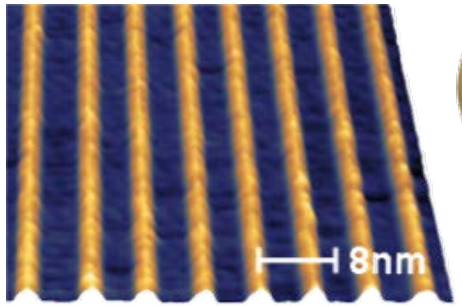
resonator states



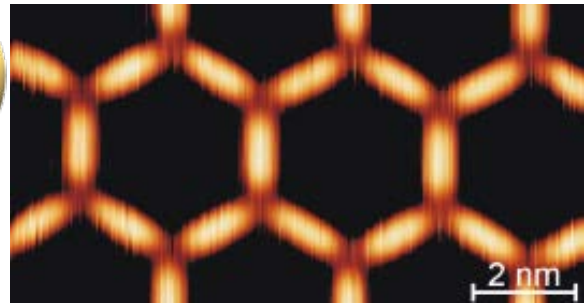
saddle-shaped porphyrin

Supramolecular Architecture

metal-ligand interactions,
hierarchic assembly,
dynamic phenomena



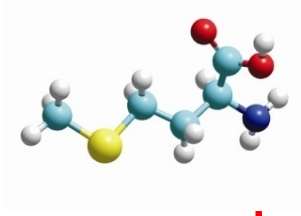
1D biomolecular grating



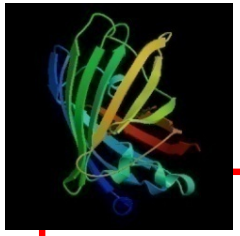
metal-organic nanomesh

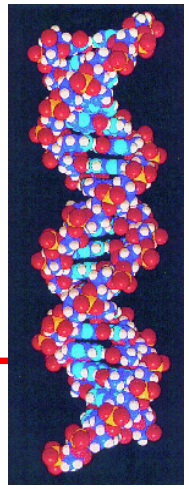
Length Scales & Organization of Matter

amino acid
~ 1nm

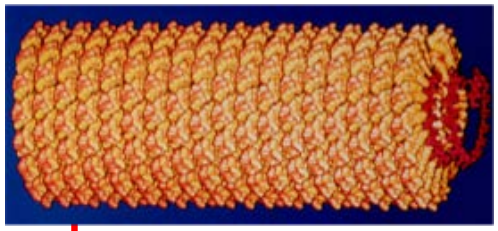


DNA
proteins
nm

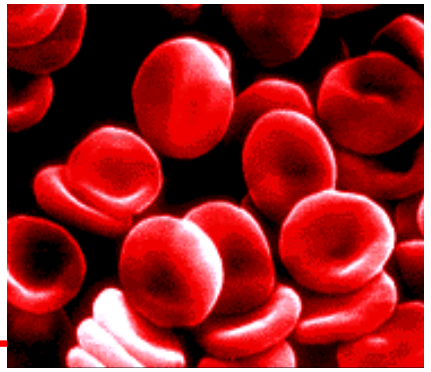




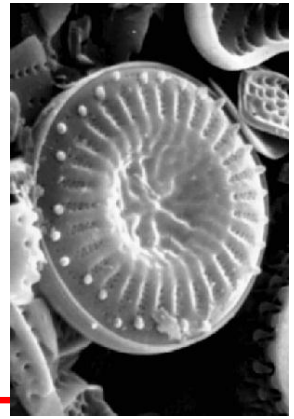
TMV virion
~ 300 nm long

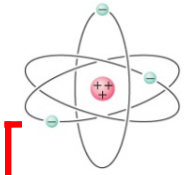


red blood cell
~5 μm (SEM)



diatom
30 μm

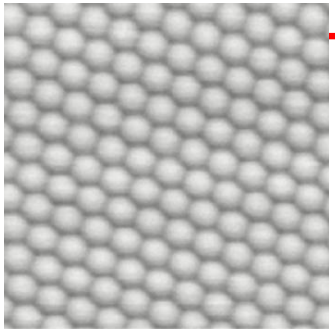




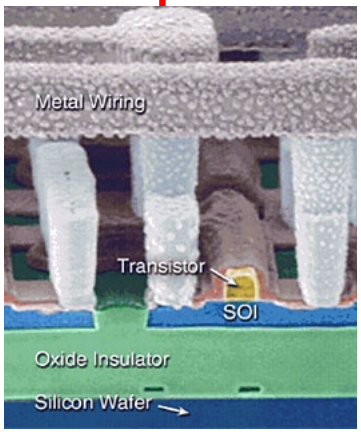
atoms

m

10^{-10} 10^{-9} 10^{-8} 10^{-7} 10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-2}

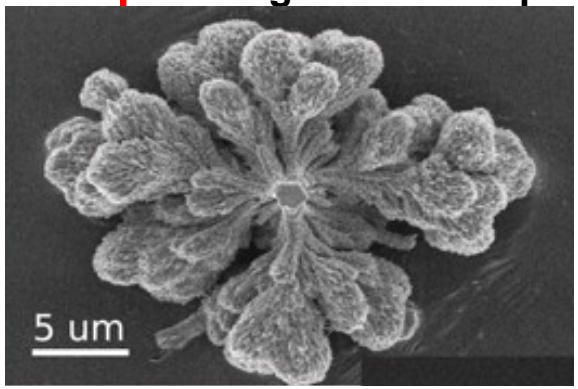


atomic
resolution
STM image

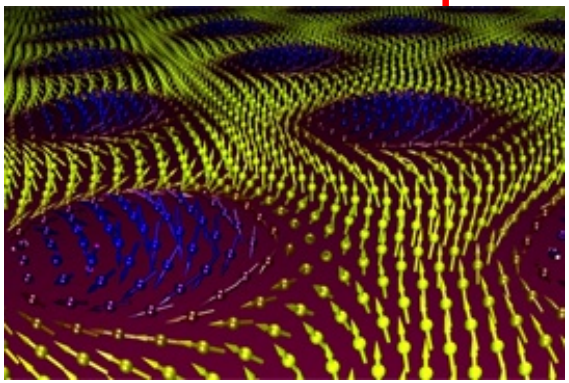


SOI transistor
width 0.12μm

self-organized growth
of inorganic biomorph

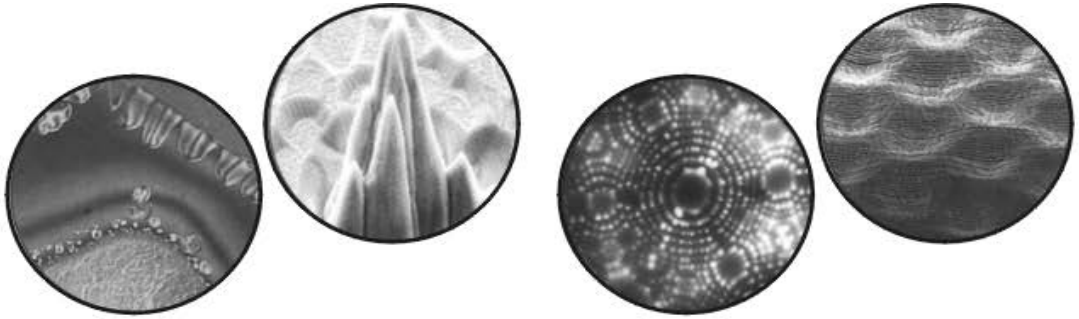


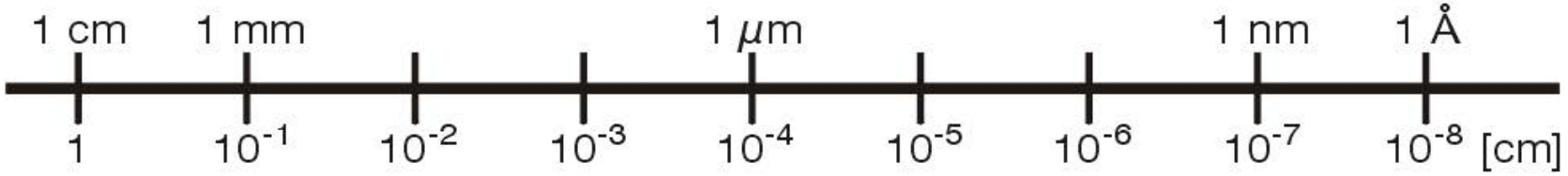
crystalline structure -
rough diamond with
octahedral shape



skyrmion spin
texture in MnSi
chiral magnet

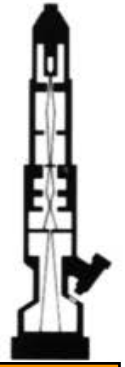
Imaging at the Atomic Scale



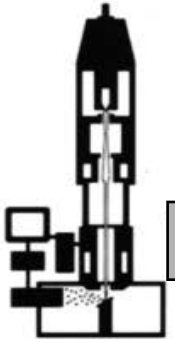


Human Eye

Light Microscope

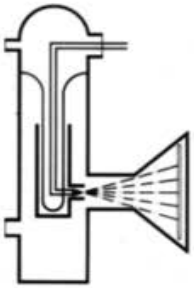


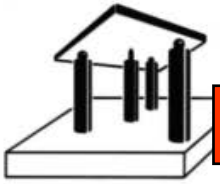
Transmission Electron Microscope (TEM)



Scanning Electron Microscope (SEM)

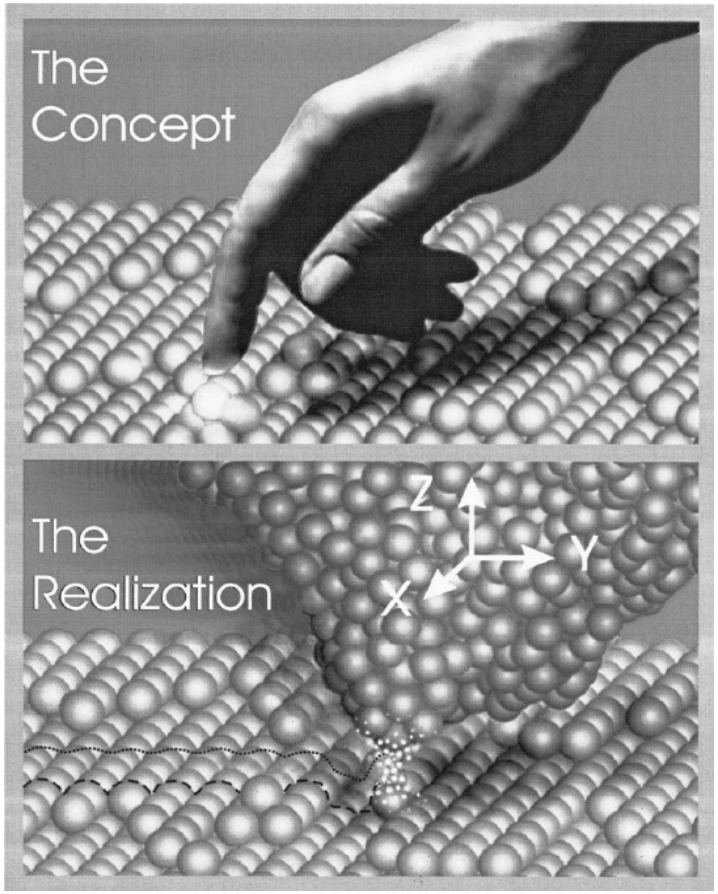
FIM



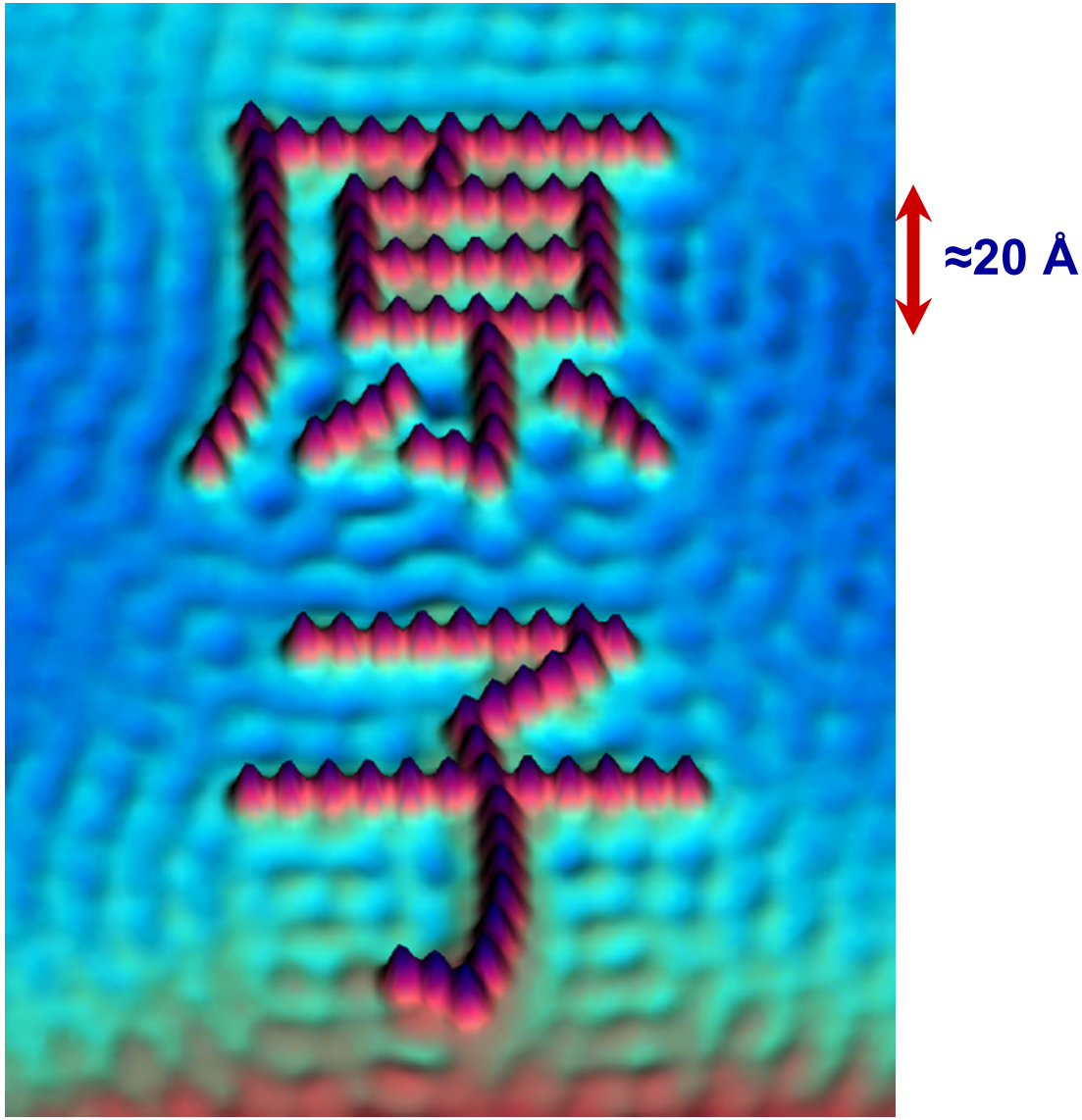


Scanning Probe Microscopy (SPM)

In Touch with Single Atoms Using STM



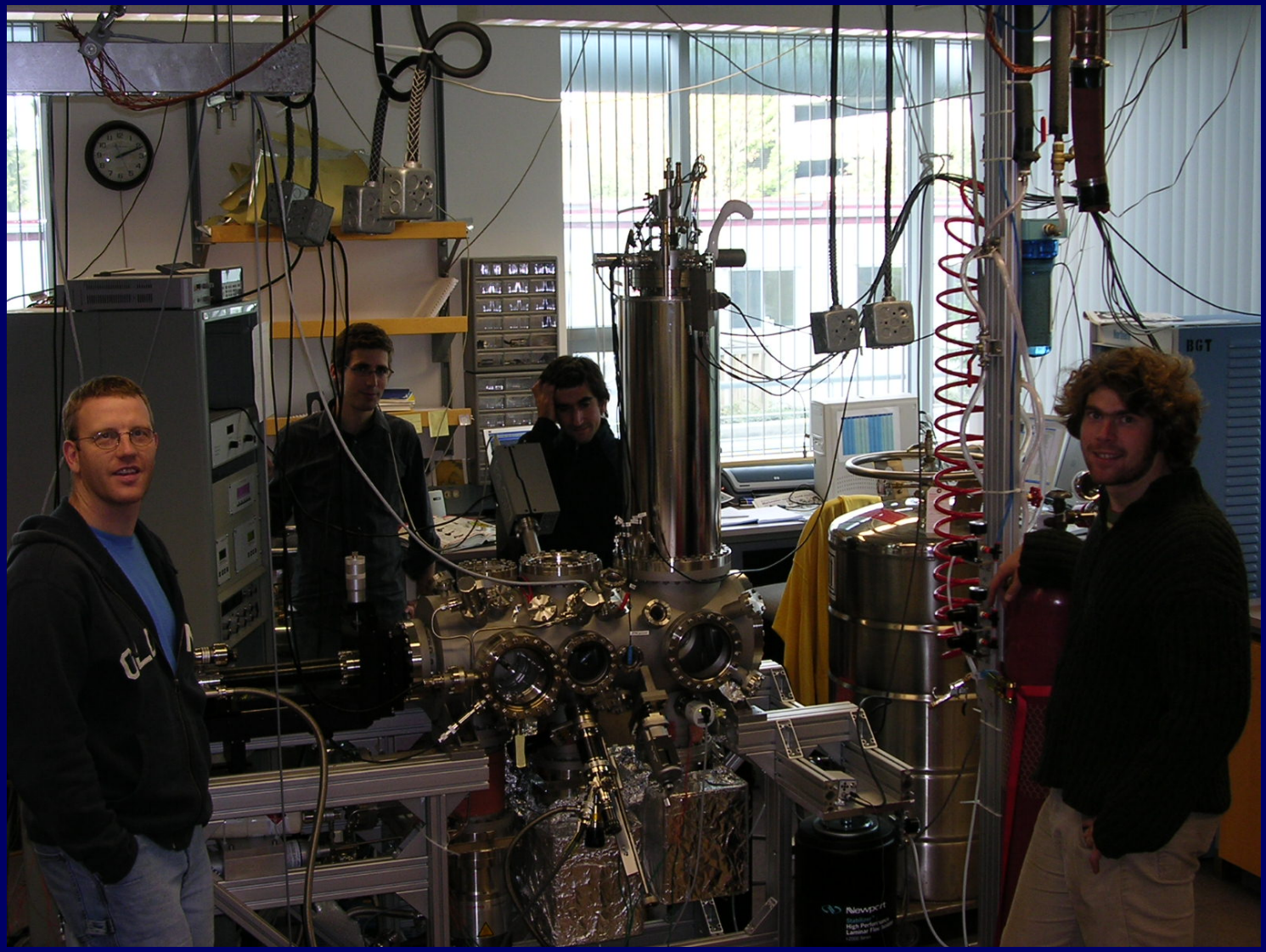
Rev. Mod. Phys. **71** (1999) S234



Don Eigler Lab (IBM Almaden); Nature 344 (1990) 524

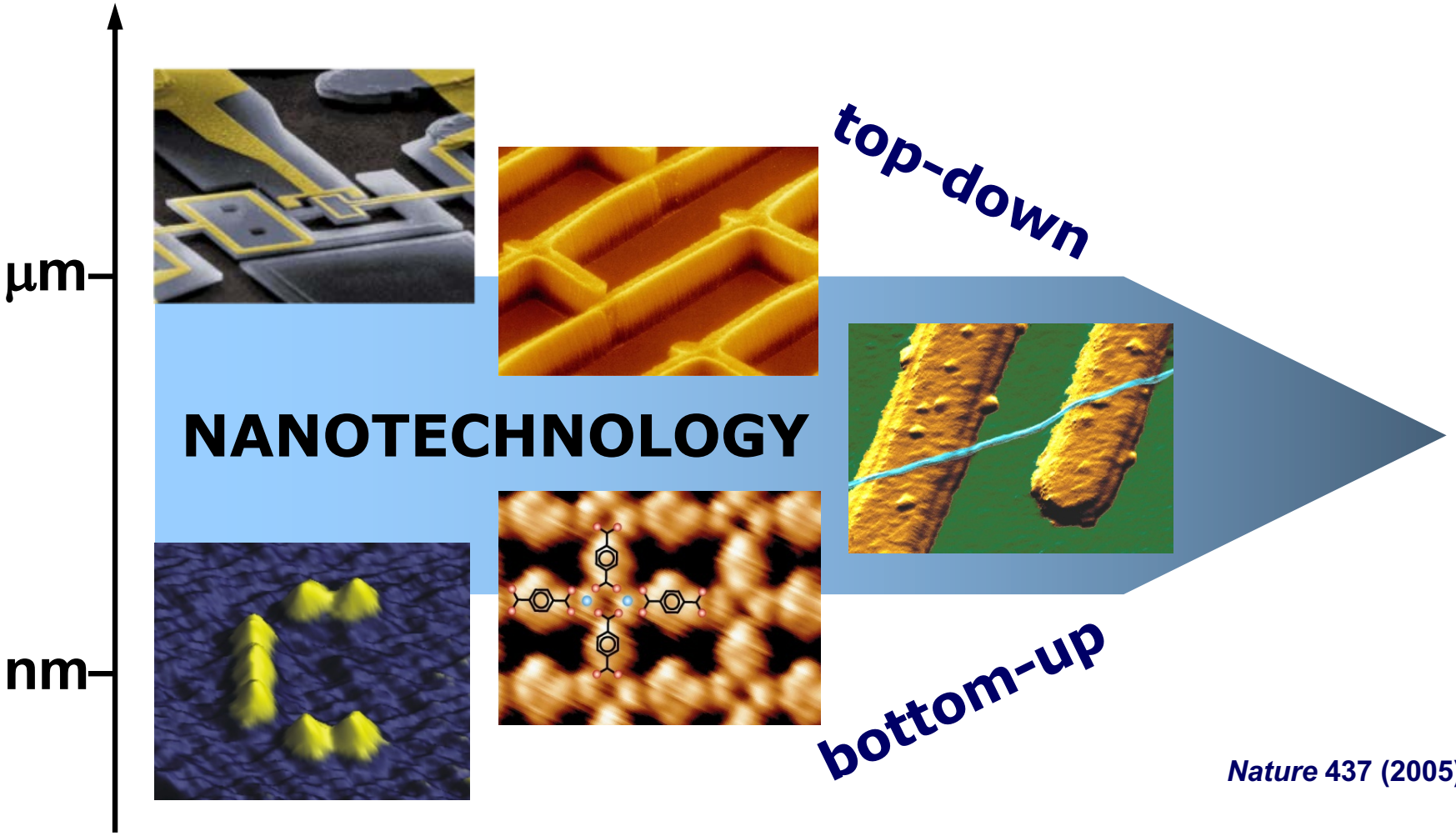
Positioning of Fe atoms on Cu(111)

Low-Temperature STM



- ultra-high vacuum setup, p < 1(-10) Torr, T = 5 - 400 K
  ⇒ atomistic studies, manipulation, spectroscopy

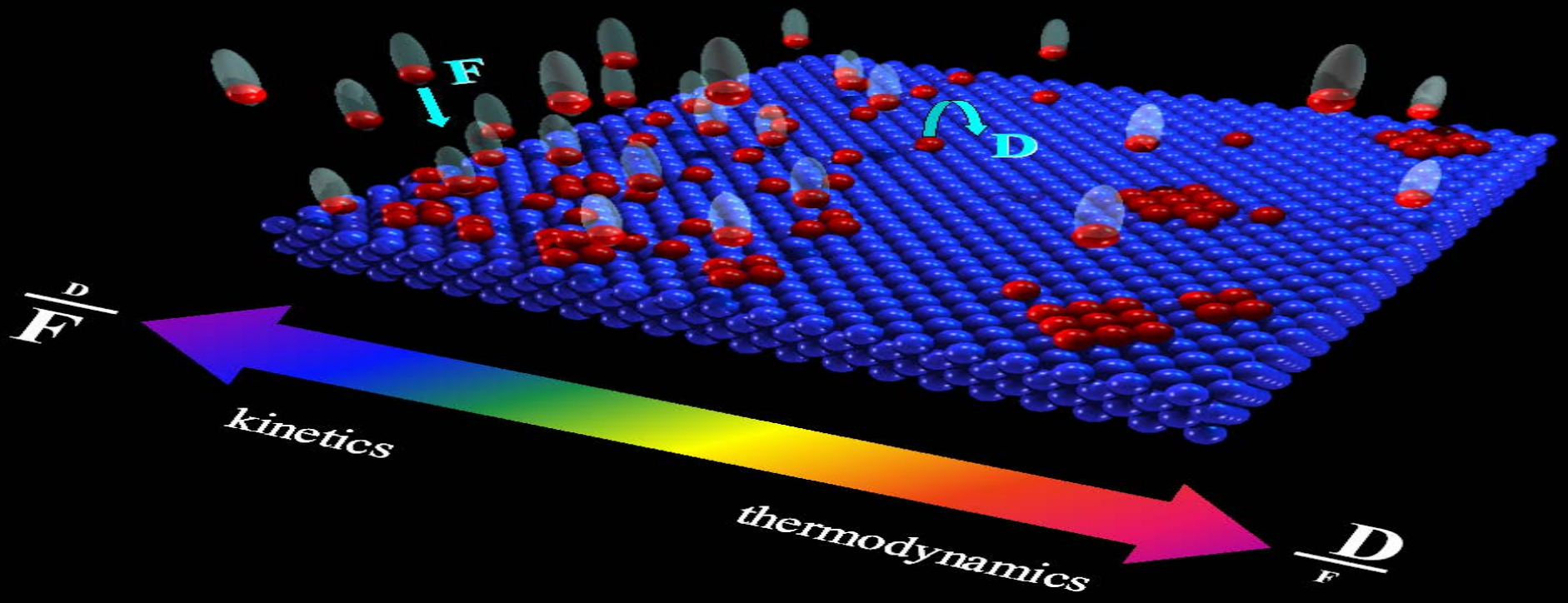
Approaches to Nanofabrication at Interfaces



Nature 437 (2005) 671

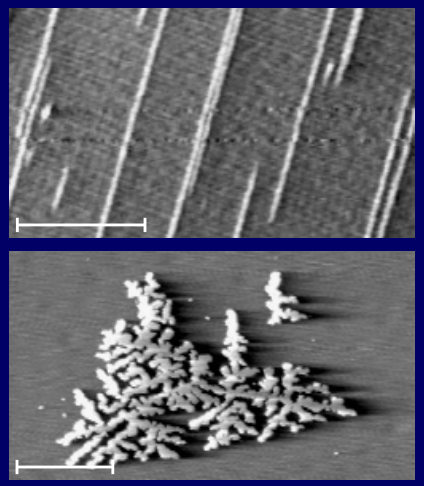
- 'top-down' lithography & printing → mature serial processes
  → limited in sub-x nm range
- 'bottom-up'/self-assembly → molecular-level feature definition
  → need of fundamental research
  → new materials & functional systems

Surfaces as Platforms for Bottom-Up Constructions

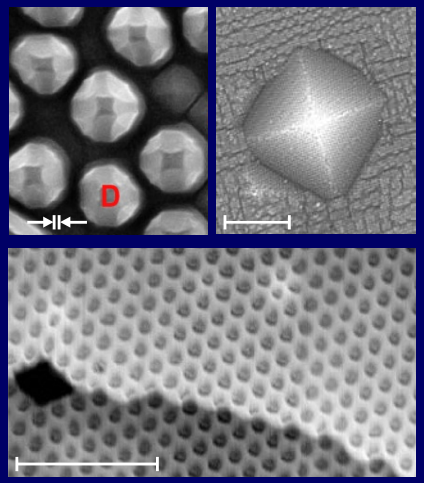


Nature 437 (2005) 671

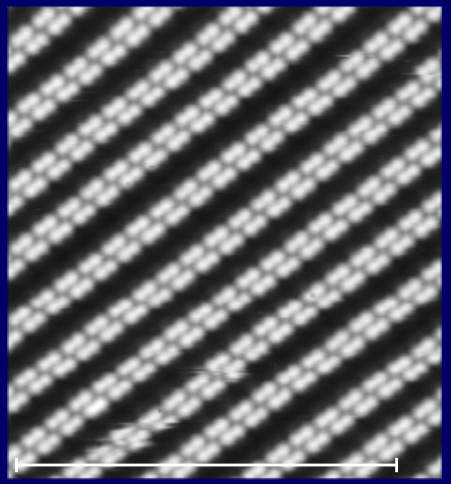
Scale 20 nm



Metal nanostructures in diffusion limited regime

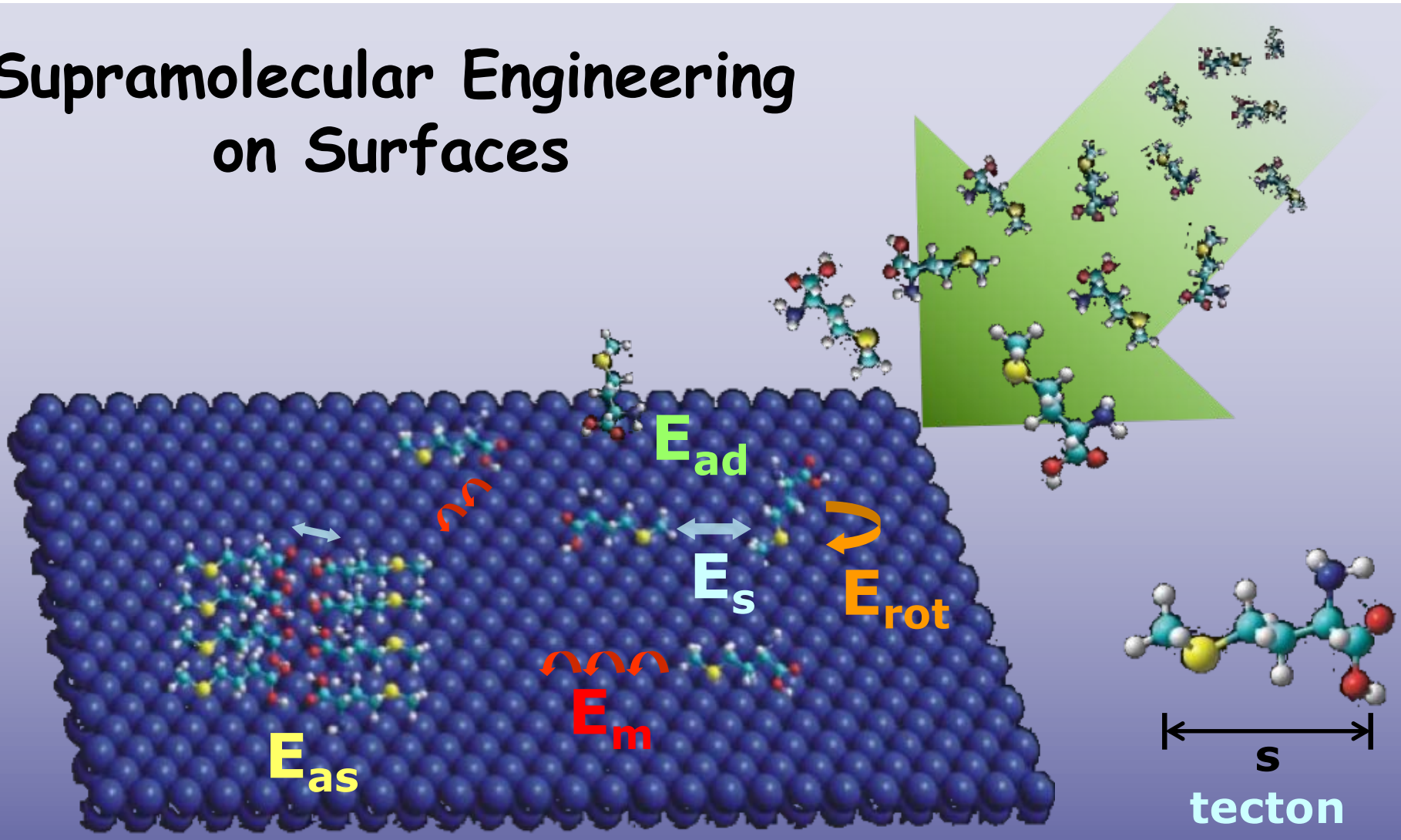


Mesoscopic arrangements via strain relaxation



Molecular self-assembly near equilibrium

Supramolecular Engineering on Surfaces



balanced interactions

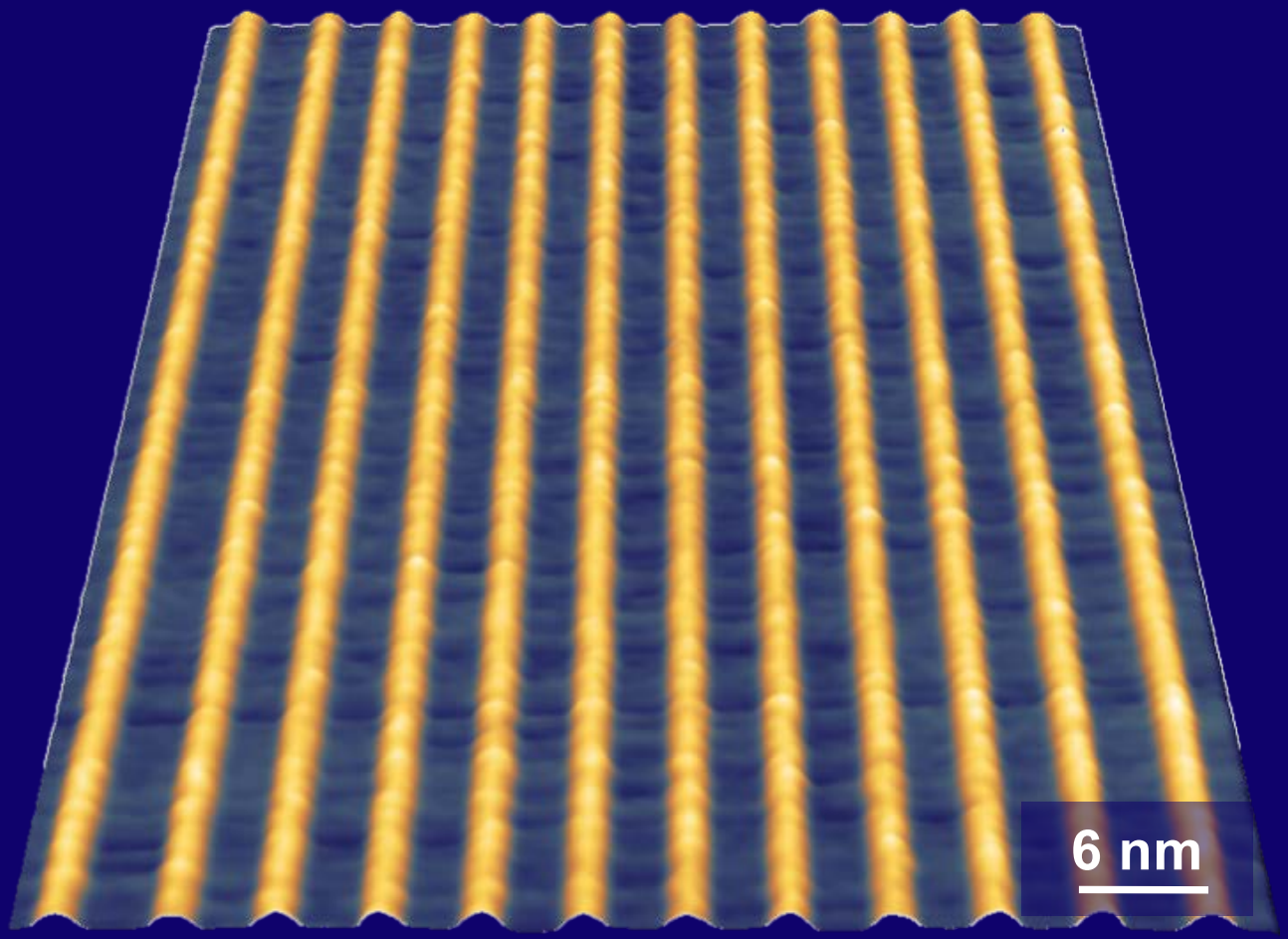
substrate
atomic structure
chemical nature
nano-templates

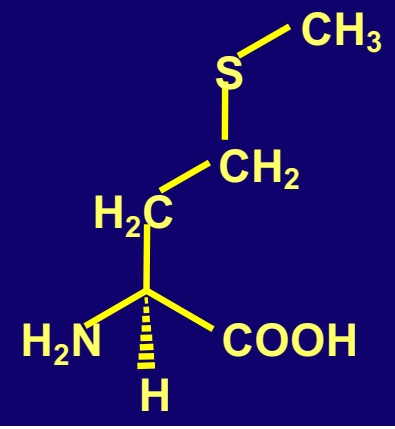
self-assembled architectures

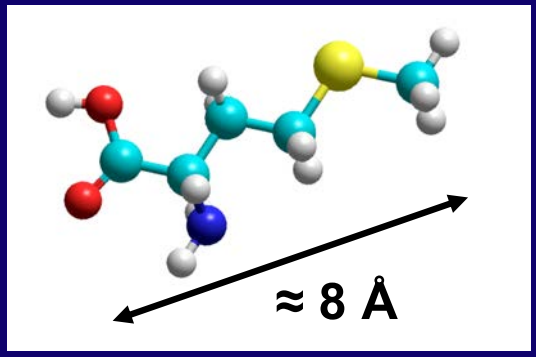
tectons
shape & symmetry
functional groups
concentration

Annu. Rev. Phys. Chem. **58** (2007) 375

Methionine Nanograting on Ag(111)







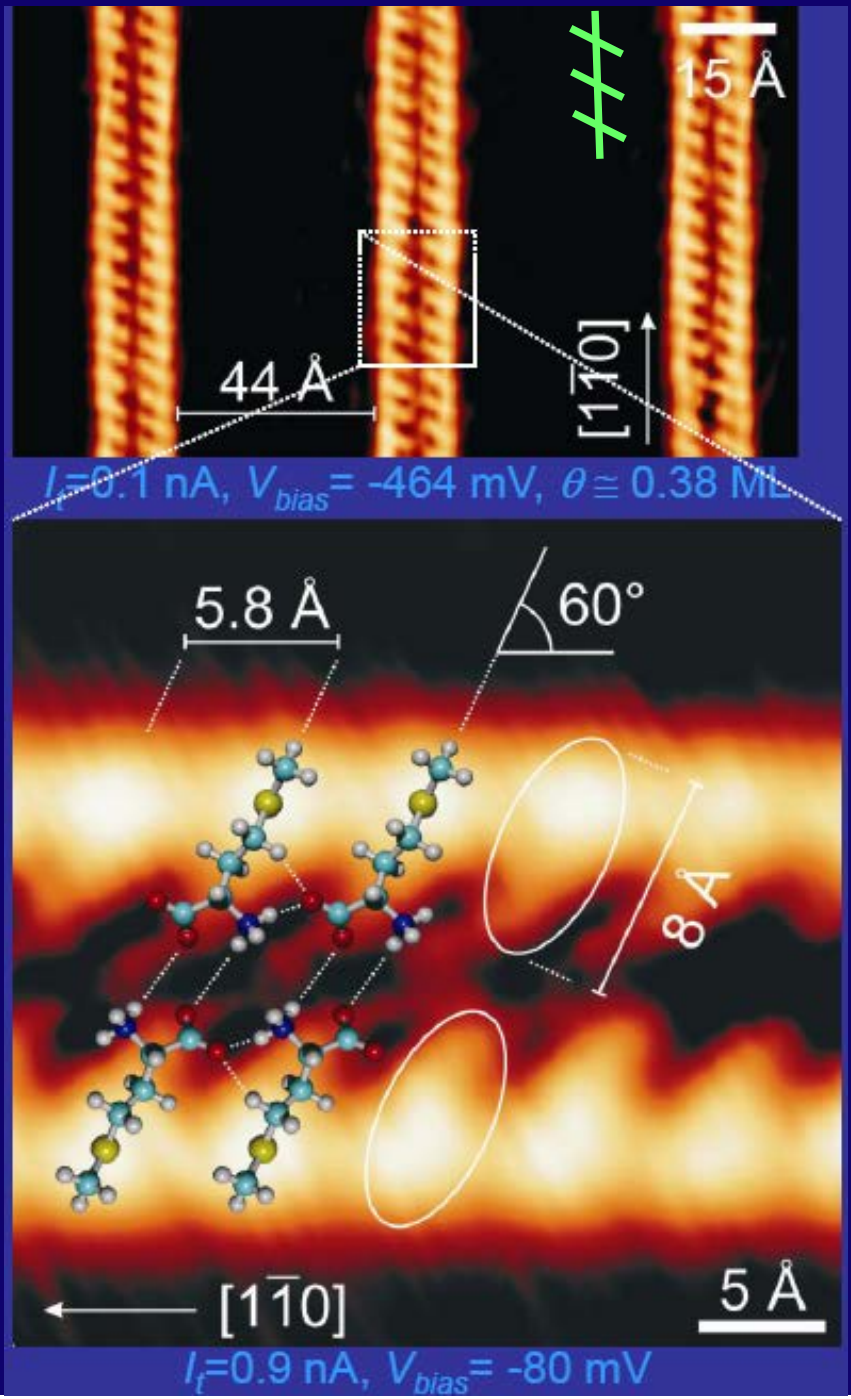
L-methionine

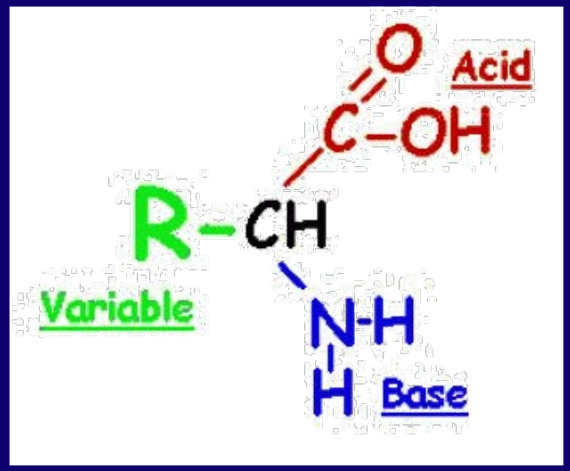
T_{as} = 320 K; T_{STM} = 18 K

- 1D H-bonded self-assembly, mesoscopic order at µm scale

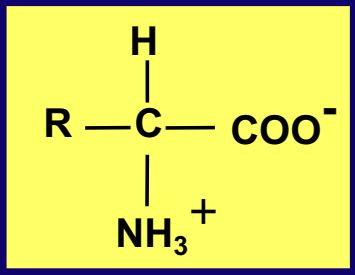
PNAS **104** (2007) 5279

Chirality & Nature of L-Methionine Assembly

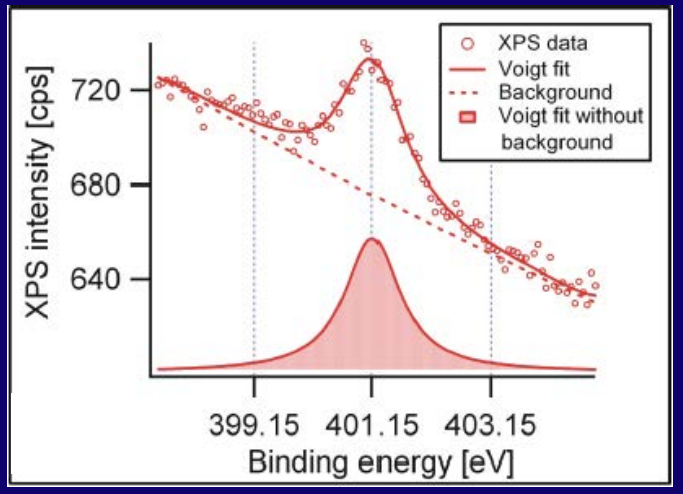




- acidic
- anionic – cationic
- zwitterion



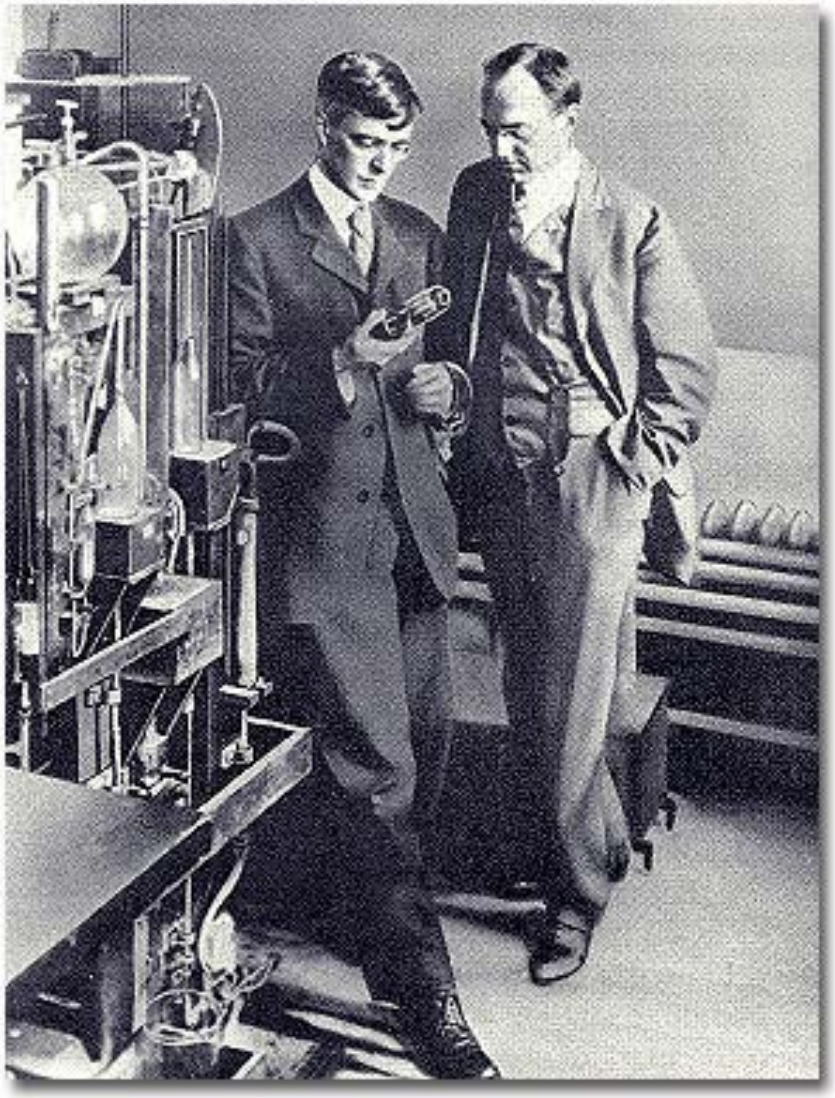
zwitterionic state in amino acid crystals



XPS of O and N 1s → zwitterions

- molecular chaining reflects zwitterionic coupling scheme

PNAS 104 (2007) 5279



Irving Langmuir

Irving Langmuir
1881 – 1957
Nobel Prize 1932

The Langmuir Checker-Board

The forces exerted by the underlying solid on adsorbed atoms or molecules tend to hold the molecules in definite positions fixed by the lattice of the solid.

The solid surface is thus to be looked upon as a type of checker-board containing definite numbers and arrangements of elementary spaces, each of which is capable of holding an adsorbed molecule.

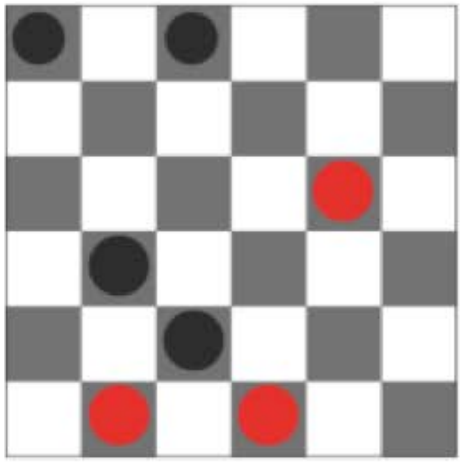
I Langmuir
NL Lecture 1932

G Ertl
NL Lecture 2007

cf. Angew. Chem. Int. Ed., 47, 3524 (2008)

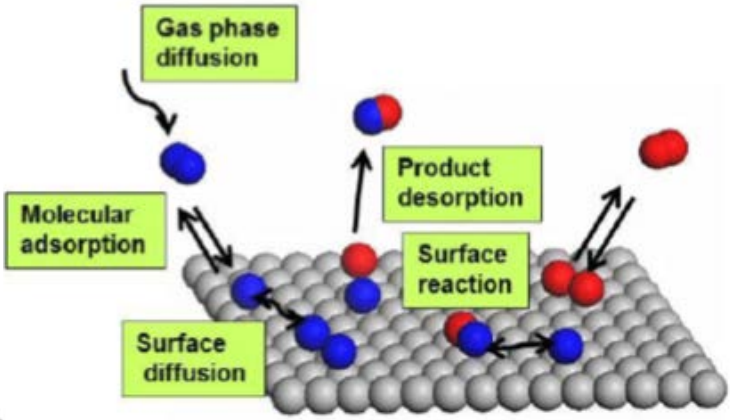
Active Sites in Heterogeneous Catalysis

Langmuir school of thought



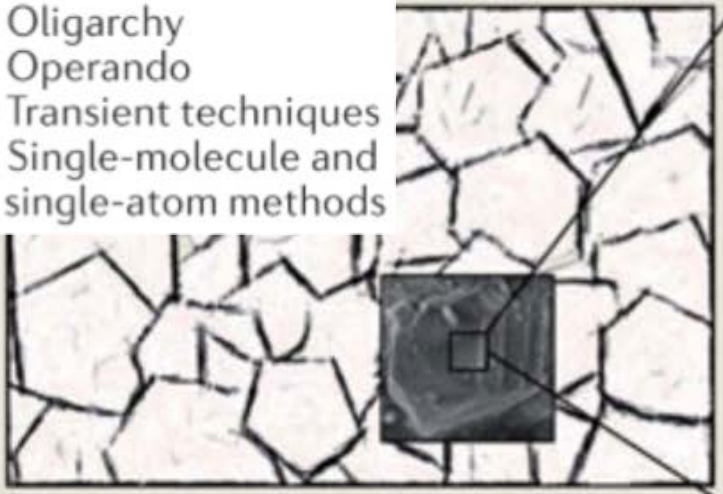
- Polycracy
- Surface science
- Ultrahigh vacuum
- Model surfaces as catalysts

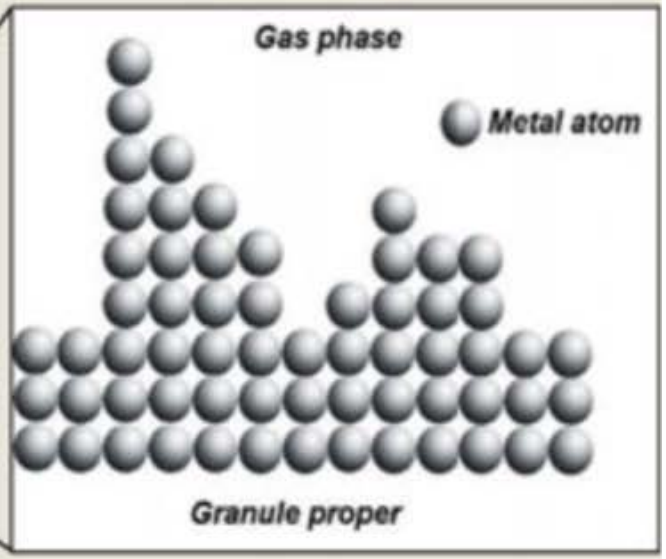
∑ Elementary steps ↔ Catalytic cycle



Taylor school of thought

- Oligarchy
- Operando
- Transient techniques
- Single-molecule and single-atom methods





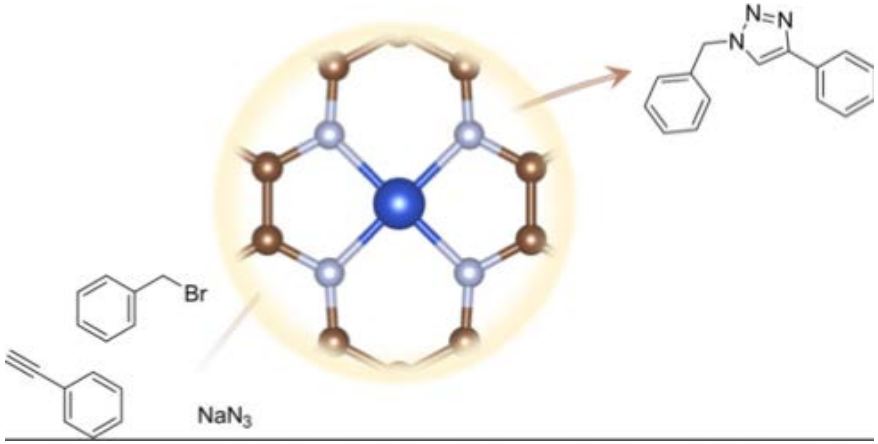
Hugh Taylor (1890-1974)

H. S. Taylor, Proc. R. Soc. London A 1925, 108

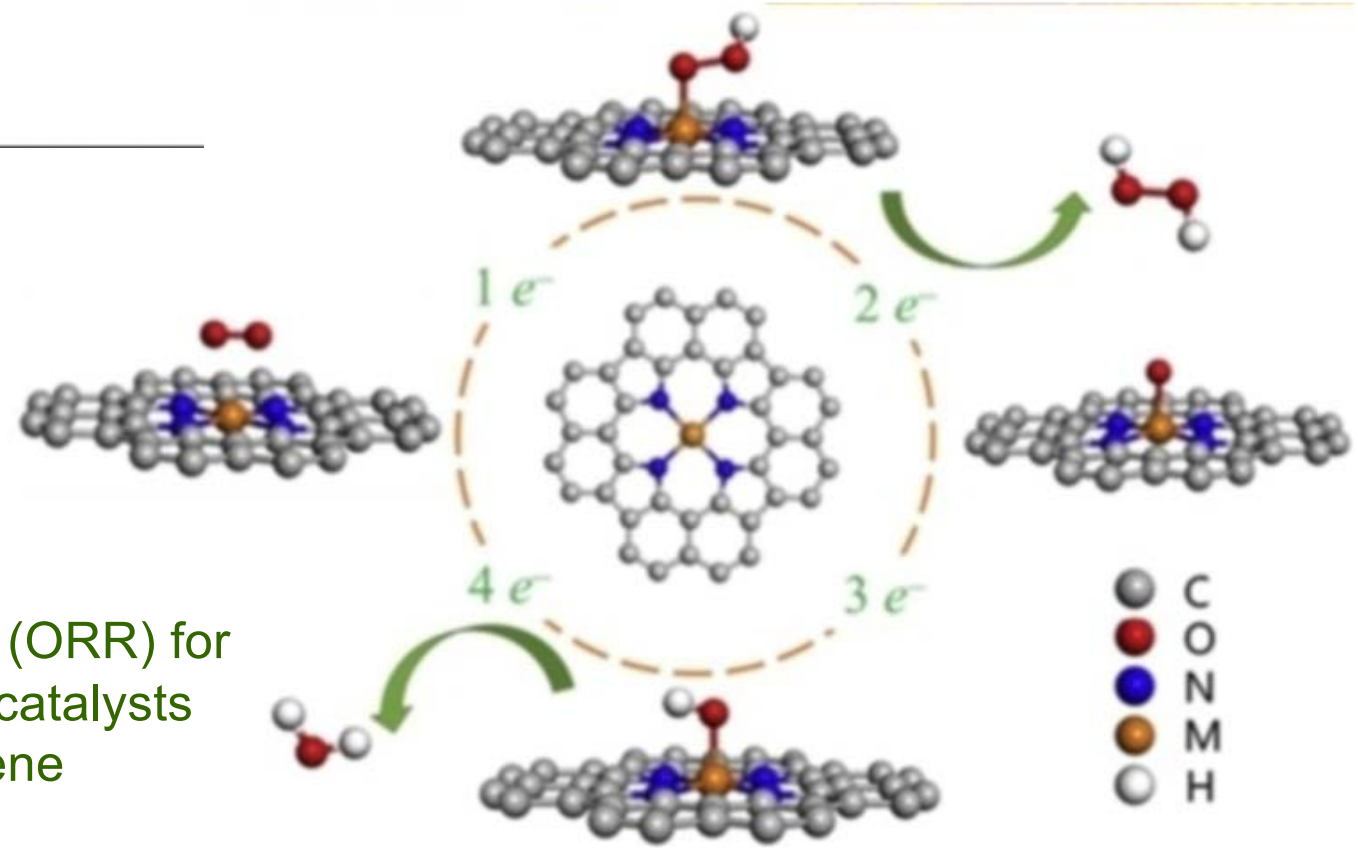
M. Piumetti: “A brief history of the science of catalysis - I “ | Chemistry Today 2014

Vogt & Weckhuysen: The concept of active site in heterogeneous catalysis | Nature Reviews Chemistry 6, 89 (2022)

Single Atom {Sites in Heterogeneous} **Catalysis**



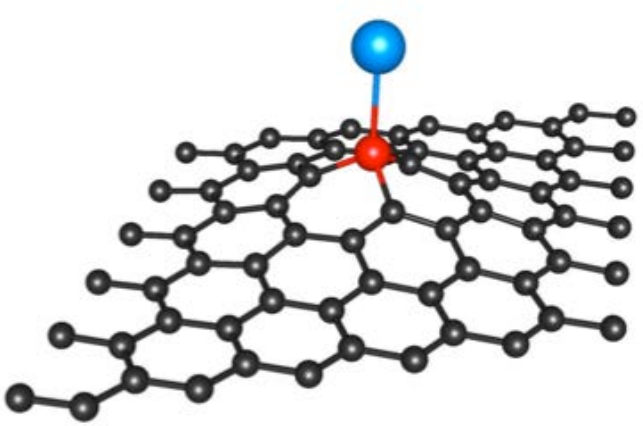
local coordination markedly affects catalytic activity

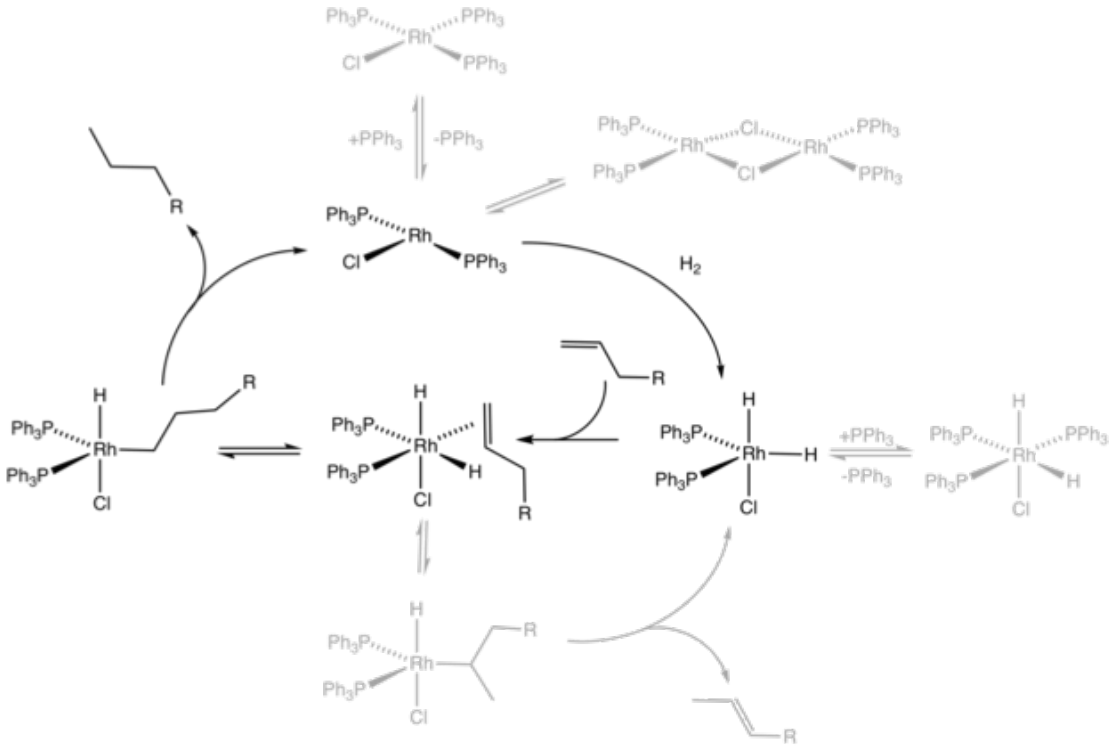


Oxygen Reduction Reaction (ORR) for transition metal single atom catalysts anchored in N-doped graphene

ACS Catal. 12 (2022) 2947 „*Azide-Alkyne Click Chemistry over a Heterogeneous Copper-Based Single-Atom Catalyst*“
ChemCatChem 2022, e202200611 „ *Single Atom Catalysts: What Matters Most, the Active Site or The Surrounding?* “
Chemistry - Methods 1 (2021) 278 “*Single Atom Catalysts: A Review of Characterization Methods*“

Single Atom Catalysis and Halpern's Tenet



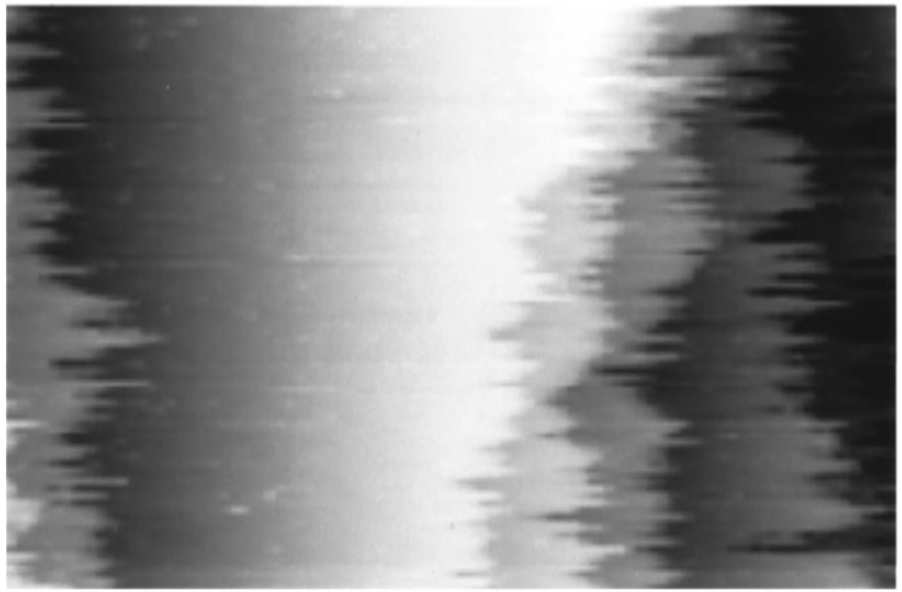


Jack Halpern (1925–2018)

"If you can identify a compound from a catalytic system, it is probably not the catalyst !"

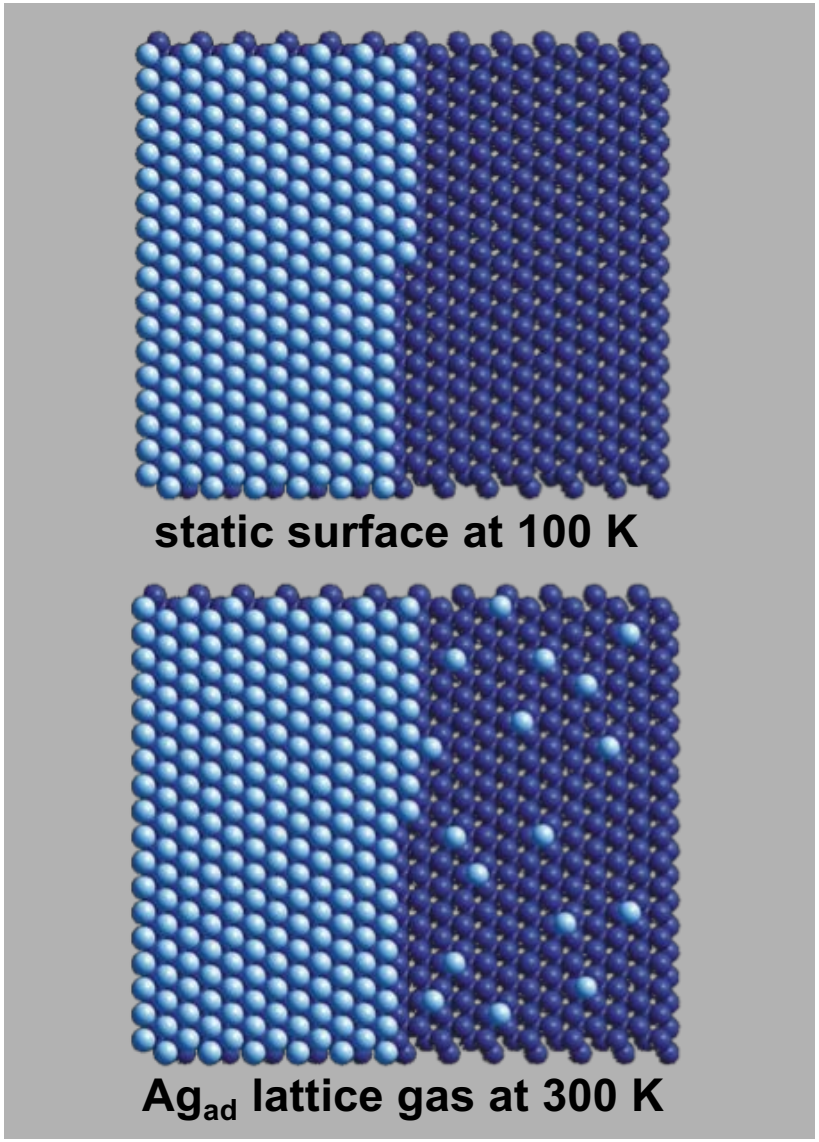
phys.org/news/2021-08-anchoring-atoms-catalysis „*Anchoring single atoms for catalysis*" | *ACS Nano (2021). 10.1021/acsnano.1c03535*
PNAS | 2018 | vol. 115 | no. 20 | 5049 „ *Jack Halpern - Pioneer of homogeneous catalysis*"
en.wikipedia.org/wiki/Wilkinson's_catalyst

Step Fluctuations and Adatom Gas at Metal Surfaces



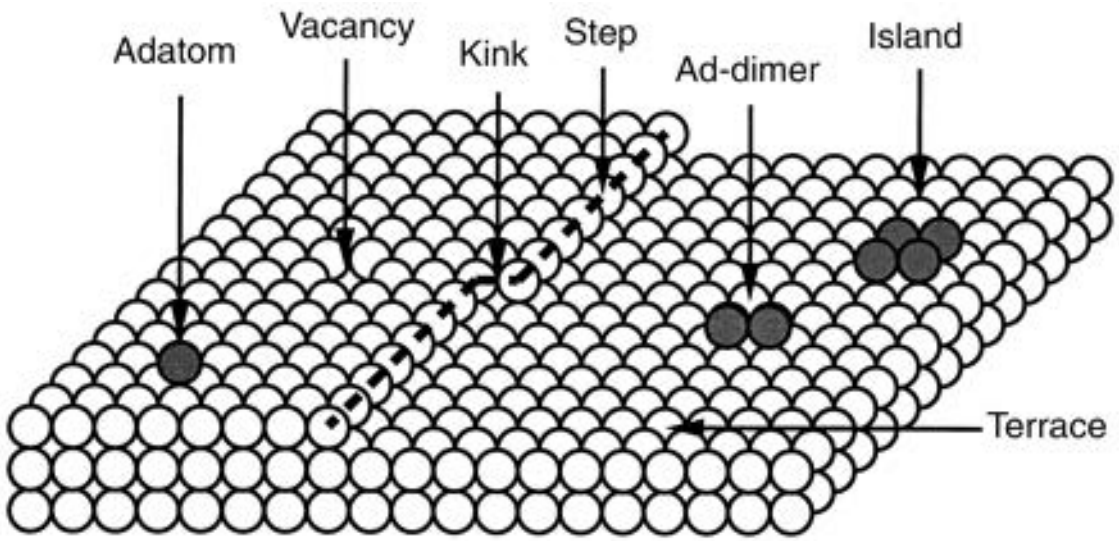
STM image of the clean Ag(110) at 300 K

PRB 58 (1998) 12663



- **dynamic coexistence of adatoms and step-kink configuration**
  - **concentration dependends on material properties and temperature**
  - **pronounced effect on Cu, Ag surfaces at RT**

Adatom Generation in Terrace-Step-Kink (TSK) Model



Adatoms
- feature lowest coordination
- release / condensation at steps by thermal processes

Face specificity and the role of metal adatoms in molecular reorientation at surfaces

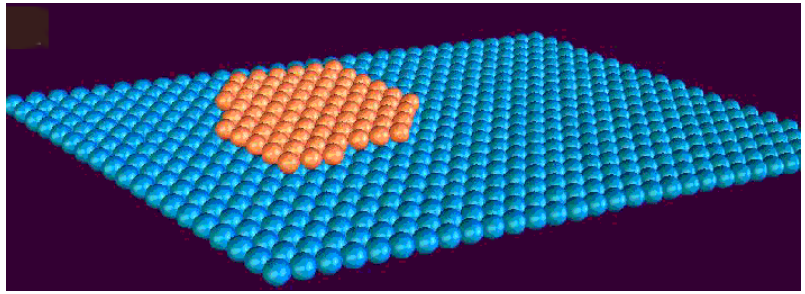
Calculated formation and migration energies (eV) of adatom defects and surface energies on Cu(111), Cu(100), and Cu(110)

Surface	(111)	(100)	(110)
Surface energy (erg cm^{-2})	1214[a]	1319[a]	1446[a]
	1215[d]	1321[d]	1487[d]
E_m	0.0028[a]	0.481[a]	0.241[a]
		0.40[c] (exp.)	0.244[d]
		0.39, 0.53[d]	0.26[e]
$E_{f\ ad\text{-}vac}$	1.688[a]	1.306[a]	0.601[a]
	2.21[b]		
Terrace atom coordination (nn)	9	8	7
Terrace adatom coordination (nn)	3	4	5
Ledge (eV Å^{-1})	0.103[a]	0.068[a]	0.0054[a]
(eV/lattice constant)	(0.26)	(0.17[h]–0.25[g])	(0.014[h], 0.019[g])
Coordination (nn)	7[h]	6[g], 7[h]	6[g], 7[h]
Δn ledge→terrace	4[h]	2[g], 3[h]	1[g], 2[h]
E^f ($2\Delta nE^{coh}/12$)	2.33	1.16–1.75	0.58–1.16
Kink (eV/kink)	0.059[a]	0.108[a]	0.245[a]
		0.101[f] (exp.)	
Coordination (nn)	5, 6	5[g], 6[h]	6[k]
Δn kink→terrace	2[i], 3[j]	1[g], 2[h]	1[k]
E^f ($2\Delta nE^{coh}/12$)	1.16–1.75	0.58–1.16	0.58

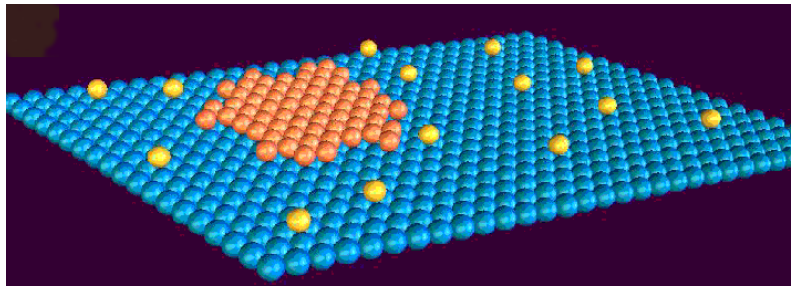
cf. M. Giesen *Prog. Surf. Sci.* 2001, *68*, 1.

B.G. Frederick *et al. Surf. Sci.*, **1998**, *409, 512–520*

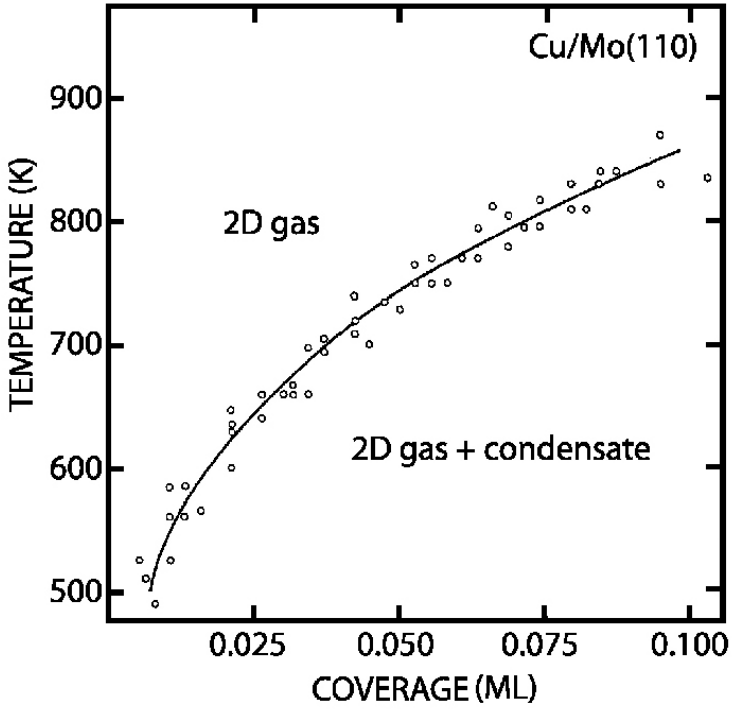
2-D Gas-Condensate Equilibrium in Heterosystems



static island at low T



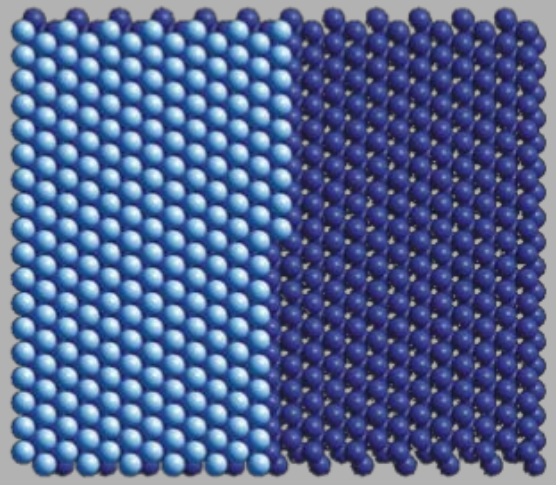
2-D adatom gas at high T



- **coexistence of mobile adatoms at surface with condensate**
  - concentration dependends on material properties and temperature

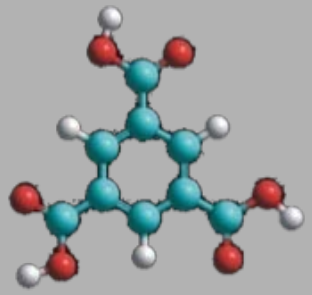
Angew. Chem. Int. Ed. **44** (2005) 1488

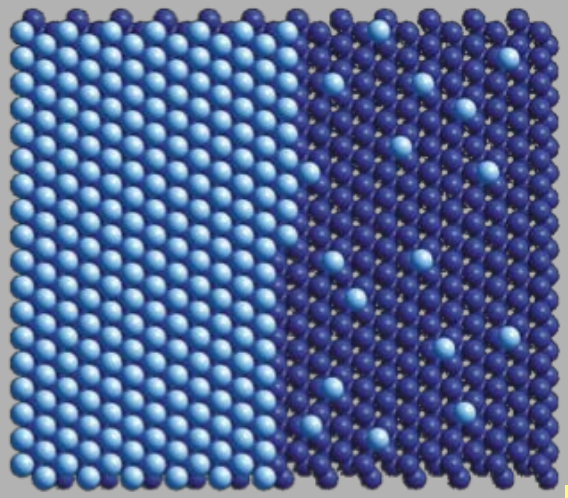
Intrinsic Adatoms Reacting with Molecular Functional Groups



frozen Cu islands at 100 K

carboxylic acid



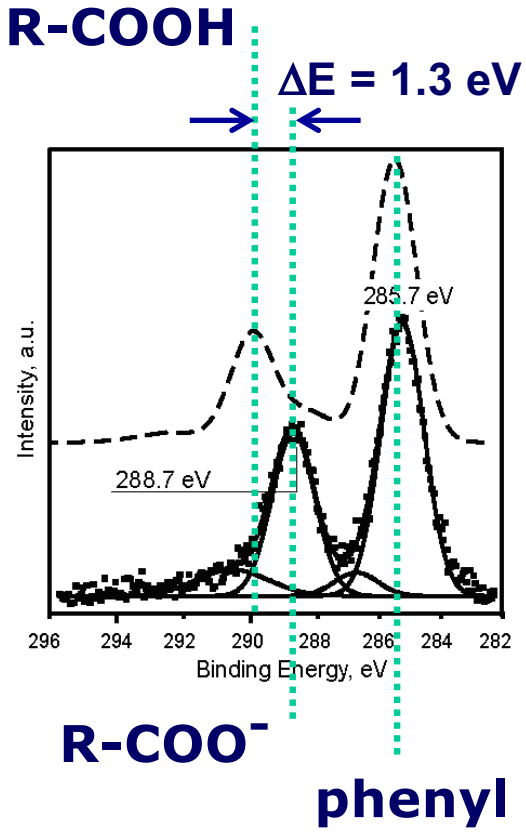


Cu_{ad} lattice gas at 300 K

carboxylate

$R\text{-}COOH + 2e \rightarrow RCOO^- + \frac{1}{2} H_2\uparrow$

X-ray Photoelectron Spectroscopy



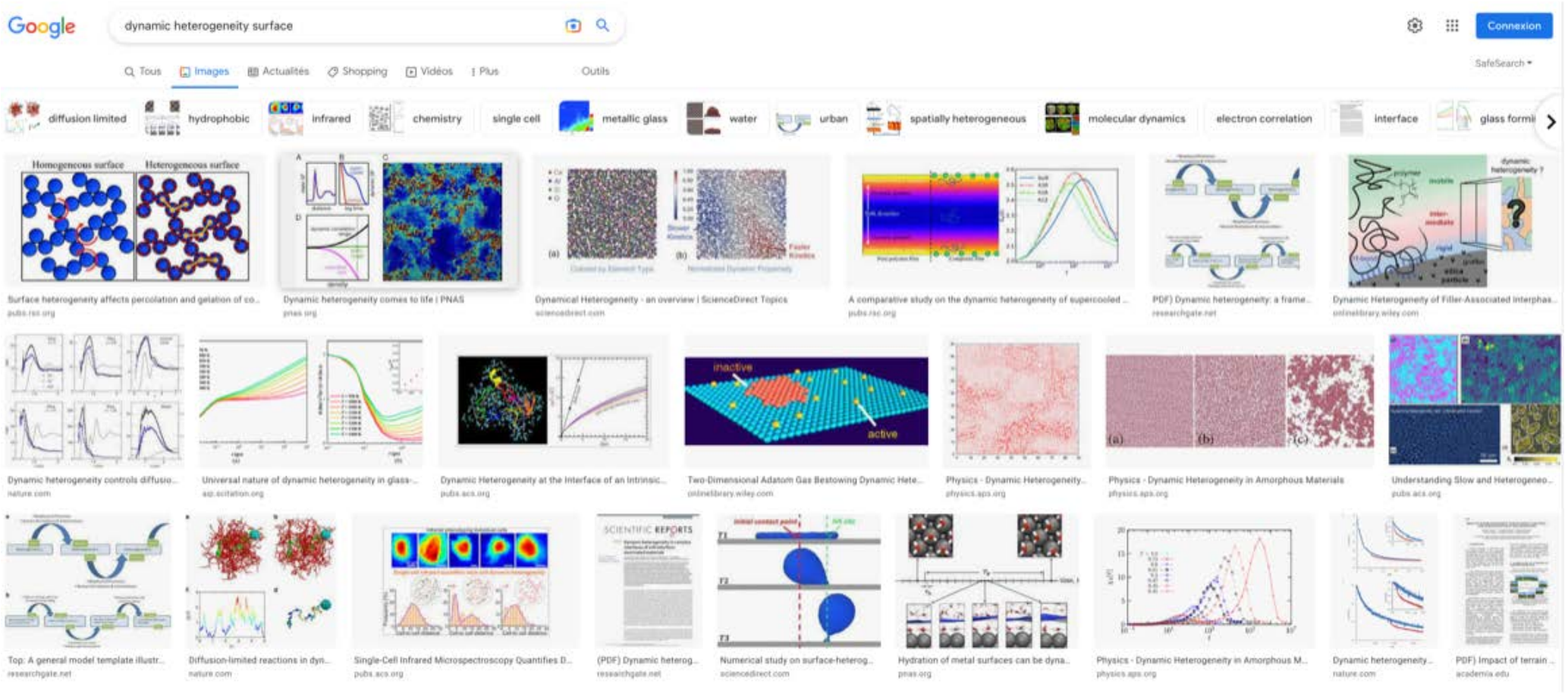
C1s core level shift

- reactivity increased by Cu adatoms on Ag(111) → carboxylate formation

➔ 2-dim Adatom Gas Bestowing Dynamic Heterogeneity

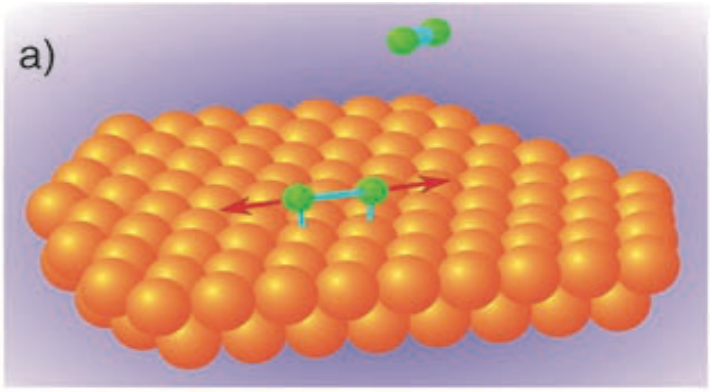
J. Phys. Chem. B **108** (2004) 19392; Angew. Chem. Int. Ed. **44** (2005) 1488

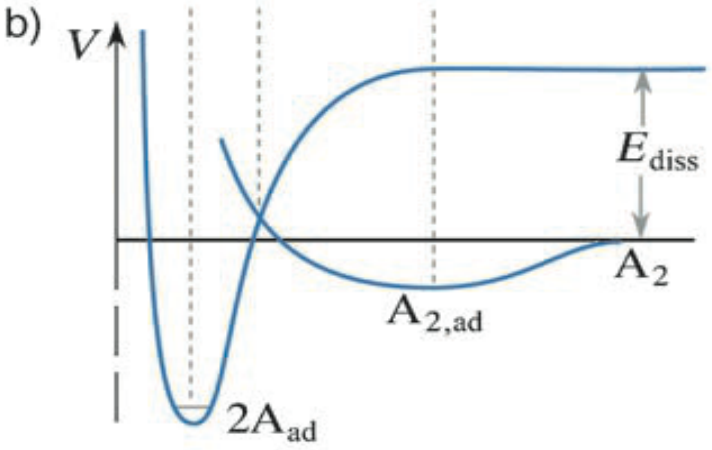
What I {don't} **mean by** *Dynamic Heterogeneity at Surfaces*

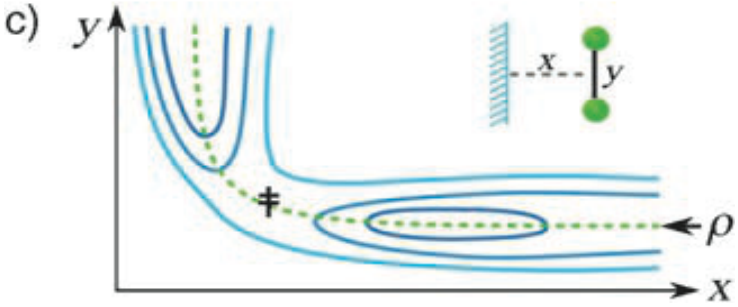


Key Terms : supported lipid bilayers | biological interfaces | supercooled liquid | structural relaxation in disordered materials | hydration of metal surfaces | glass transition phenomena | heterogenous catalysis

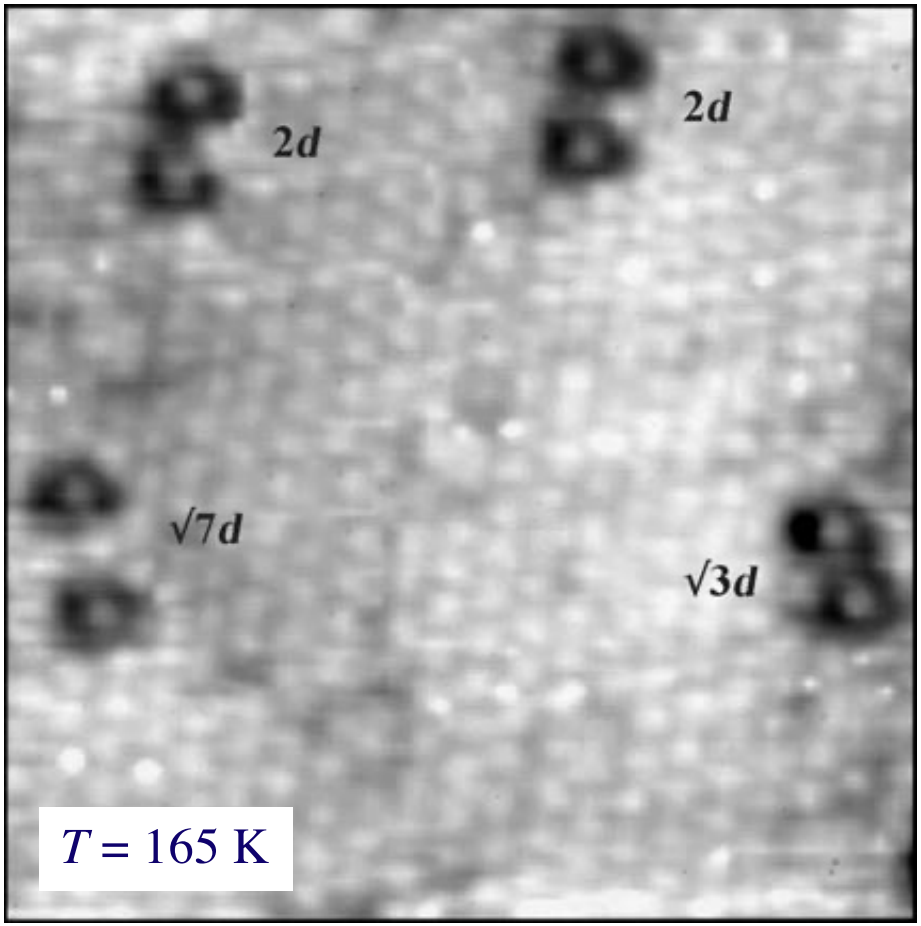
Dissociative Adsorption of Dioxygen on Pt(111)







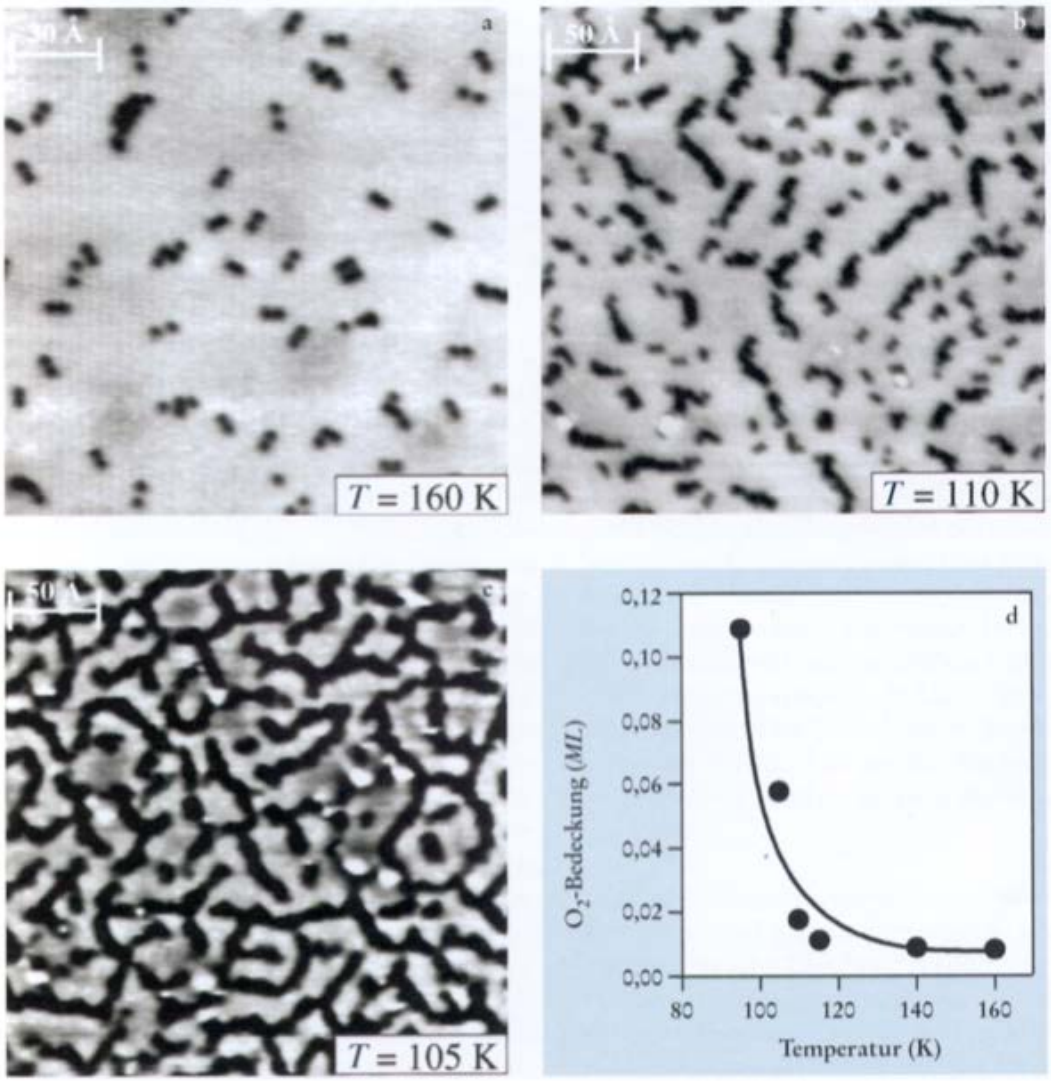
a) dissociative chemisorption of a diatomic molecule;
b) 1-dim Lennard–Jones diagram;
c) 2-dim view of equipotential lines (distance *x* of the molecule from the surface; adatom separation *y*)



Pt(111) after exposure to a small concentration of O_2 molecules (5.3 x 5.5 mm)

G. Ertl, Angew. Chem. Int. Ed., 47, 3524 (2008) & PRL 1996, 77, 123.

More Dissociative Adsorption of Dioxygen on Pt(111)

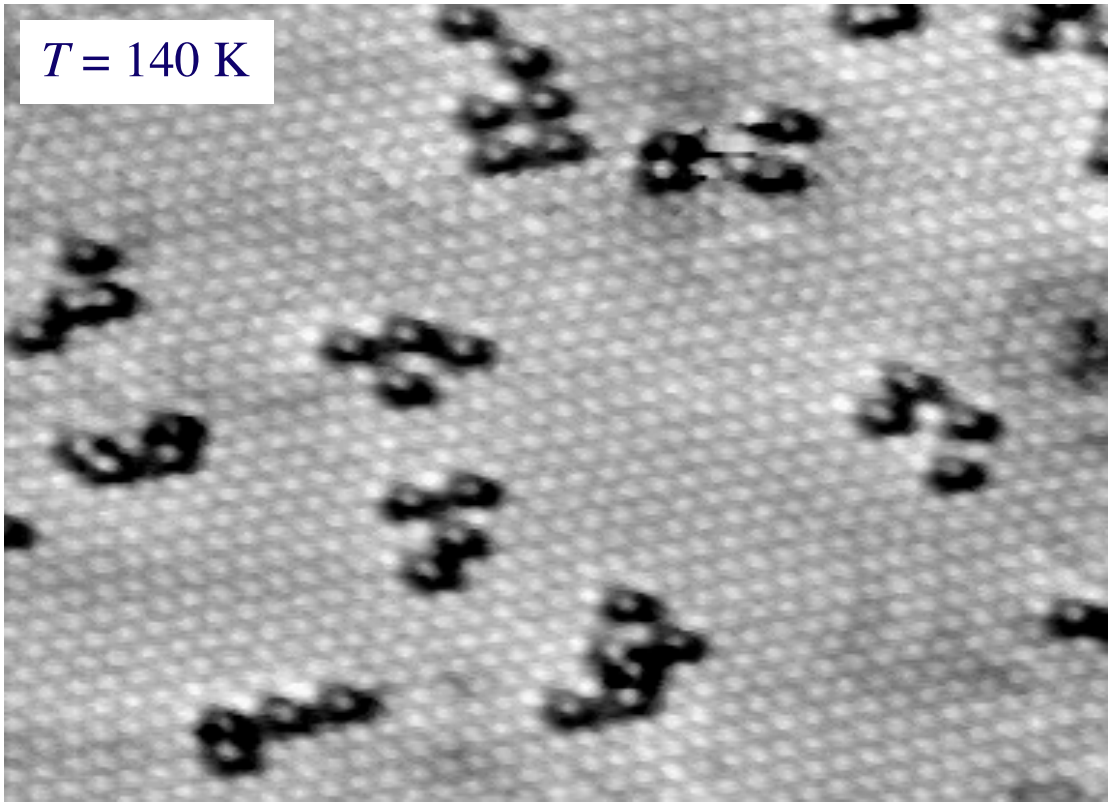


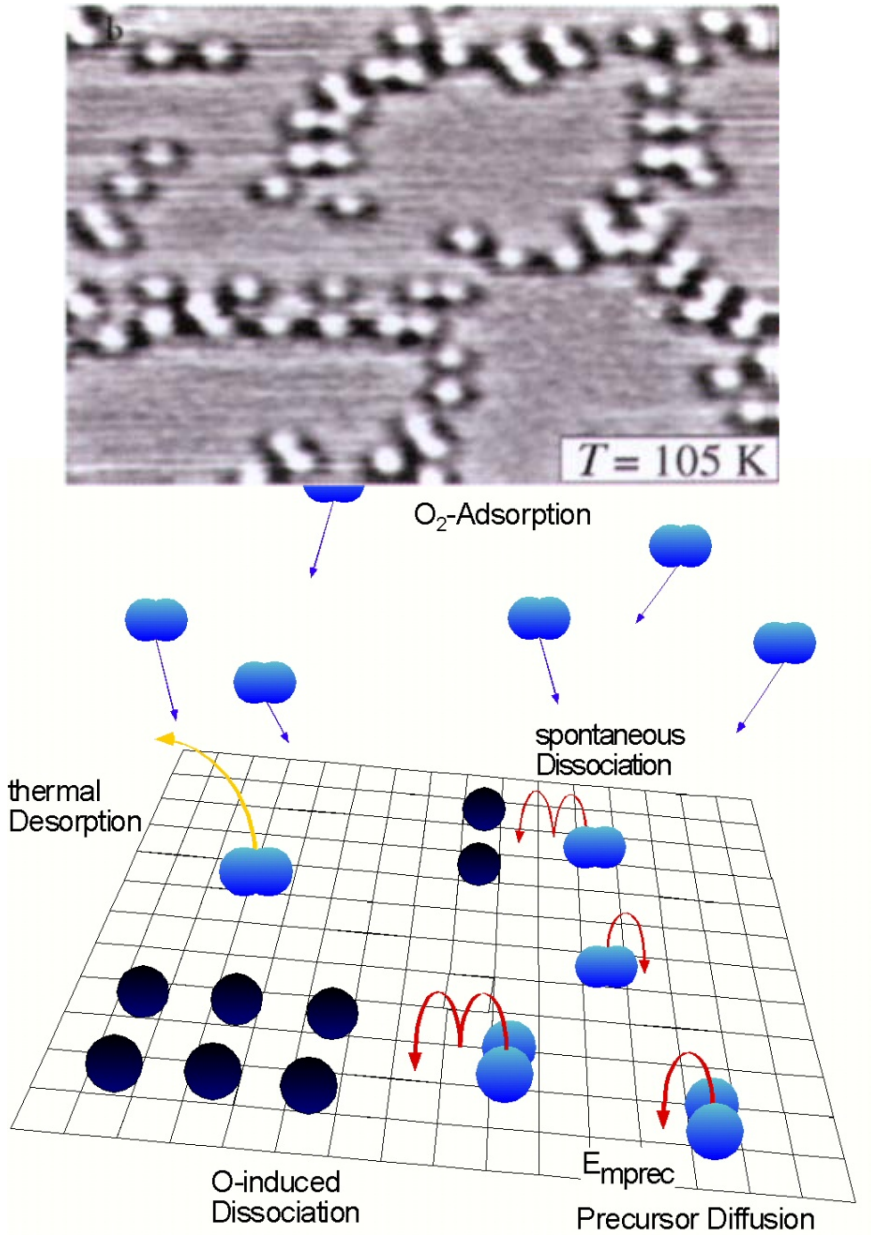
1 L exposure

- **strongly increasing oxygen uptake with decreasing temperature for T<160 K**
- **clustering of oxygen pairs with some directional order**

Nature 390 (1997) 495

Complex Pathways in Dissociative Adsorption of Oxygen on Pt(111)



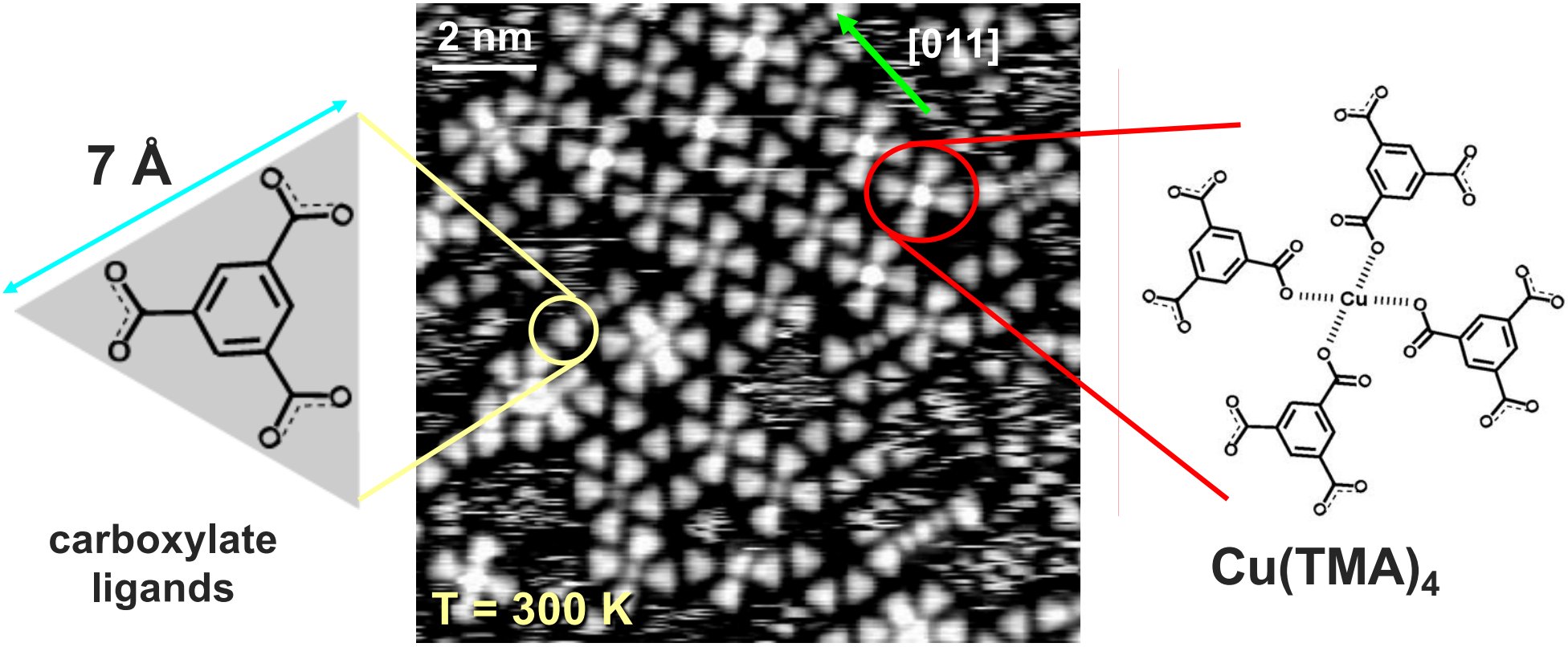


- diffusion of O_{ad} frozen at low T
- formation of islands due to preferred dissociation of molecular precursor at O_{ad}

➔ DYNAMIC HETEROGENEITY in the adsorption mechanism

Nature 390 (1997) 495

Coordination Reaction between Cu and Carboxylate on Cu(100)



T > 250 K

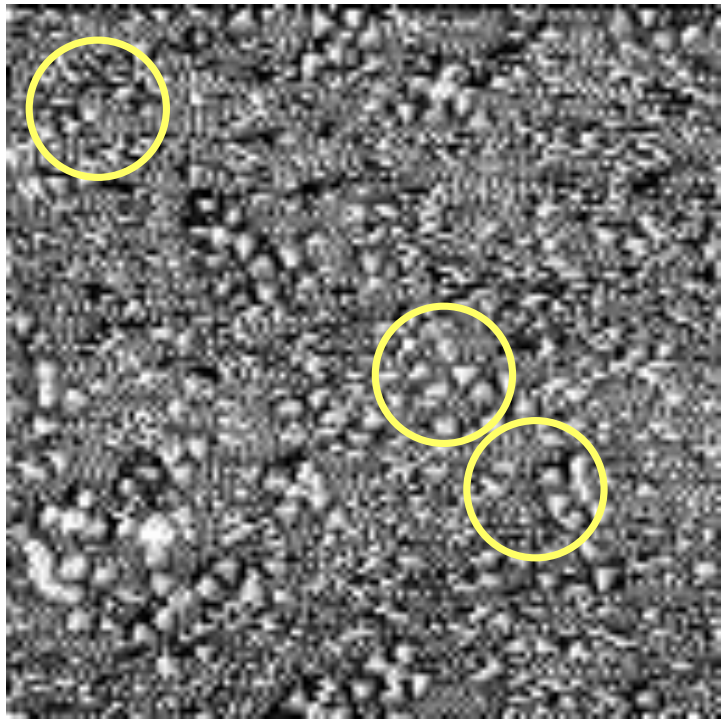
- deprotonation of the three TMA carboxyle groups
- 2-D Cu adatom lattice gas (atomic step evaporation)

Adatoms attracted & immobilized by carboxylate moieties

⇒ formation of Cu-TMA metal-organic complexes

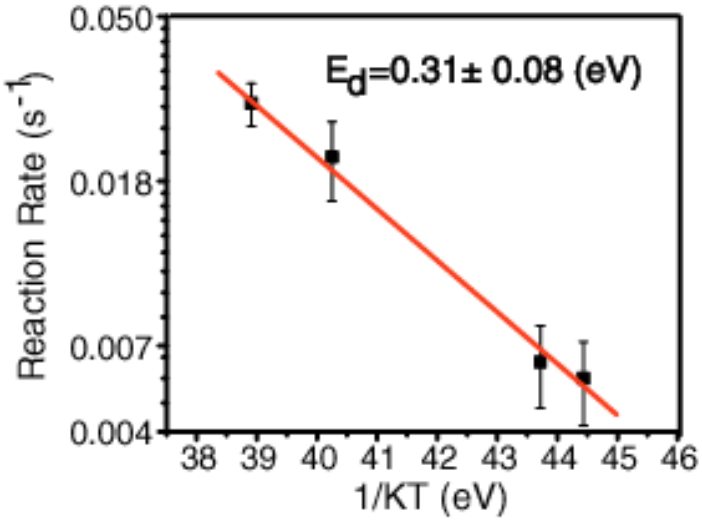
Angew. Chem. Int. Ed. **41** (2002) 4779

Energetics of Complexation Reaction



T = 300 K

Dissociation rates for 260 – 300 K



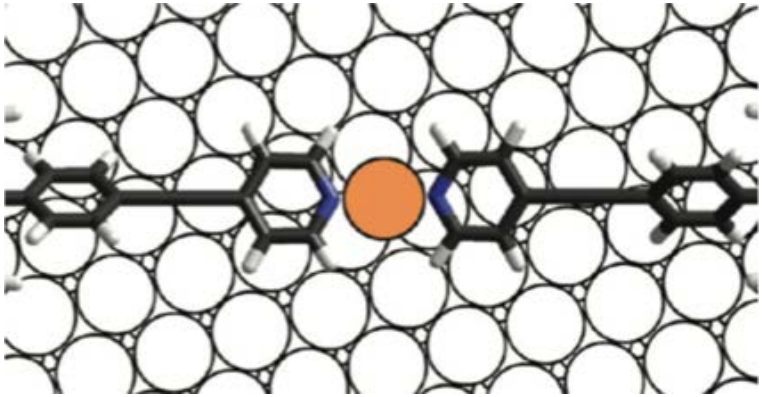
- **small reactant concentration**

$\Rightarrow$ **dissociation & association rates of single $Cu(TMA)_4$**

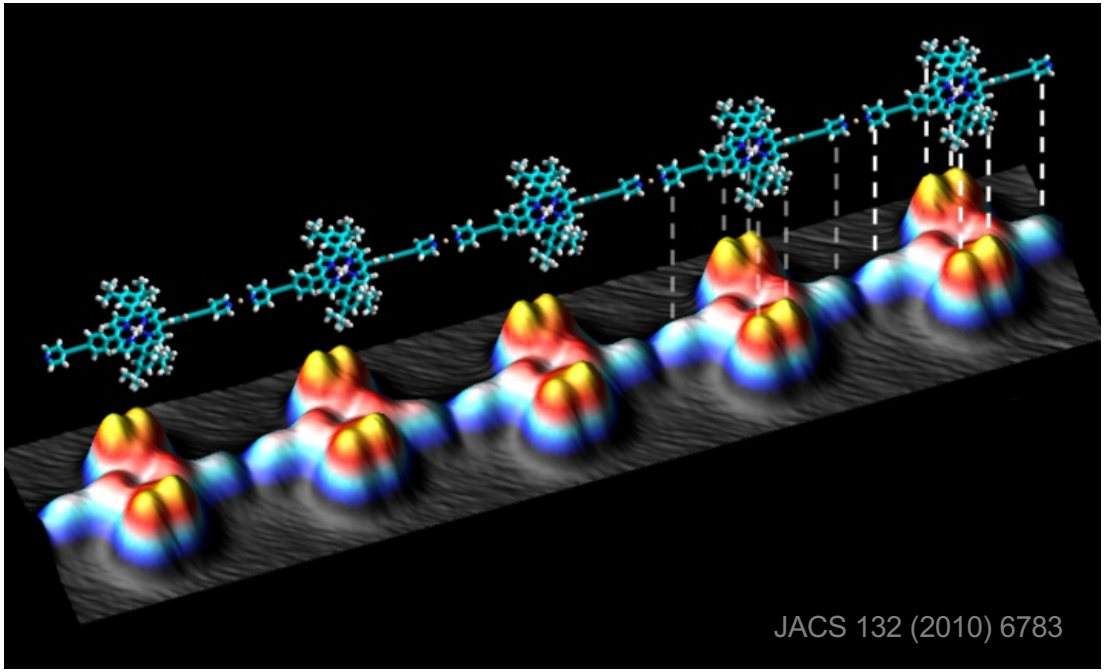
$\Rightarrow$ **energy barrier for dissociation : 0.31 ± 0.08 eV**

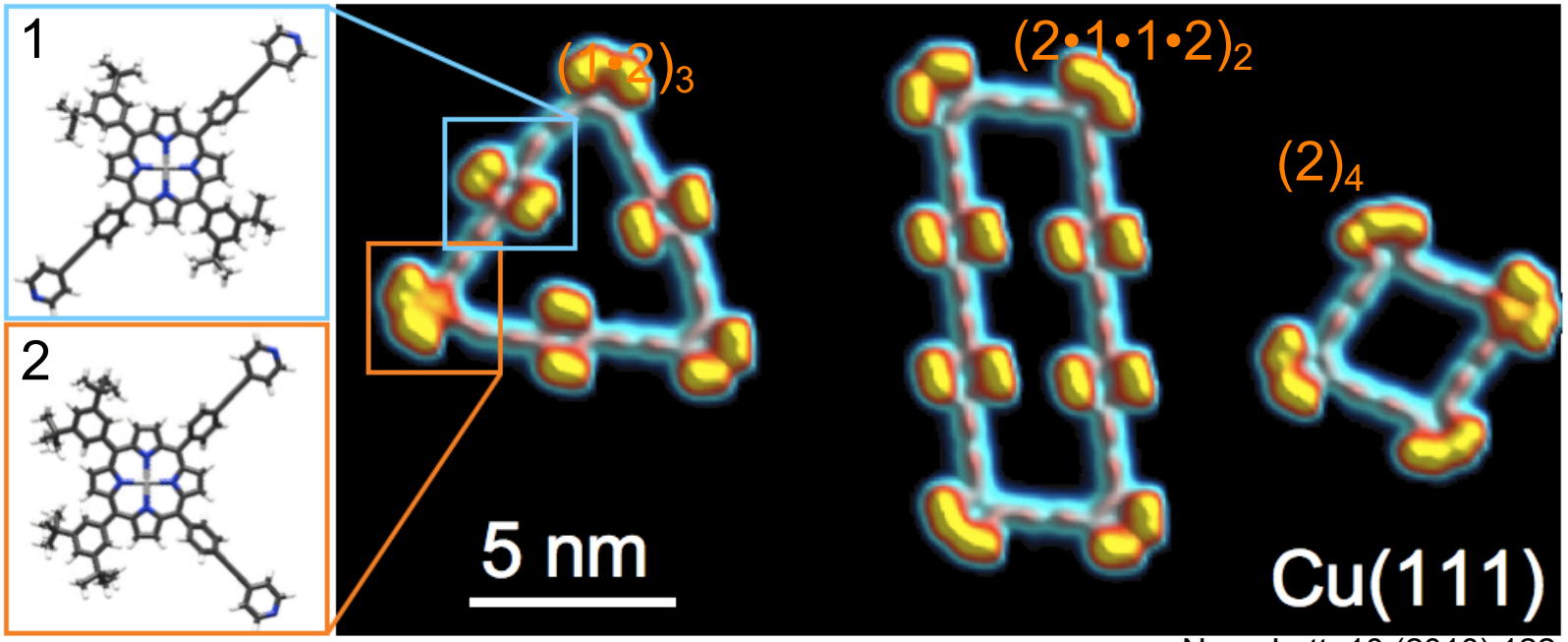
Angew. Chem. Int. Ed. **41** (2002) 4779

Cyclic & 1D-Flexible Coordination Polymers



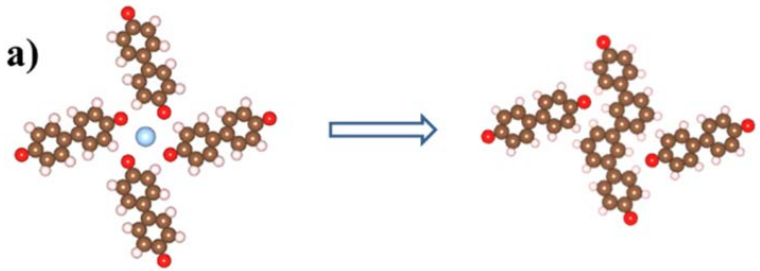
- two-fold Cu-pyridyl coordination motifs
→ adatoms provided by Cu(111) substrate

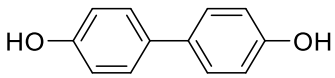




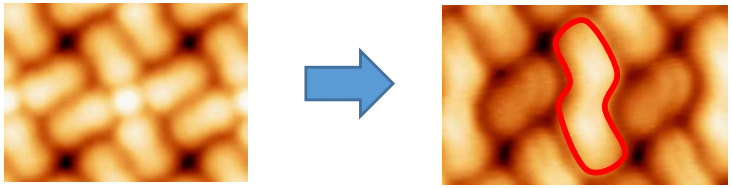
Nano Lett. 10 (2010) 122

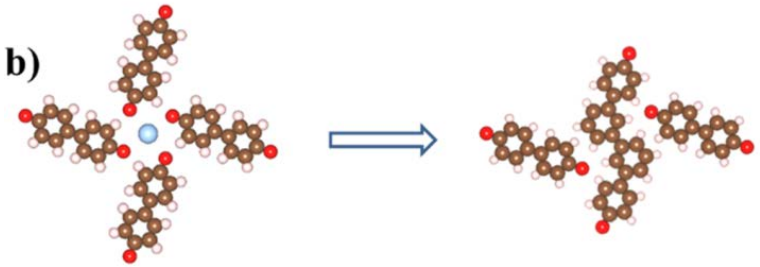
Adatoms Stabilize Intermediate States Steering Chirality Transfer

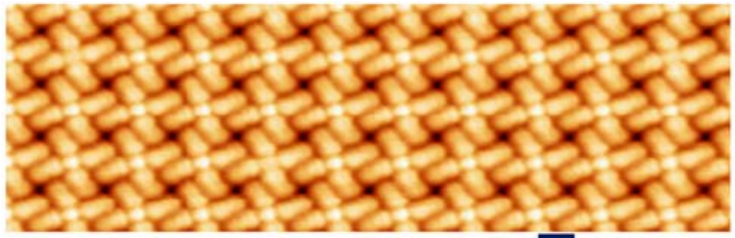


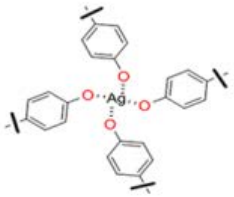


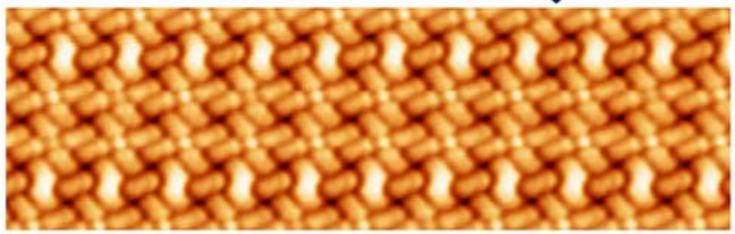
on Ag(100)

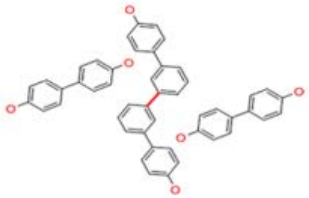


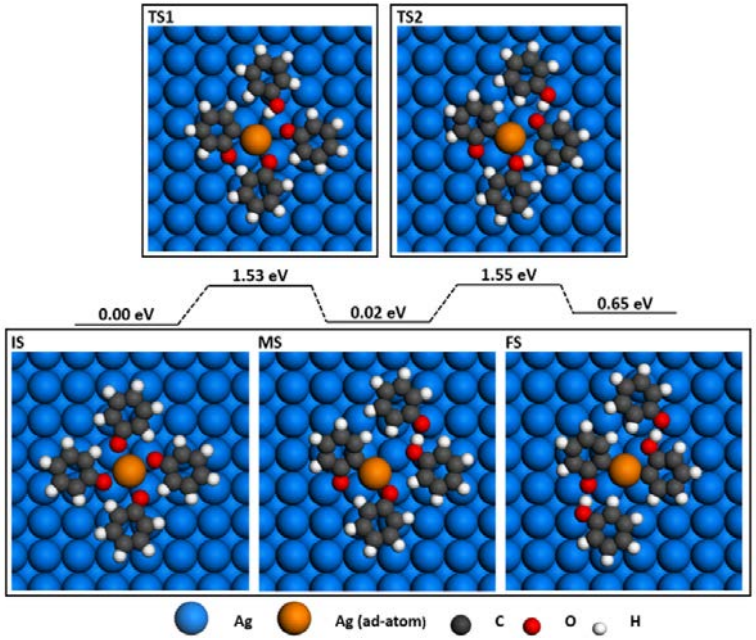










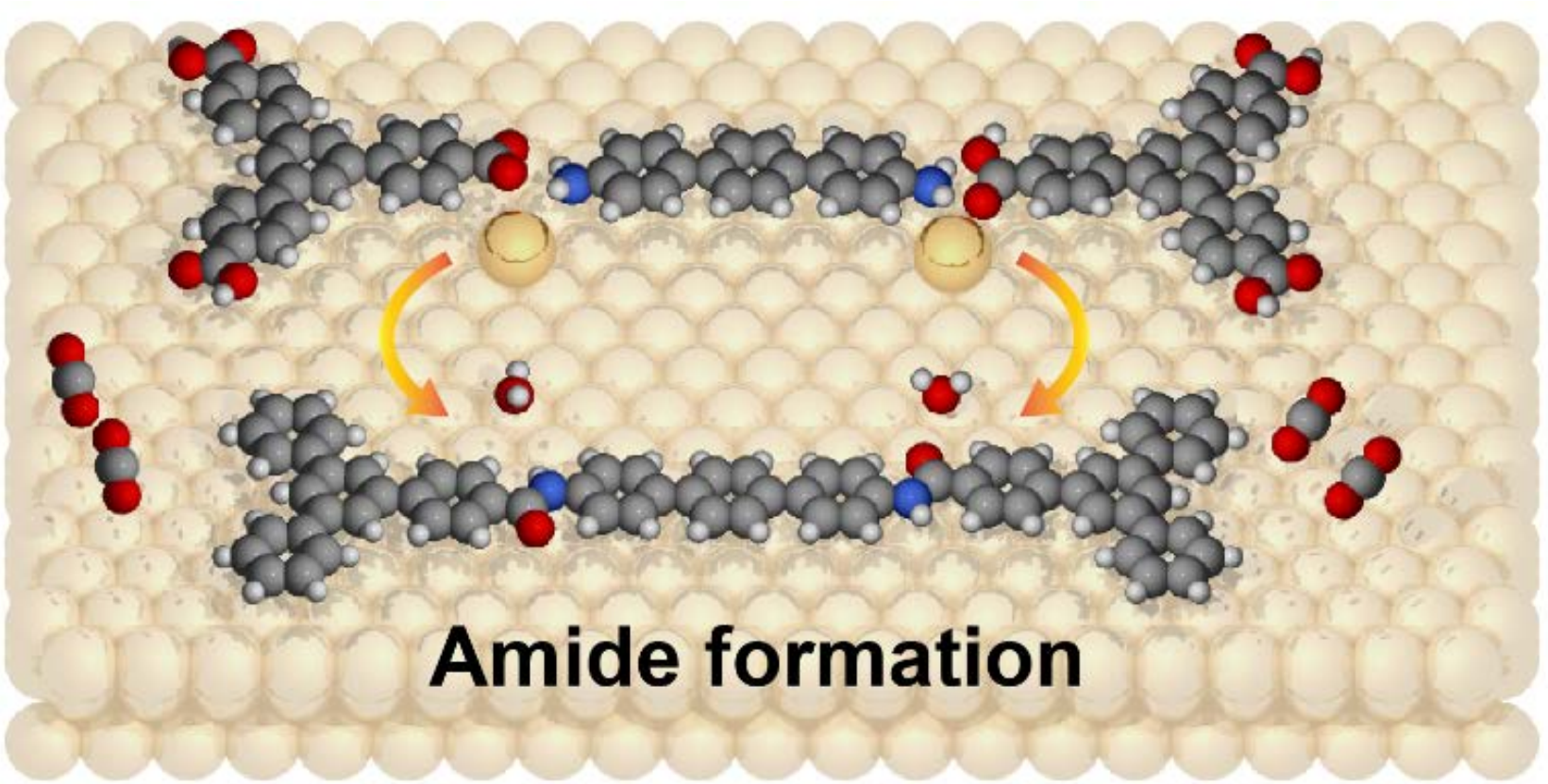


➔ tetrameric metal-organic intermediate states on Ag(100)

➔ formation of dimeric covalent products retaining previous chirality signature

B. Yang *et al.* J**. Am. Chem. Soc.** 2019, 141, 168 (Soochow Univ,).

Abiotic Formation of an Amide Bond via Direct Carboxyl–Amine Coupling



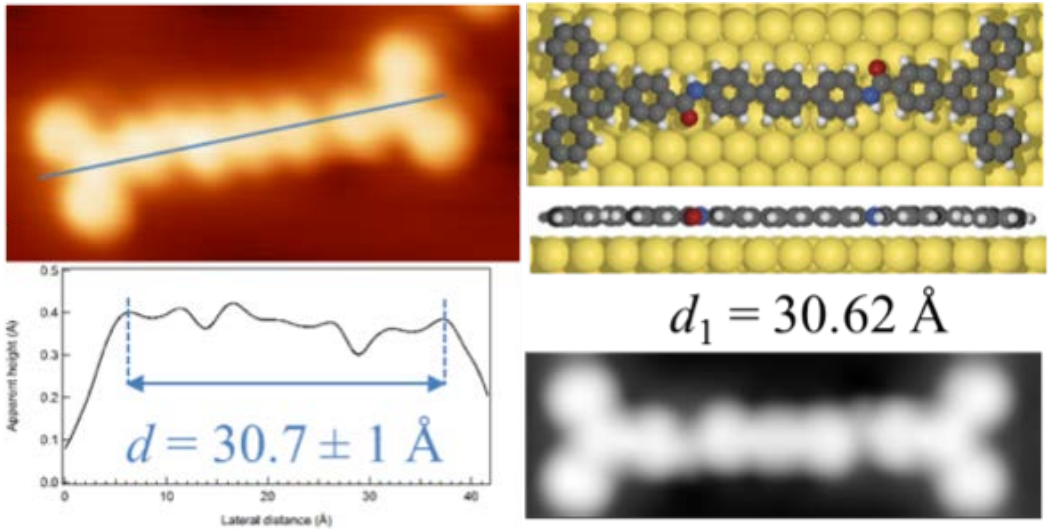
Demonstrated on Au(111) surface

(competition between cross-coupling amide formation and decarboxylation reactions
different reaction scenarios prevail on Ag(111) and Cu(111))

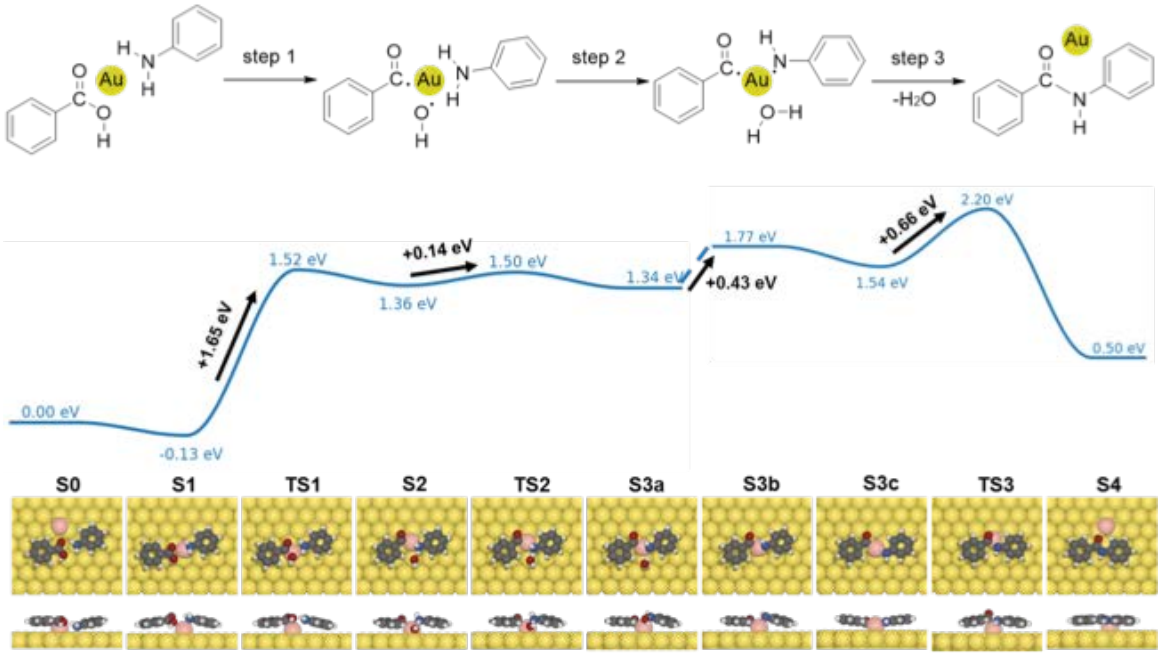
- **archetypical bio-related molecules can be abiotically synthesized in clean environments without water or oxygen**

B. Yang *et al. Angew. Chem. Int. Ed.* **2022**, *61*, e202113590

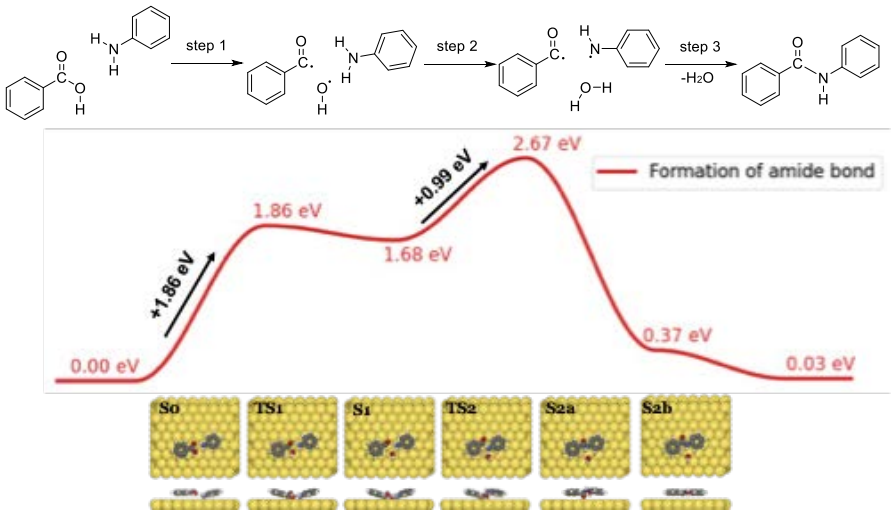
Modeling the Amide Bond Formation



Calculated reaction pathway 1:
Energy barrier of **2.20 eV with Au adatom**



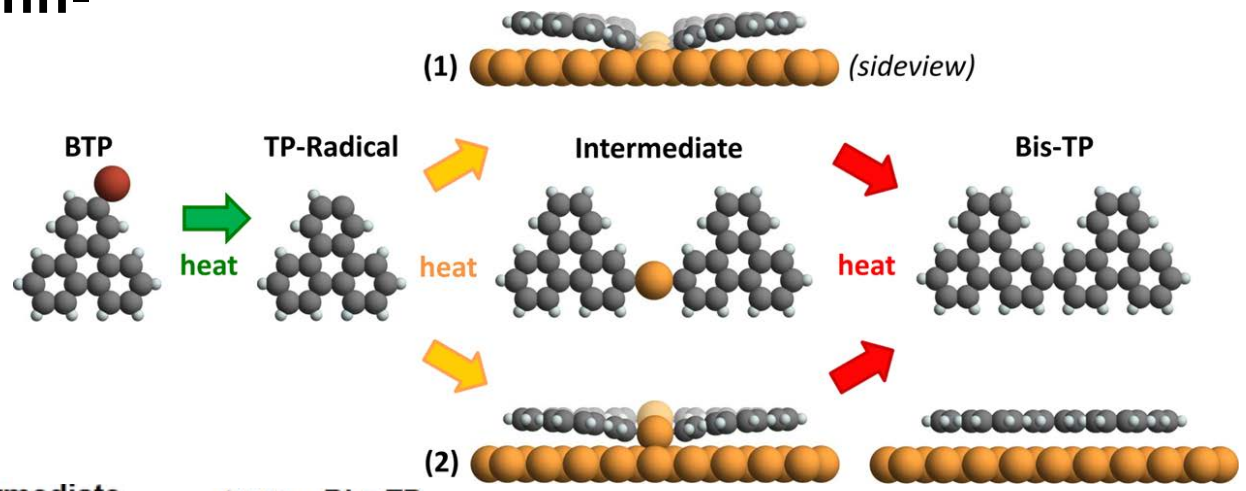
Energy barrier of 2.67 eV with (111) substrate lattice only



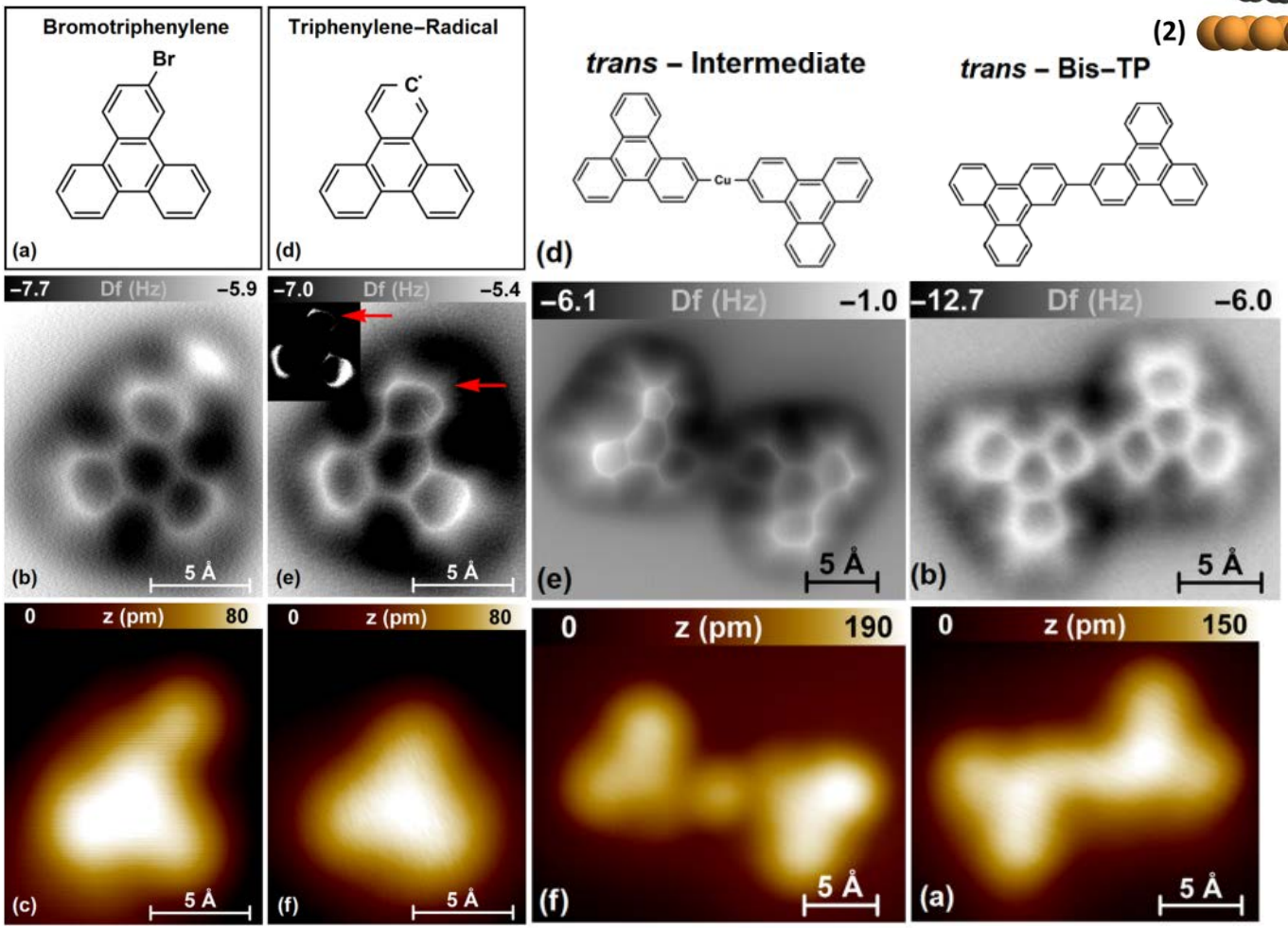
➢ **Au adatom interference promotes reaction**

B. Yang *et al. Angew. Chem. Int. Ed.* **2022**, *61*, e202113590

Adatoms interfering in Ullmann-type Surface Reactions



Cu(111) substrate



ncAFM

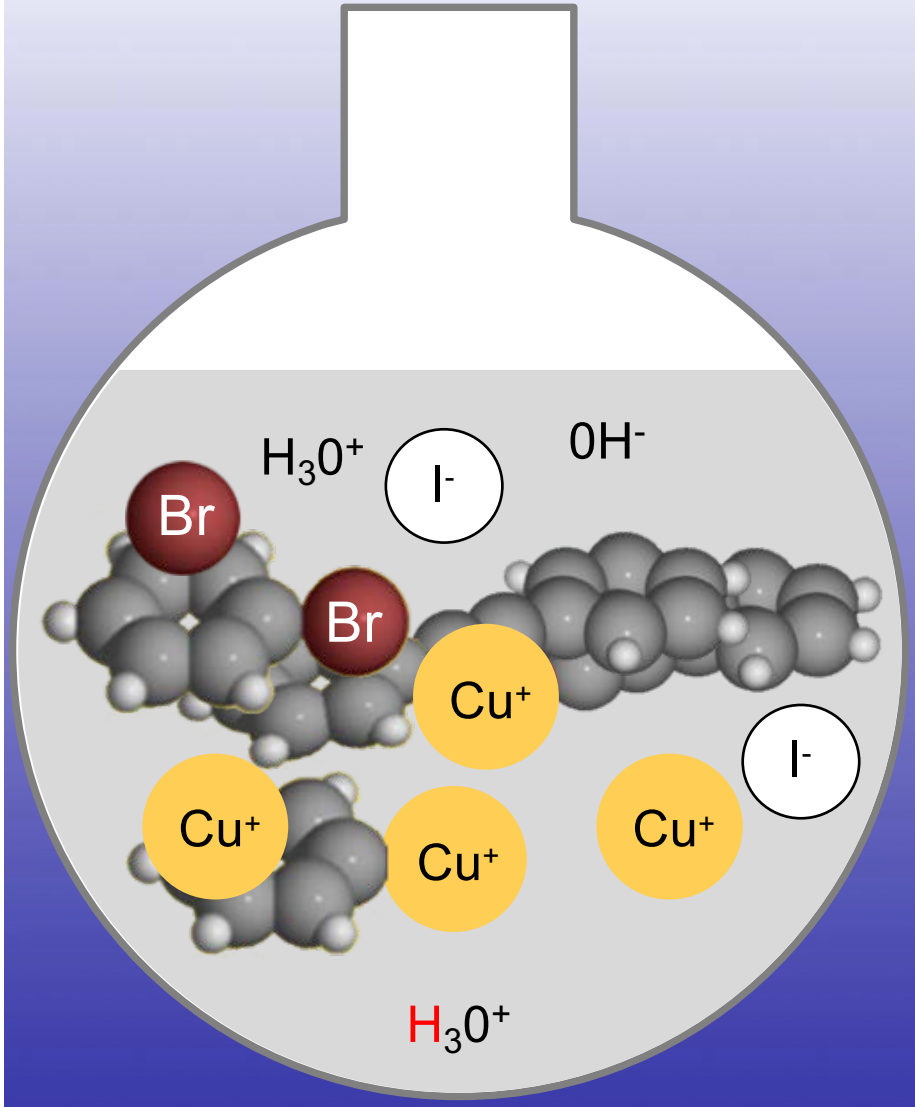
- **sequentual chemical conversions in on-surfac Ullmann-type reaction**

STM

Wegner, Schirmeisen et al.
ACS Nano 2017, *11*, 4183−4190

On-surface synthesis: approaches

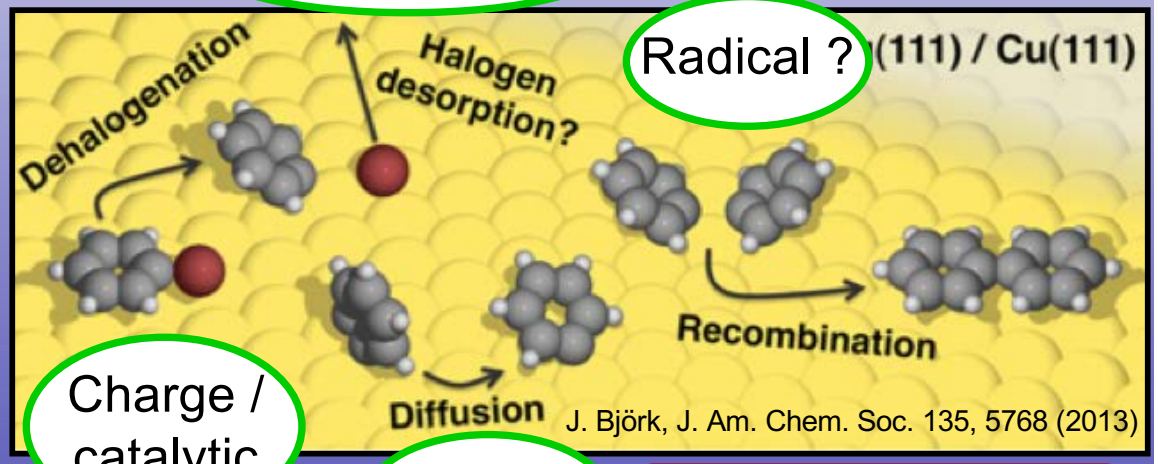
Why is it interesting to do on-surface synthesis?



New means of characterization

New pathways / reactions

Reversibility



Radical ?

Charge / catalytic

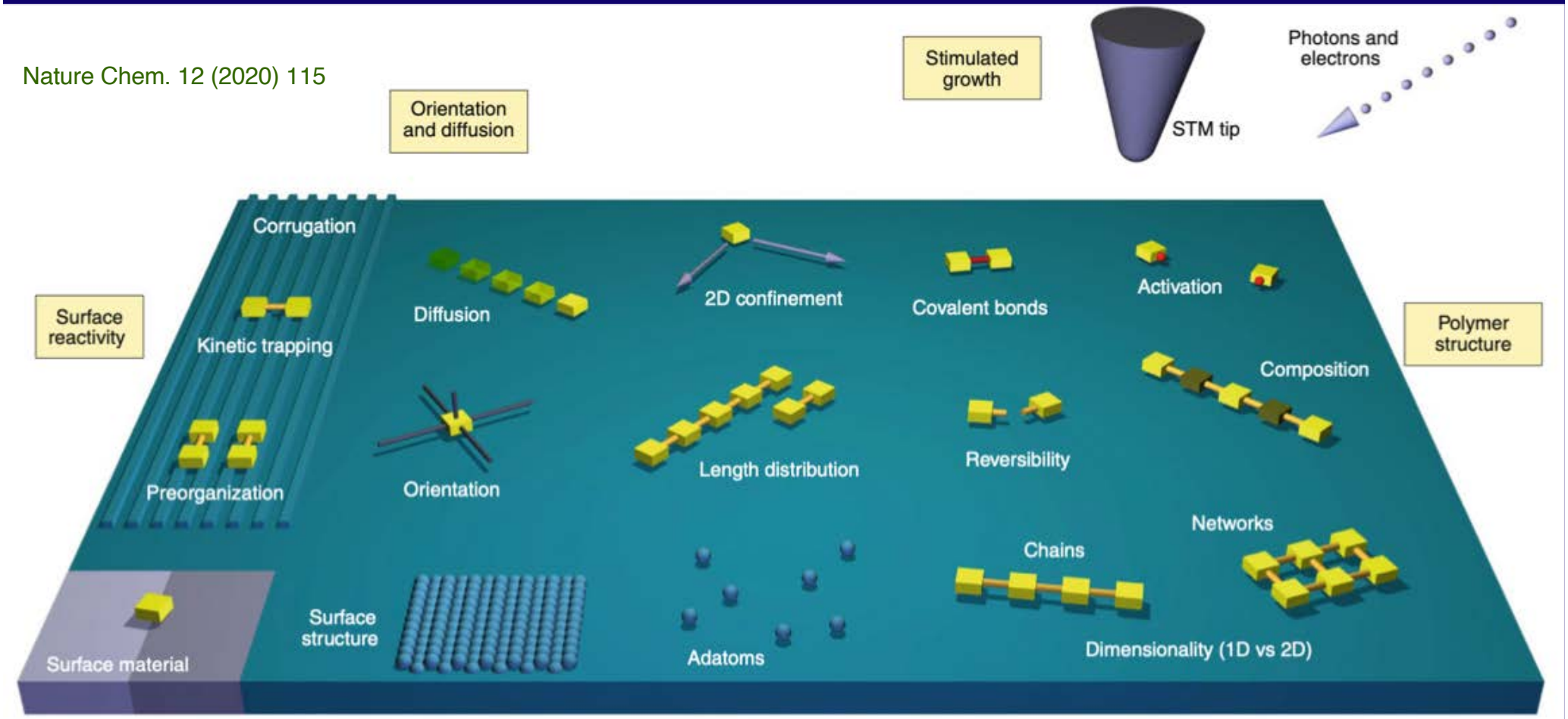
Kinetics

Temperature-control

Surface templating with atomistic precision

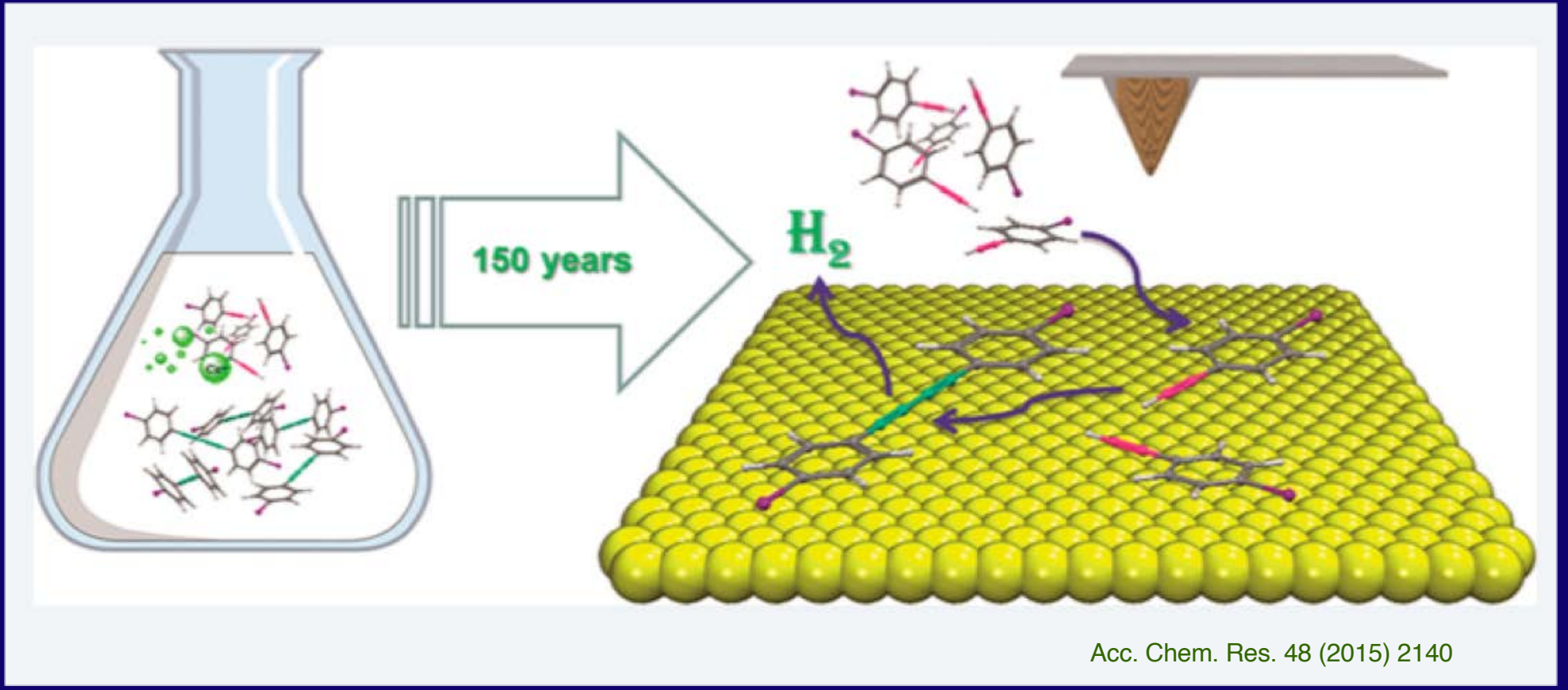
Exploring Novel Materials via On-Surface Synthesis

Nature Chem. 12 (2020) 115



- 2D confinement affects chemical pathways and product formation
- systems amenable to surface & nanoscale techniques
- frequent interference of adatom-mediated processes

All-Carbon Scaffolds via On-Surface Synthesis



Acc. Chem. Res. 48 (2015) 2140

- 2D confinement affects chemical pathways and product formation
- systems amenable to surface & nanoscale techniques
- frequent interference of adatom-mediated processes

Homo-Coupling of Terminal Alkynes

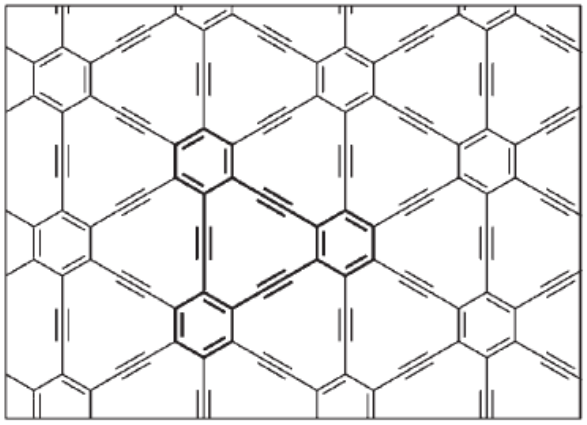
$$2RC \equiv CH + \tfrac{1}{2}O_2 \xrightarrow{Cu(II)} RC \equiv C - C \equiv C - CR + H_2O$$

$$2RC \equiv CH + 2Cu(II) \rightarrow RC \equiv C - C \equiv CR + 2H^{+}2Cu(I)$$

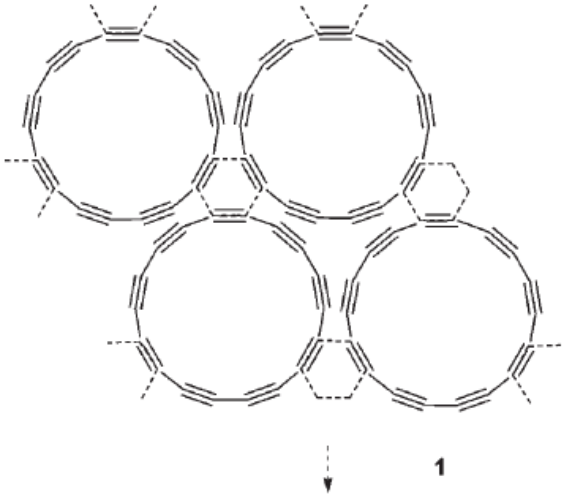
$$2Cu(I) + \tfrac{1}{2}O_2 \rightarrow 2Cu(II) + 2OH^{-}$$

- more lately: Ag-acetylide catalysis & Sonogashira reactions (transition metals, Pd)

  → **all-carbon scaffolds by rational design** (Diederich & Kivala, Adv. Mater. 2010)



graphyne, **2**



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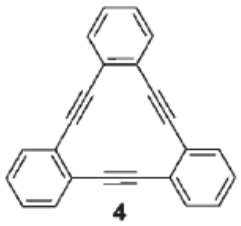

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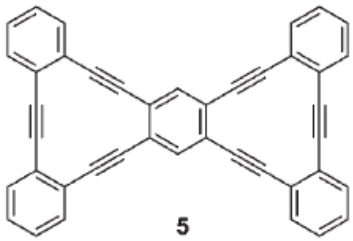

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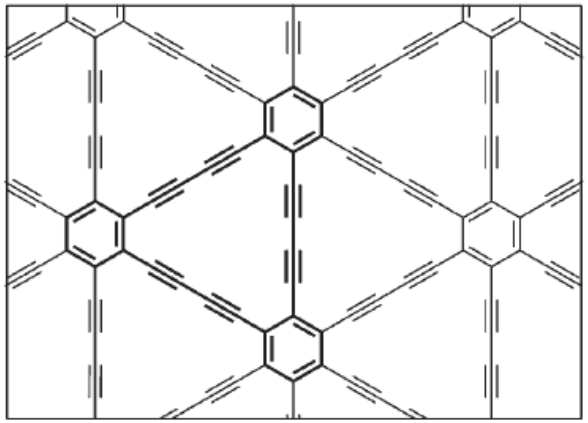
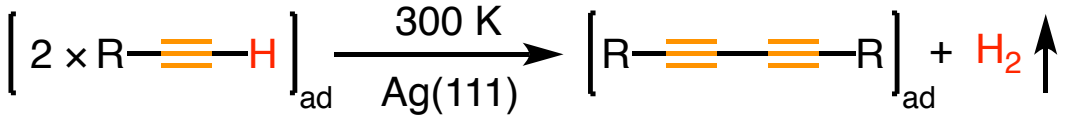
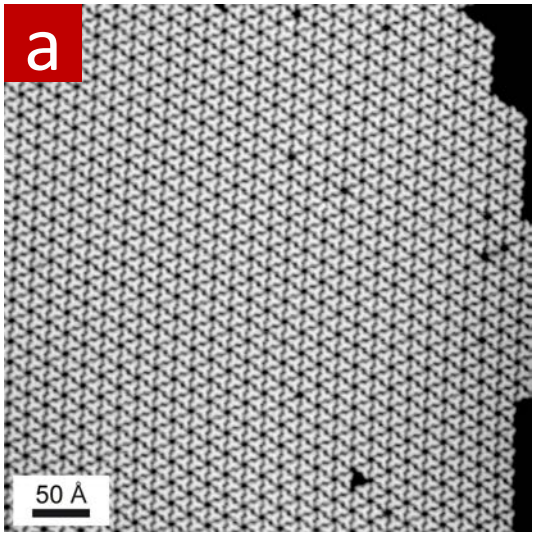


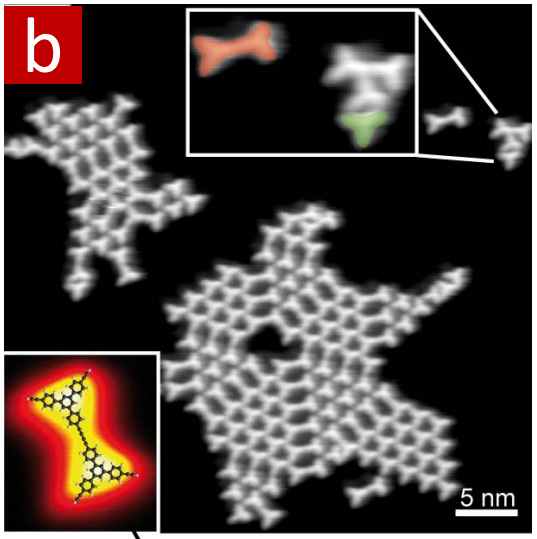
graphdiyne, **3**

Homocoupling of Terminal Alkynes on Ag(111)

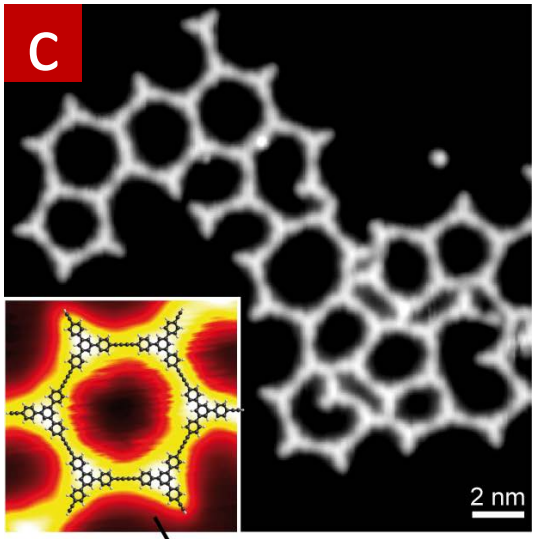




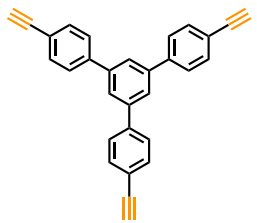
T_{sub} = 200 K



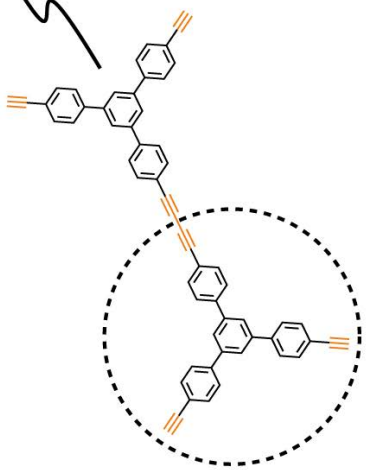
T_{ann}=300K

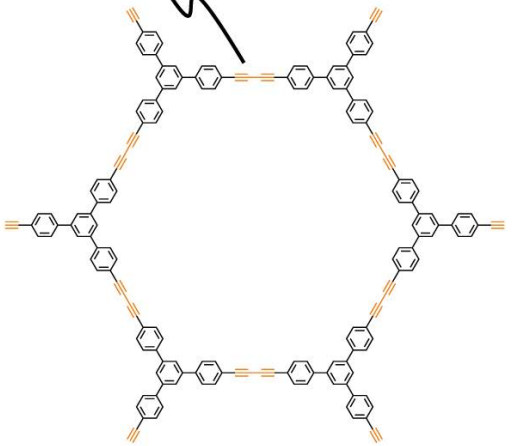


T_{ann}=400K



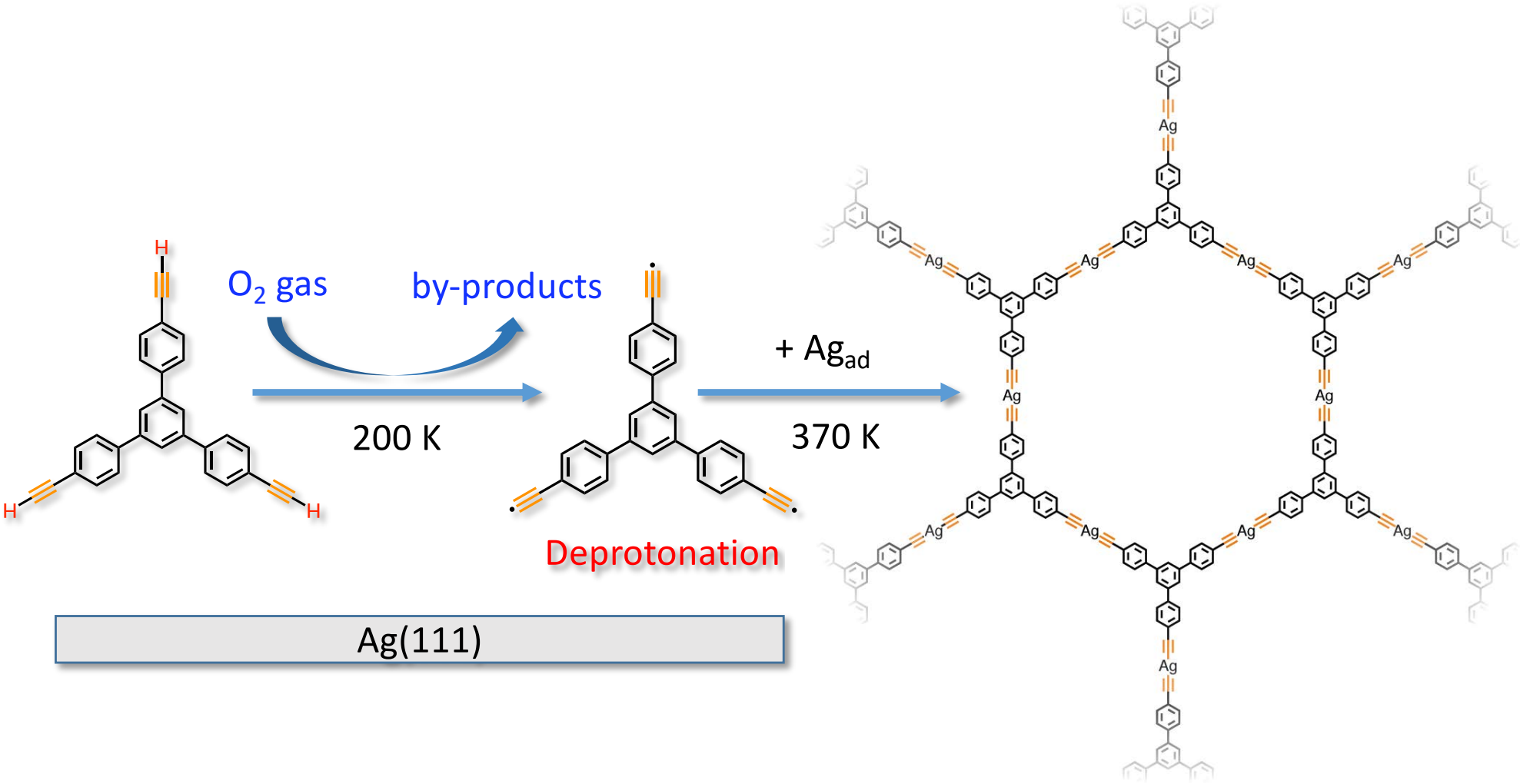
1,3,5-tris-(4-ethynylphenyl)benzene
Ext-TEB





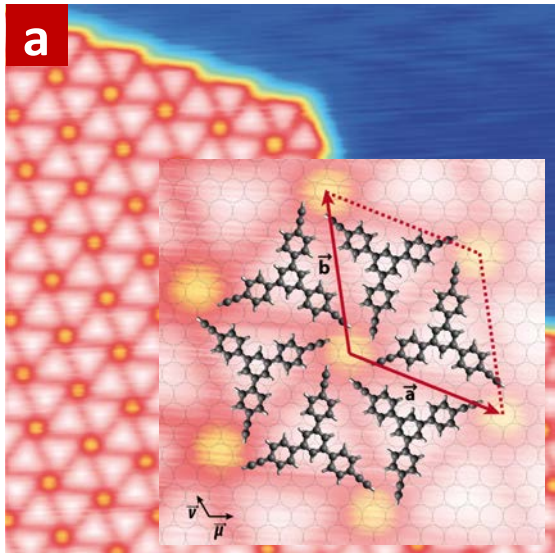
Yi-Qi Zhang, N. Kepčija, *et al.*, *Nat. Commun.* **3**, 1286 (2012).

2D Organometallic Graphdiyne-like Network



Y.-Q. Zhang, T. Paintner, *et al.*, **J. Am. Chem. Soc. 141**, 5087 (2019).

STM and XPS Characterization



T_{ann} = 200 K

T_{ann} = 200 K

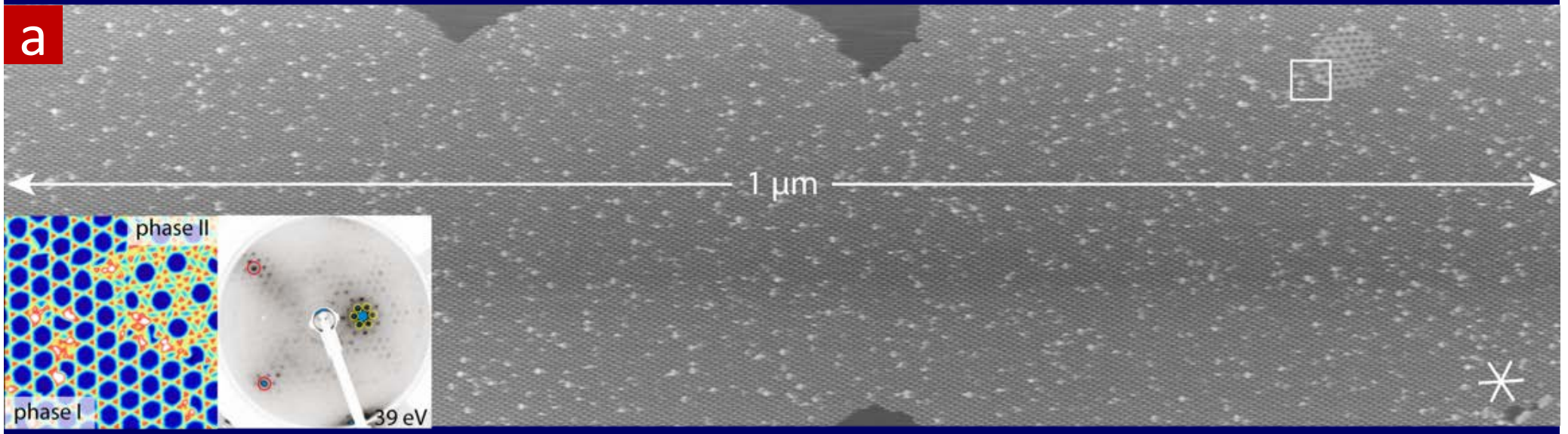
T_{ann} = 250 K

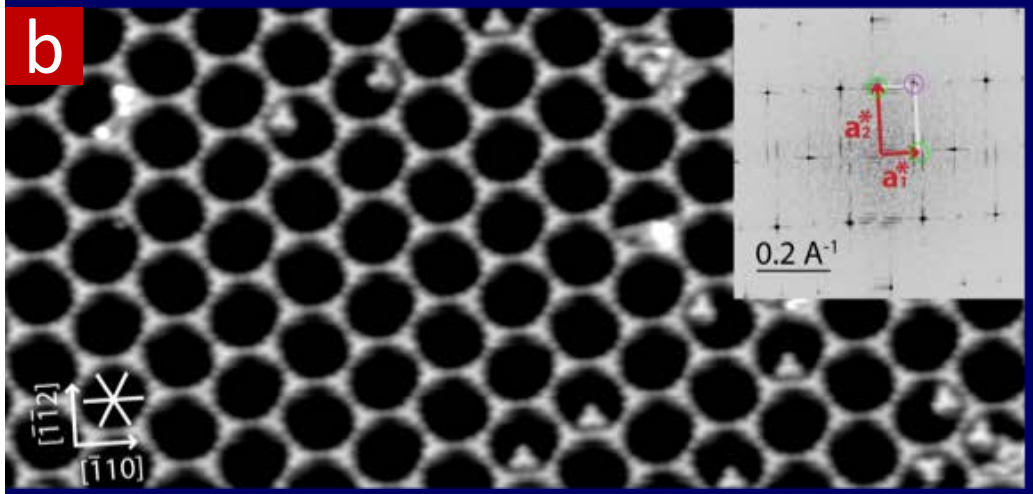
T_{ann} = 300 K

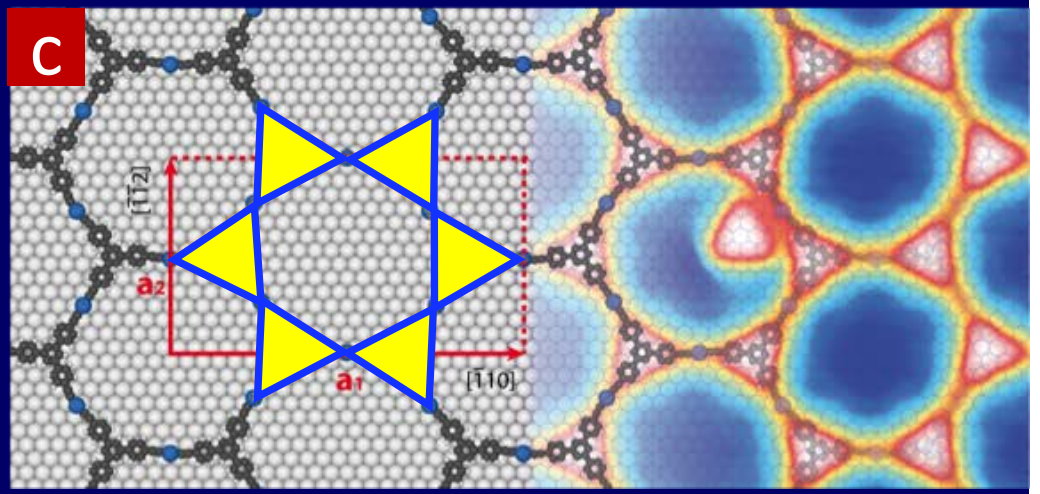
Y.-Q. Zhang, T. Paintner, *et al.*, **J. Am. Chem. Soc. 141**, 5087 (2019).

Single-Layer Network at the Micrometer Scale

2D organometallic graphdiyne analogue



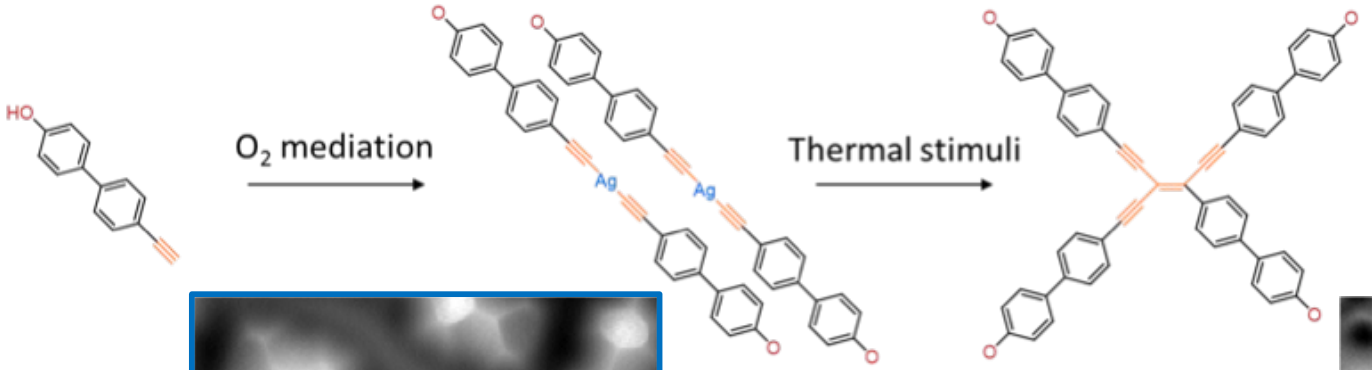


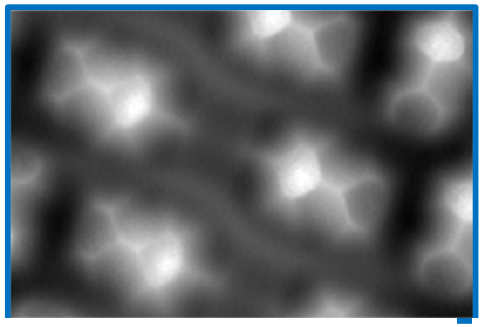


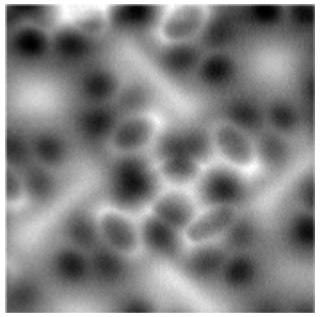
- possible approach towards 2D organic topological insulators
- ARPES investigation suggests decoupled 2D electronic system (to be publ.)

Y.-Q. Zhang, T. Paintner, *et al.*, **J. Am. Chem. Soc. 141**, 5087 (2019).

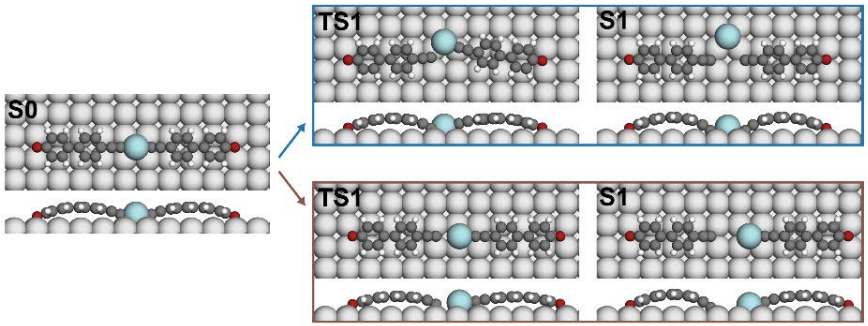
On-surface Synthesis of Enetriynes on Ag(100)

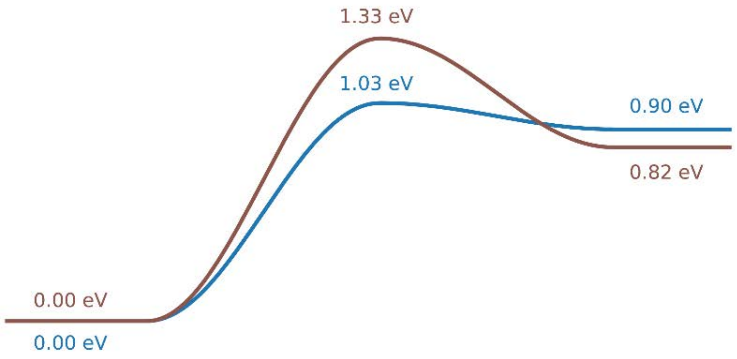


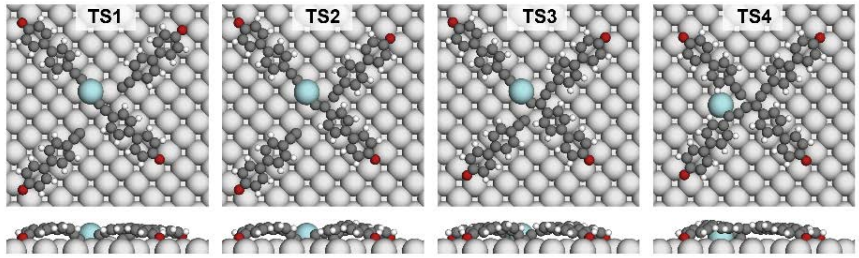


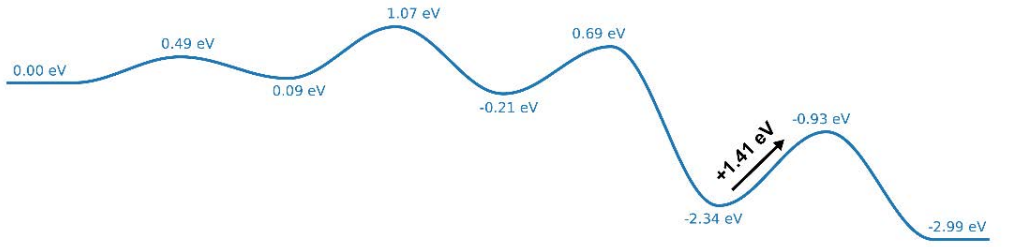


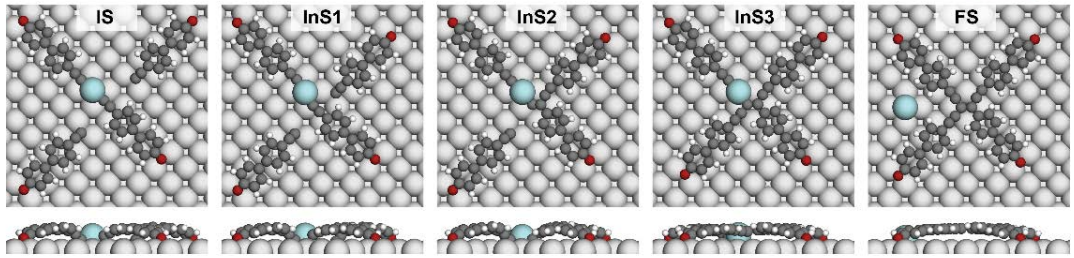
Organometallic intermediates
→ covalent products





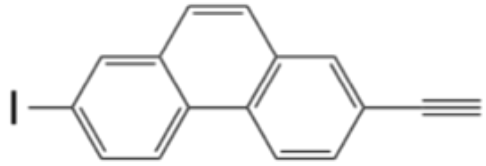






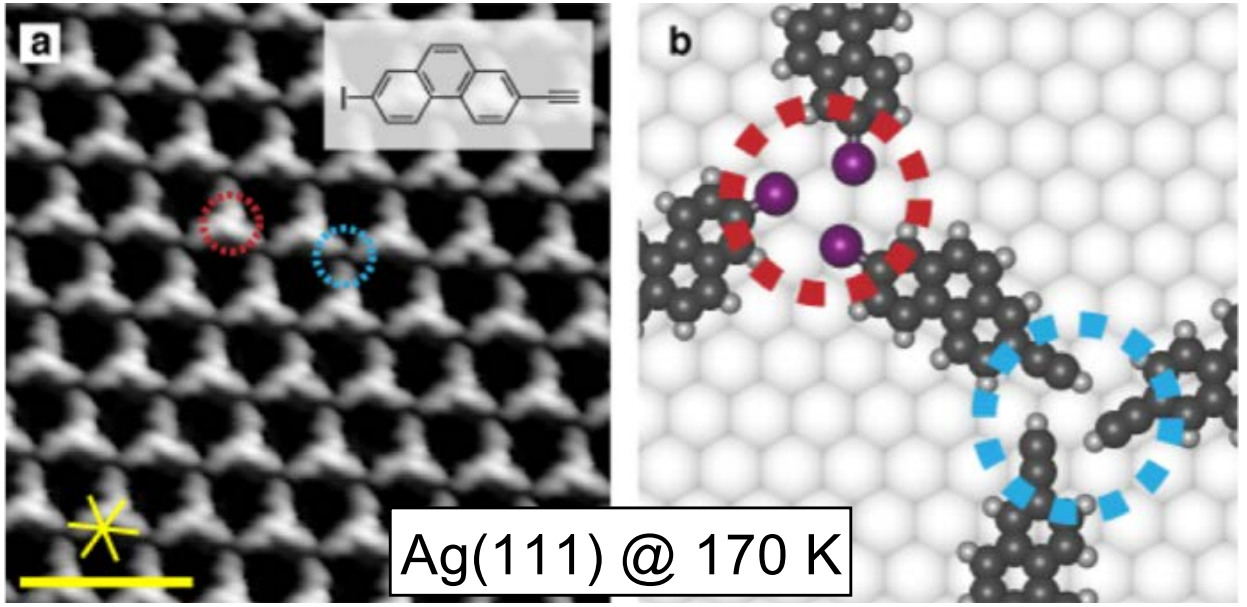
N. Cao, B. Yang *et al.* Nature Comms. 2023

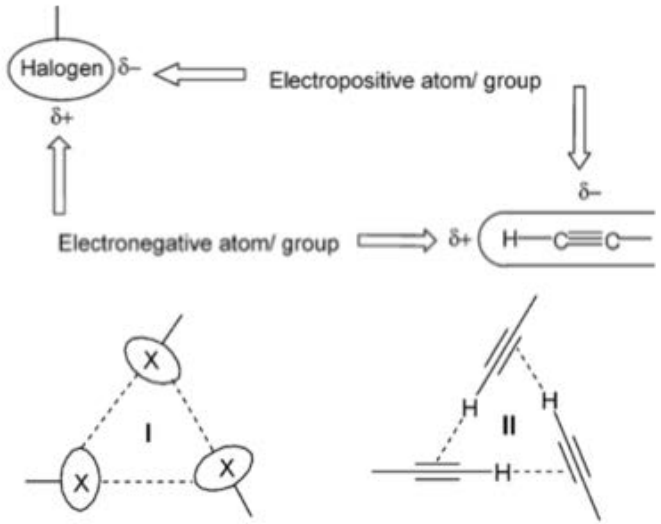
Supramolecular Assembly of EIP on Ag(111)

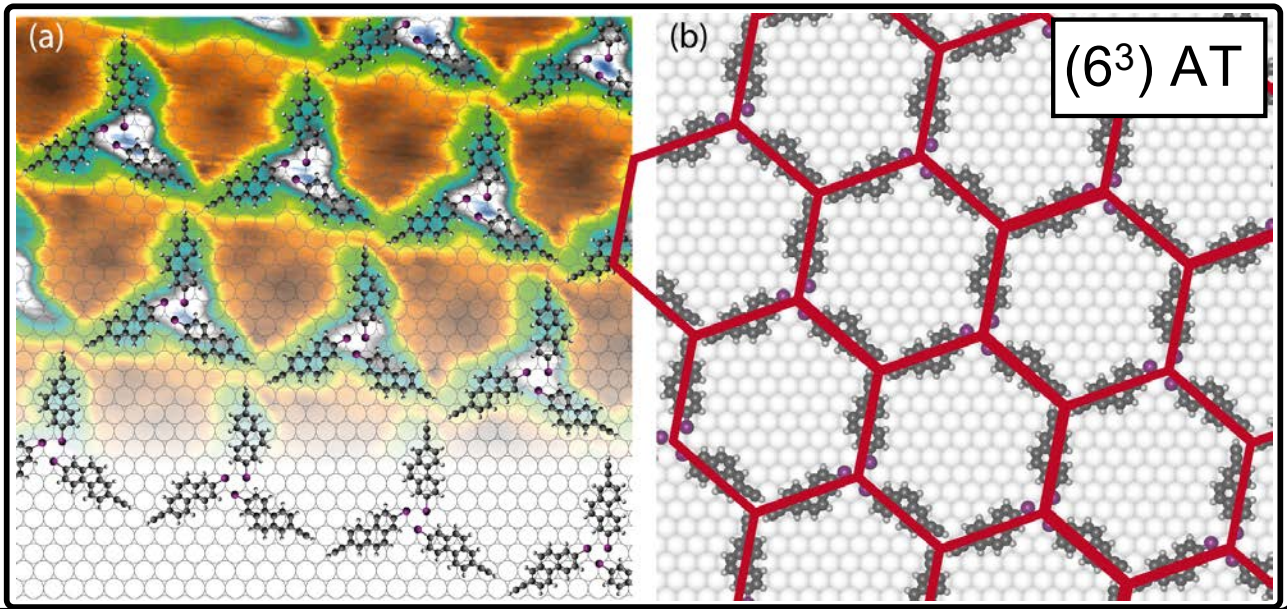


Ethynyl-iodophenanthrene - **EIP**

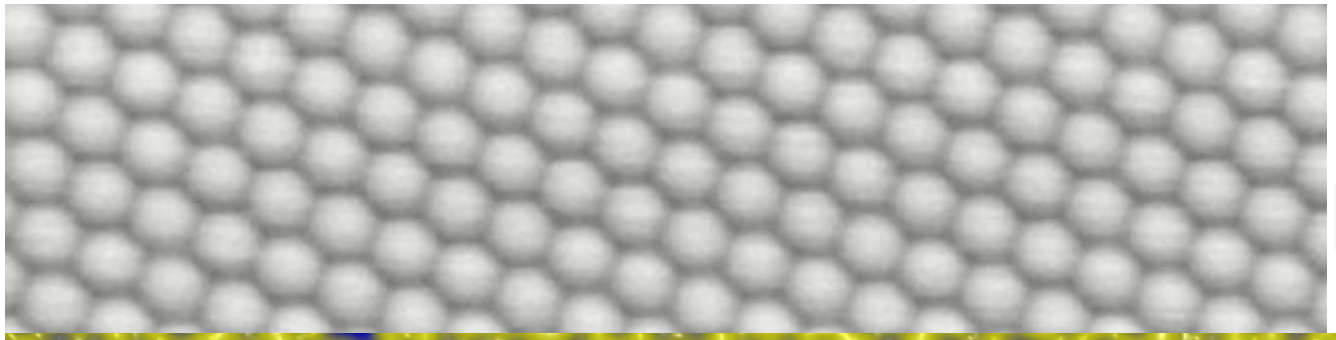
- 2 different functional groups
  → self-recognition
  → distinct reaction sites
- asymmetry in planar backbone

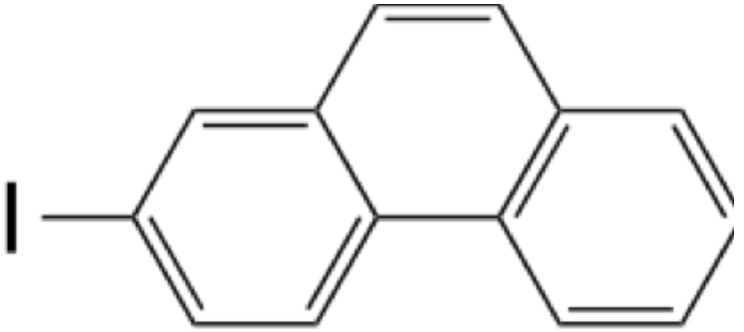


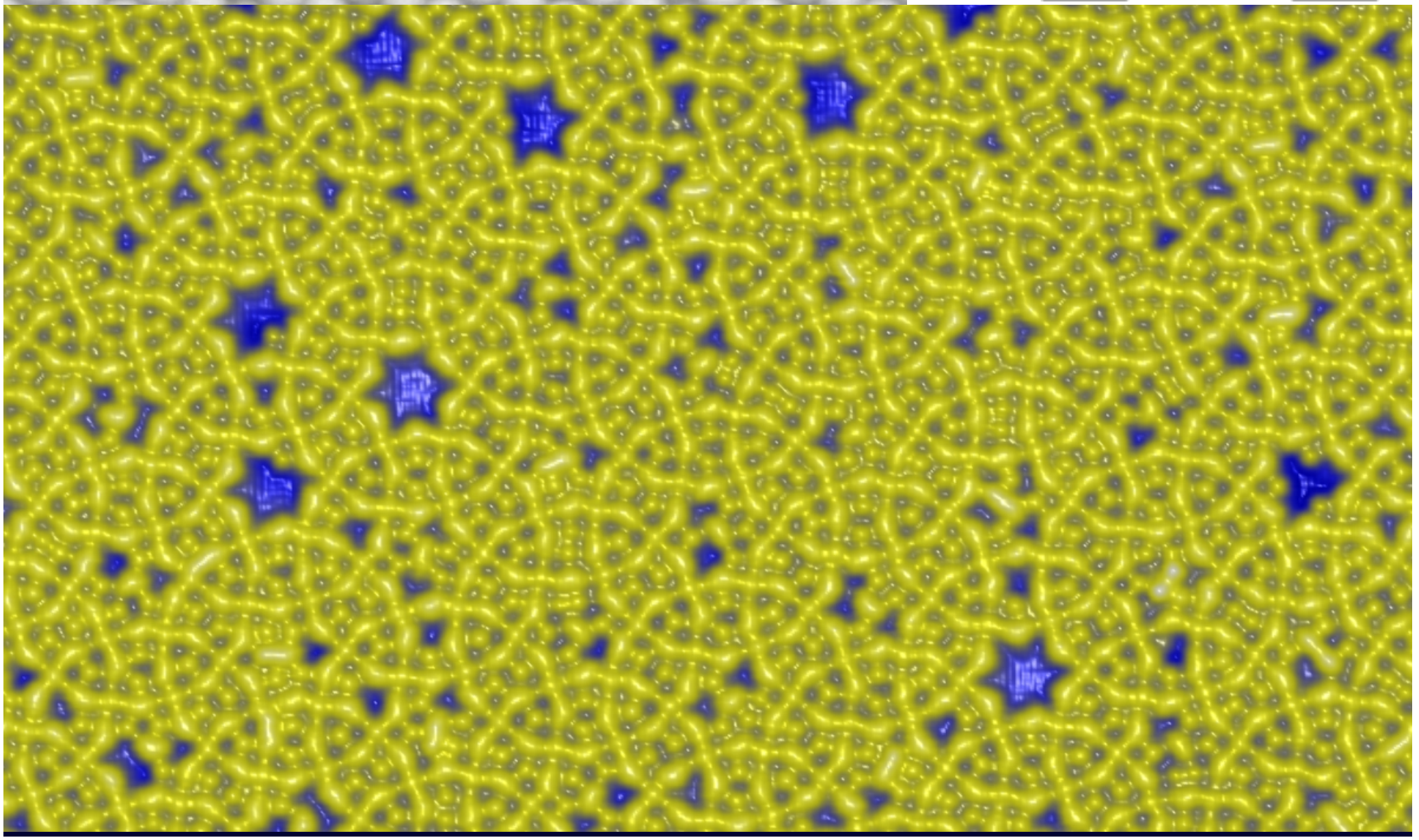




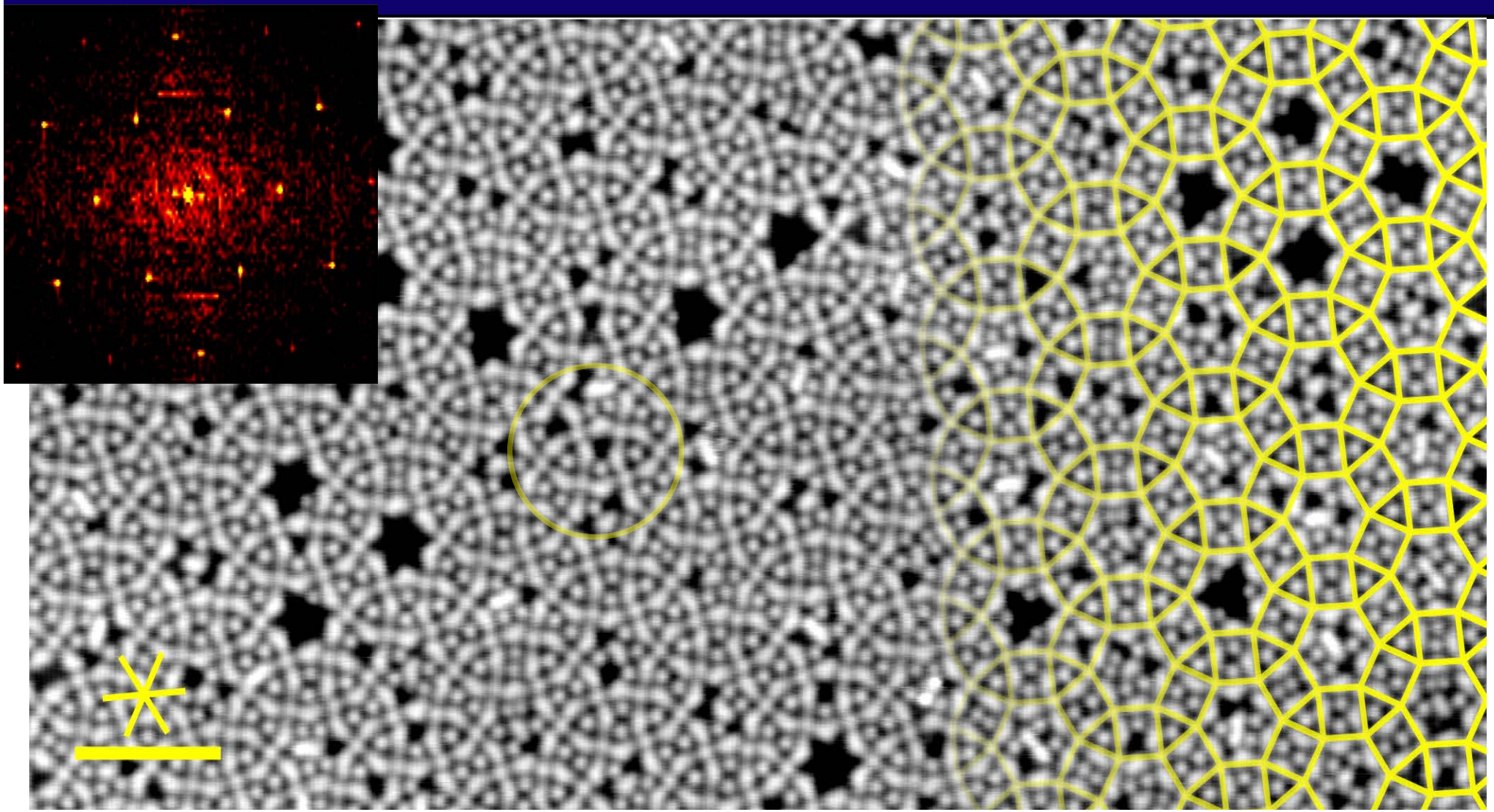
Nature Chem. 2018 - 10.1038/NCHEM.2924




I



Regular Network with Long-Range Order

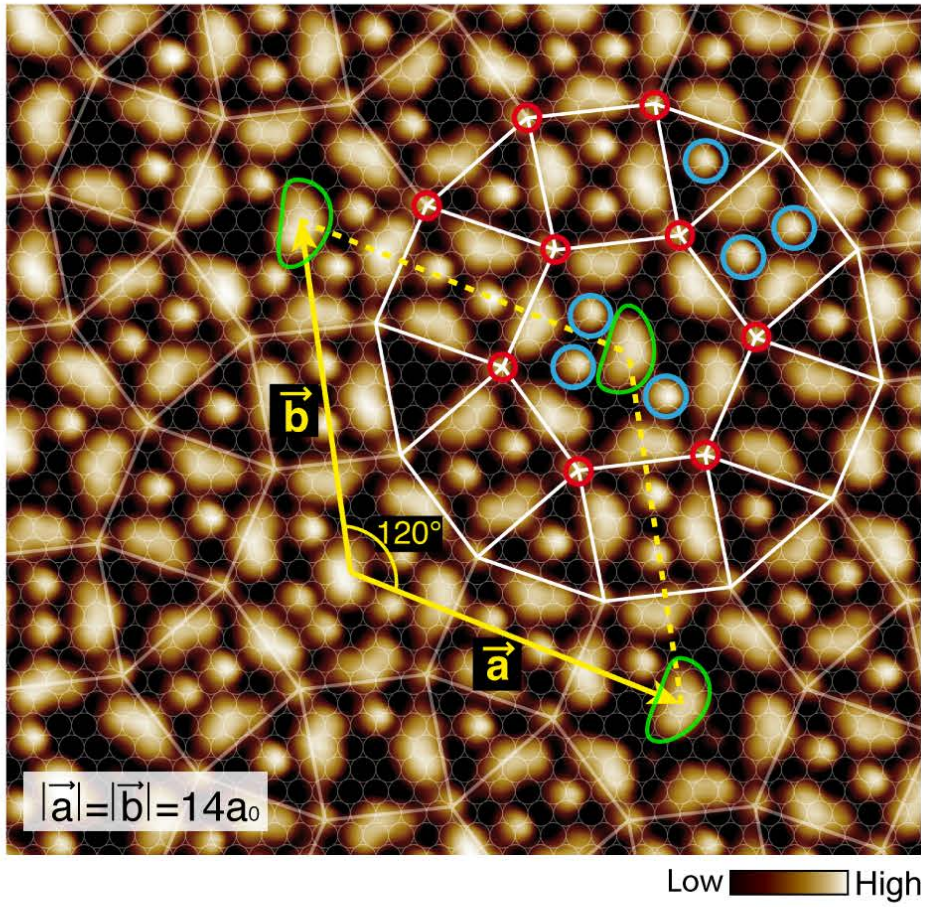


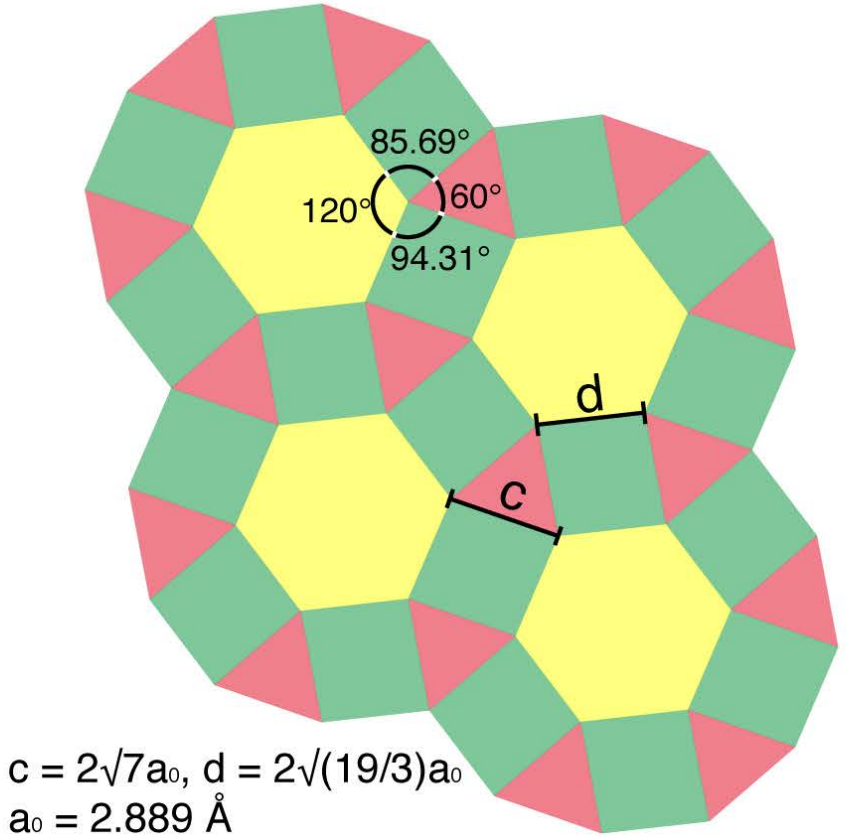
V_B = -50 mV; I = 0.05 nA

- **transformation upon annealing molecular layer to 300 - 350 K**
- **complex superlattice with hexagonal symmetry**

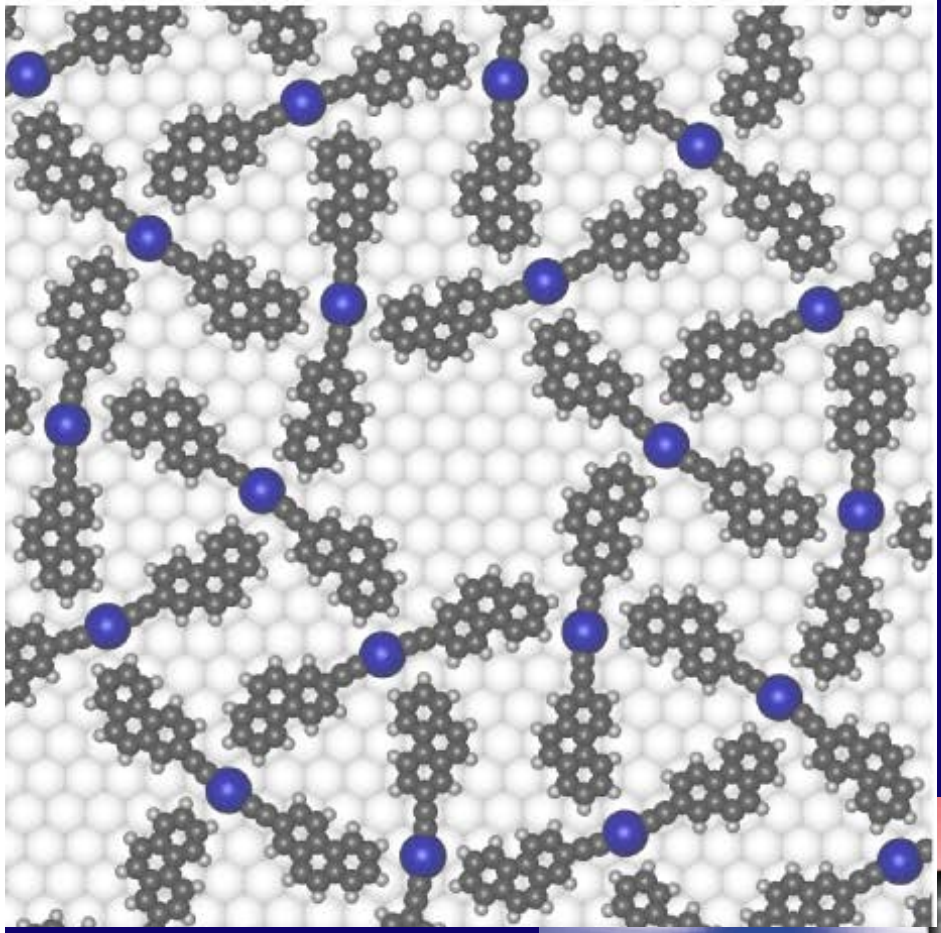
Nature Chem. 2018 - 10.1038/NCHEM.2924

Network Structure and Elements



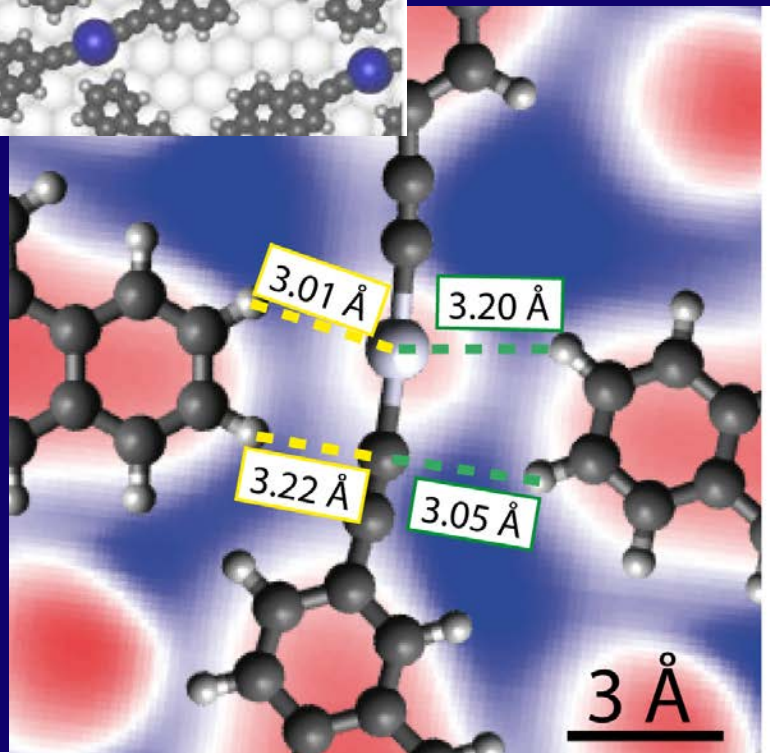


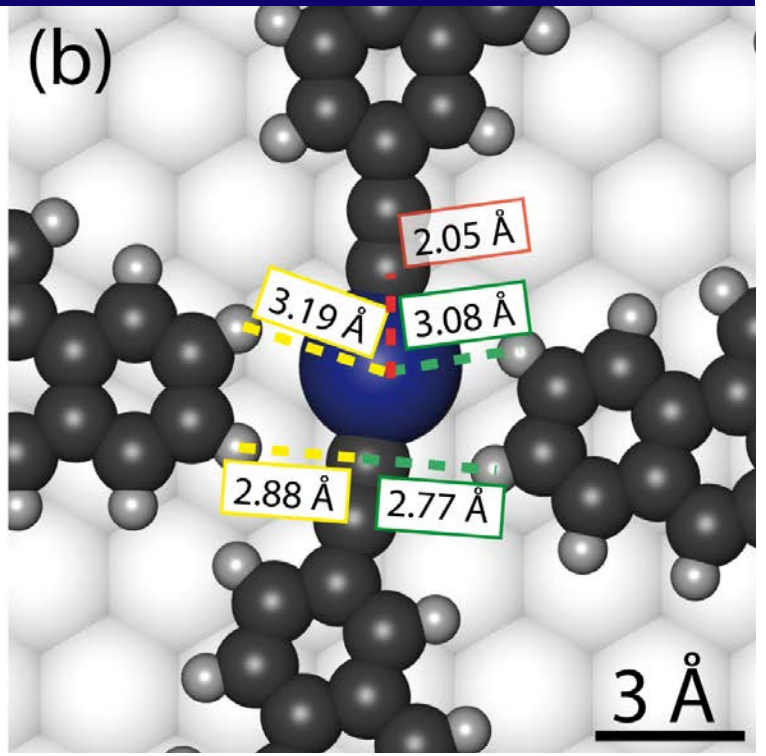
- **pattern close to ideal 3.4.6.4 Archimedean tessellation**
- **molecular backbones span superlattice elements**
- **released iodine atoms in lattice voids**



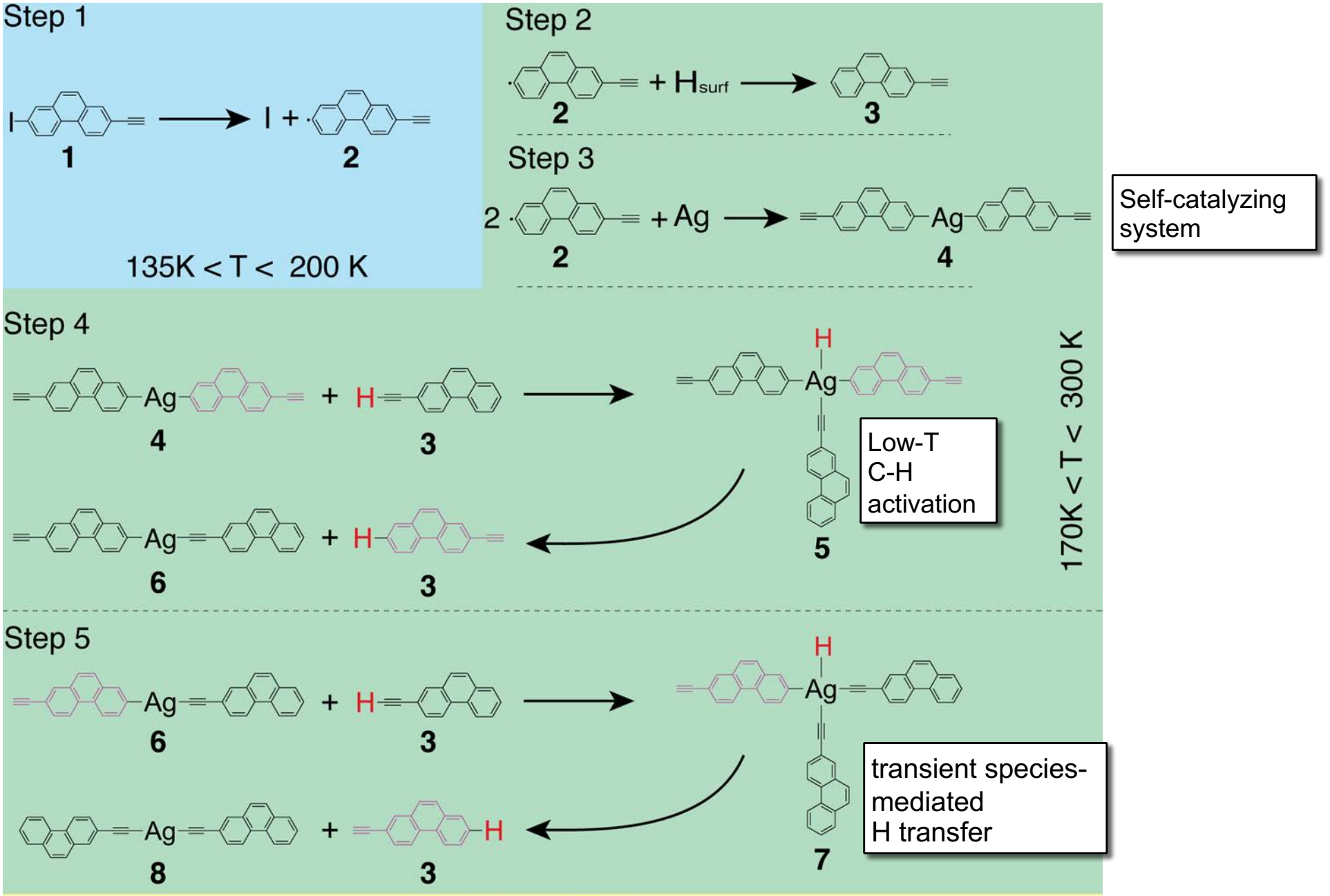
Idealized DFT Model

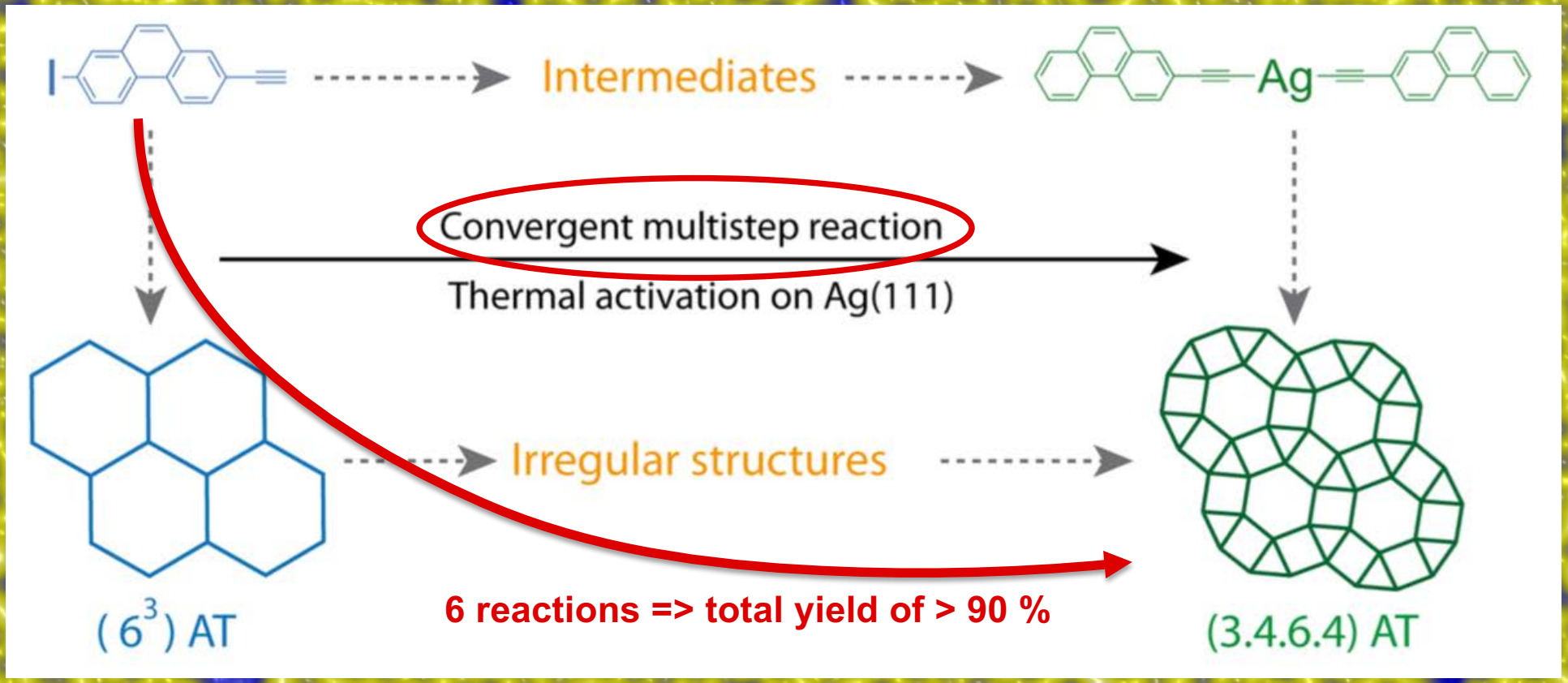
- from combined XPS, NEXAFS and STM observations over 200K T-range
- Convergent transformation affords **alkynyl–Ag–alkynyl bridges**
- EIP backbones recombined with released H





Convergent Multi-Step Synthesis Protocol




I
Intermediates
Ag
Convergent multistep reaction
Thermal activation on Ag(111)
Irregular structures
(6 3) AT
6 reactions => total yield of > 90 %
(3.4.6.4) AT

Conclusions & Inspirations [not necessarily exhaustive]

Adatom-mediated chemical conversions on surfaces

- many aspects elusive and hard to quantify
- convincing evidence for significance & chemical impact
- catalytic relevance supported by sophisticated simulations
- possibly ubiquitous though underestimated
- further implications and detailed mechanisms to be explored
  - ➔ instrumental for many on-surface synthesis protocols
  - ➔ serve to achieve novel compounds and 2D-materials
  - ➔ mediate emergence of functional architectures

- mobile adatoms can be interpreted as a SAC variant
- phenomenology underpins notion of *surface dynamic heterogeneity*