Investigation of Low-Dimensional Conjugated Nanostructures on Metal Substrates Using Scanning Tunneling Microscopy

Ran ZHANG

Supervisor: Prof. Nian LIN

Outline

➢ Introduction

- Low-dimensional conjugated nanostructures
- Fabrication of low-dimensional conjugated nanostructures

➢ Supramolecular templates:

- **Metal quantum dots:**
  -Growth of Bi nanocluster arrays directed by supramolecular templates
- **Chemical reactions:**
  -Sonogashira coupling directed by supramolecular templates

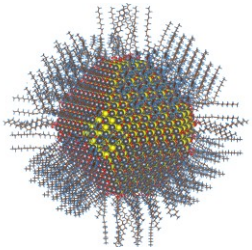
➢ On-surface synthesis:

- **2D conjugated MOF:**
  -$Cu_3(C_6O_6)$ Metal-Organic Monolayer
- **2D conjugated COF:**
  -Chemical reactions of aryl-dibromo molecules on metal surfaces

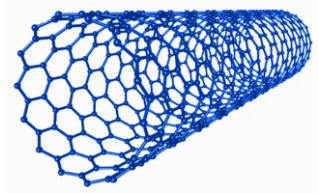
➢ Summary

Introduction: Low-dimensional conjugated nanostructures

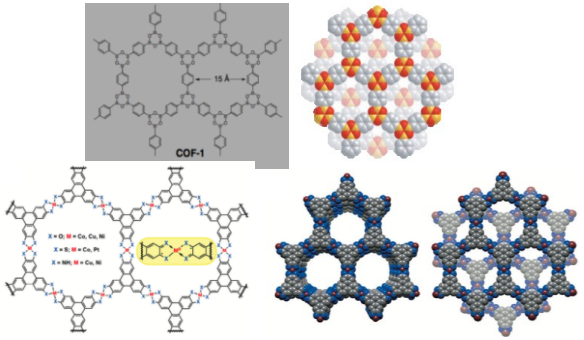
Nanomaterials: sizing from 0.1 to 100 nm



Quantum dots



Single-walled CNTs

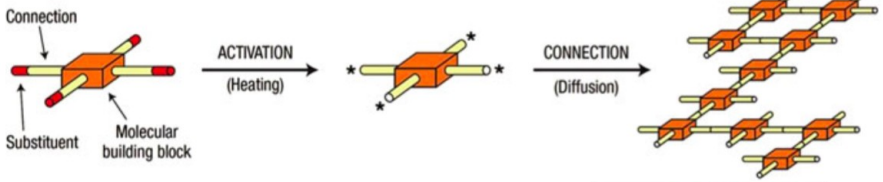


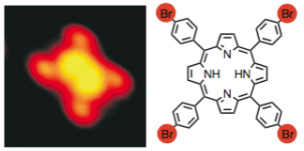
Staggered COF/π-d conjugated MOF

0D **1D** **2D**

Atomic precision

On-surface synthesis

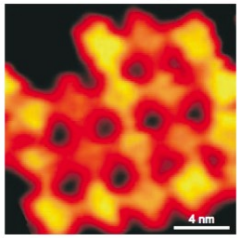




Molecular Precursors

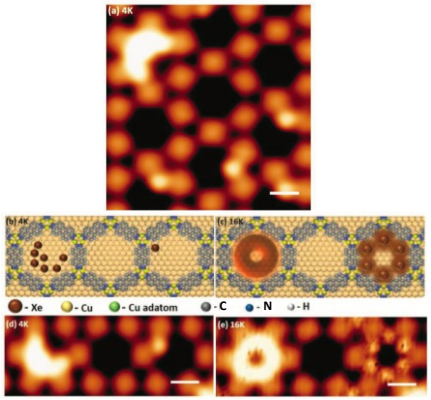
Annealing

Au(111)

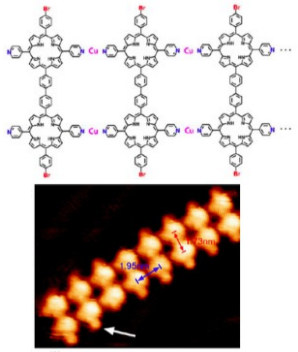


2D COF

Supramolecular templates



➢ **Cage metal clusters**



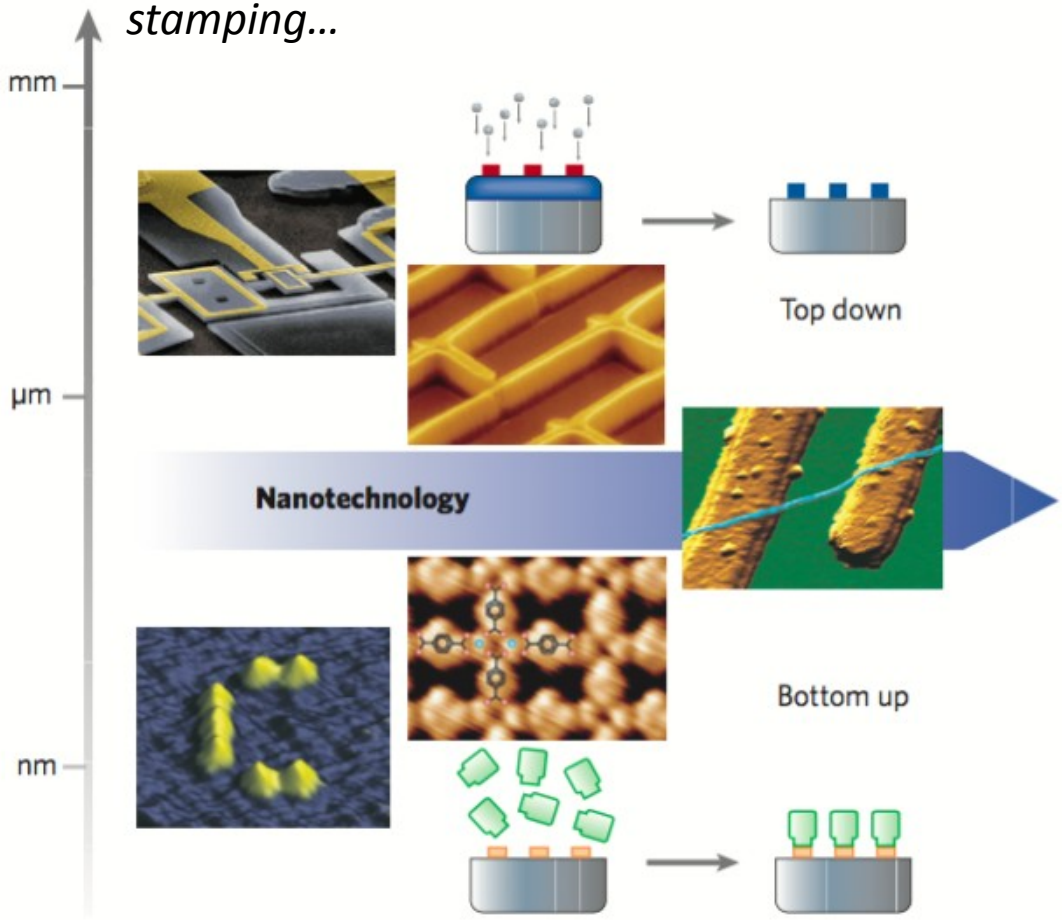
➢ **Direct on-surface synthesis**

QD: https://en.wikipedia.org/wiki/Quantum_dot
CNTs:
http://large.stanford.edu/courses/2015/ph240/kumar1/
Science ***310***, 1166-1170(2005).
Angew. Chem. Int. Ed. ***55***, 3566 – 3579(2016).

Nat.Nanotechn. ***2,*** 687–691 (2007).
Small ***15,*** 1803169(2019).
J. Am. Chem. Soc.***135***, 3576-3582(2013).

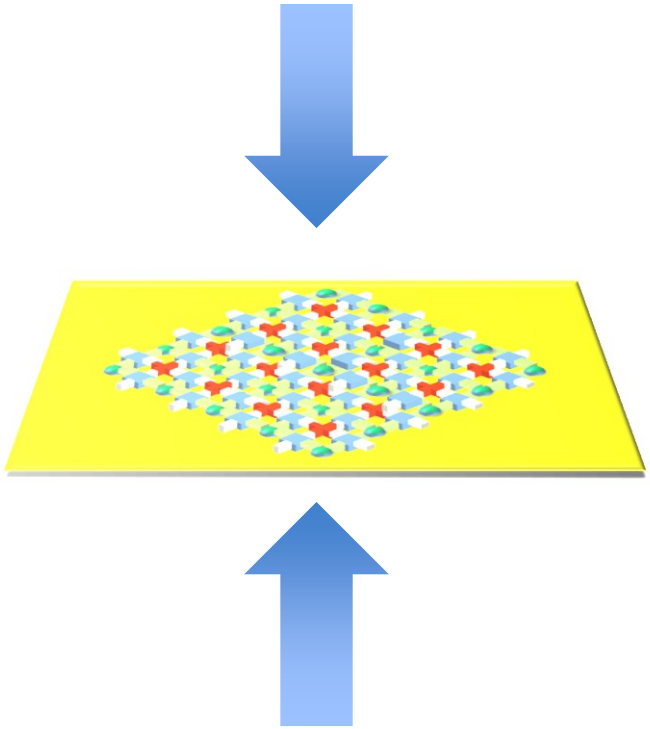
Introduction: Fabrication of Low-dimensional nanostructures

photolithography etching, electron-beam writing, stamping…



Covalent/non-covalent interaction

Top down

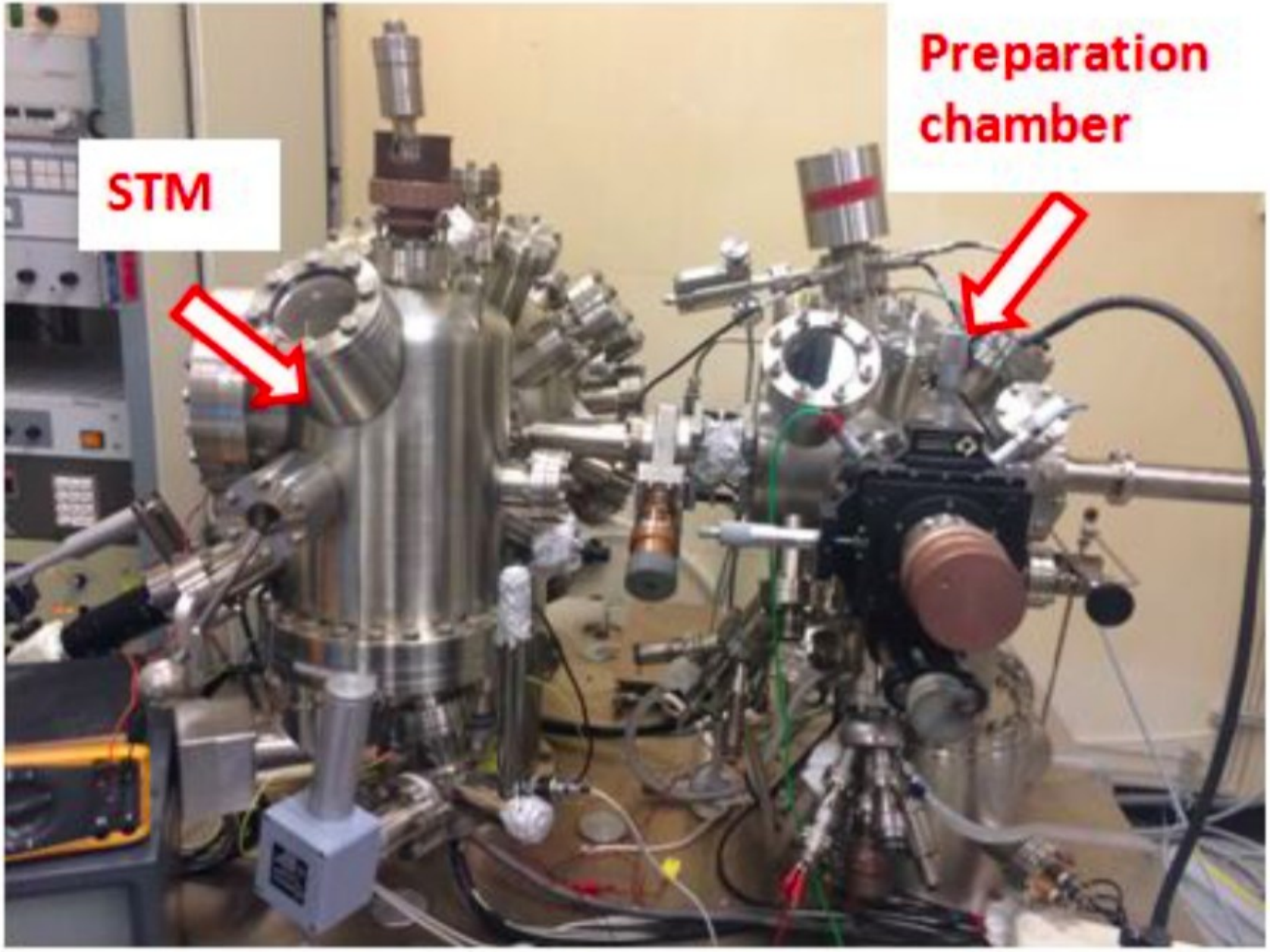


Atomic precision: 0.1nm

Bottom up

Nature ***2005,*** 437, 671–679.

Introduction: Experimental Setup



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Introduction

2D superlattices of metal quantum dots

Optical and electronic properties:

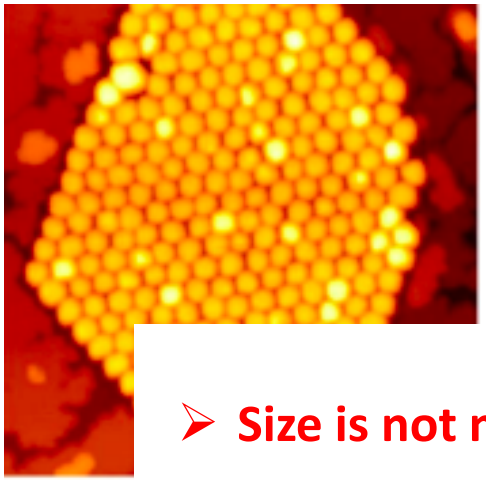
- ✓ Structure
- ✓ Periodicity
- ✓ Intercluster spacing

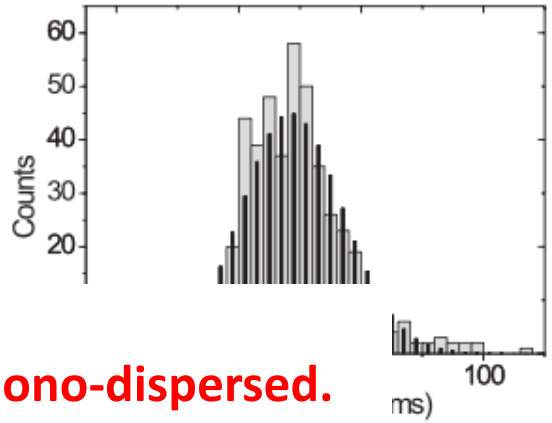
Bismuth:

- ✓ *High carrier mobility*
- ✓ *Strong SOC*
- ✓ *D_w of Bi: Semimetal –>semiconductor*

…

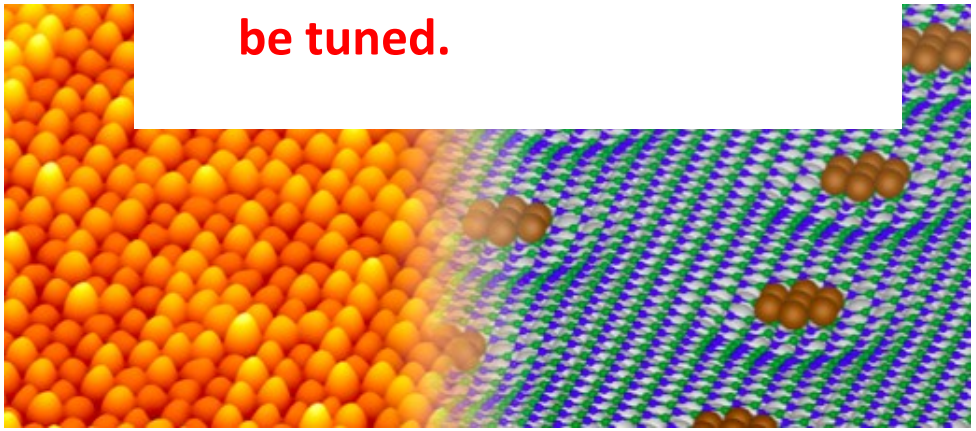
Metal clusters grown on substrates





Ir /Gra

- ➢ **Size is not mono-dispersed.**
- ➢ **Intercluster spacing cannot be tuned.**



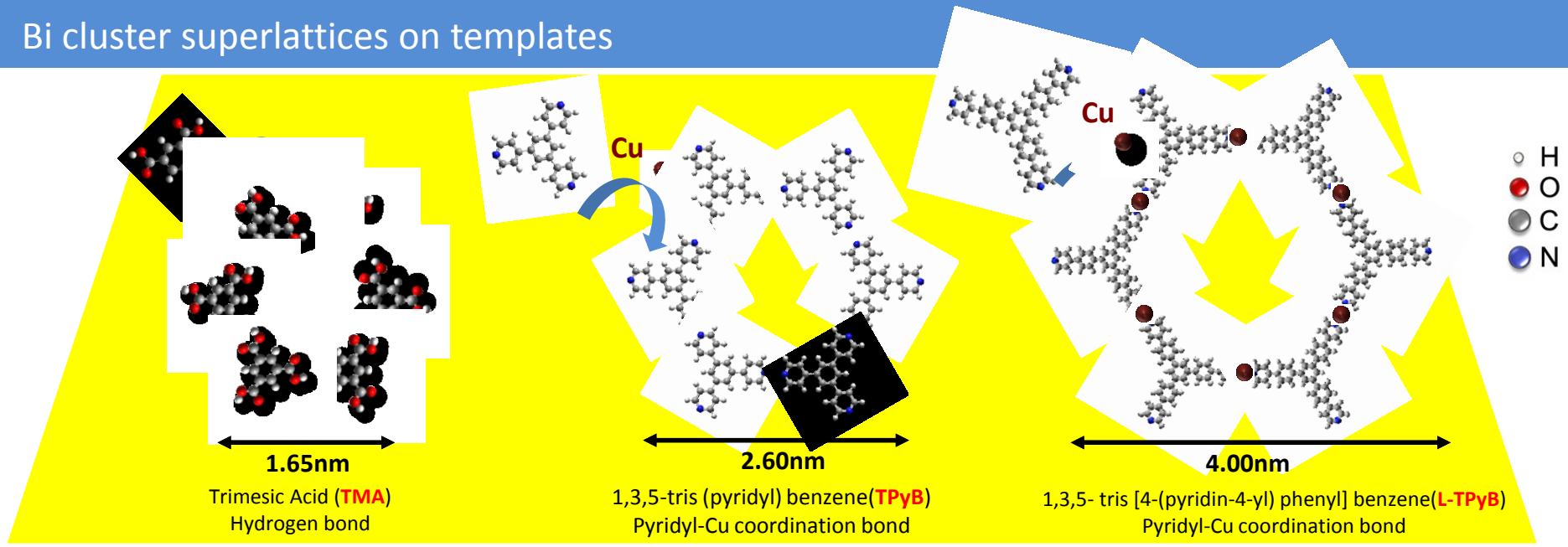
Ir /h-BN/Ir(111)

Materials Science and Engineering C ***23****, 129–140(2003)*

Ultramicroscopy **42-44**, 556 (1992)
Phys.Rev.Lett. **110**, 086102(2013)
N'Diaye. *et. al., New J Phys.* **11**, 1 –19(2009)

Results and Discussion

Bi cluster superlattices on templates



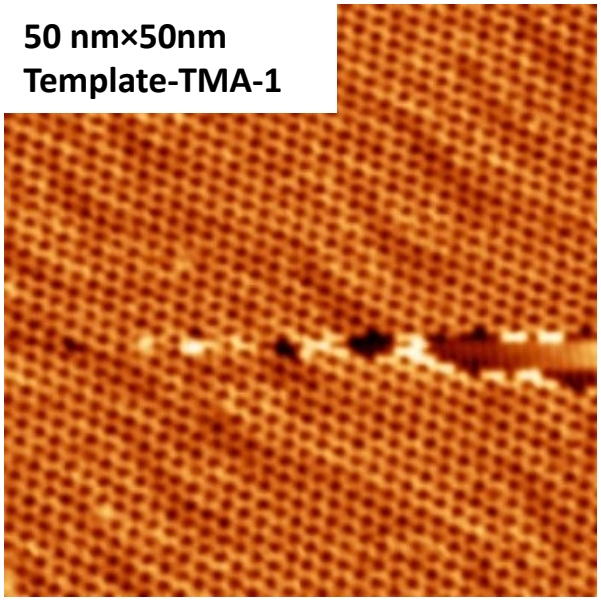
Trimesic Acid (**TMA**)
Hydrogen bond

1,3,5-tris (pyridyl) benzene(**TPyB**)
Pyridyl-Cu coordination bond

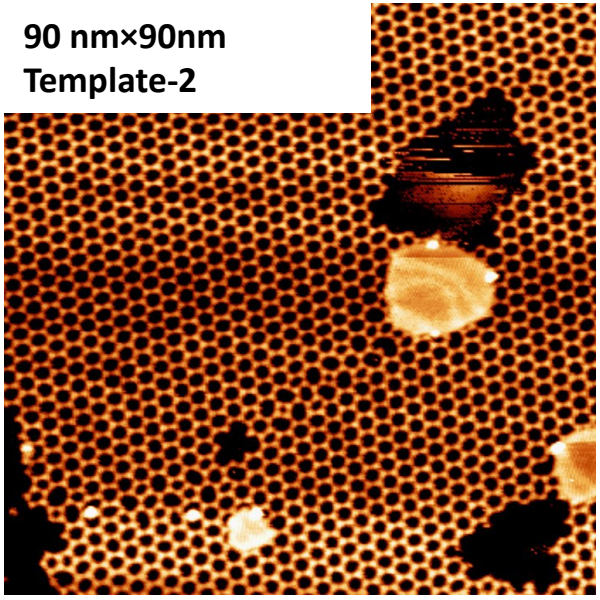
1,3,5- tris [4-(pyridin-4-yl) phenyl] benzene(**L-TPyB**)
Pyridyl-Cu coordination bond

Au(111)

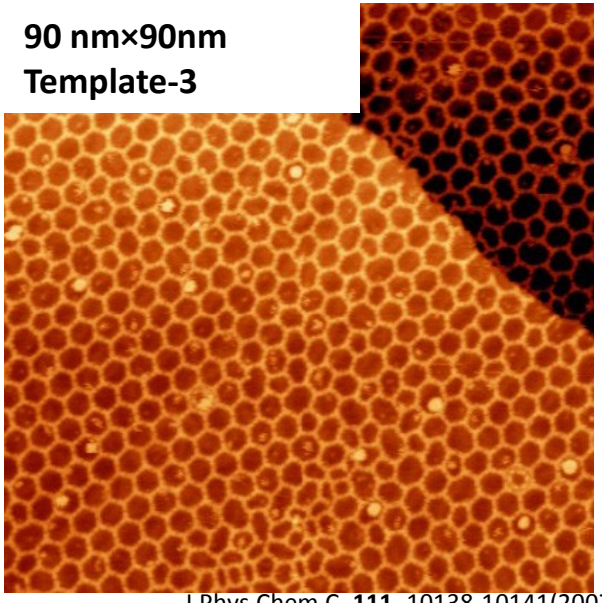
50 nm×50nm
Template-TMA-1



90 nm×90nm
Template-2



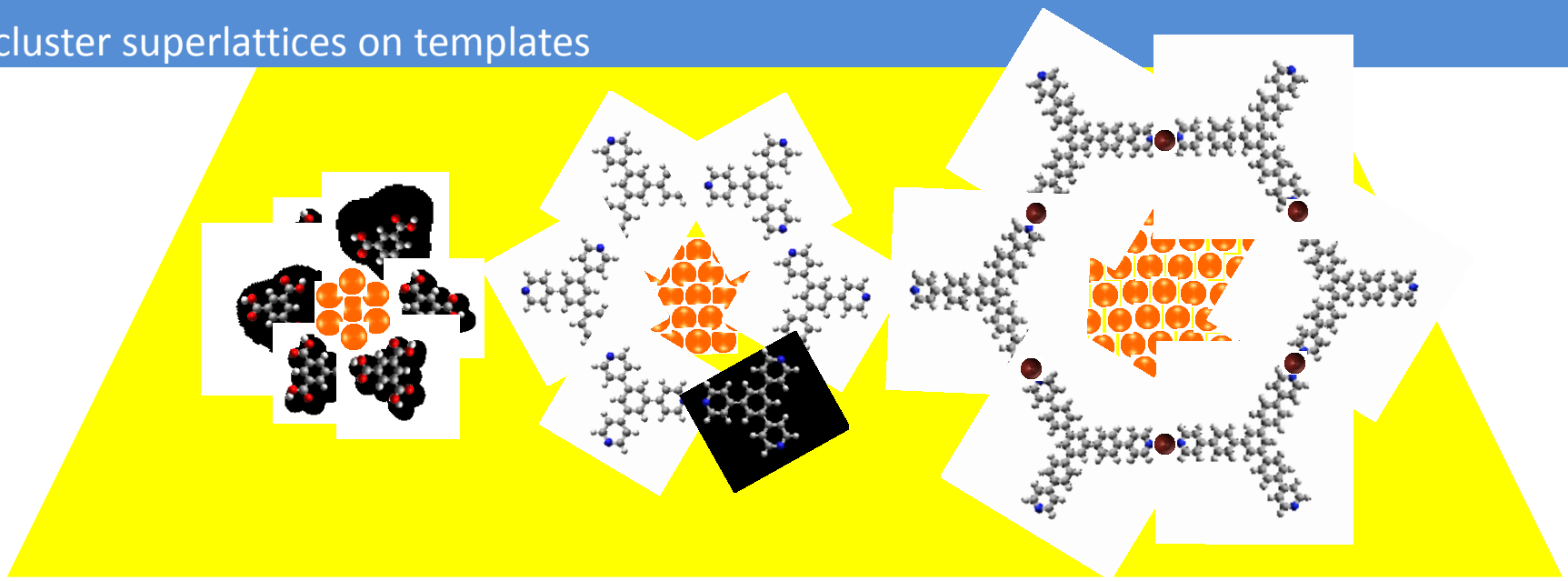
90 nm×90nm
Template-3



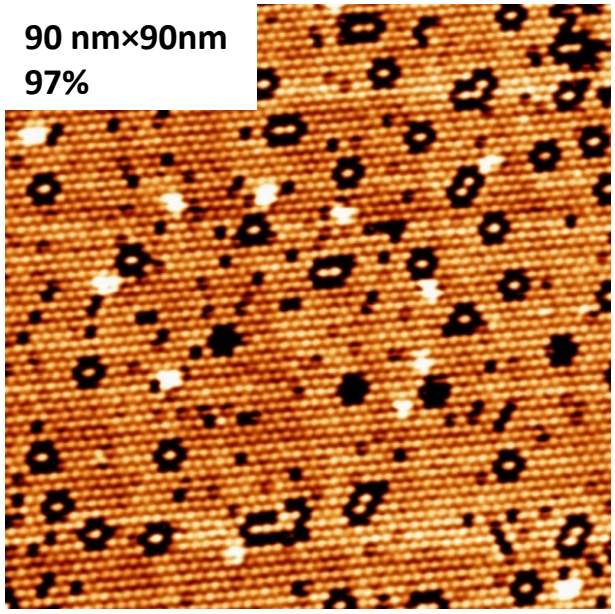
J.Phys.Chem.C. **111**, 10138-10141(2007);
J. Am. Chem. Soc., ***133***, 6150-6153(2011).

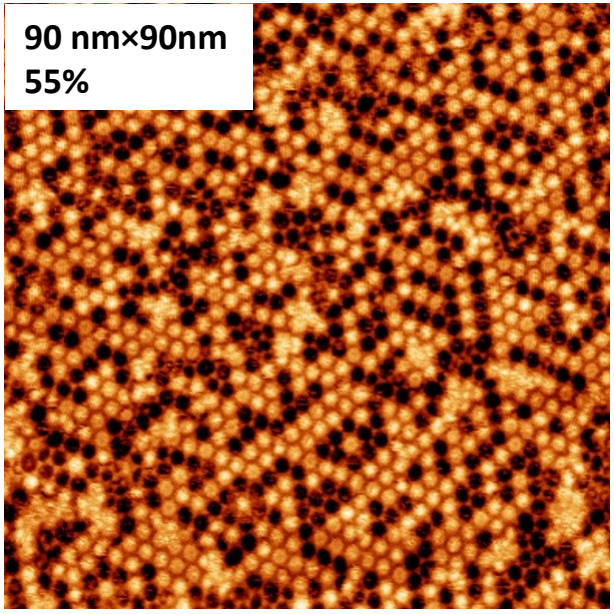
Results and Discussion

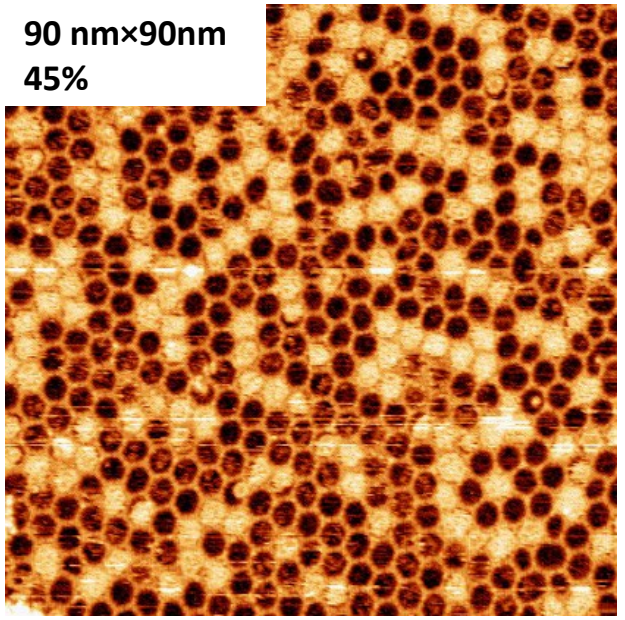
Bi cluster superlattices on templates



Au(111)

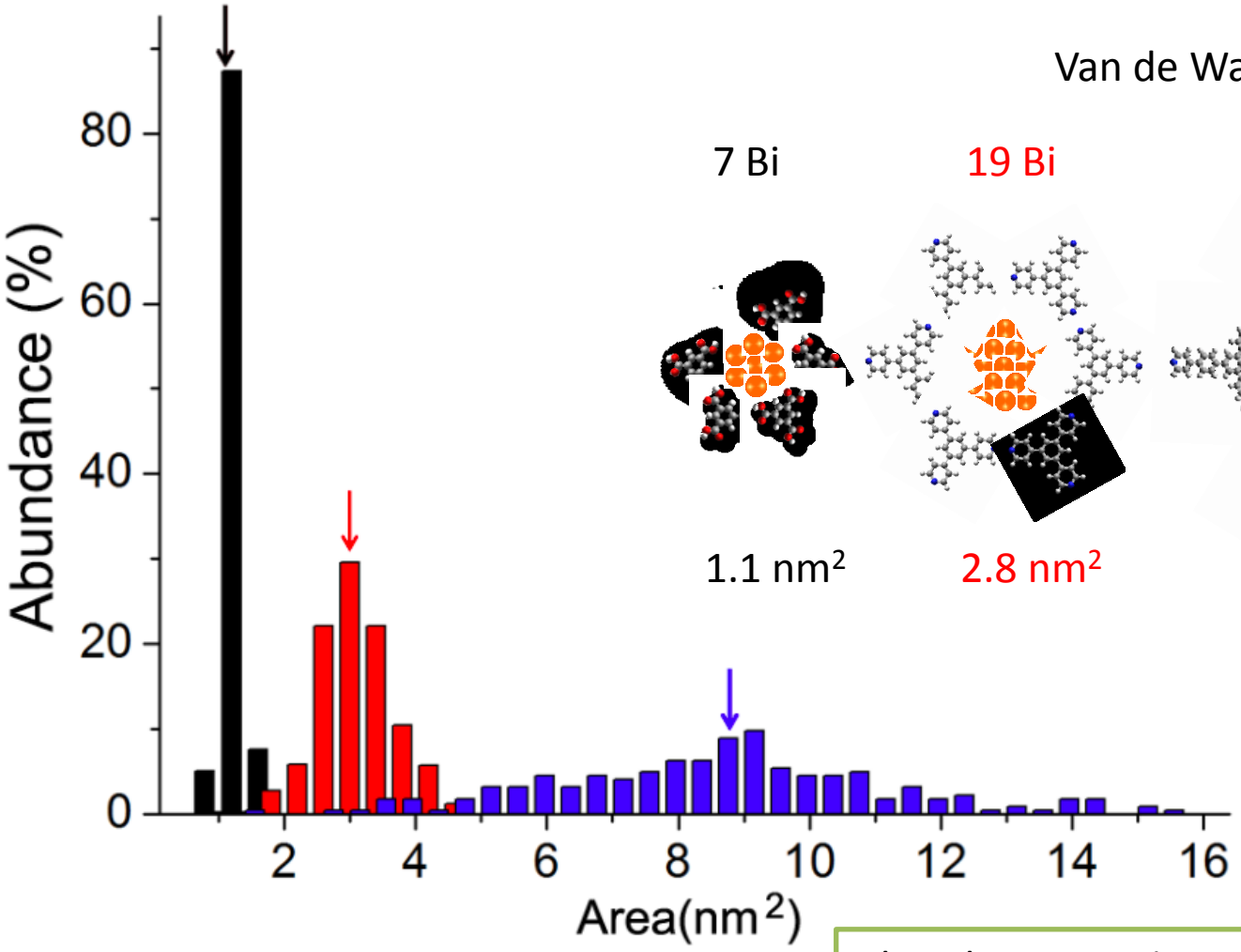






Results and Discussion

Size distribution of Bi clusters



Van de Waals pore size

7 Bi

19 Bi

61 Bi

1.1 nm^2

2.8 nm^2

Bi-Bi: 0.33nm

Abundance: 87%; Area:1.3 ± 0.2 nm^2

Abundance: 30%; Area: 3.0 ± 0.2nm^2

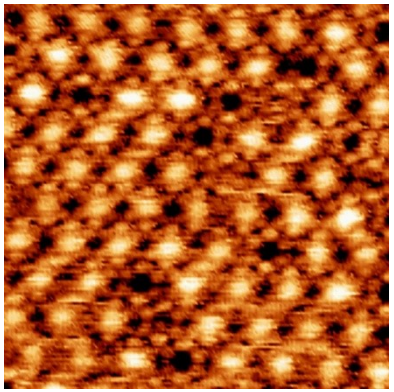
Abundance: 10%; Area: 9.0 ± 0.2nm^2

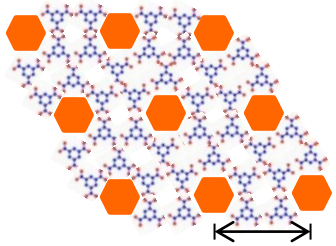
Results and Discussion

Bi cluster superlattices on TMA templates

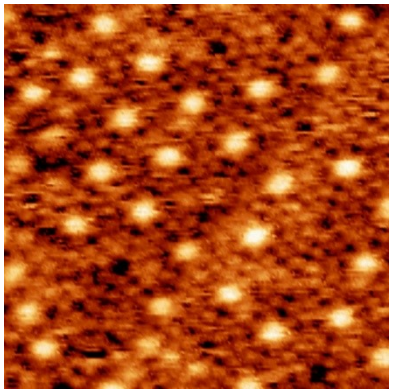
0.6ML molecules; TMA-**n** templates **(20 nm×20 nm)**

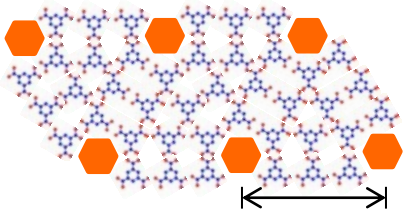
TMA-**2**



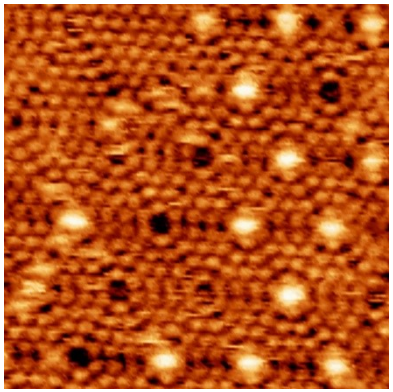


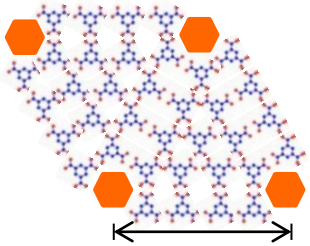
TMA-**3**



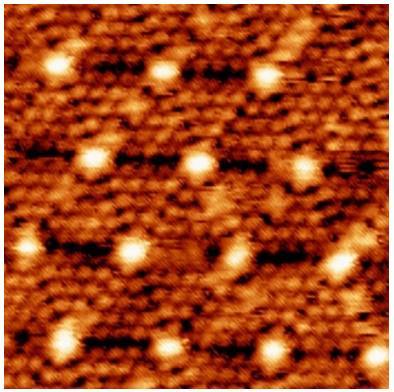


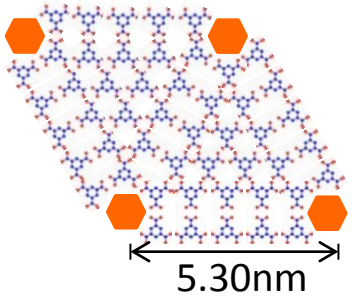
TMA-**4**





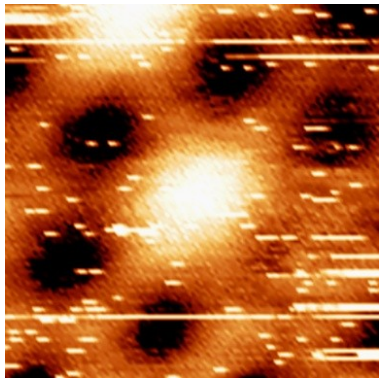
TMA-**5**

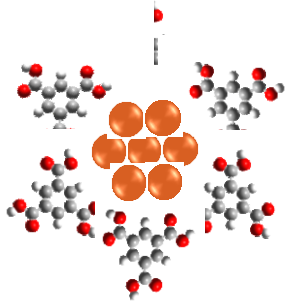




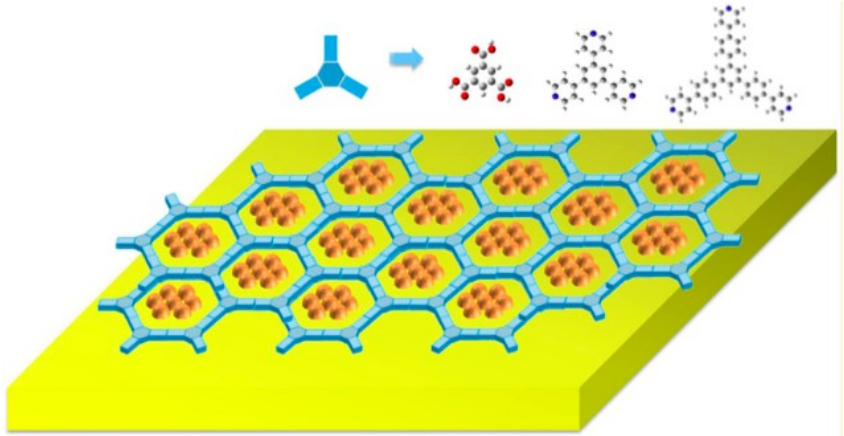
Conclusion

- ✓ Bi quantum dot superlattices.
- ✓ Atomic precision by supramolecular templates
- ✓ Tuning nanocluster size and superlattice periodicity





TMA +Bi



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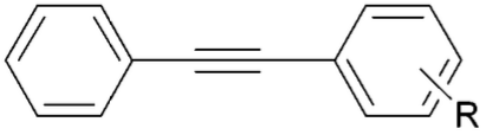
Introduction

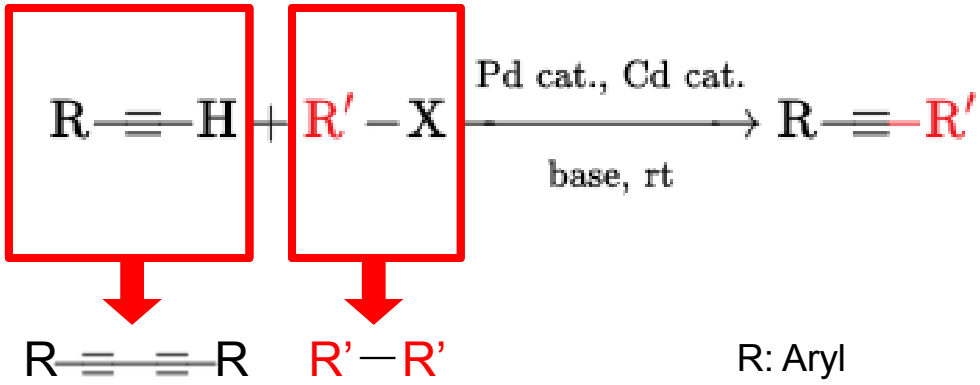
Sonogashira cross-coupling

Aryl-ethynyl compounds



Sonogashira cross-coupling(SCC)

Homo coupling



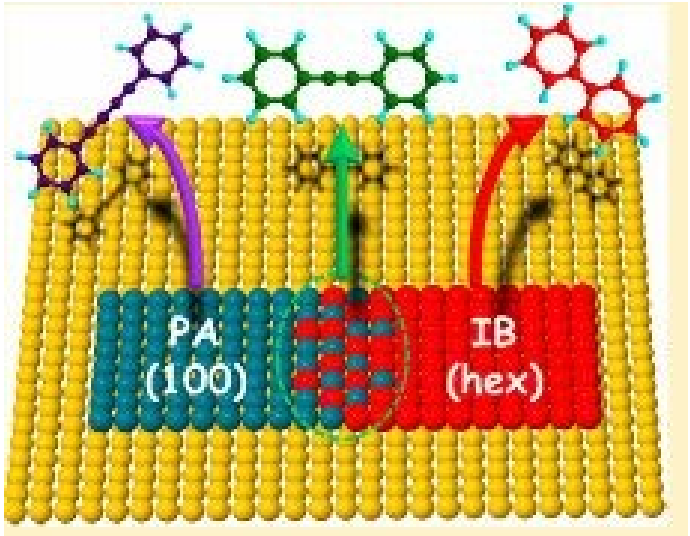
Glaser coupling

…

Ullmann coupling

…

R: Aryl
R': Aryl or Vinyl
X:I,Br, Cl or OTf



Au(100)

On-surface SCC coupling only took place at island boundaries.

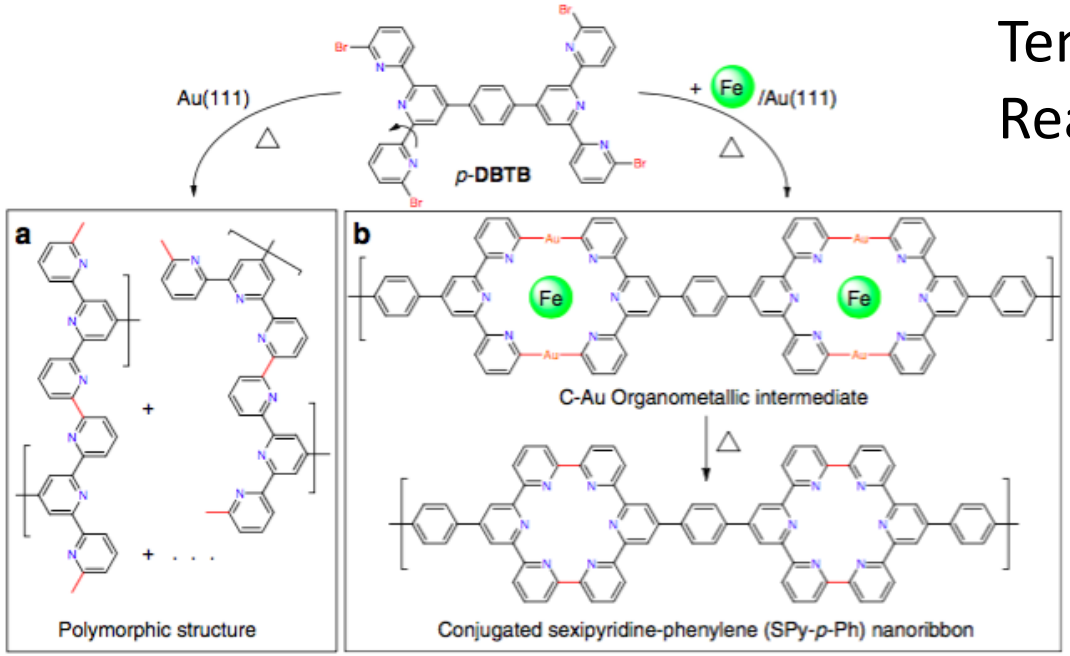
Org. Lett., Vol. 5, *No. 11*, 2003
J. PHYS. CHEM. C. **2014,** *118*, 11677–11684

Introduction

Chemical templates

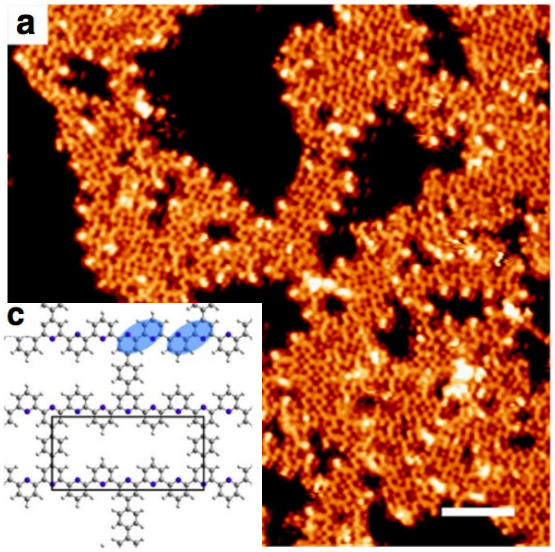
Template:

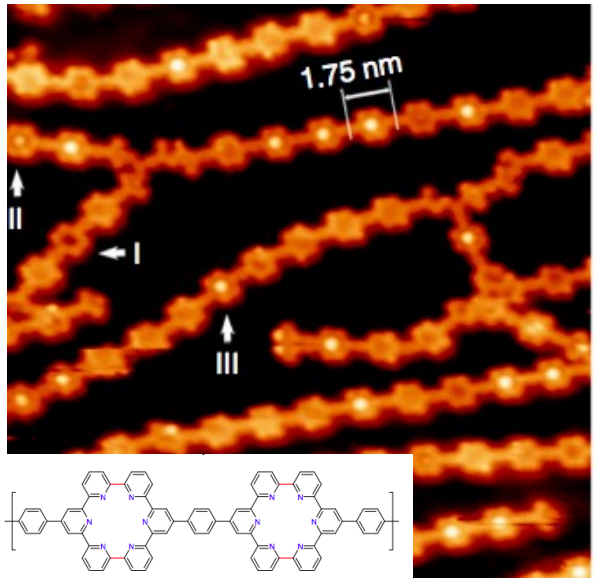
Reactant + metal –> *coordination*



With template

Without template



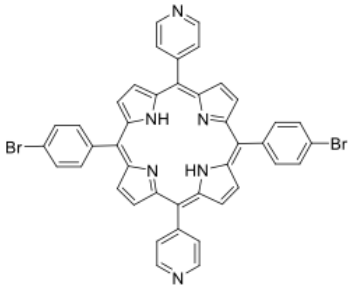


doi.org/10.1038/s41467-018-07933-0

Results and Discussion

Reaction without templates on Au(111)

Reactant 1:



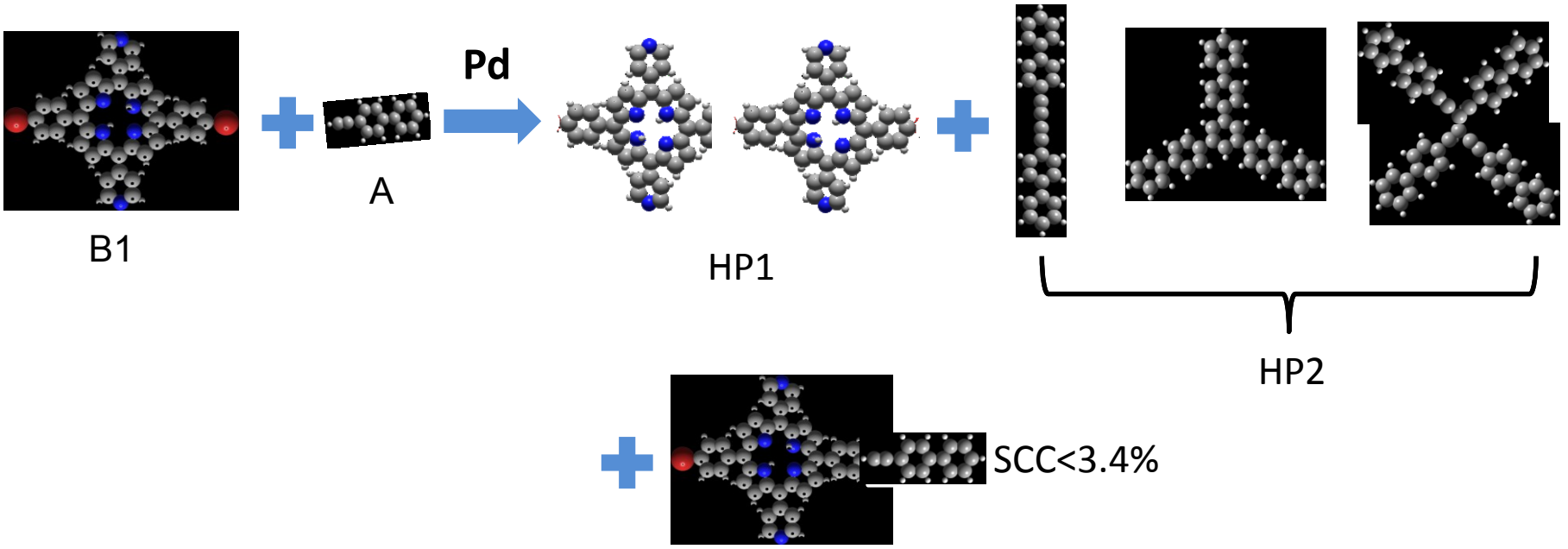
B1:

5,15-di-(4-pyridyl)-10, and 20-bromophenyl porphyrin

Reactant 2:

A:

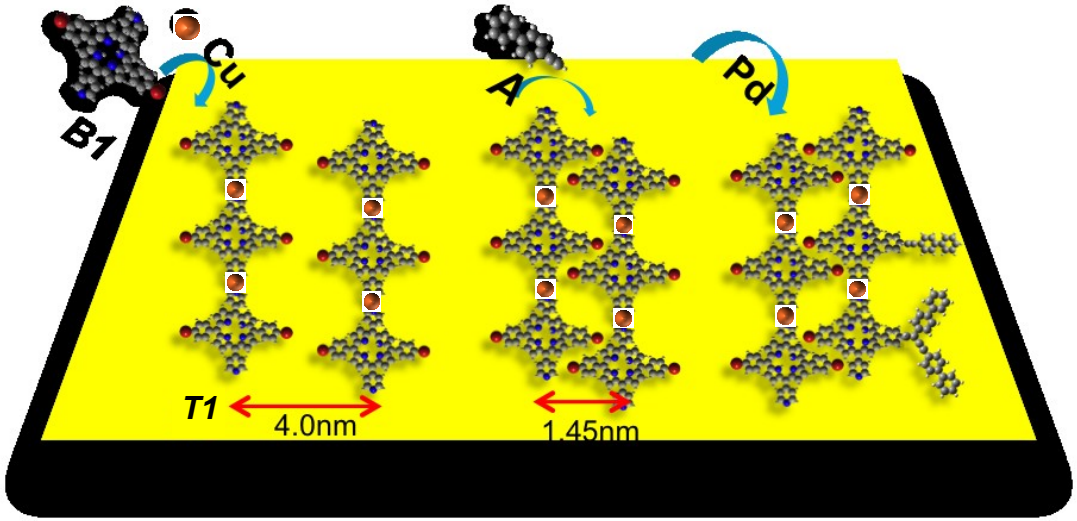
4-ethynylbiphenyl

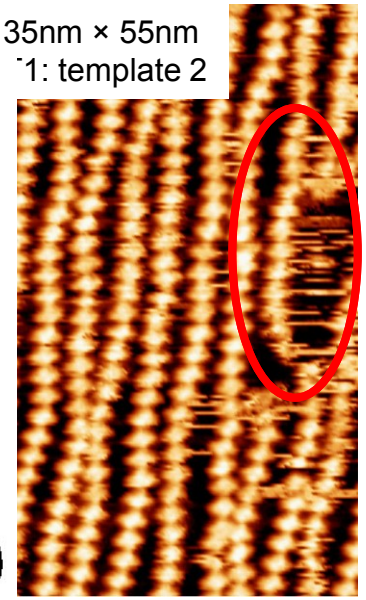


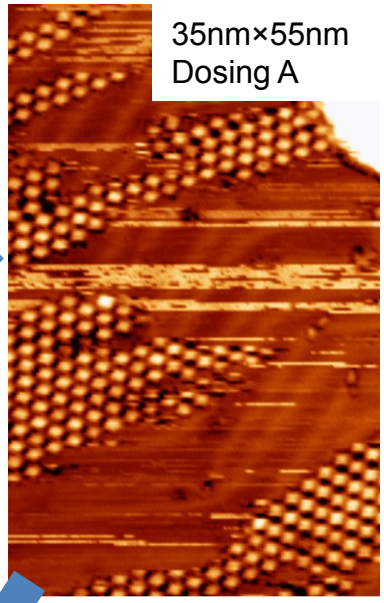
1. B1 form 2D islands; A occupy the surface as 2D gas phase at room temperature.
2. Annealing promotes homo-coupling.
3. SCC<3.4%.

Results and Discussion

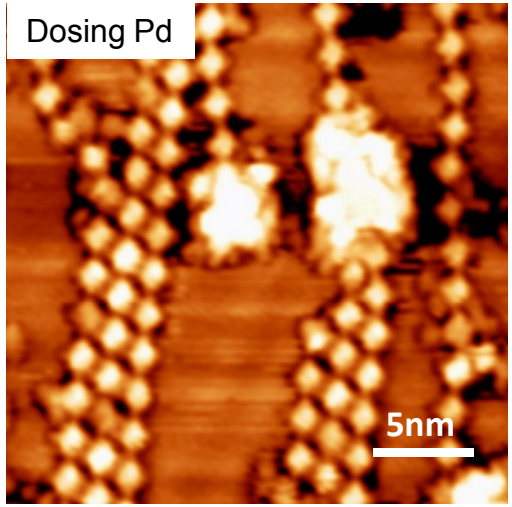
SCC in template 1 on Au(111)

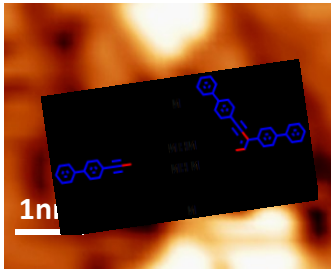






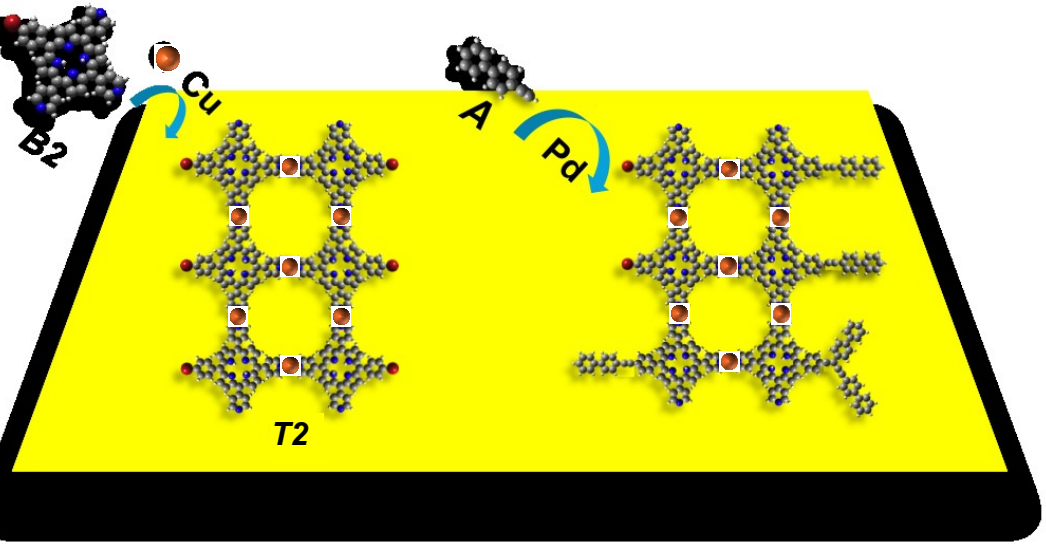
- Phase separation of T1 and A greatly decreases reaction sites.
- Y shape features are binding to B1.
- T1 is unstable even at RT, which cannot inhibit homo-coupling.



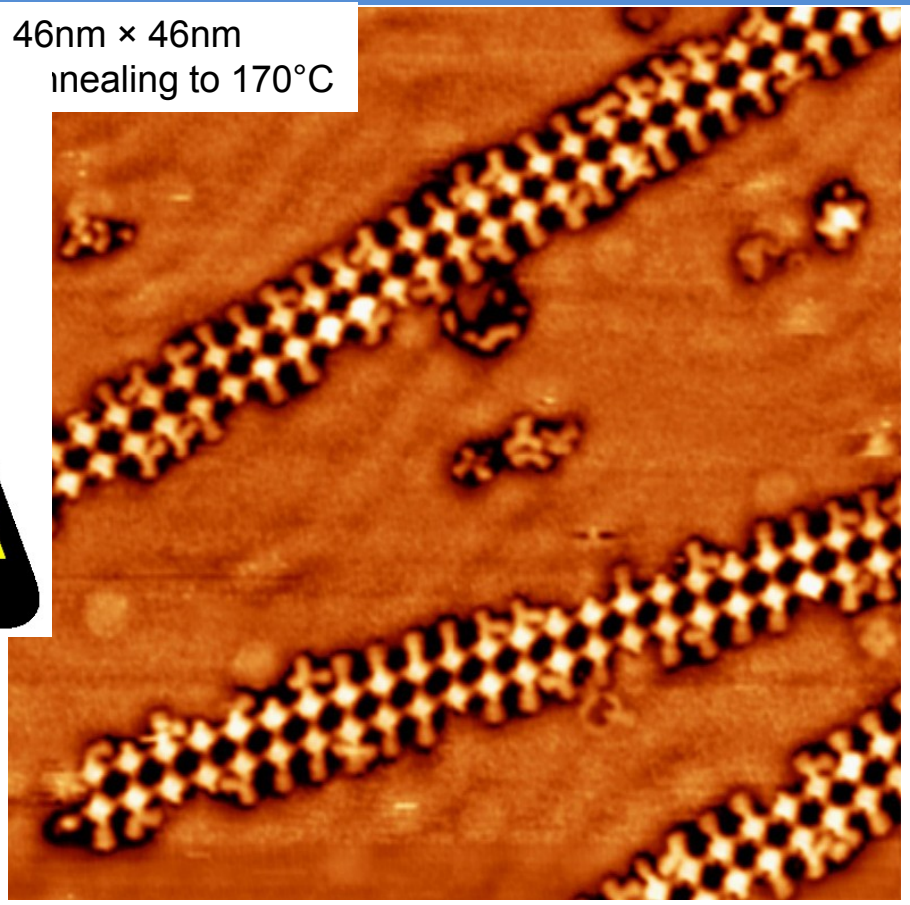


Results and Discussion

SCC in template 2 on Au(111)



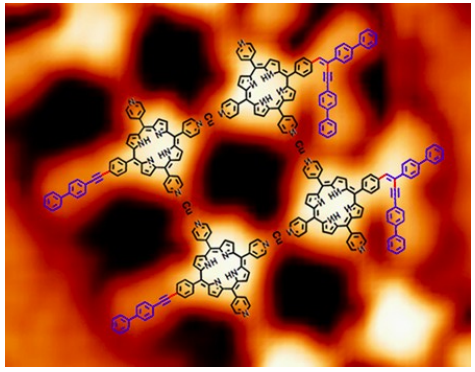
46nm × 46nm
ınealing to 170°C



- Yield at RT ~10%
- Yield at 170°C annealing ~67%
- T2 is an effective template for on-surface SCC.

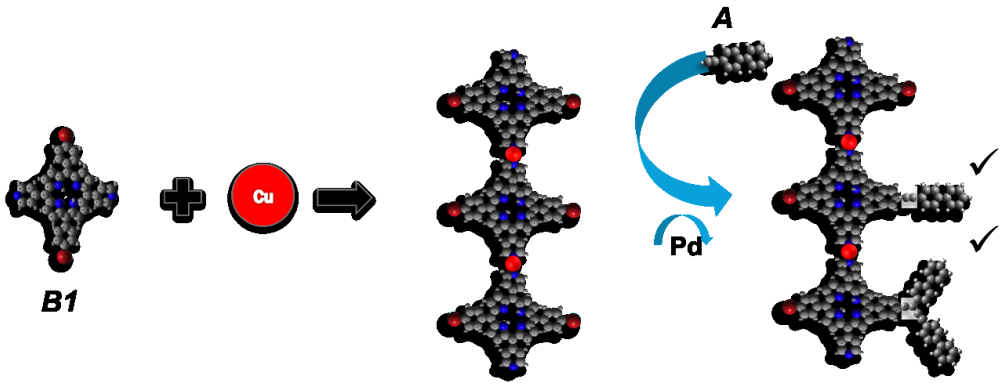
$$Yield = \frac{[SSC]+[CP2]}{[B2]} \times 100\%$$

Molecular model of SCC



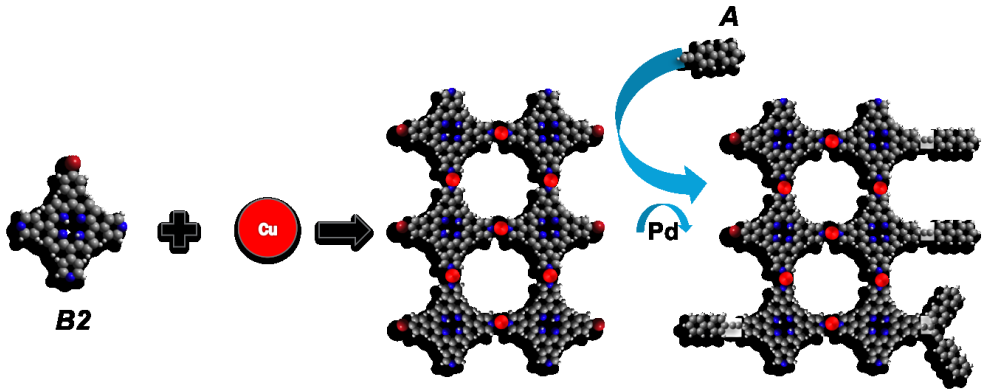
Molecular model of CP2

Conclusion



✓ T1 is not rigid enough. (Structural rigidity)

✓ T1 is not robust enough. (Thermal stability)



✓ T2 is rigid enough and robust enough.

✓ T2 has accessible reaction sites for A.

Outline

➢ Introduction

- Low-dimensional conjugated nanostructures
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- **Metal quantum dots:**
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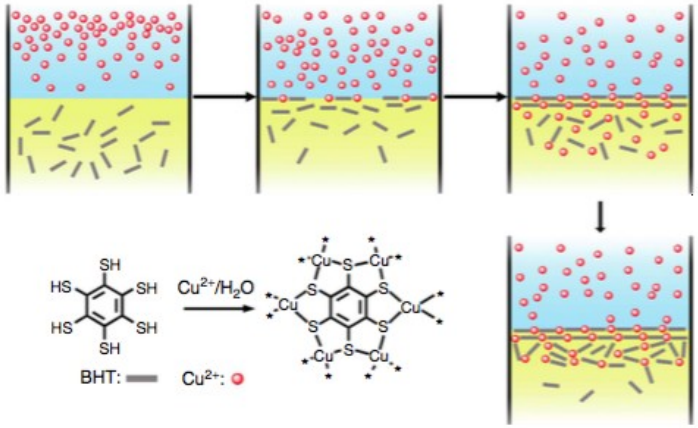
- **2D conjugated MOF:**
  -$Cu_3(C_6O_6)$ Metal-Organic Monolayer
- **2D conjugated COF:**
  -Chemical reactions of aryl-dibromo molecules on metal surfaces

➢ Summary

Introduction

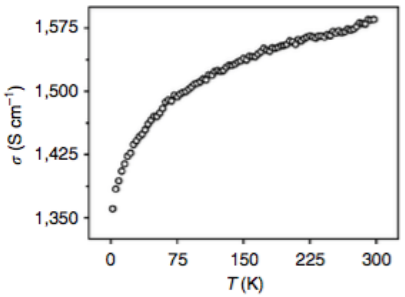
Conductive 2D metal-organic networks



✓ Cu-BHT film

✓ Thickness: 15-500nm

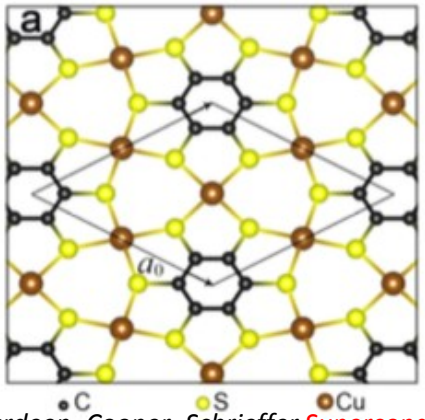
✓ Multilayers



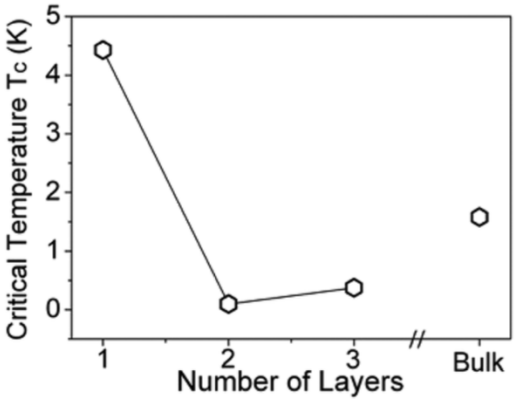
$[Cu_3(C_6S_6)]_n$ formed from liquid-liquid interface reaction

RT conductivity: 1,580 S cm^{-1}

The highest value of coordination polymers



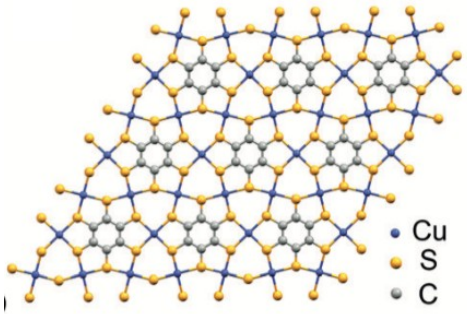
A Bardeen–Cooper–Schrieffer Superconductivity



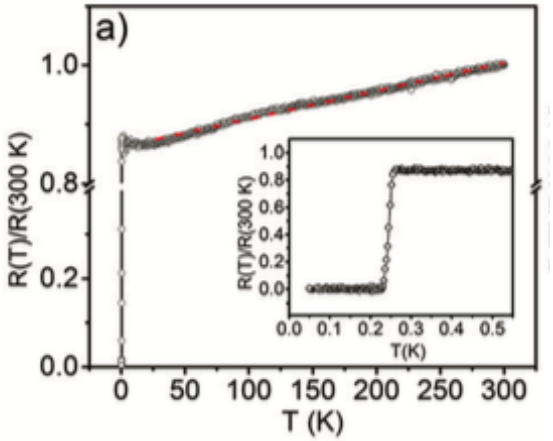
✓ Tc of monolayer Cu-BHT: 4.43 K

✓ Tc of bulk Cu-BHT :1.58 K

Thickness: 800nm



Cu-BHT film



Bulk SC : Tc = 0.25 K

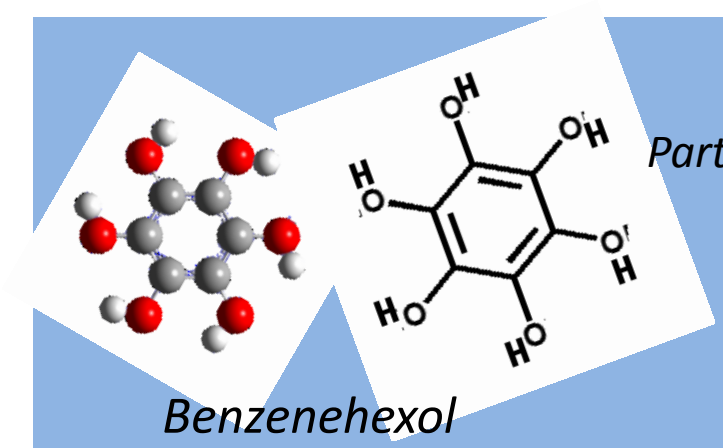
Nat. Commun. 2015, 6, 1 – 8.

Nano Lett. 2017, 17, 6166−6170.

Angew. Chem. 2018, 130, 152 –156.

Results and Discussion

BHO/Cu(111) at RT

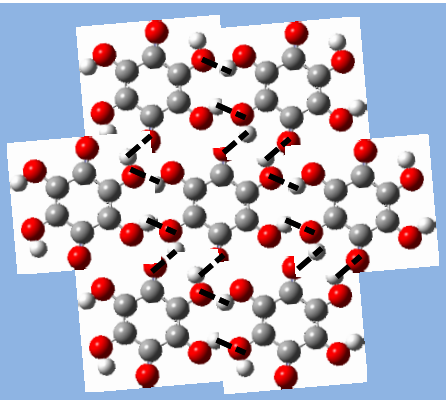


Benzenehexol

Partially deprotonated

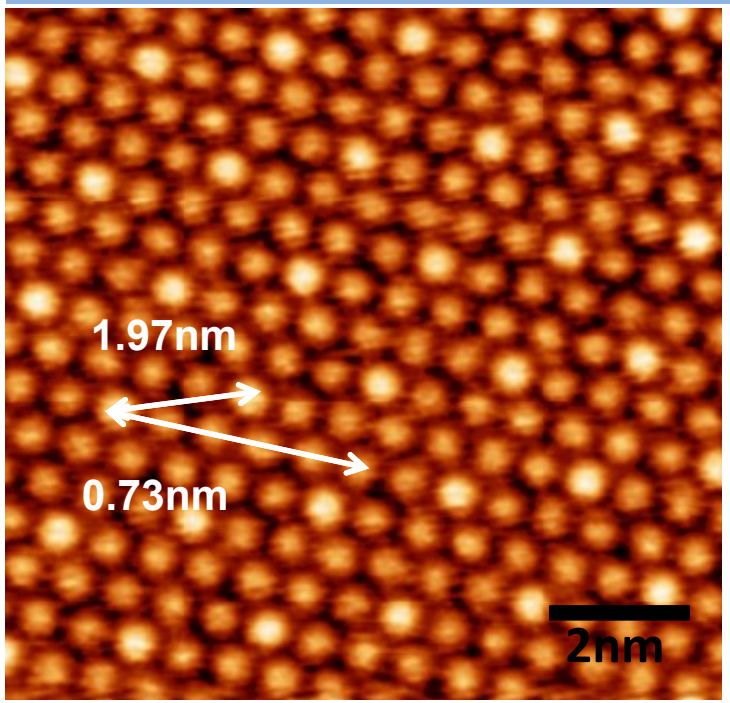
Cu(111)

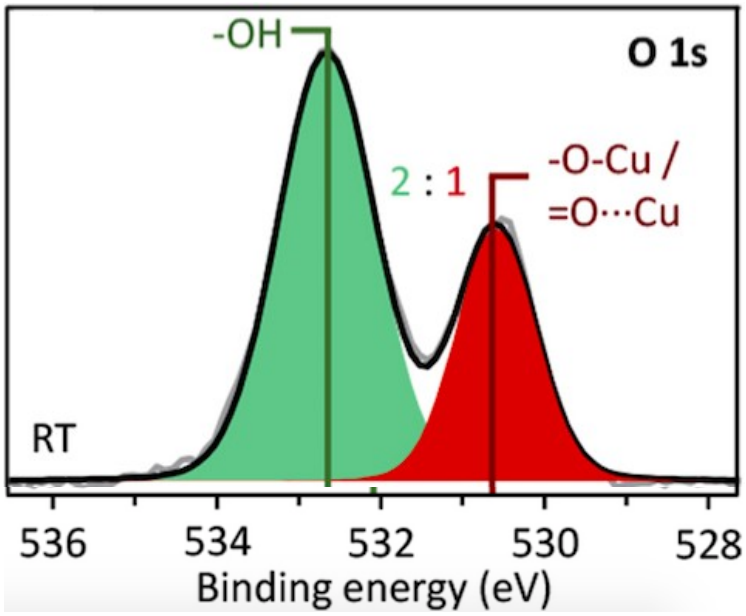
RT



tetrahydroxyquinone (THQ)

HB phase ***O—H:0.18nm***



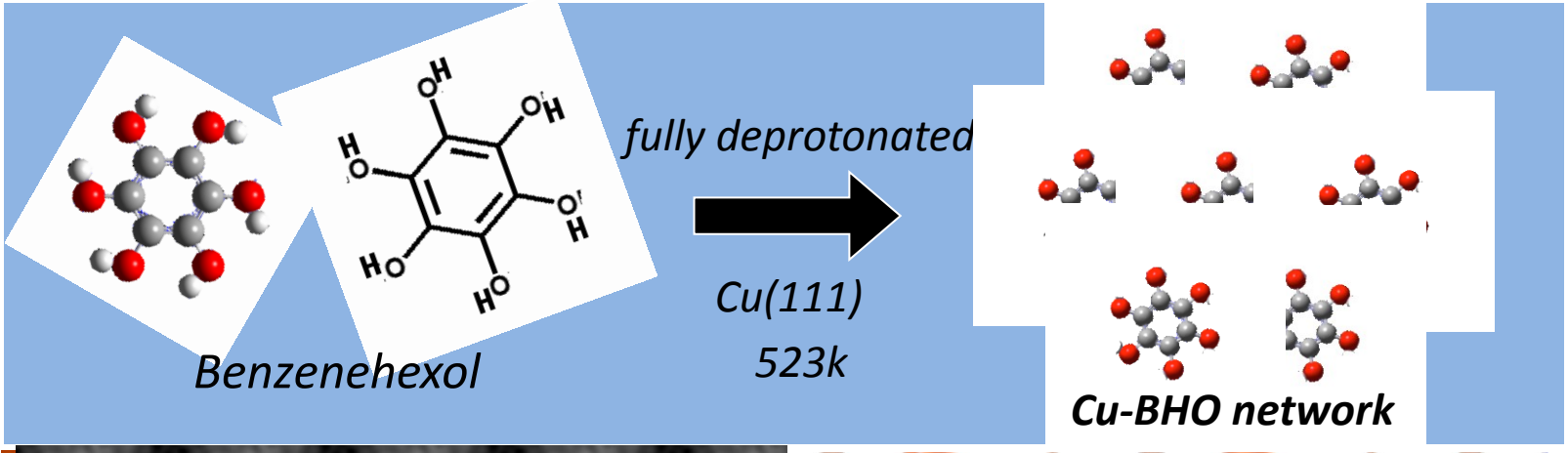


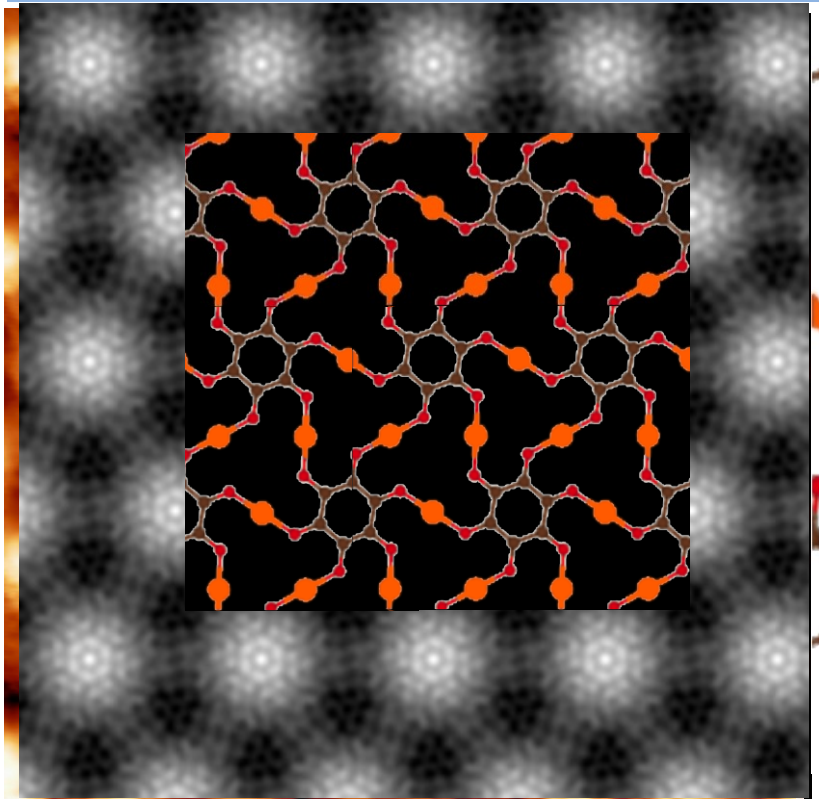
J. Chem. Phys. 2017, 147, 214706

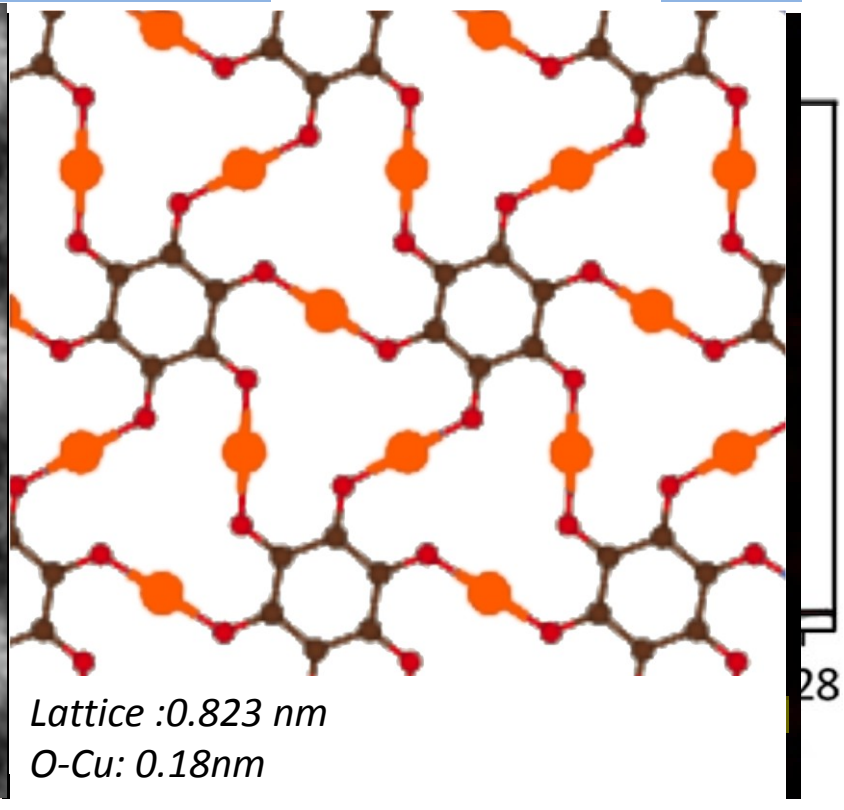
PHYSICAL REVIEW B 2008, 77, 085410

Results and Discussion

BHO/Cu(111) at 523K





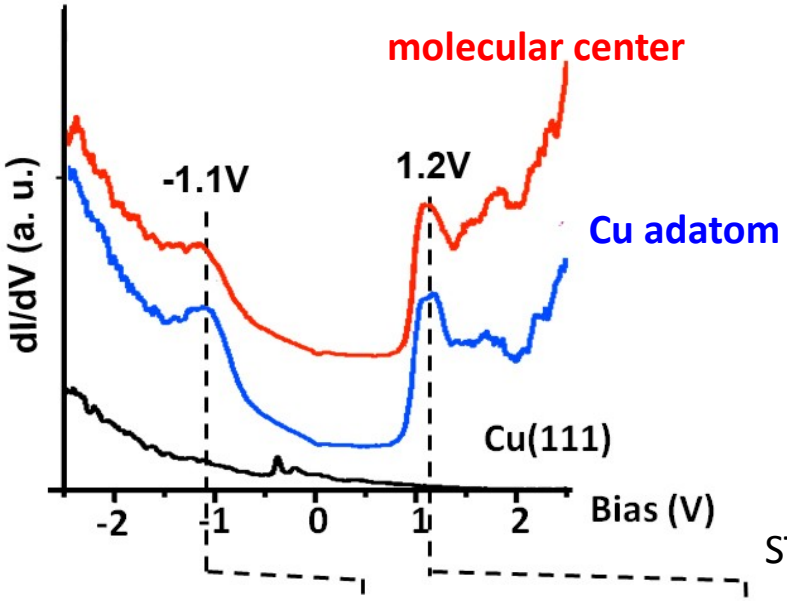


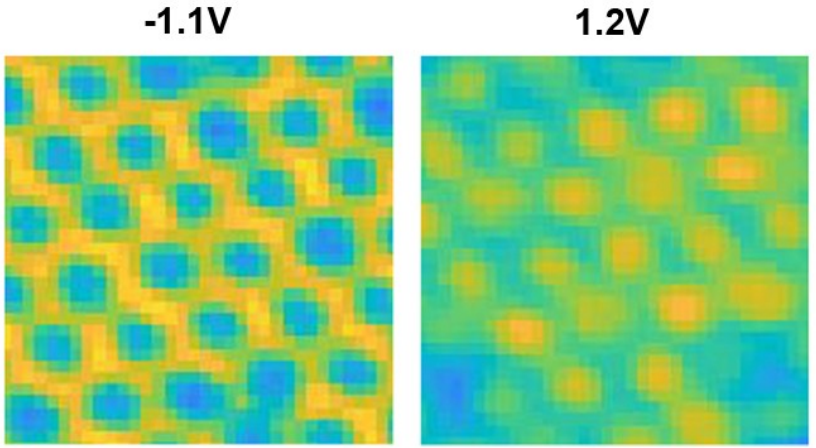
Lattice :0.823 nm

O-Cu: 0.18nm

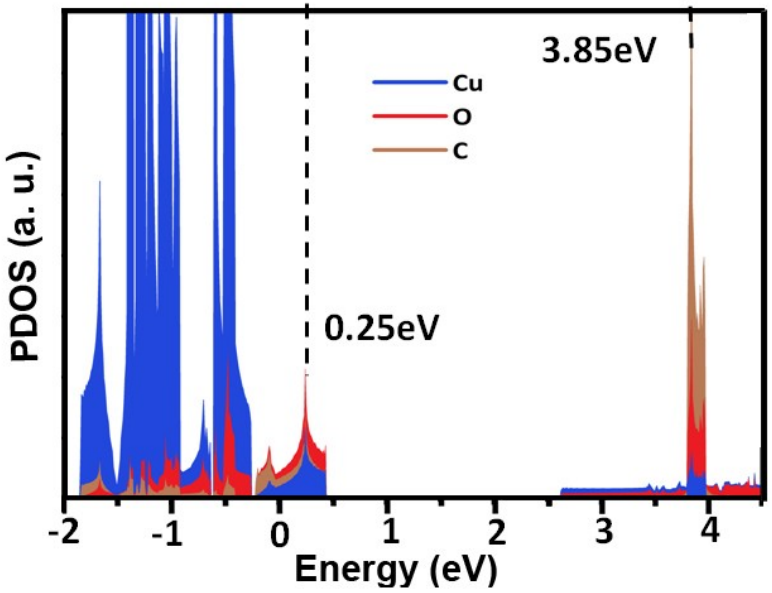
Results and Discussion

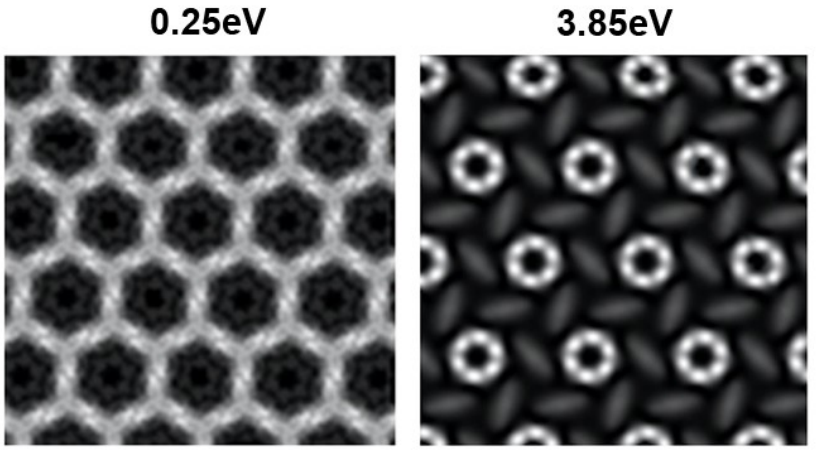
STS, PDOS and STS mapping of $Cu_3(C_6O_6)$ network





STS, STS mapping of a $Cu_3(C_6O_6)$ network on Cu(111)

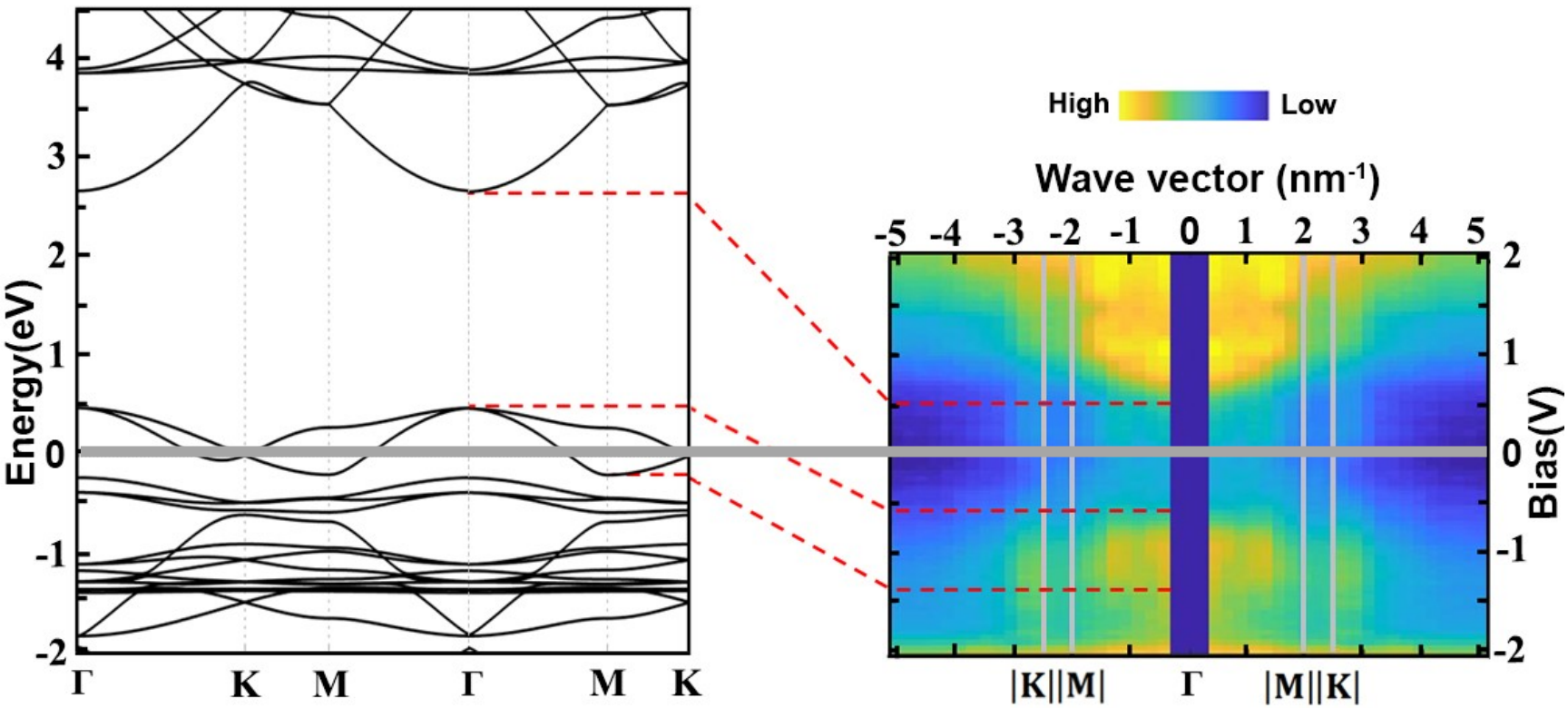




PDOS, simulated mapping of a free-standing $Cu_3(C_6O_6)$ network

Results and Discussion

FT-STS of a $Cu_3(C_6O_6)$ network on Cu(111)



Free standing MOF:

✓ Two bands crossing Fermi level

MOF adsorbed on Cu(111):

✓ band gap: 1.5 V

- **Single layered $Cu_3(C_6O_6)$ framework (metallic)**
- **A monolayer on Cu(111) (semiconductive)**
- **O-Cu-O bonding motif offers efficient charge delocalization**

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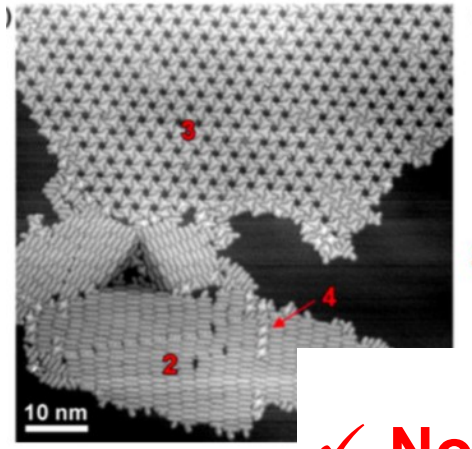
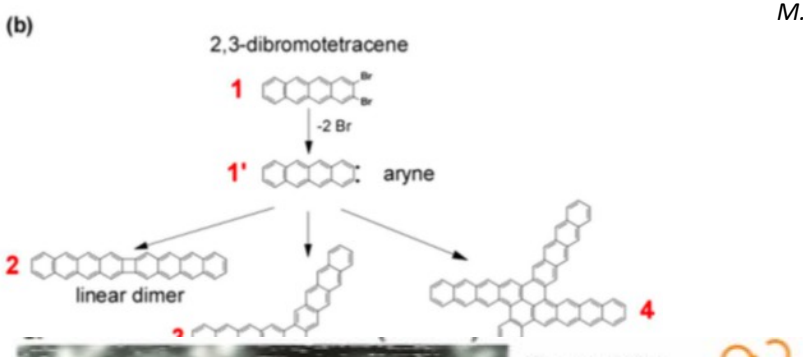
➢ Summary

Introduction

On-surface synthesis of dibromo aryls





*M. Koch, et al. in From Polyphenylenes to Nanographenes and Graphene Nanoribbons, Springer International Publishing, Cham, **2017**, pp. 99-125.*

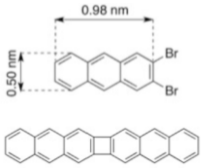
J. Am. Chem. Soc. 2017, 139, 17617−17623

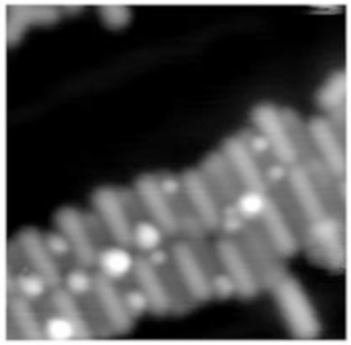
Chem. Commun., 2018, 54, 7948--7951

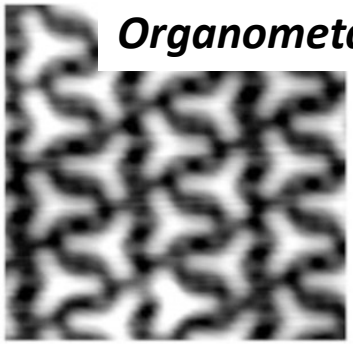
[2+2] cycload

✓ **No intermediate states**

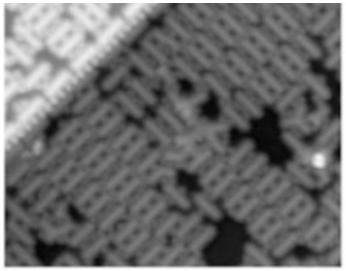
✓ **No extended covalent networks**





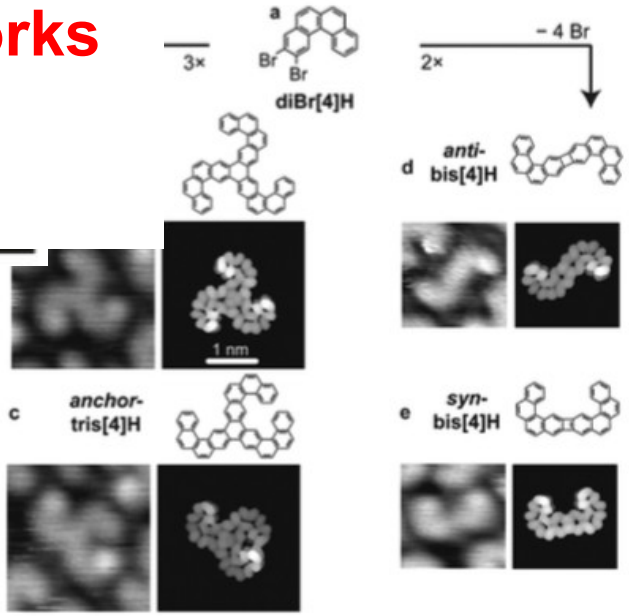


Organometallic structure/Cu(111)



Au(111)

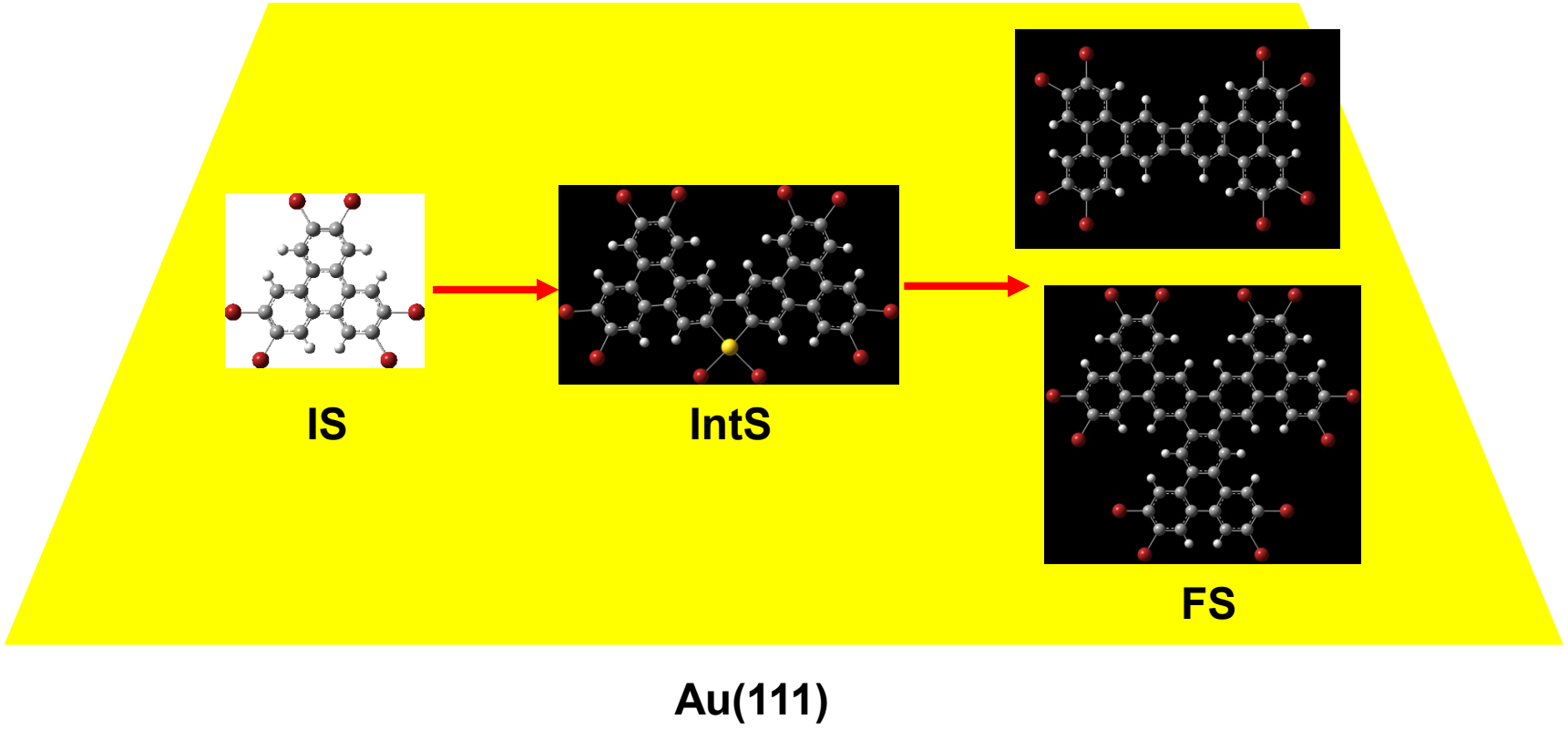
Au(100)



Ullmann reaction/Au(111)

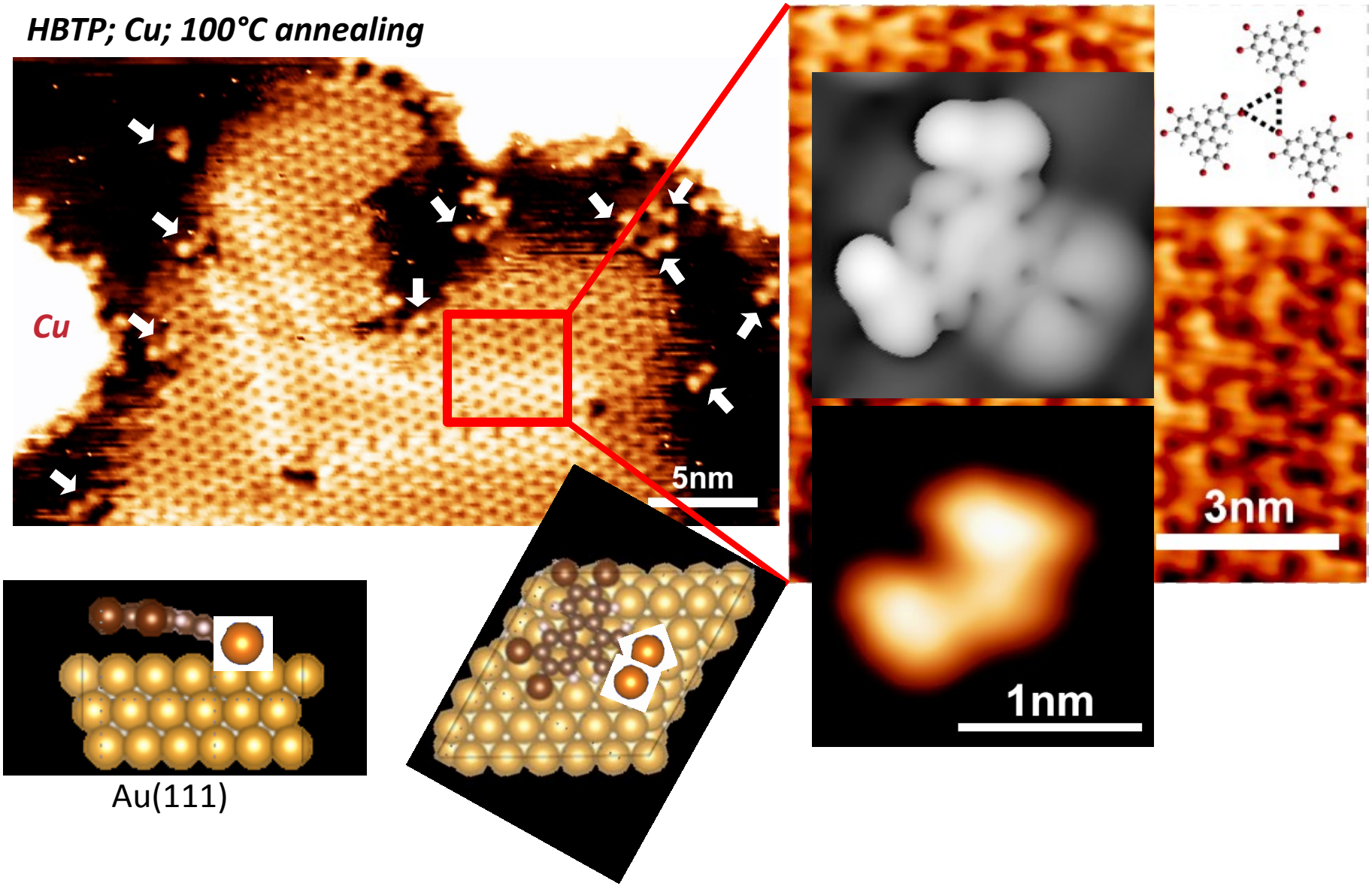
Results and Discussion

HBTP on Au(111)



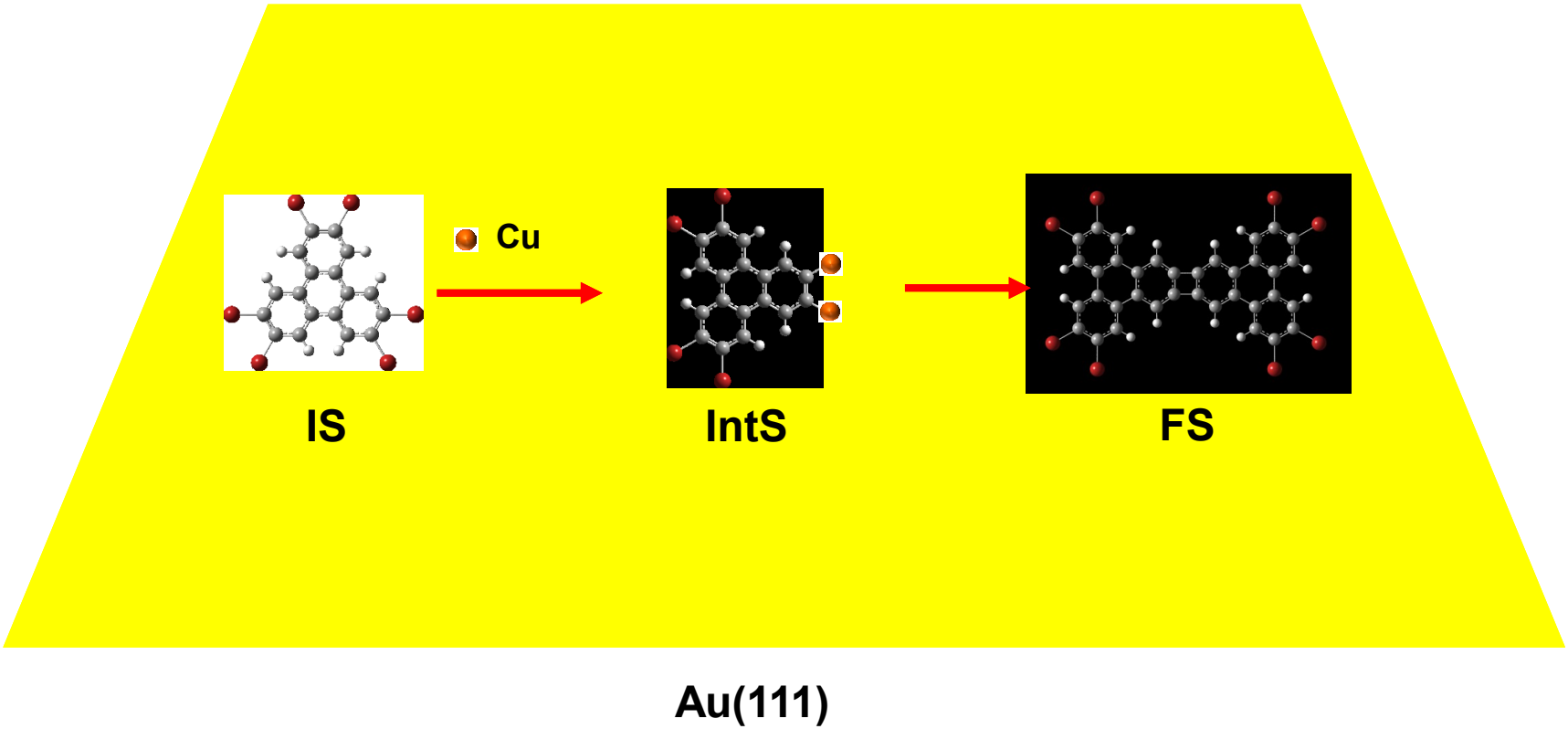
Results and Discussion

HBTP on Cu-dosed Au(111)



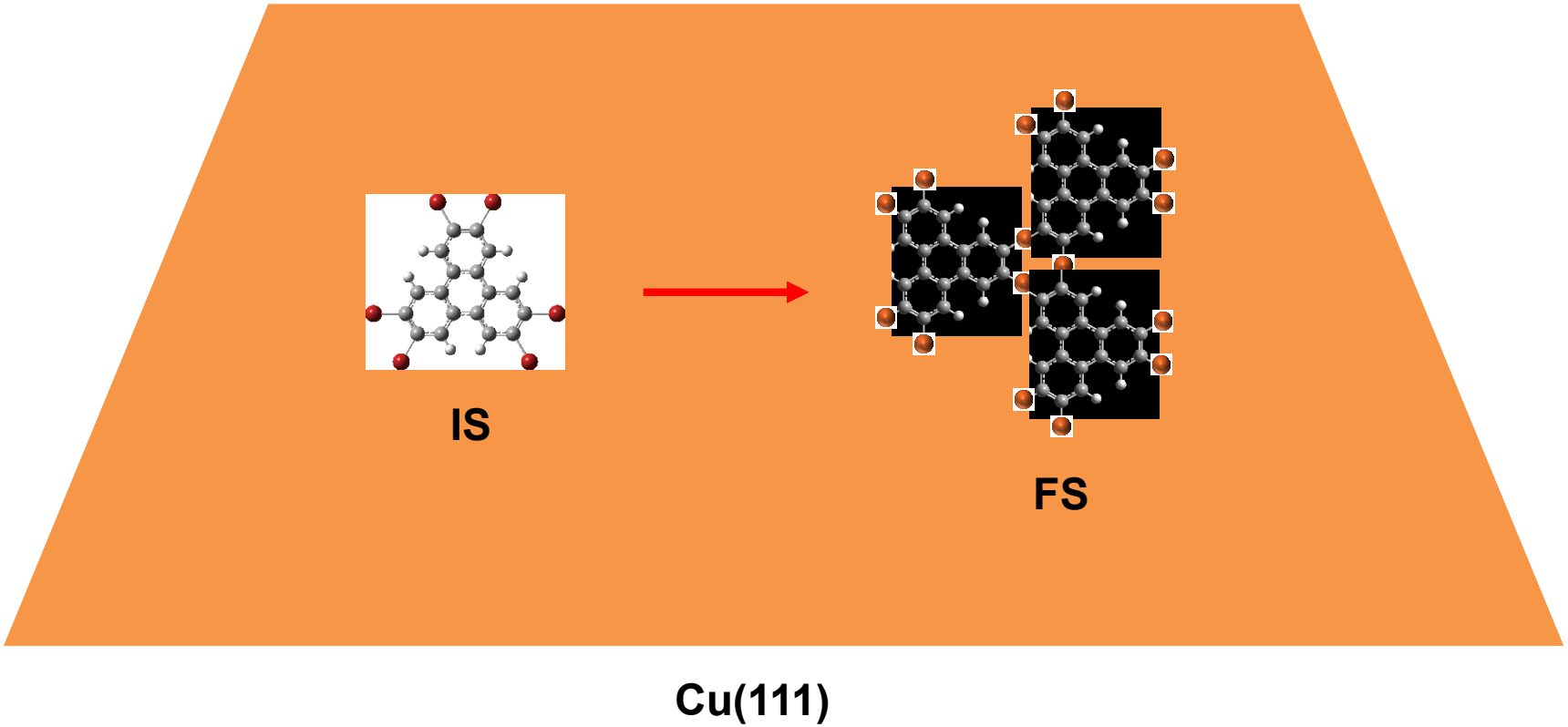
Results and Discussion

HBTP on Cu-dosed Au(111)



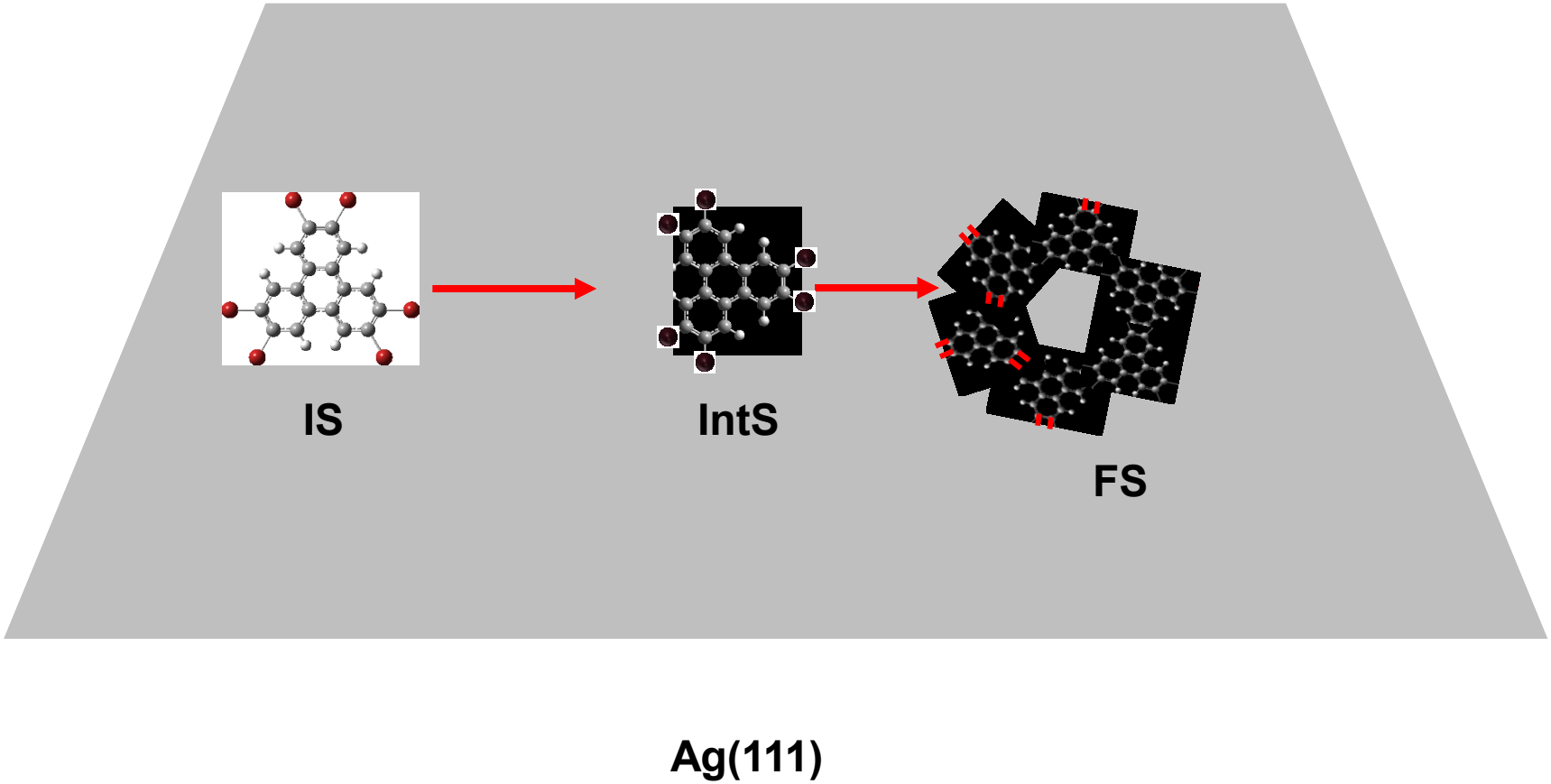
Results and Discussion

HBTP on Cu(111)



Results and Discussion

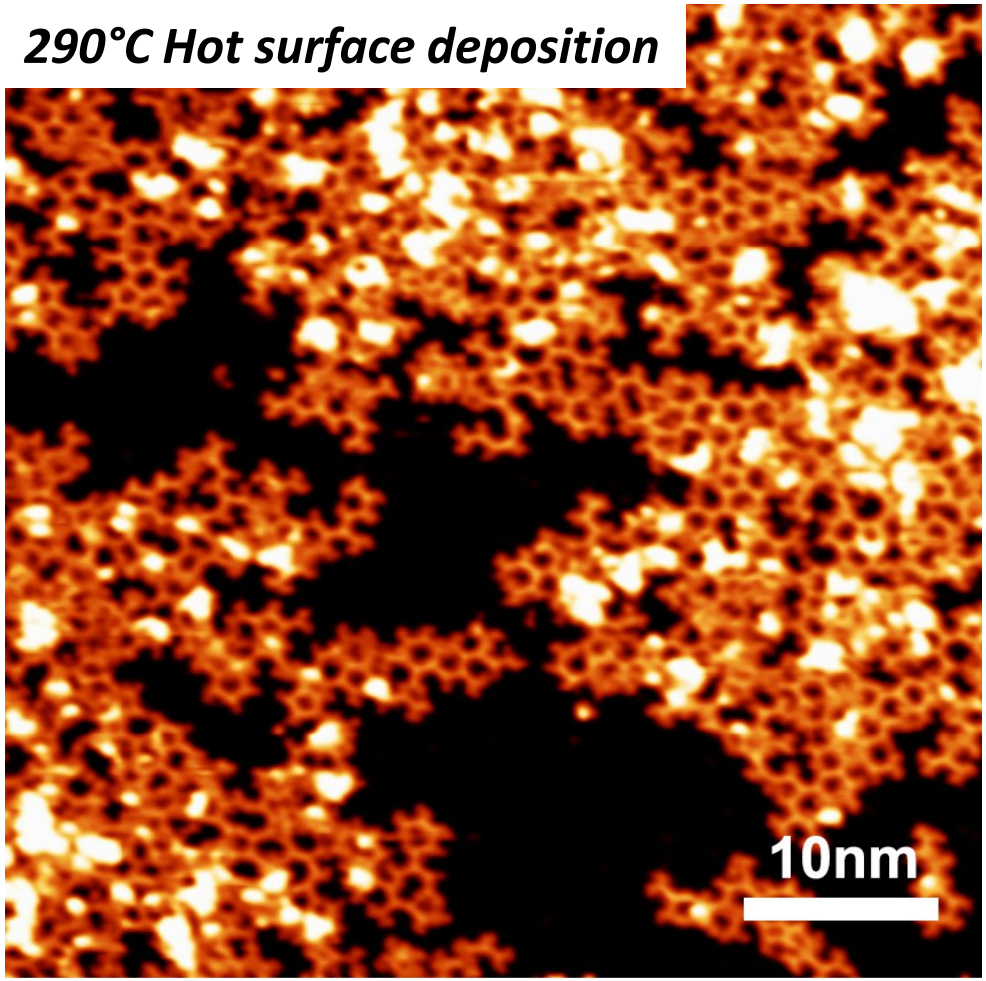
HBTP on Ag(111)



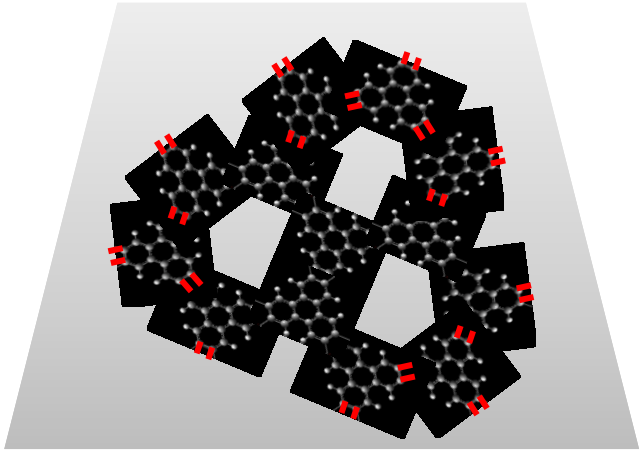
Results and Discussion

HBTP on Ag(111)

290°C Hot surface deposition

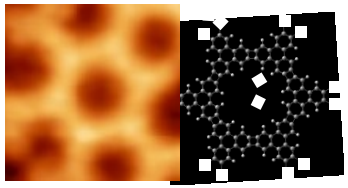


C2 network

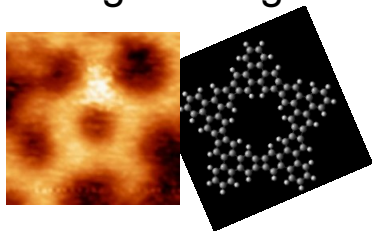


Ag(111)

- ✓ Hexagonal oligomers

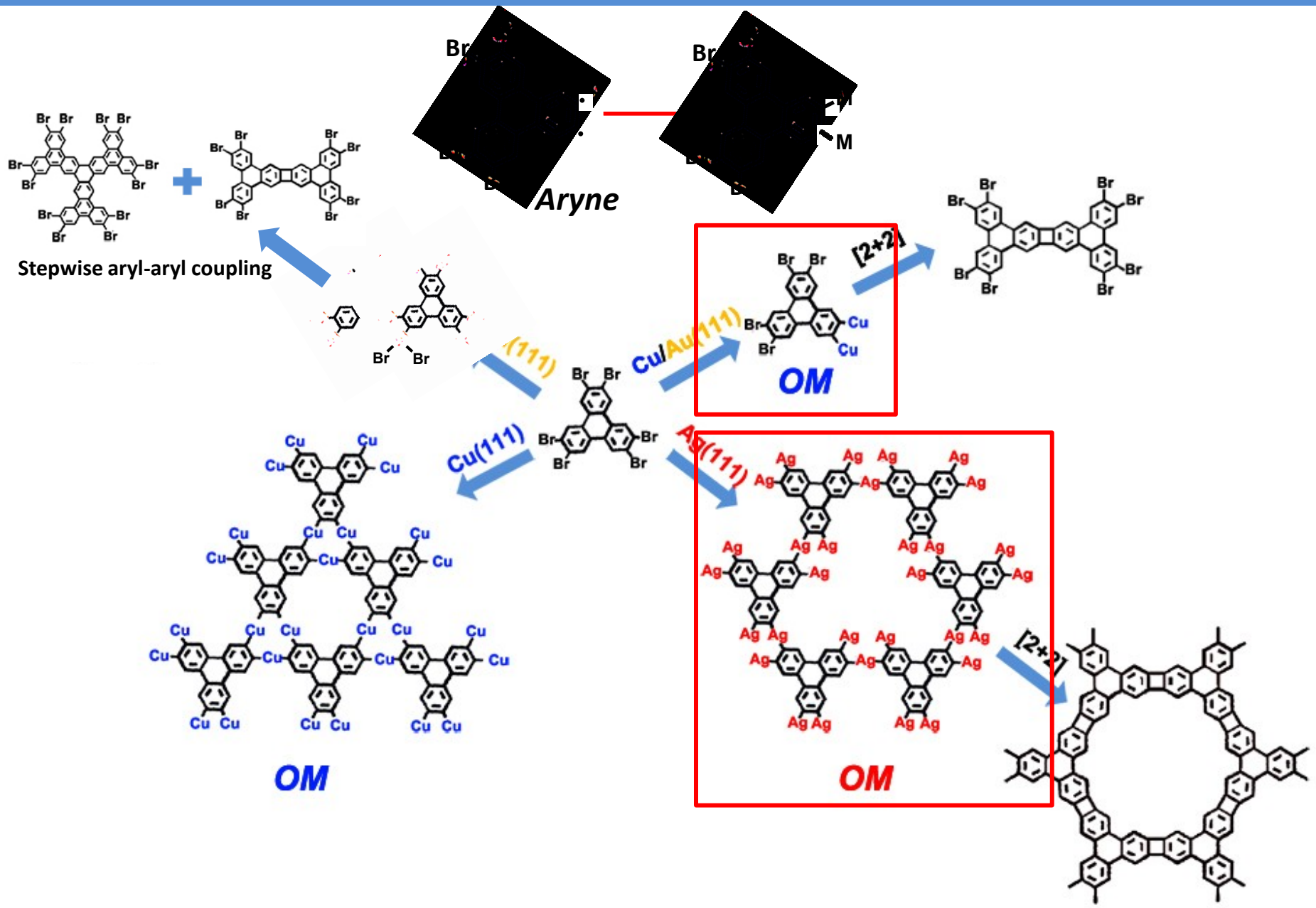


- ✓ Pentagonal oligomers



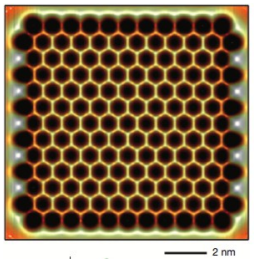
- ✓ Inreversibility of covalent bonds

Conclusion


Br
Br
M
Aryne
Stepwise aryl-aryl coupling
(111)
Cu/Au(111)
[2+2]
OM
Cu(111)
Ag(111)
OM
OM
[2+2]

Summary

Next step:



Artificial Graphene:

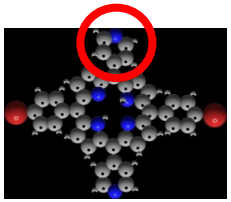
- Decoration of 2DEG of metal surfaces
- Strong SOC effect in Bi
- Artificial 2D quantum spin-hall insulator

Nature, **483**, 306-310.(2010)
Phys. Rev. B **86**, 201406(2012)

Next step:

- **Enhance the conjugation along the chains**

Eg: **π-d conjugation**

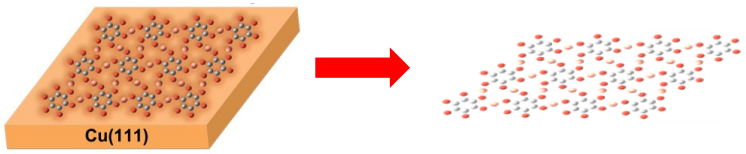


Pyridyl –> *-OH* –> *-O-Cu-O-*

Atomic precision

Next step:

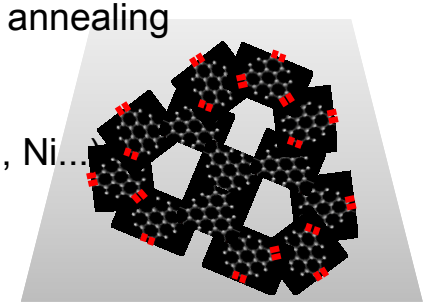
- **Transport measurement**
  1. Desorption at 650K annealing
  2. Different orientations



Nanoscale, 2017, 9, 2785–2792

Next step:

- Kinetic control (Coverage, annealing temperature, duration…)
- Extrinsic catalysts (Cu, Pd, Ni…)



Publication

[10] [2+2] cycloaddition reactions on metal surfaces, R. Zhang, B. Xia, Z. Gao, H. Xu, N. Lin, *Manuscript.*

[9] Kinetically-controlled synthesis of four-member and six-member cyclic products via sequential aryl-aryl coupling on a Au(111) surface, R. Zhang, B. Xia, H. Xu, N. Lin, *ChemPhysChem, Accepted.*

[8] $Cu_3(C_6O_6)$ metal-organic monolayer exhibiting highly dispersive electronic band, R. Zhang, J. Liu, Y. Gao, M. Hua, B. Xia, P. Knecht, A. C. Papageorgiou, J. Reichert, J. V. Barth, L. Huang, H. Xu, N. Lin, *Submitted.*

[7] Template-controlled Sonogashira cross-coupling reactions on Au(111) surface, R. Zhang, G. Lyu, D. Y. Li, P. N. Liu, N. Lin, *Chem. Commun*. 53, 1731(2017).

[6] Two-Dimensional Superlattices of Bi Nanoclusters formed on a Au(111) Surface using Porous Supramolecular Templates, R. Zhang, G. Lyu, C. Chen, T. Lin, P. N. Liu, N. Lin, *ACS Nano*, 9, 8547- 8553 (2015).

[5]On-surface coupling reactions with extrinsic catalysts, W. Zhao, L. Dong, R. Zhang and N. Lin, ***Book Chapter, On-surface synthesis II***.

[4] Selective on-surface covalent coupling based on metal-organic coordination template, S. Xing, Z. Zhang, X. Fei, W. Zhao, R. Zhang, T. Lin, D. Zhao, H. Ju, J. Fan, J. Zhu, Y.-Q. Ma, Z. Shi, ***Nat. Commun.*** 1, 10(2019).

[3]Synthesis and characterization of a single-layer conjugated metal-organic structure featuring a non-trivial topological gap, Z. Gao, C.-H. Hsu, J. Liu, F.-C. Chuang, R. Zhang, B. Xia, H. Xu, L. Huang, Q. Jin, P. N. Liu, N. Lin, ***Nanoscale***, 11, 878 (2019).

[2] Quasicrystallinity expressed in two-dimensional coordination networks, J. Urgel, D. Ecija, G. Lyu, R. Zhang, C. A. Palma, W. Auwärter, N. Lin, J. V. Barth, Johannes, ***Nature Chemistry***, 8, 657 (2016).

[1] On-surface assembly of low-dimensional Pb-coordinated metal-organic structures, G. Lyu, R. Zhang, X. Zhang, P. N. Liu, N. Lin, ***J. Mater. Chem. C.*** 3, 3252 (2015).

Acknowledgement

- **Supervisor:**
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- **Examination committee members:**
  - Prof. Yilong Han
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  - Prof. Haibin Su
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  - Prof. Hu Xu(SUSTC)
  - Prof. Li Huang(SUSTC)
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  - Prof. Johannes V. Barth(TUM)
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  - Dr. Lei Dong
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  - Mr. Qiushi Zhang
  - Dr. Jing Liu

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  - Mr. Zi'ang Gao
  - Mr. Bowen Xia
  - Mr. Yifan Gao
  - Mr. Muqing Hua
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Thanks for your attention!