Precise Functional Assemblies: First Glimpses and Upcoming Challenges

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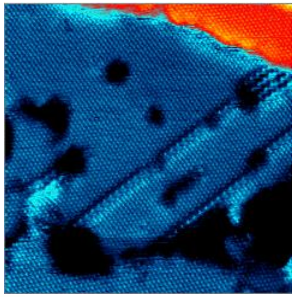
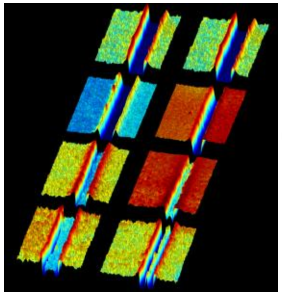
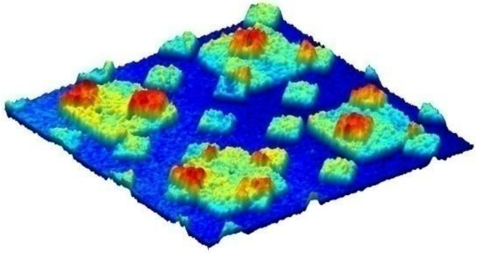
Exploit and expand our knowledge of the placement, reaction, and control of single molecules and assemblies

Exploit and expand our enabling ability to "see" structures and to measure function at these scales

Produce and apply new functional materials controlled to the sub-molecular level

Develop the requisite and *enabling* metrology tools

Use these materials as platforms to measure and to control the chemical and biological worlds that operate at these scales

Grand Challenges for Precise Assembly and Nanomanufacturing of Functional Nanostructures

Precise structures

- **Can be treated simultaneously with theory, experiment, and simulation**
- **Are the ultimate in control**
- **Enable us to learn the rules of supramolecular and nanostructure function – interference vs. cooperativity**

Design interactions into precise molecular and supramolecular structures

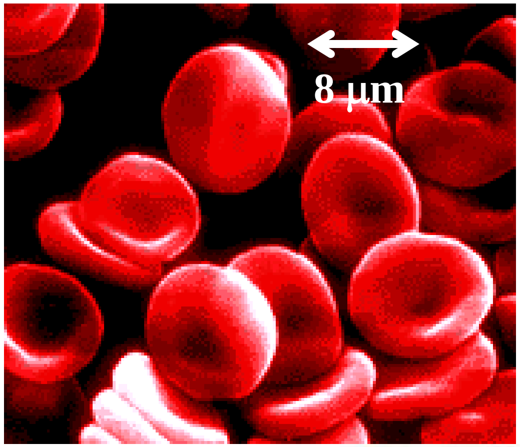
Then, apply these in the macromolecular, materials, and other nanomanufacturing communities

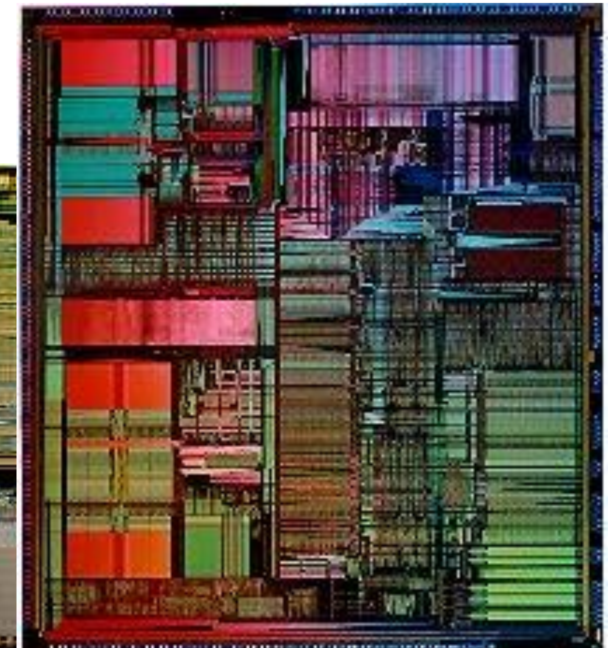
We now have the ability to carry out this work because we have the tools "to see" but we need more simultaneously applied functional and spectroscopic tools with ultrahigh spatial resolution.

Mieko Yuki
Ippodo

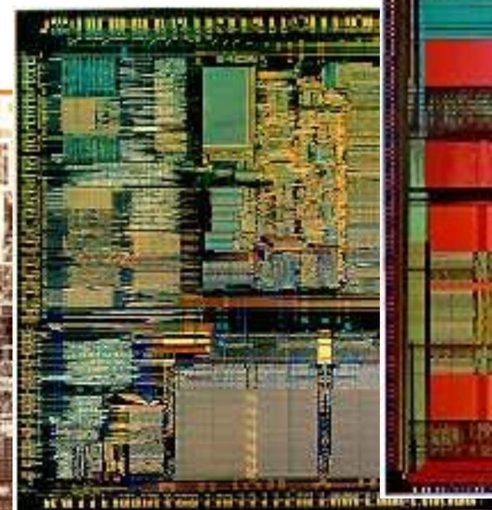
Scaling and Moore's "Laws"

Intel Itanium 2 (2003)
410 million transistors
0.13 µm minimum feature size
(⇒ 0.06 µm gate length)

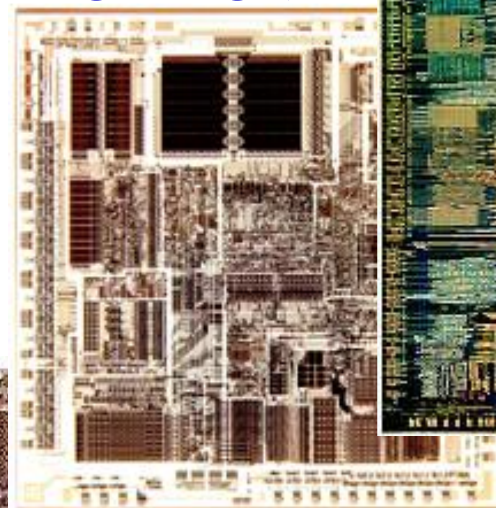




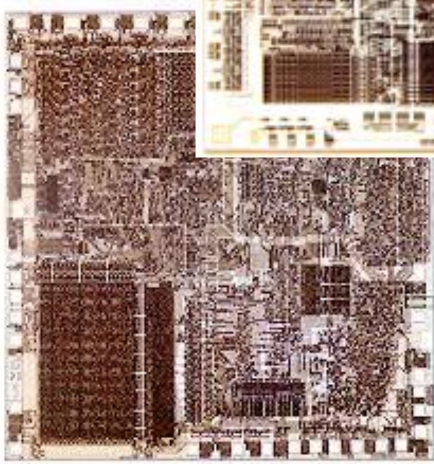
Early Pentium
(1993 3,100,000 0.8 µm)



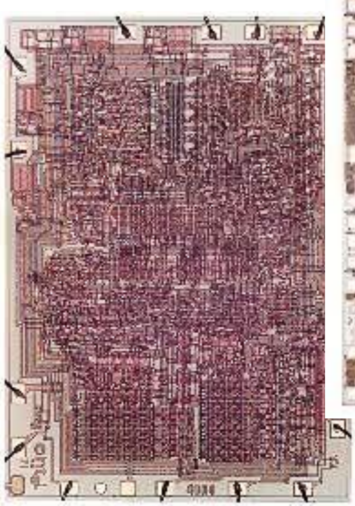
80386
(1985 275,000 1.5 µm)



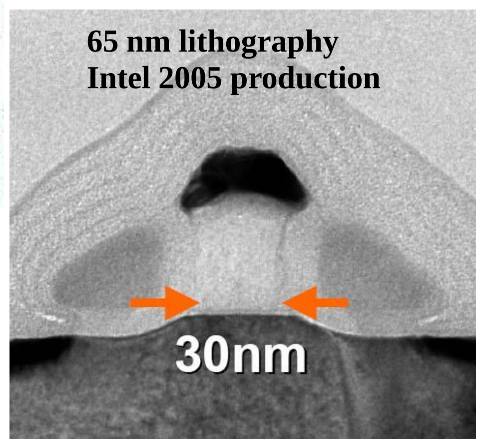
80286
(1982 134,000 1.5 µm)



8088
(1979 29,000 3 µm)

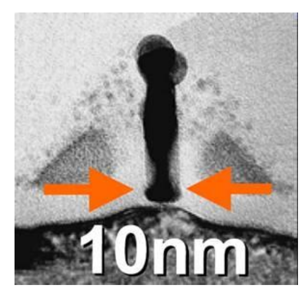


4004
(1971 2250 10 µm)
Courtesy Tom Jackson

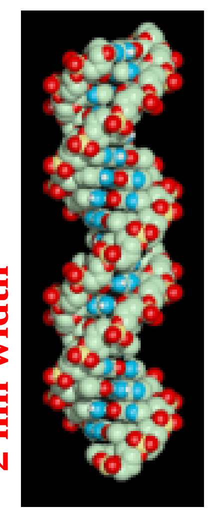


HIV virus ~100 nm

22 nm lithography
Intel 2011 production



2 nm width



Catalyze Collaboration & Innovation I: Centers @CNSI

Center for Environmental Implications of Nanotechnology (CEIN) (Nel+)

Emerging Infectious Diseases Center (Godwin, Miller+)

Functional Engineered Nano Architechtonics (FENA) (Wang+)

Western Institute of Nanoelectronics (Wang+)

Nano Renewable Energy Center (NREC) (Yang)

Institute for Digital Research & Education (IDRE)

Center for Reticular Chemistry (Yaghi, Kaner)

Center for International Science, Technology & Cultural Policy (Darby, Zucker)

Art | Sci Center (Vesna, Gimzewski)

Three WPI centers (Japan) (Gimzewski, Rome, Weiss, Yaghi)

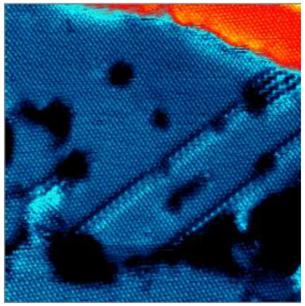
Leading Foreign Research Institutes (Korea) (Wang+)

Controlling the Placement and Environments of Molecules at All Scales: New Strategies and Chemistries

Defects

Use defects for film control – type, density, processing

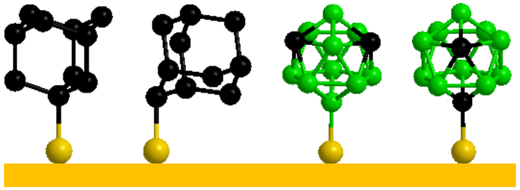
Simplify defect types by eliminating molecular tilts



Cage molecules

Control interaction strengths

Build off surface into three dimensions

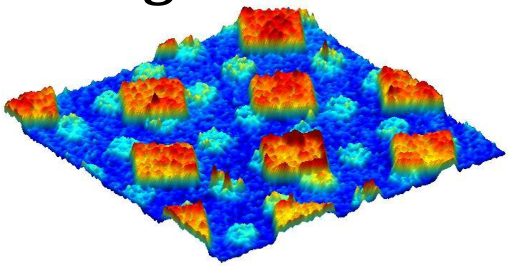


Patterning

Use intermolecular and directed interactions to advantage

Add surface functionality, enable sensing, capture

Develop metrology tools for chemical patterns



Information

Collection, mining, and extraction

Saavedra, Mullin, Zhang, Dewey, Claridge, & Weiss, *Rep Prog Phys* 73, 036501 (2010)

Laboratory Rules & Themes

Cardinal rule of nanoscience:

Compare cartoons to reality.

Themes and challenges in self-assembly:

Control assembly via intermolecular interactions.

Control type and density of defects to control structure at the nanometer scale.

Control and pattern chemical functionality

Themes and challenges in single-molecule measurements:

Record substantial data sets on single molecules/particles.

To have the statistics to elucidate the effects of:

- **Molecular design**
- **Molecular environment**
- **Cooperative molecular effects**
- **Measurement conditions**

Retain single-molecule information for further analysis and insight.

Design tools for functional measurements at the nanoscale.

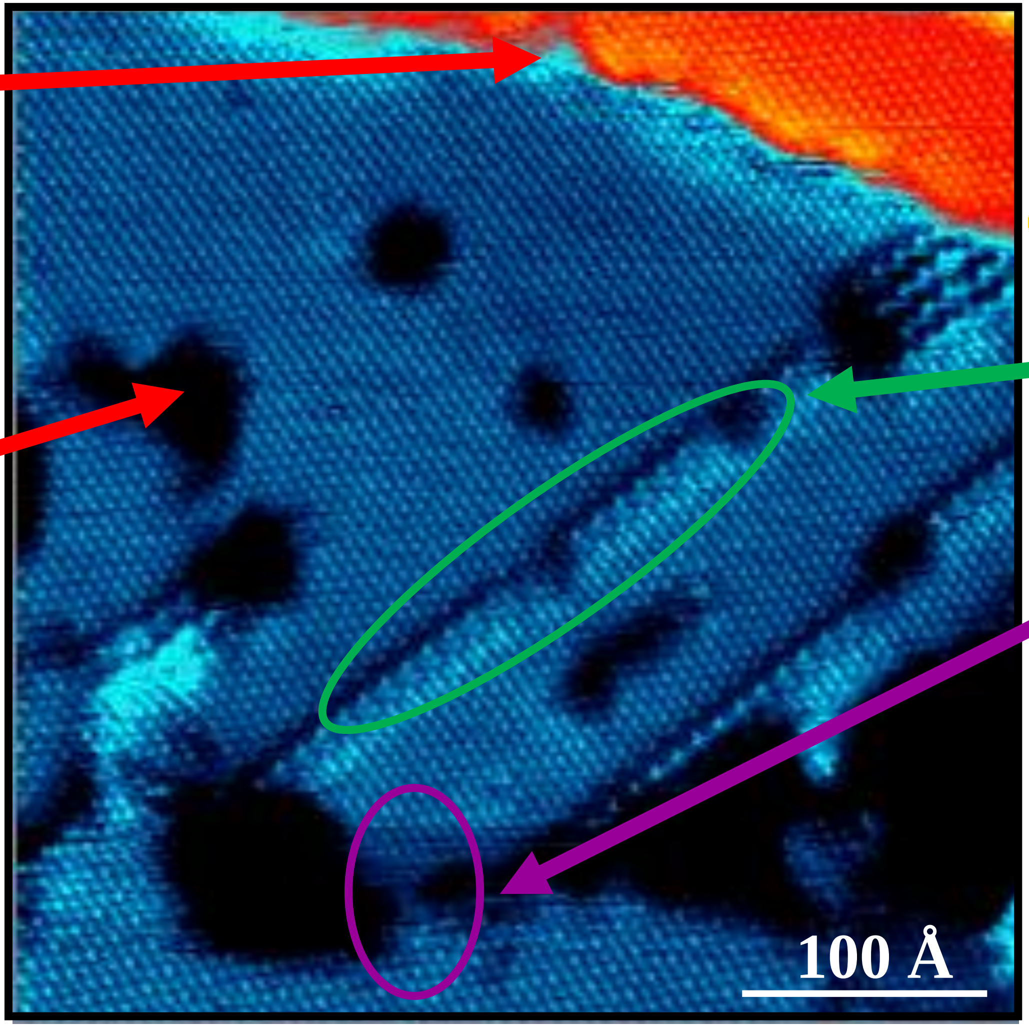
Combine structural and spectroscopic measurements.

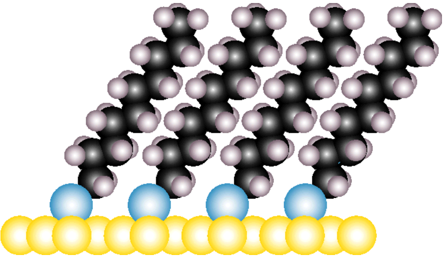
Defects in Self-Assembled Monolayers are Key to Control

Defects can be exploited for patterning but can also lead to pattern dissolution

Au substrate step edge

Au substrate vacancy island

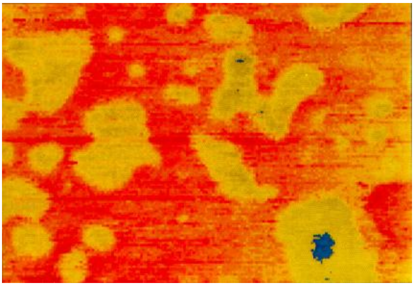




SAM structural domain boundary

Region of SAM disorder

Mixed monolayers can phase separate



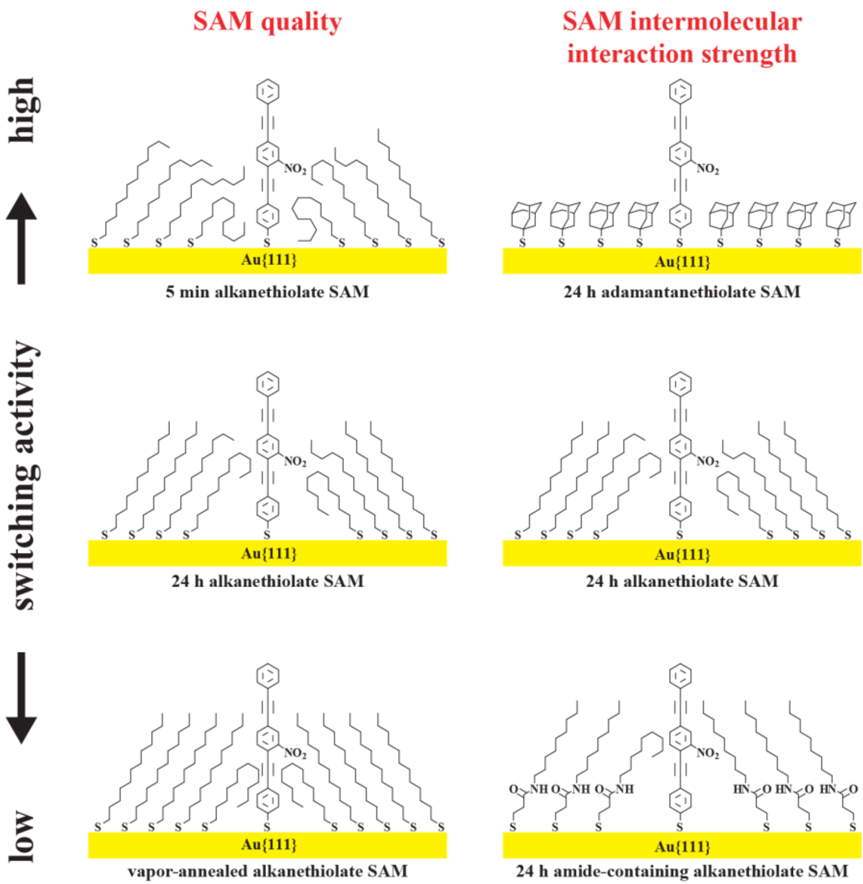
Dodecanethiolate on Au{111}
V_{sample}= -1.0 V, I_{tunnel} = 1.0 pA

Scanning tunneling microscopy

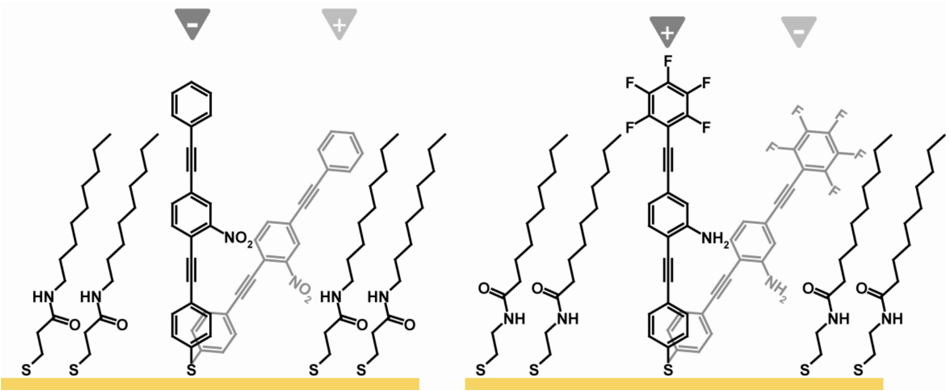
Weiss, Allara

Weiss, *Accounts of Chemical Research* 41, 1772 (2008)

Controlling Single-Molecule Switching Activity



Put single molecules in controlled environments with tailored intermolecular interactions



Donhauser *et al.*, *Science* 292, 2303 (2001)

Donhauser, Price, Tour & Weiss, *JACS* 125, 11462 (2003)

Lewis, Inman, Yao, Tour, Hutchison & Weiss, *JACS* 126, 12214 (2004)

Moore, Mantooth, Donhauser, Maya, Price, Yao, Tour & Weiss, *Nano Lett* 5, 2292 (2005)

Lewis, Inman, Maya, Tour, Hutchison & Weiss, *JACS* 127, 17421 (2005)

Moore, Dameron, Mantooth, Maya, Ciszek, Tour & Weiss, *JACS* 128, 1959 (2006)

Moore, Mantooth, Donhauser, Yao, Tour & Weiss, *JACS* 129, 10352 (2007)

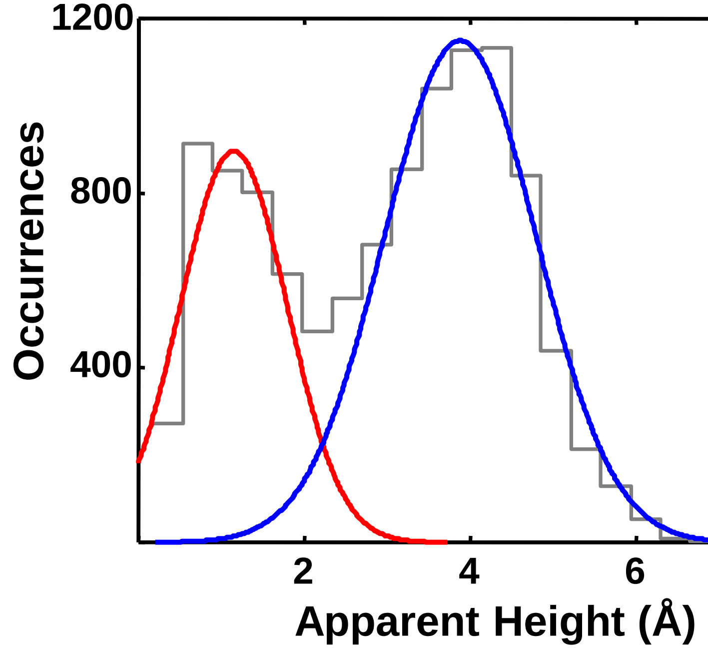
Weiss, *Acc Chem Res* 41, 1772 (2008)

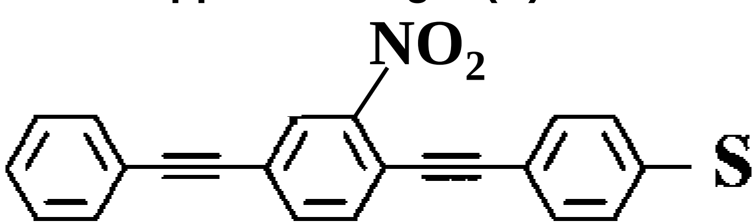
Weiss, Allara, Hutchison, Tour

Molecular Switching: Dynamic Range

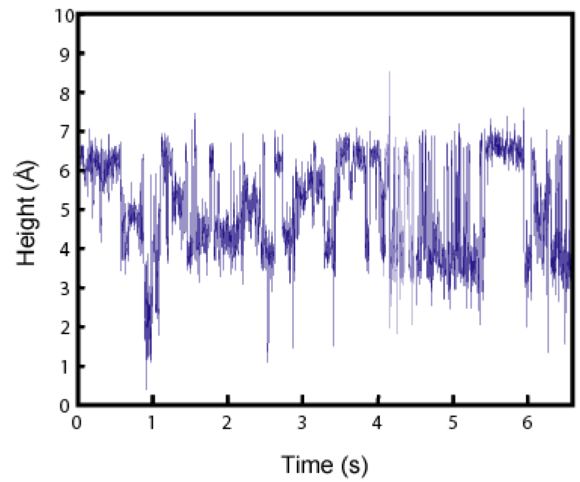
Span time scales by selecting measurement*

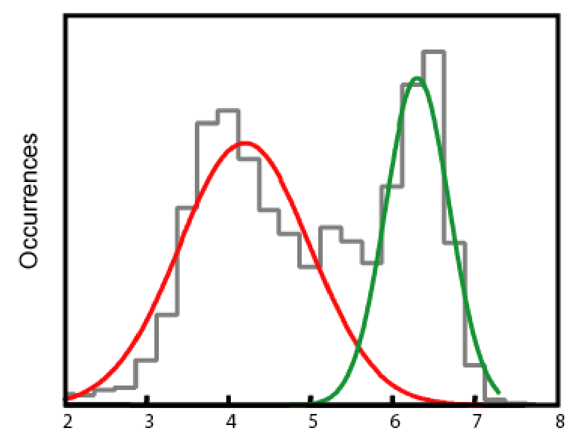
Accumulated 10^0-10^5 sec time scale measurements of ~50 isolated switches





Real time measurements of an active switch 10^{-3}-10^1 sec time scale



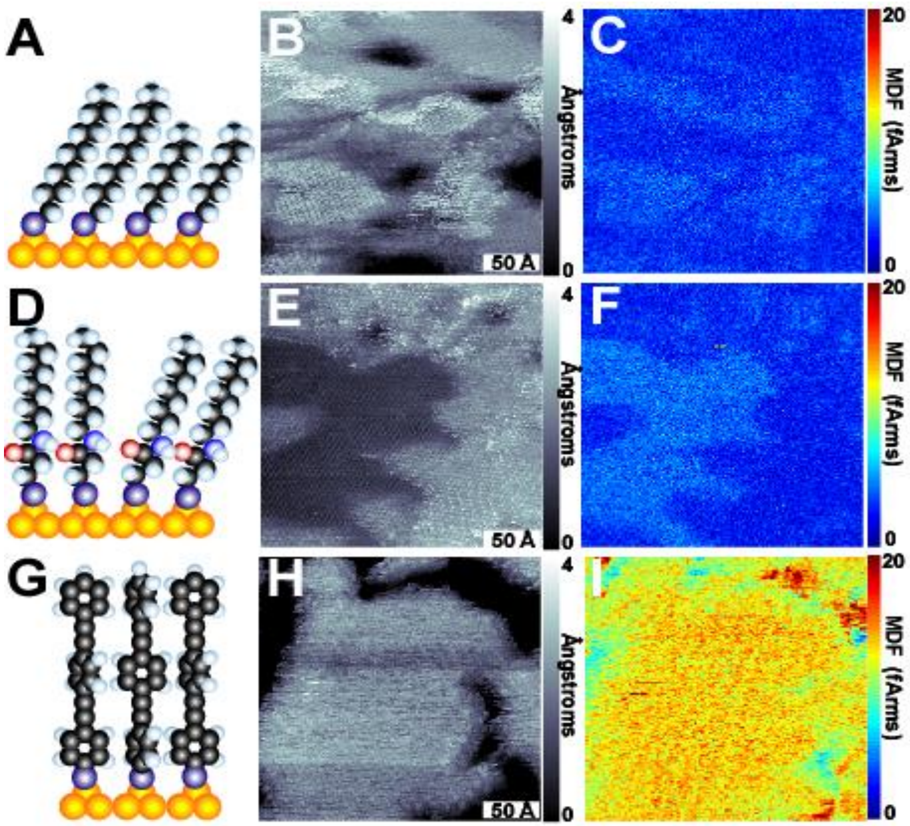


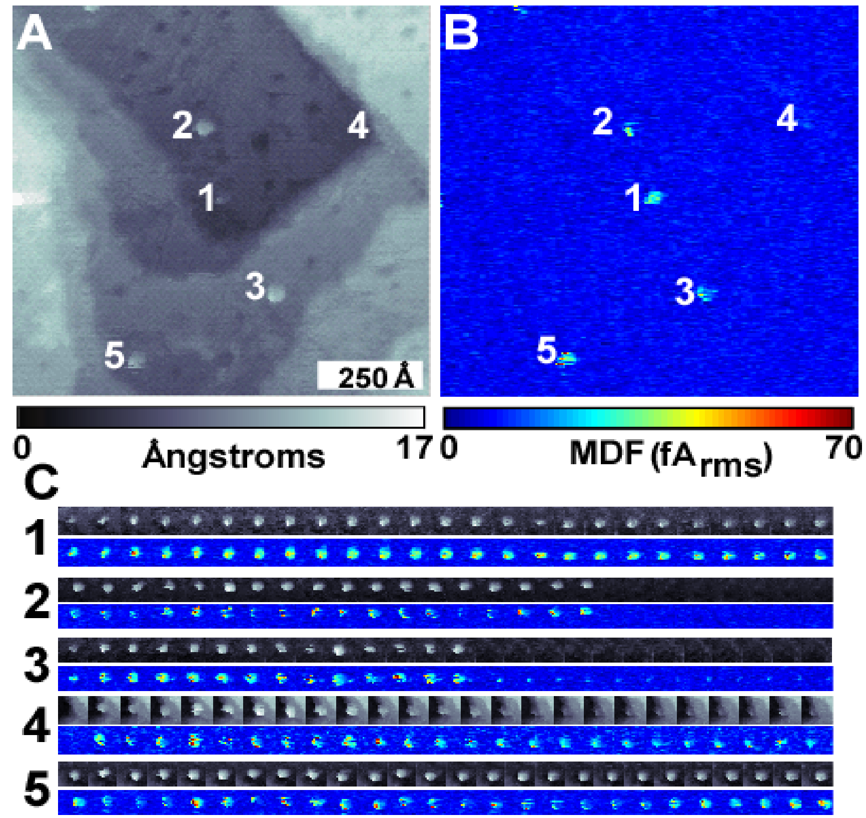
*Mark Ratner challenge – can reach <10^{-10} sec

Moore, Mantooth, Donhauser, Yao, Tour & Weiss, *JACS* 129, 10352 (2007)

Measure "Connection" of Molecules to Substrate

Polarizability can be used for chemical contrast and to measure coupling of molecular and substrate electrons





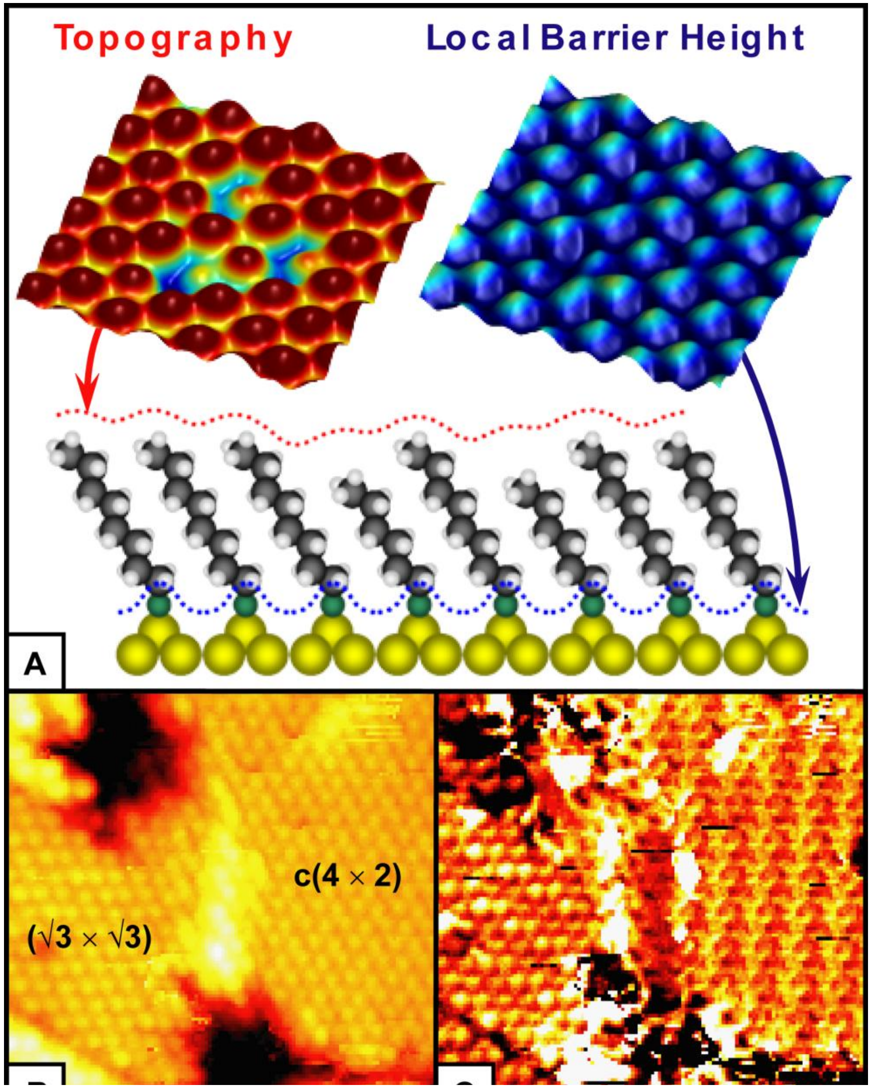
V_{sample} = 1 V, I_{tunnel} = 1 pA
Applied frequency: 2 GHz with difference: 5 kHz
Input Power level: 10 dBm
Left, gray: topography
Right, color: microwave polarizability

V_{sample} = -1 V, I_{tunnel} = 2 pA
Applied frequency: 2 GHz with difference: 5 kHz
Input Power level: 10 dBm
Left, gray: topography
Right, color: microwave polarizability

Moore, Yeganeh, Yao, Claridge, Tour, Ratner & Weiss, *ACS Nano* 4, 7630 (2010)

Measure Molecular Tilts

Measure tops and bottoms of molecules simultaneously



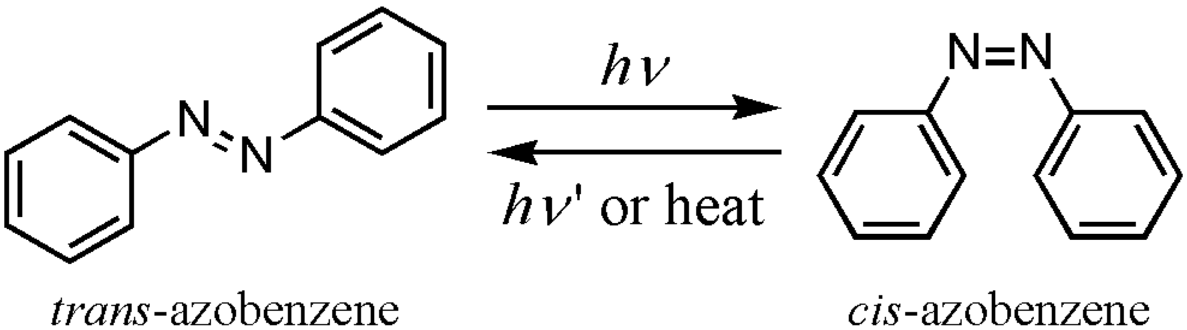
Octanethiol/Hexanethiol SAM on Au{111}
25 Å × 30 Å
V_{sample} = 1.2 V
I_{tunnel} = 11 pA
T = 4 K

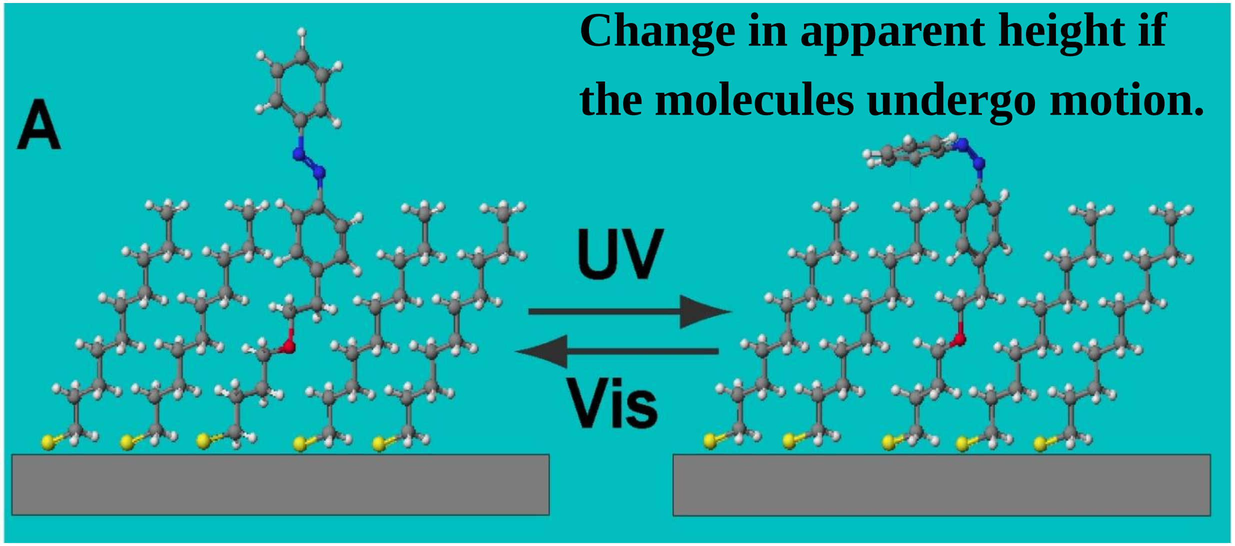
Dodecanethiol SAM on Au{111}
100 Å × 100 Å
V_{sample} = 1 V
I_{tunnel} = 15 pA
T = 4 K

Han, Kurland, Giordano, Nanayakkara, Blake, Pochas & Weiss
***ACS Nano* 3, 3115 (2009)**

Photoswitching Single Molecules

Can we photoinduce *cis-trans* isomerization in tethered azobenzene?



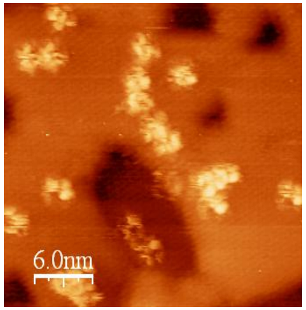


Ye, Kumar, Takami, Flatt, Yu, Tour & PSW, *Nano Letters* 8, 1644 (2008)

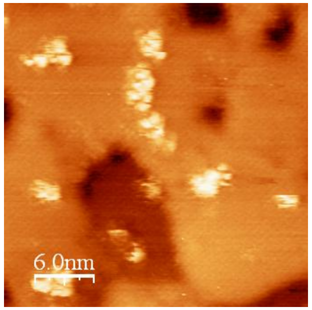
Photoswitching Single Molecules

We CAN photoinduce *cis-trans* isomerization in tethered azobenzene

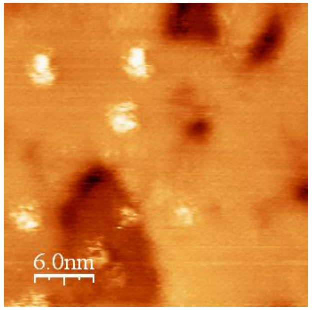
Before UV



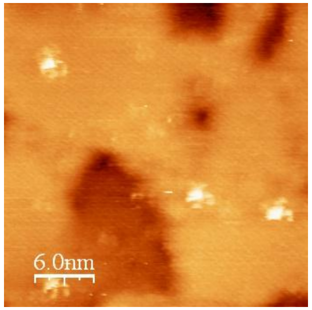
10 min UV



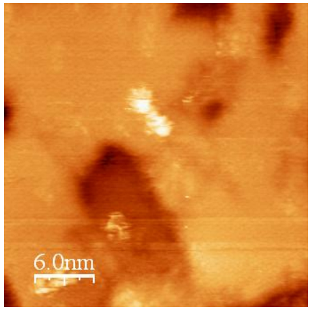
37 min UV

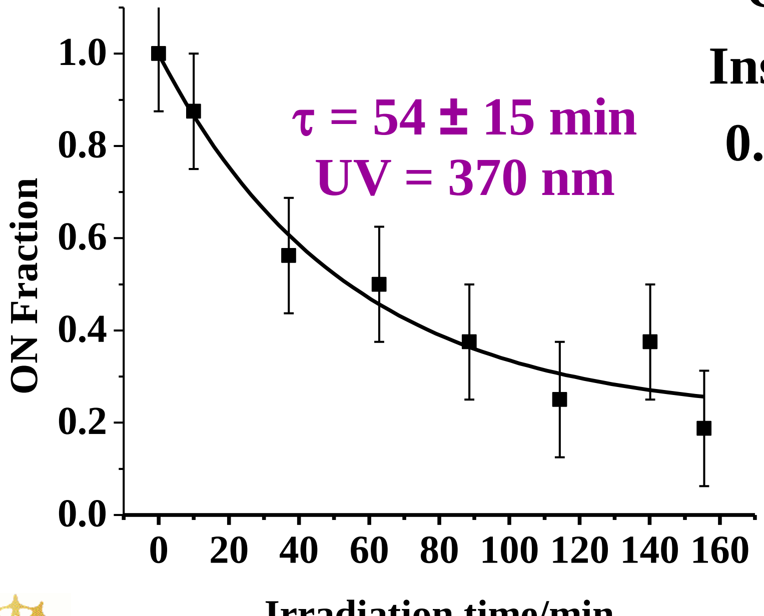


62 min UV



156 min UV

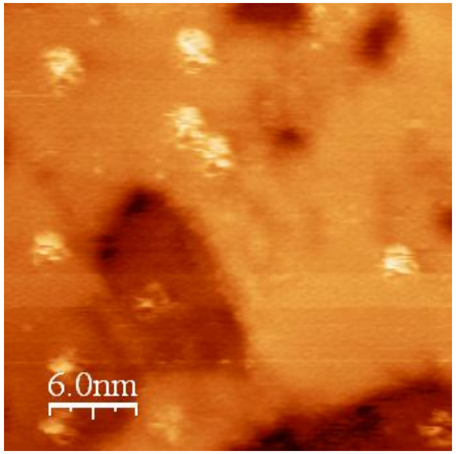




Octanethiolate matrix

Inserted alkylazobenzene

0.6 V sample bias, 2 pA

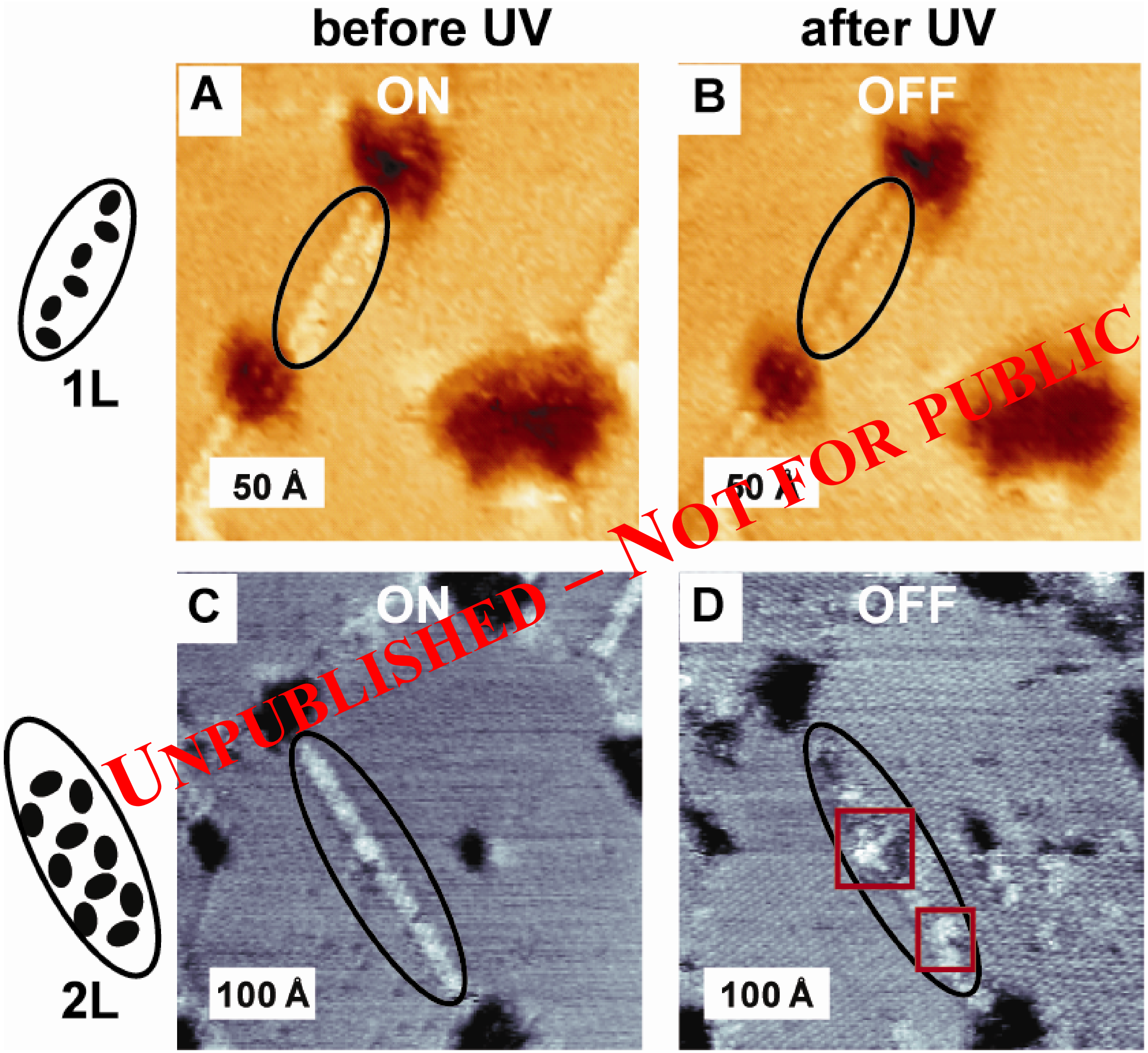


30 min vis (450 nm)

Ye, Kumar, Takami, Flatt, Yu, Tour & PSW, *Nano Letters* 8, 1644 (2008)

Actuation and Coupling in 1D Assemblies

Induce *cis-trans* isomerization in assemblies



Complete conversion (1L)

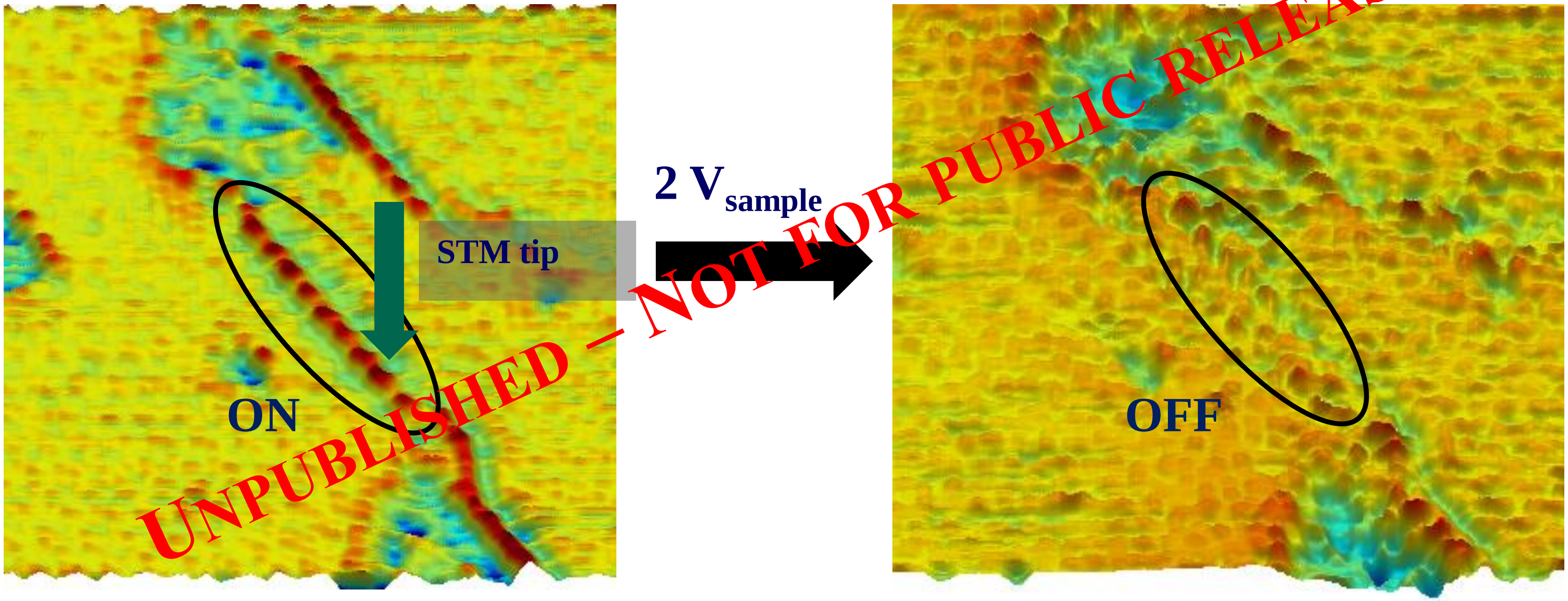
Steric interference (2L)

Kumar, Pathem, Corley, Ye, Tour, & Weiss

Trigger Actuation Locally and Test Coupling in 1D Assemblies

Induce *cis-trans* isomerization in assemblies locally with electrons

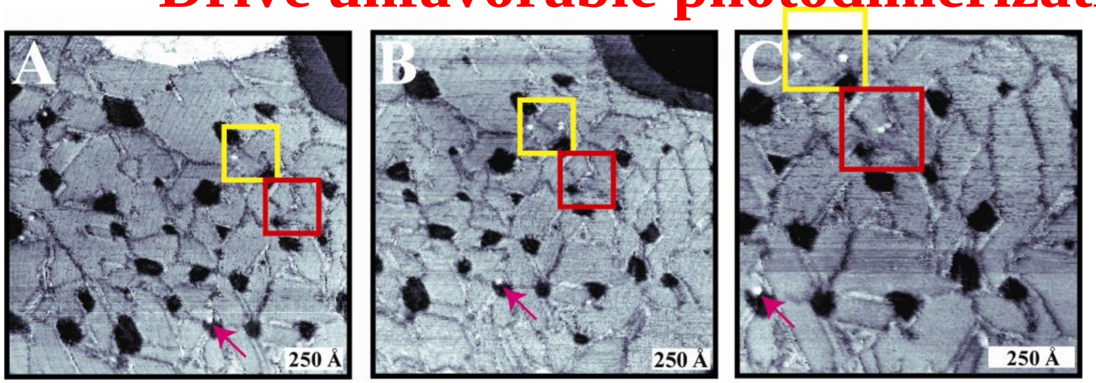
Negative ion state has lower barrier for interconversion



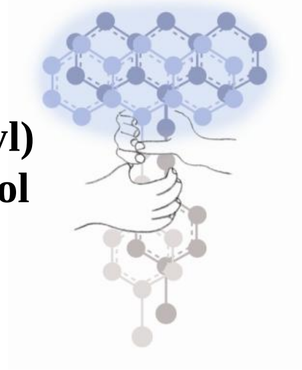
Kumar, Pathem, Corley, Tour, & Weiss

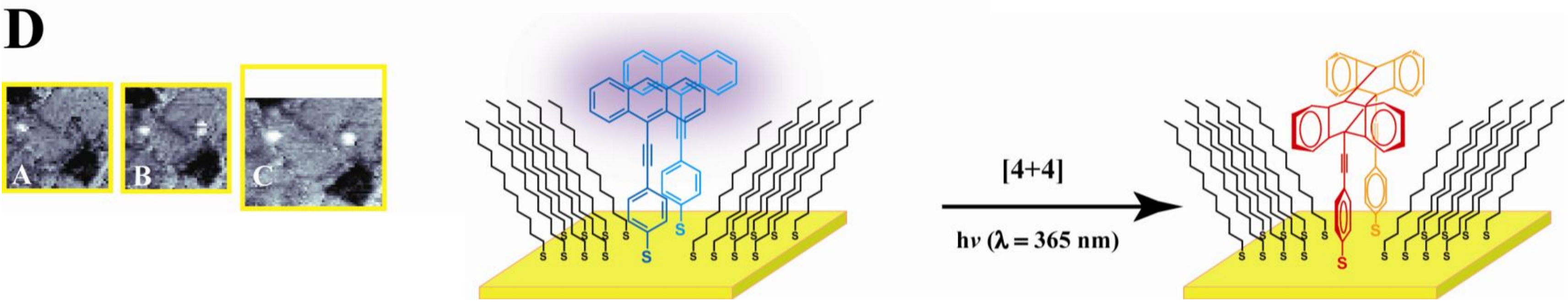
Photodimerizing Inserted *Pairs* of Molecules

Drive unfavorable photodimerization – 4+4 cycloaddition



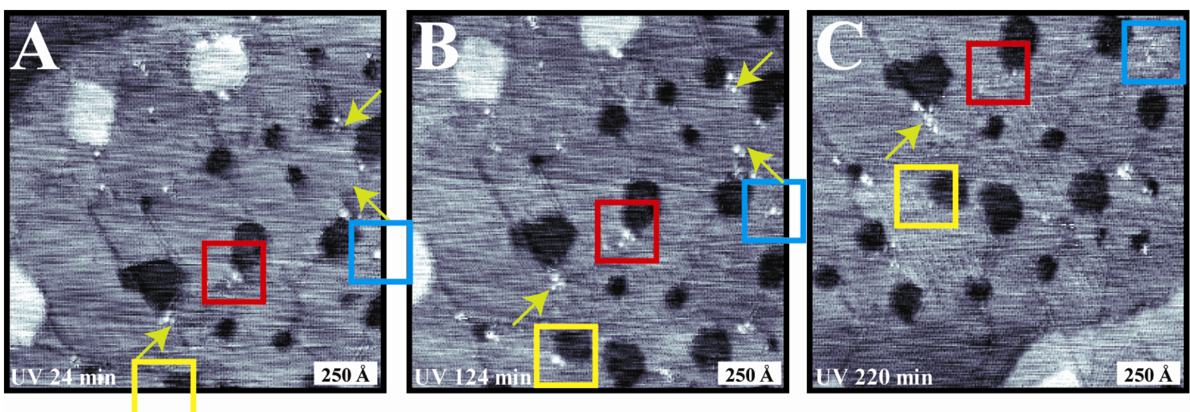
Switching of 9-(4-mercaptophenylethynyl) anthracene in dodecanethiol matrix on Au{111}





Photodimerization stops switching

([4+2] Diels-Alder reaction favored in solution)



Kim, Hohman, Cao, Houk, Ma, Jen, Weiss, *Science* (2011), in press

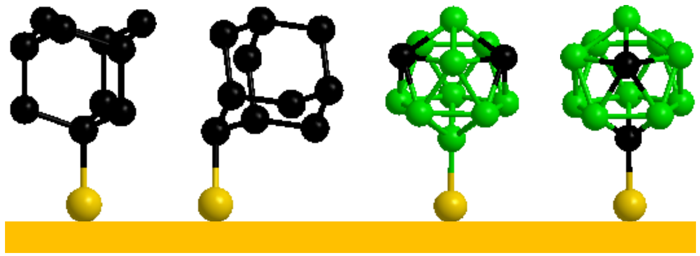
Cage Molecules

Simplicity has significant advantages

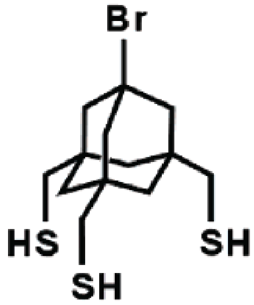
Eliminating tilt eliminates prominent defect type

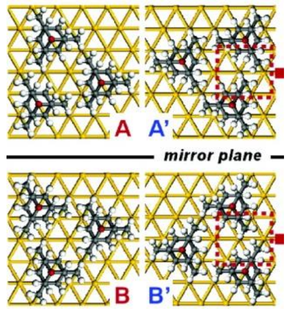
Asymmetric cages enable:

- tailored interactions
- directed interactions
- further functionalization
- supramolecular assembly
- lattice match/mismatch
- 3D supramolecular construction?



SIGMA





cf. chiral assemblies, Kitagawa, Kawai *et al.* *JACS* 129, 2511 (2007)

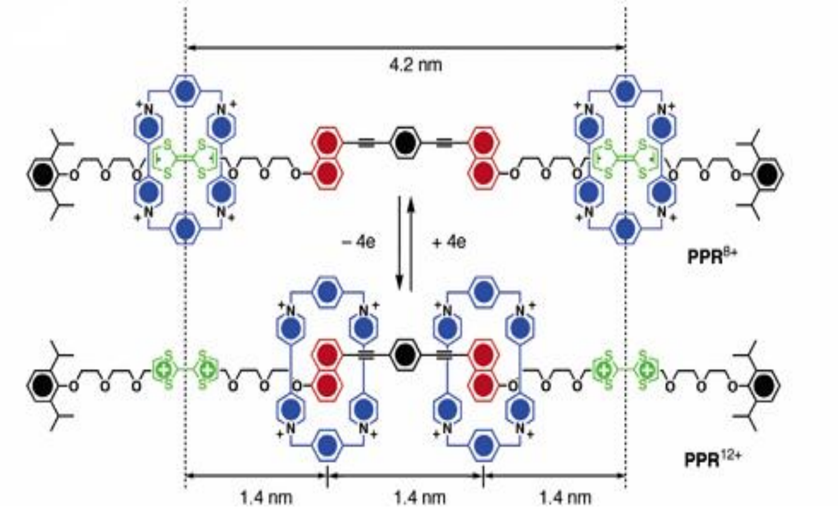
Also, see the work of Base, Kawai, Kitagawa, Michl

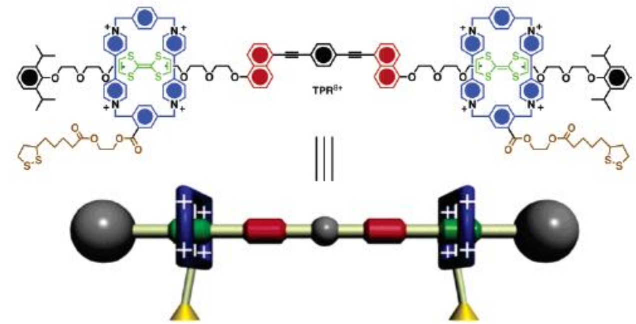
NSF

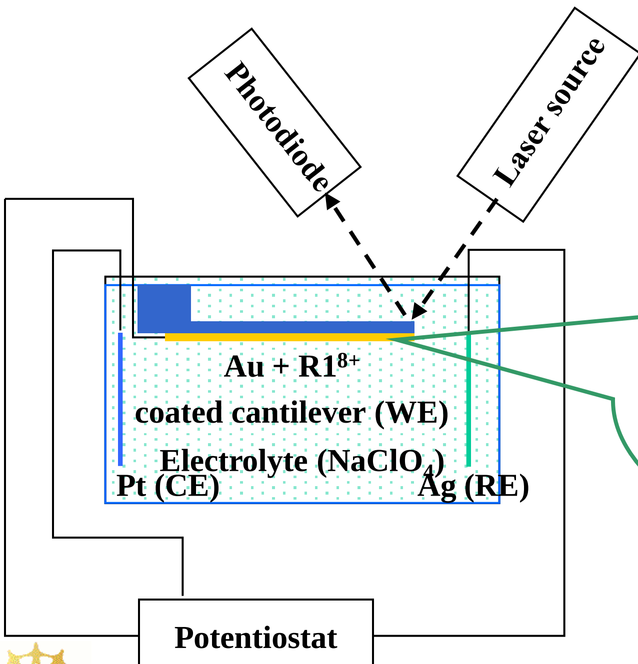
Hohman, Zhang, Morin, Han, Kim, Balema & Weiss, *ACS Nano* 3, 527 (2009)

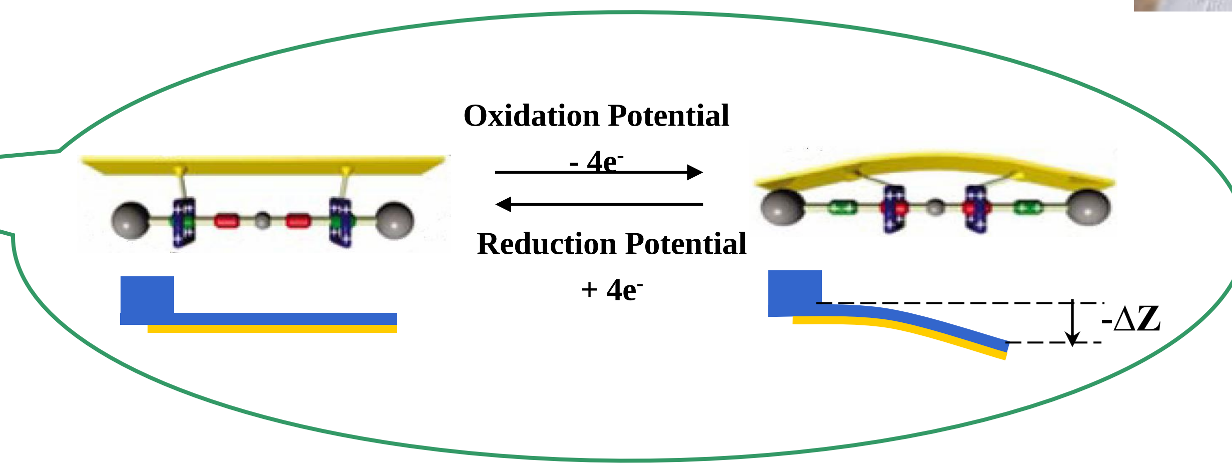
Hohman, Claridge, Kim & Weiss, *Matl Sci & Eng Rep* 70, 188 (2010)

Coordinated Motions of Rotaxane Assemblies







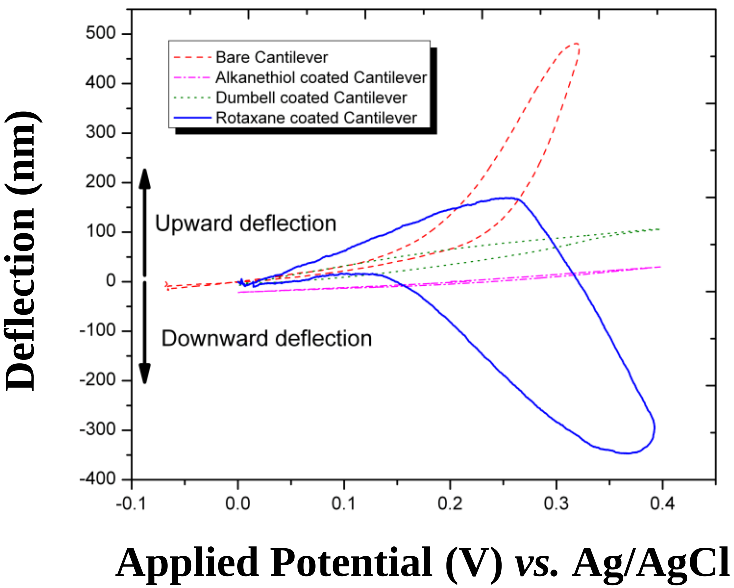


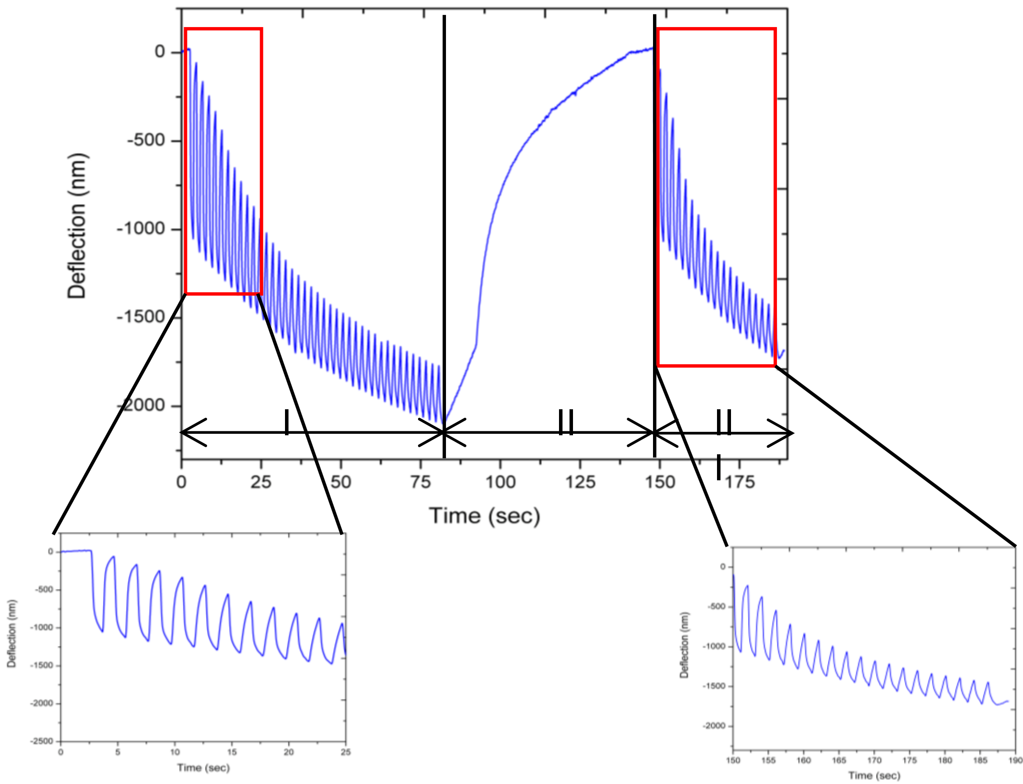
Kumar, Ye, Takami, Saha, Huang, Stoddart, & Weiss, *ACS Nano* 3, 291 (2009)

Coordinated Motions of Rotaxane Assemblies

Determine simultaneous & competing effects with control experiments

***e.g.*, Perchlorate adsorption/desorption with applied potential**





Kumar, Ye, Takami, Saha, Huang, Stoddart, & Weiss, *ACS Nano* 3, 291 (2009)

Driving & Measuring Motors, Rotors, Switches

Hierarchical assembly
- Confirm structure with nanoscale measurements.
- Use asymmetric structures to drive and to measure.
- Tie together design, synthesis, assembly, measurement, and modeling.

Combine control mechanisms
- Electric field
- Chemical
- Electrochemical
- Optical

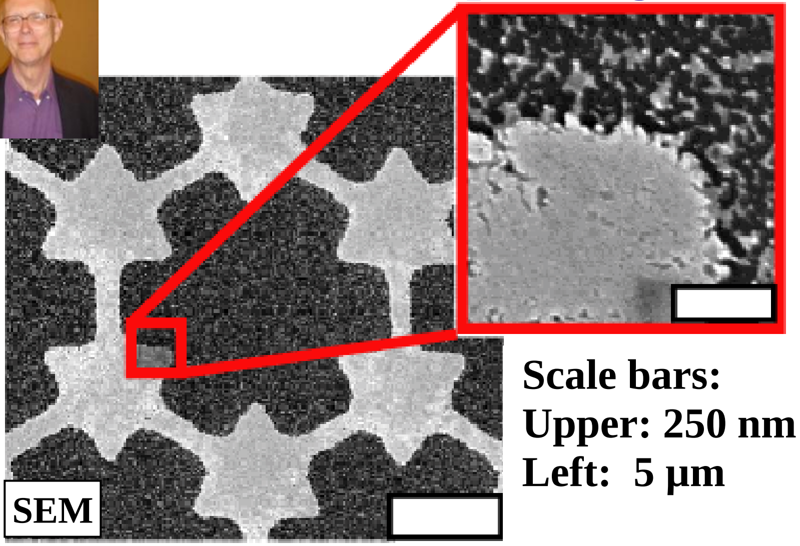
Upcoming:
- Asymmetric molecules for drive and measurements
- Coupled molecules and mechanisms through covalent coupling and assembly
- Apply new nanoscale tools:
  - High speed recording stabilized STM
  - Microwave frequency ACSTM
  - Visible absorption STM
  - FTIR absorption STM
  - Photon emission STM
  - Stabilized electrochemical STM


Mieko Yuki, Ippodo

Soft & Hybrid Lithography

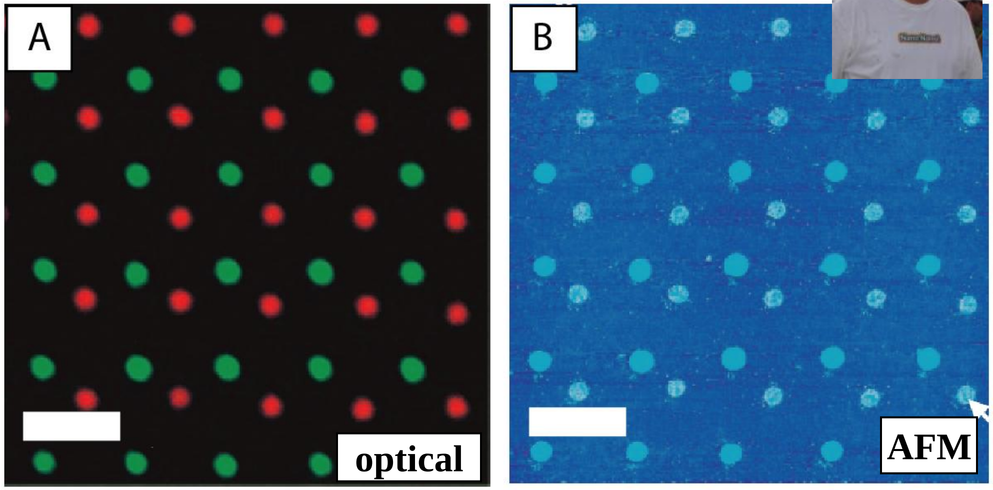
Exploit intermolecular interactions to sharpen nano-scale patterns and broaden the library of molecules that can be applied

Microcontact printing



Scale bars:
Upper: 250 nm
Left: 5 µm

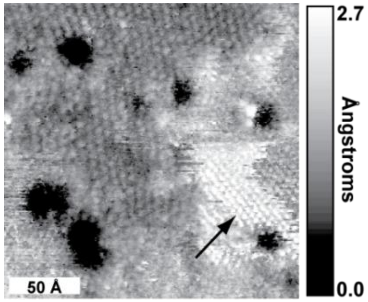
Dip-pen nanolithography



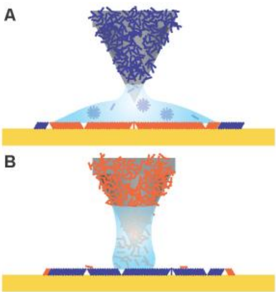
Scale bars: 4 µm

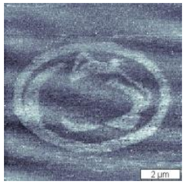
Love, Wolfe, Chabinyc, Paul & Whitesides, *JACS* 124, 1576 (2002)

Hong, Zhu & Mirkin, *Science* 288, 1808 (2000)



Control at much smaller scales
***and* improve these methods by exploiting tailored intermolecular interactions and hierarchical strategies**



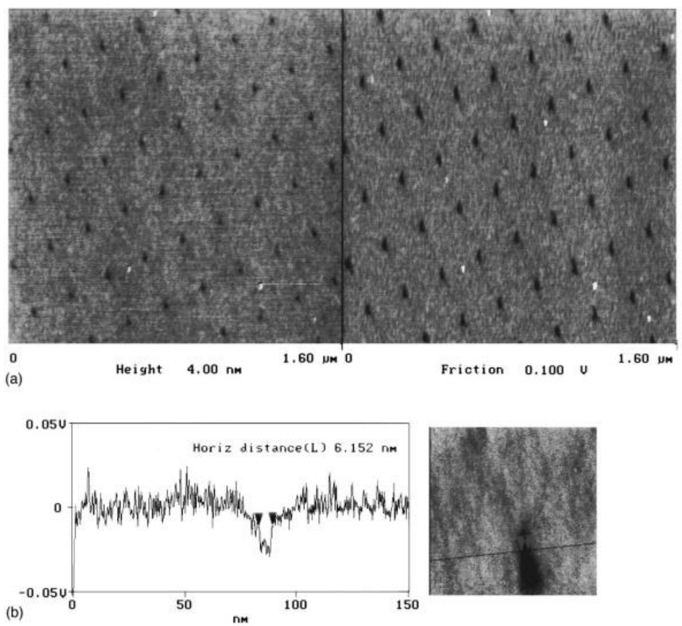


Dameron, Hampton, Smith, Mullen, Gillmor, & Weiss, *Nano Lett* 5, 1834 (2005)

Hampton, Dameron, & Weiss, *JACS* 128, 1648 (2006)

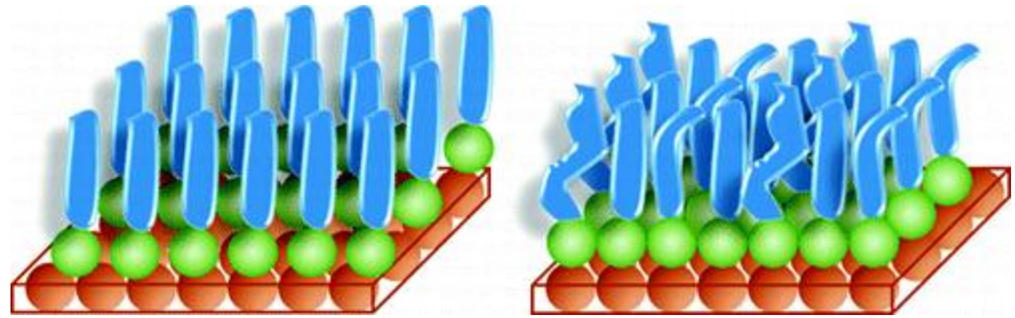
Monolayer Defects Limit Utility as Resists

Monolayers are never complete and defect-free



E-beam of monolayers on GaAs

Lercel, Craighead, Parikh, Seshadri & Allara, *APL* <u>68</u>, 1504 (1996)

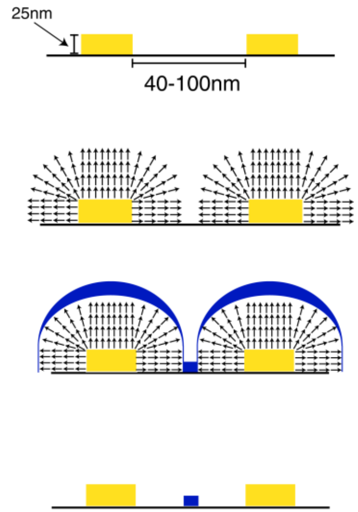


Compare monolayers on metal, group IV, and III-V substrates

Bent, *ACS Nano* <u>1</u>, 10 (2007)

Monolayers on GaAs

McGuiness, Blasini, Masejewski, Uppili, Cabarcos, Smilgies & Allara, *ACS Nano* <u>1</u>, 30 (2007)



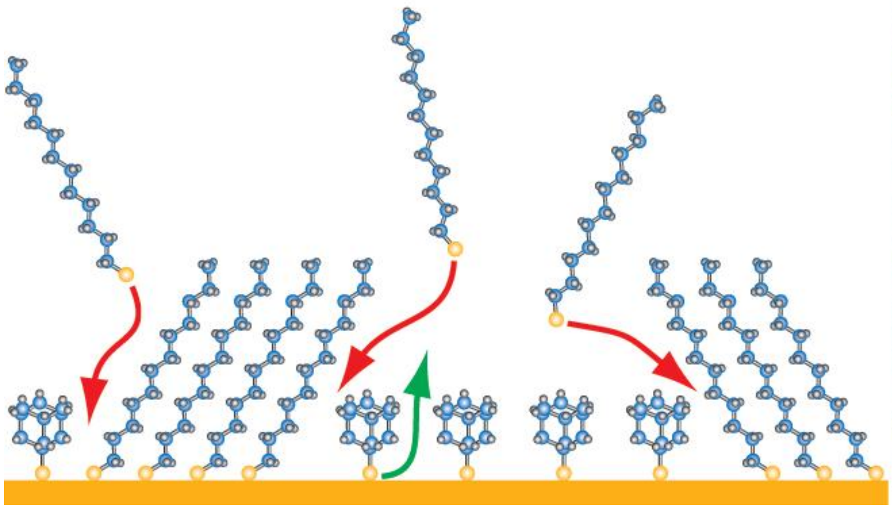
Multilayers can be used to heal defects but are not (very) useful for our purposes here

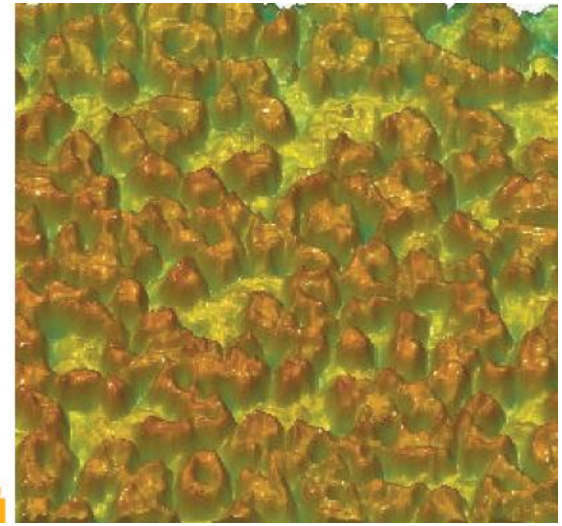
Hatzor & Weiss, *Science* <u>291</u>, 1019 (2001)

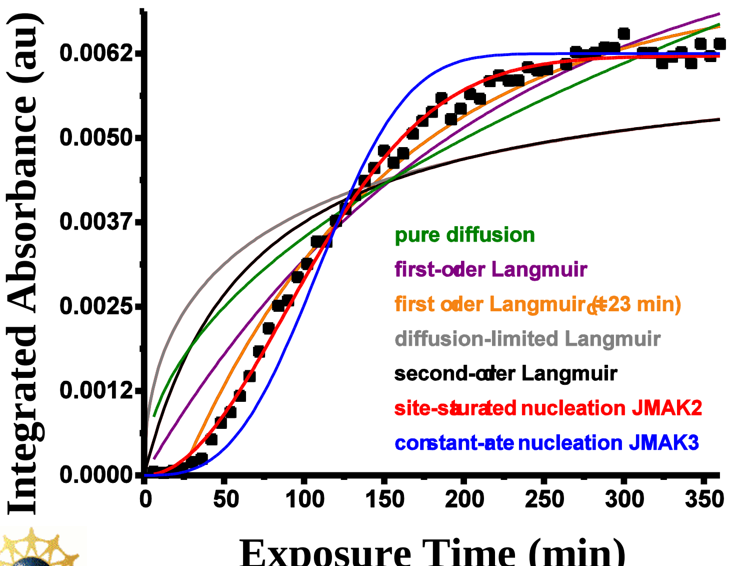
Also, see the work of Grunze, Gölzhäuser, Nuzzo, Sagiv, Zharnikov, *etc*.

Understanding Displacement

Nucleate displacement at edges, lattice mismatch "unzips" domains





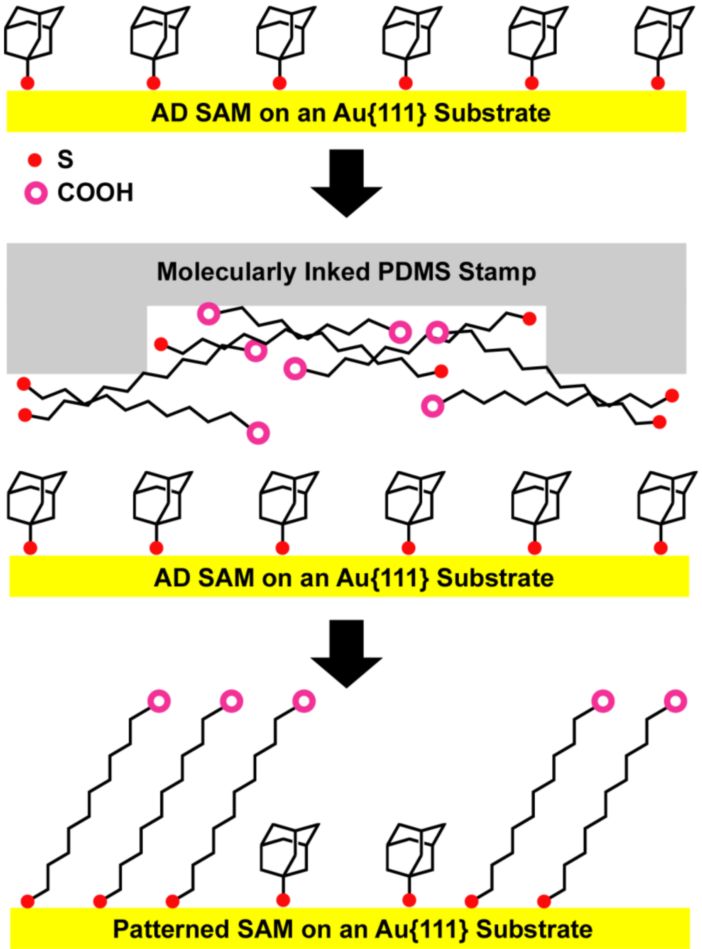


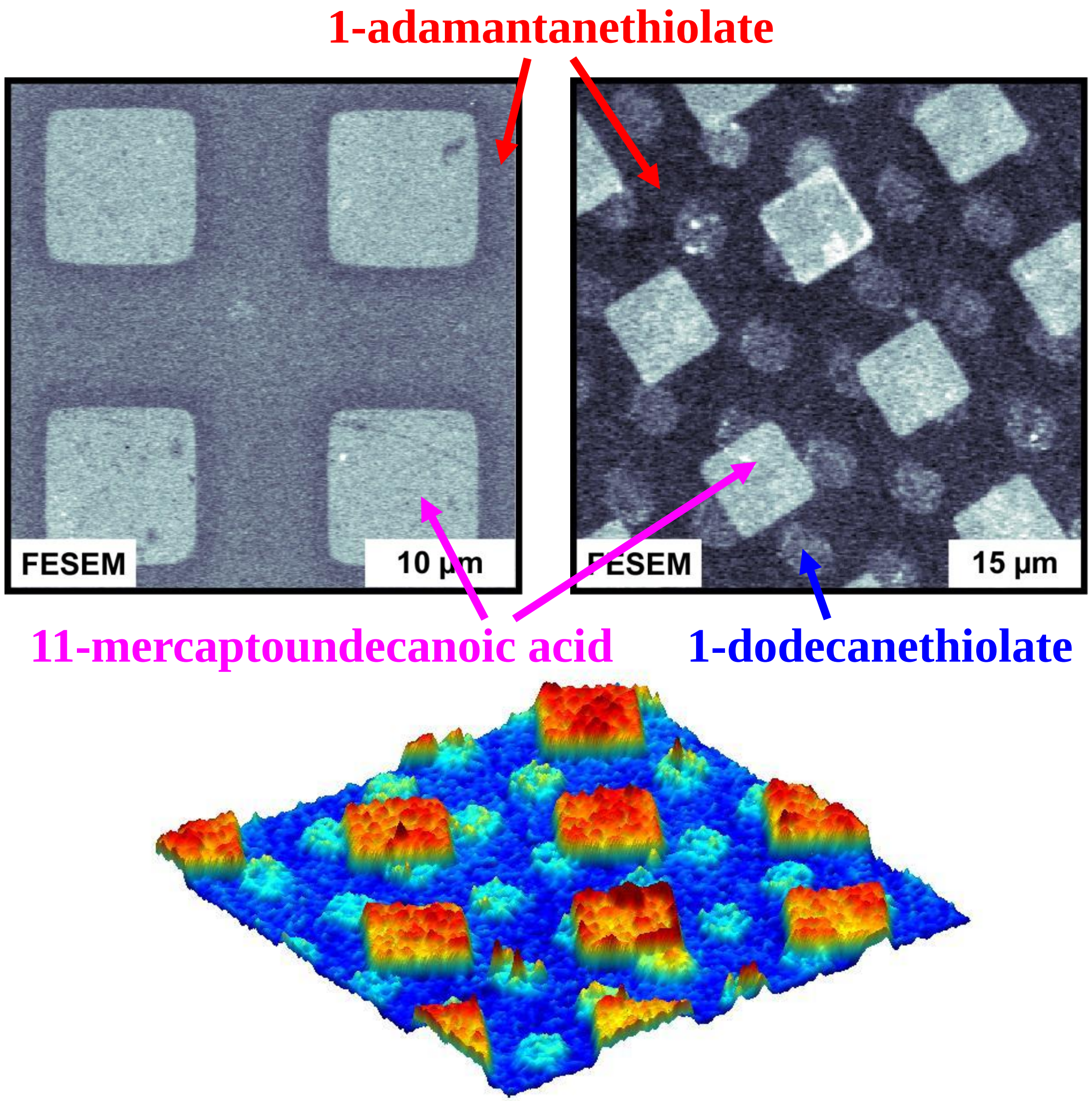
Follow displacement with STM, FTIR, XPS, and electrochemistry

Describe displacement with scale-free Johnson-Mehl-Avrami-Kolmogorov model

Saavedra, Barbu, Dameron, Mullen, Crespi, & Weiss, *JACS* 129, 10741 (2007)

Precision Patterning: Microdisplacement Printing

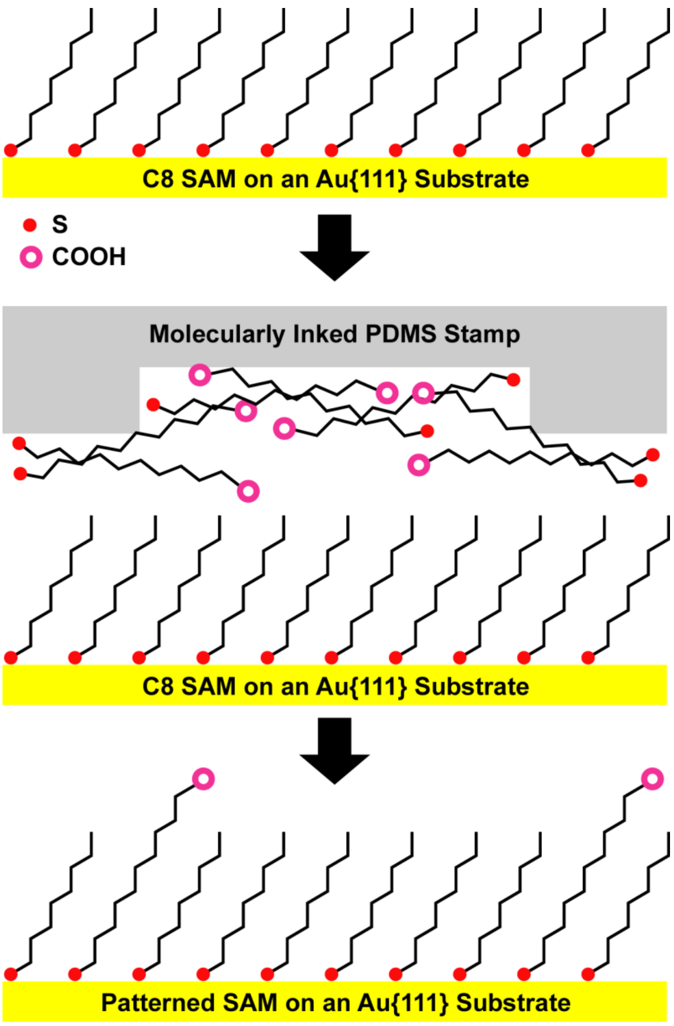




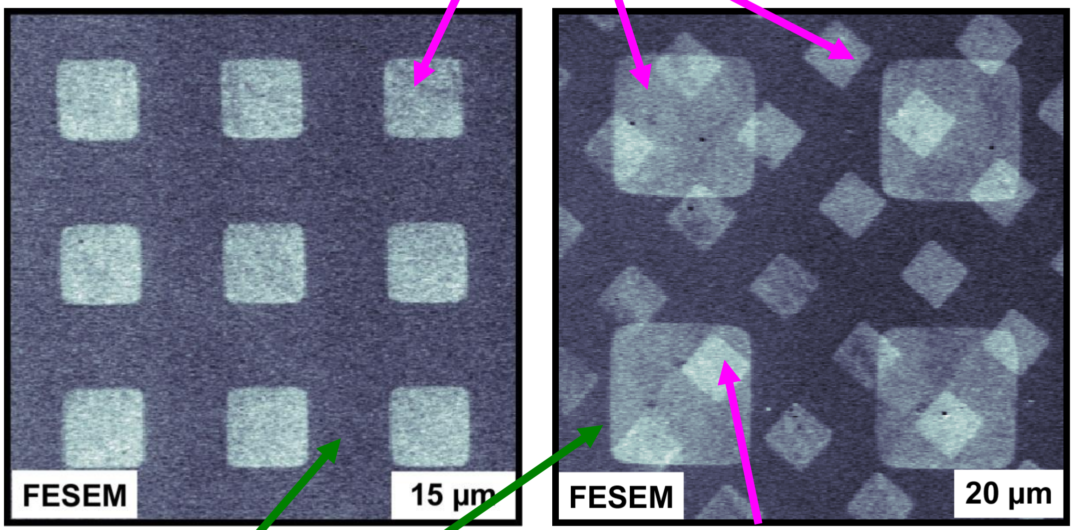
Primary Beam Energy = 1 kV
Collection Voltage = +300 V

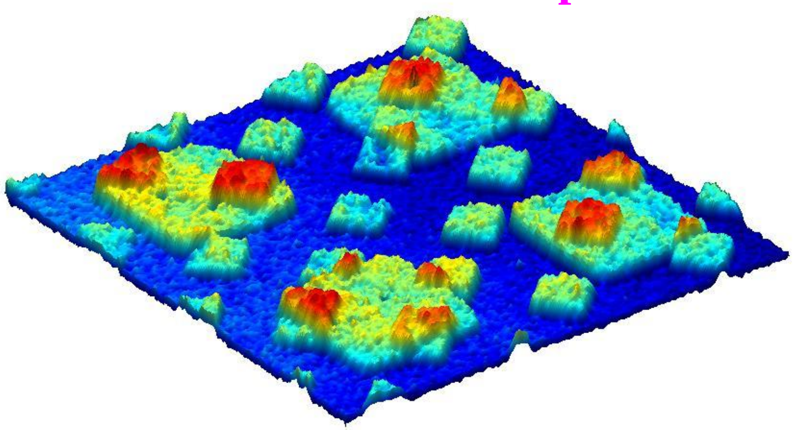
Dameron, Hampton, Smith, Mullen, Gillmor, & Weiss, *Nano Lett.* 5, 1834 (2005)
Dameron, Hampton, Gillmor, Hohman, & Weiss, *JVSTB* 23, 2929 (2005)
Mullen, Hohman, Dameron, Hampton, Gillmor, & Weiss, *Materials Matters* 1, 8 (2006)

Microcontact Insertion Printing



Primary Beam Energy = 1 kV
Collection Voltage = +300 V





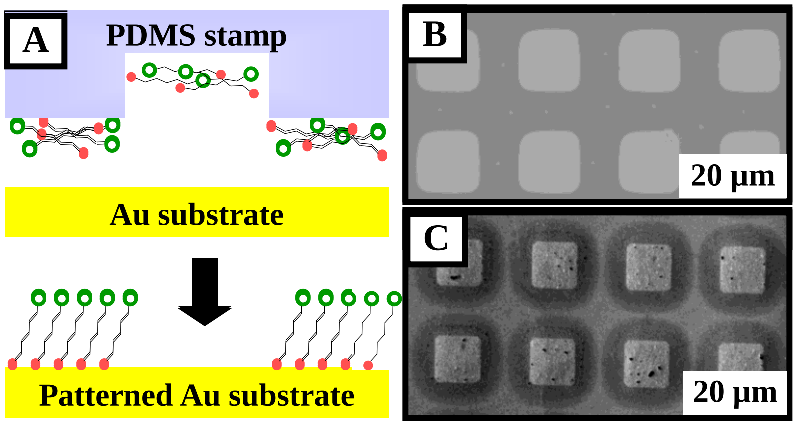
Weiss, Allara, Andrews,
Dickey, Horn, Crespi

Mullen, Srinivasan, Hohman, Gillmor, Shuster,
Horn, Andrews, & Weiss, *Appl. Phys. Lett.* 90, 063114 (2007)

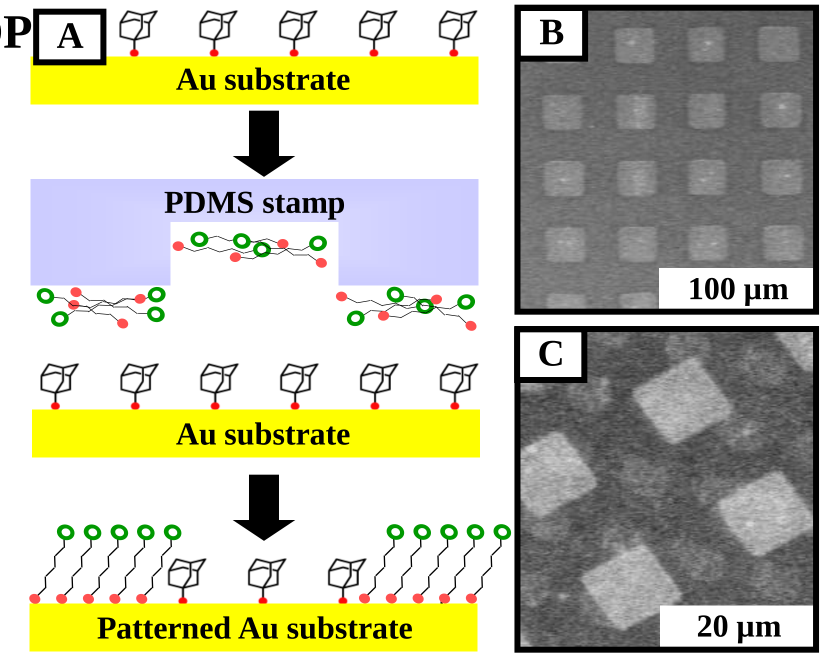
Chemical Patterning and Metrology

Use hybrid strategies to enhance precision of final structures

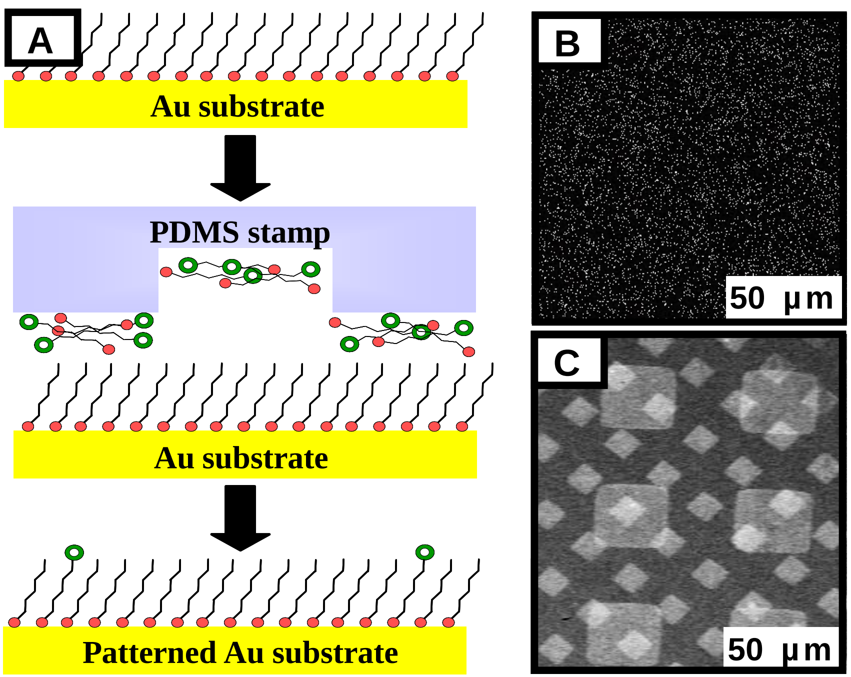
μCP



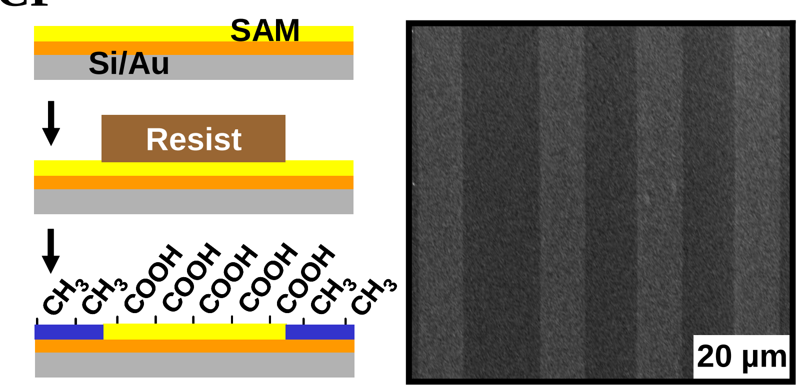
μDP



μCIP



LACP



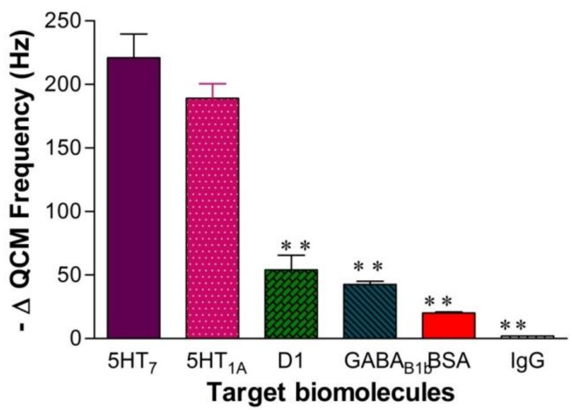
Srinivasan, Mullen, Shuster, Anderson, Hohman, Dickey, Horn, Andrews, & Weiss, *ACS Nano* 1, 191 (2007)

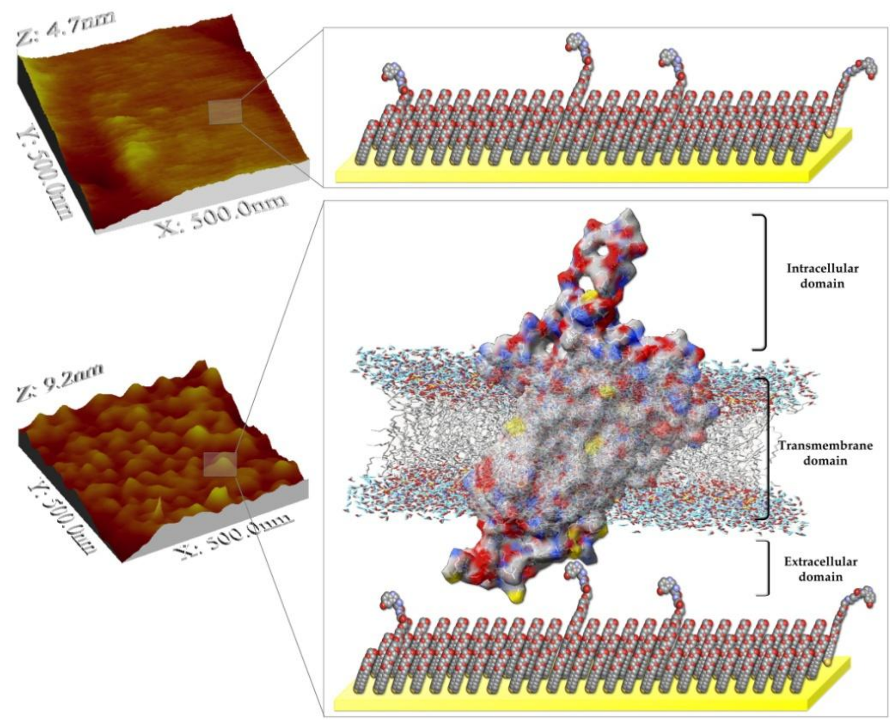
Capture of Membrane-Associated Receptor Proteins

Membrane proteins are particularly difficult to separate, and to determine structure and function - lose function and structure outside of membrane

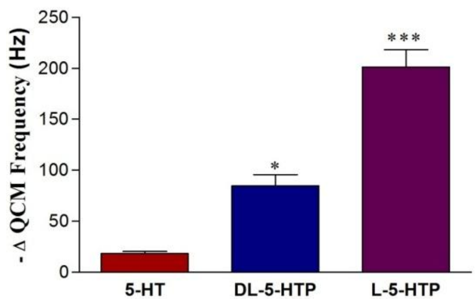
Some recombinant neurotransmitter-related proteins are available

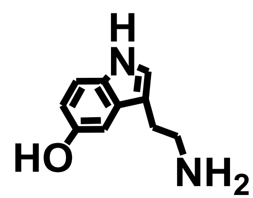
5-HTP Surface
(no stringency optimization)





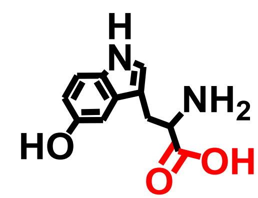
5-HT_7 Receptor Binding
5-HT/5-HTP Surface
Eniantiomeric Control





5-HT
Serotonin

vs.



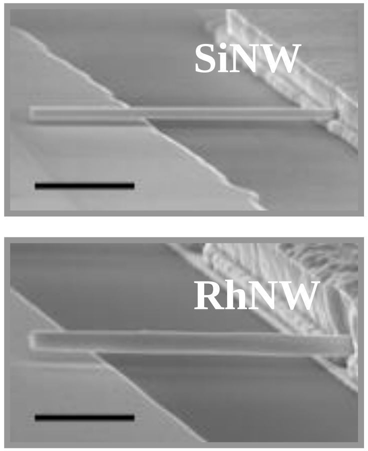
5-HTP
5-Hydroxytryptophan

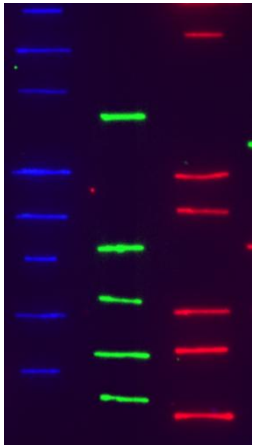
Specific exposed functionality is critical
Now developing new single-assembly structural tool based on nmr

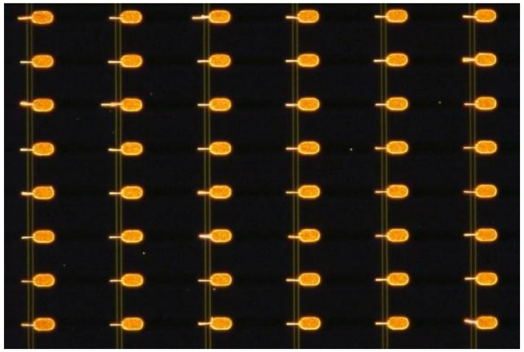
Vaish, Shuster, Singh, Weiss, & Andrews, *ACS Chem Neuro* 1, 495 (2010)

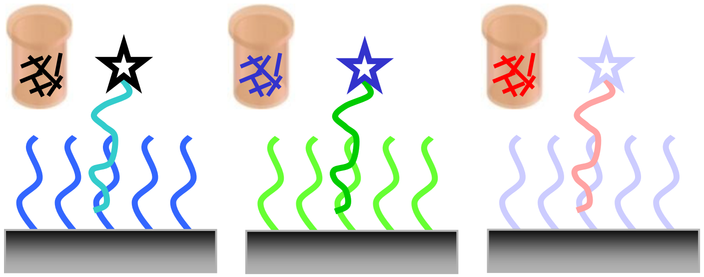
Multiplexed Nanowire Sensors: Assembly & Transduction

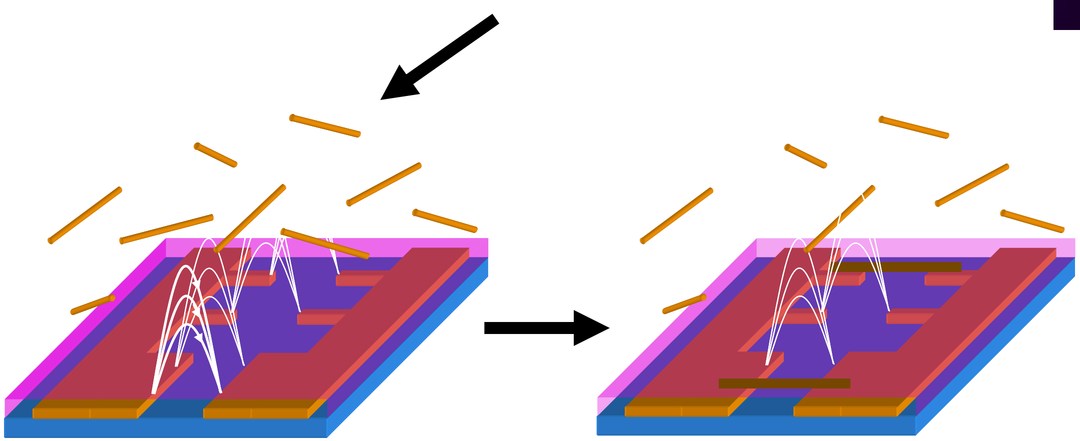
- Functionalize nanowires prior to assembly
- Post-assembly/integration hybridization with excellent positioning & retention of bioselectivity
- CMOS-compatible, three versatile platforms for chip-based multiplexed sensing

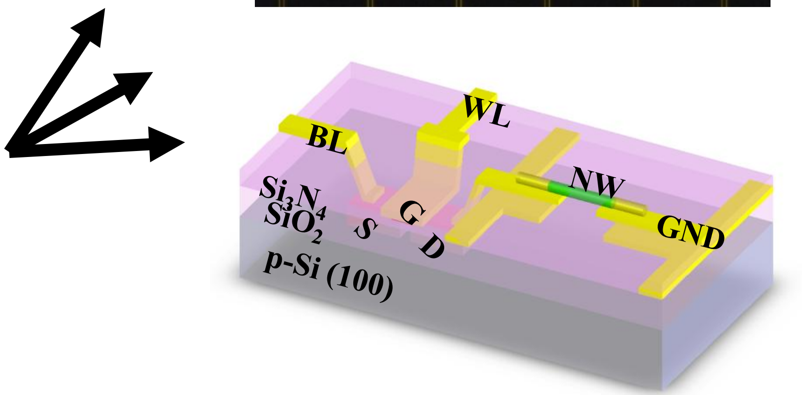








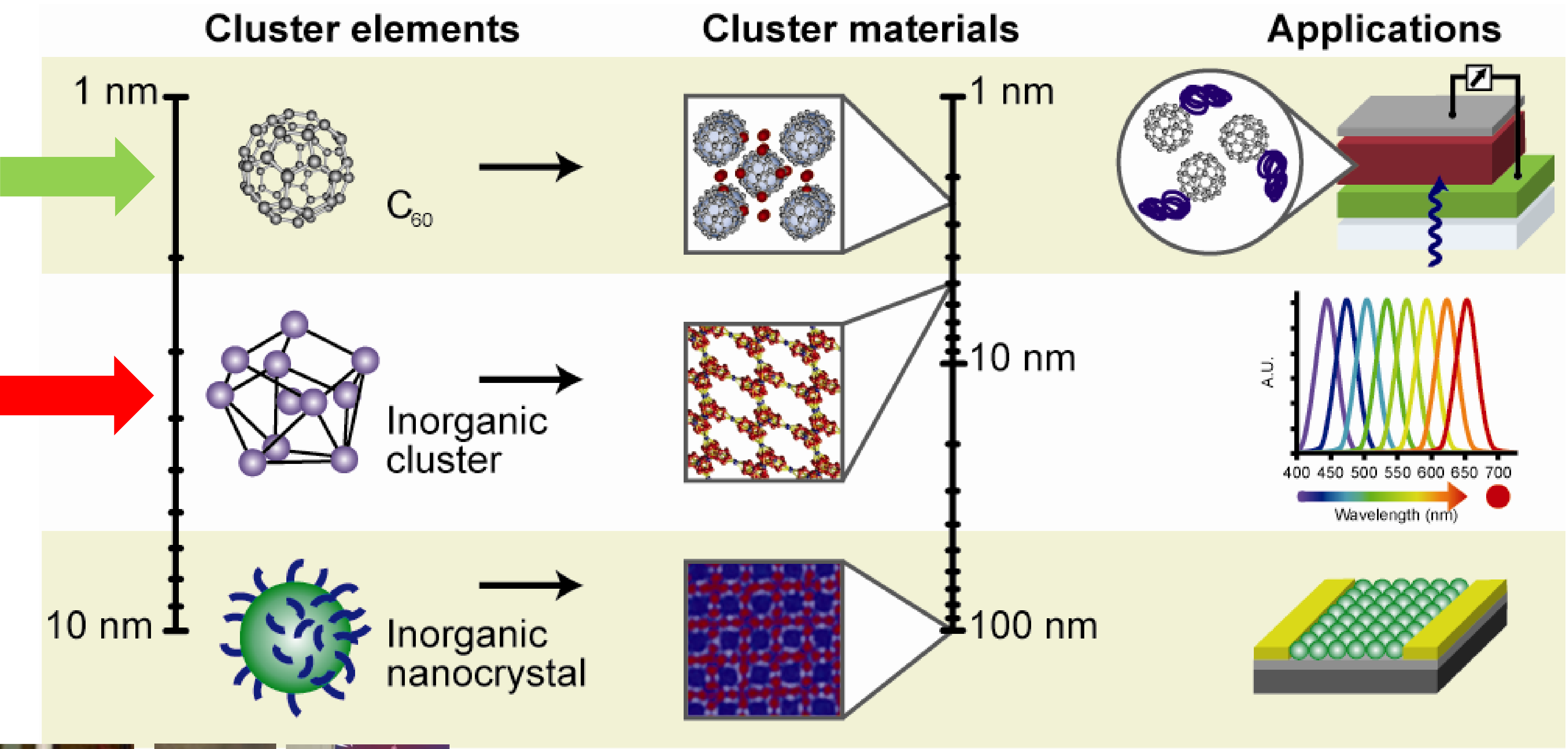


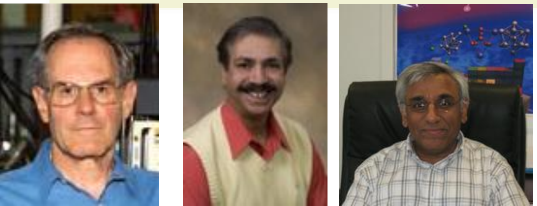


Keating, Mayer, Redwing, Cho, Huffaker, Weiss, & Andrews

Precise Cluster-Assembled Materials

Coupling of physical properties in assembled clusters creates materials with tailored properties





Claridge, Castleman, Khanna, Murray, Sen, & Weiss
ACS Nano 3, 244 (2009)

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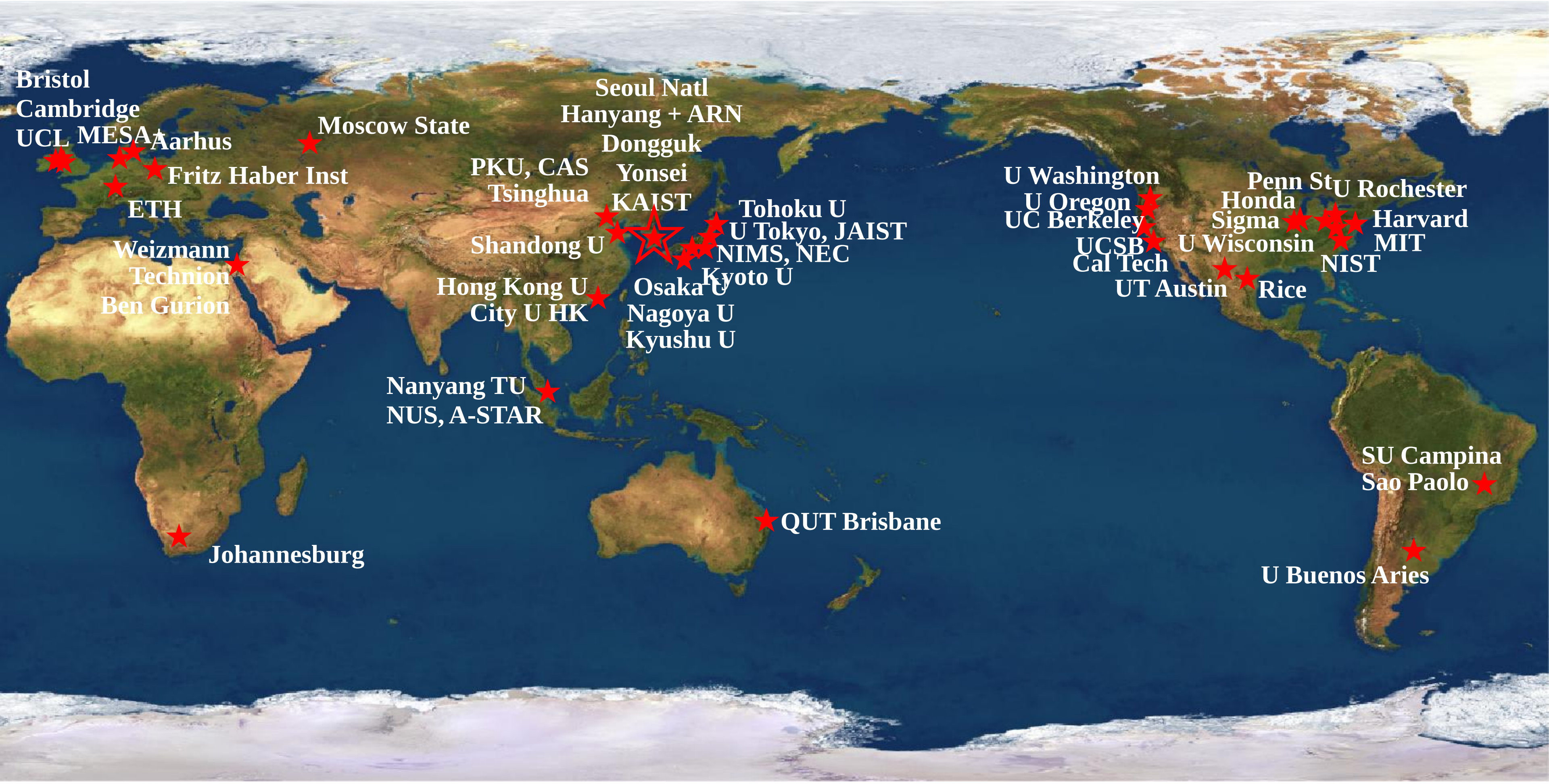

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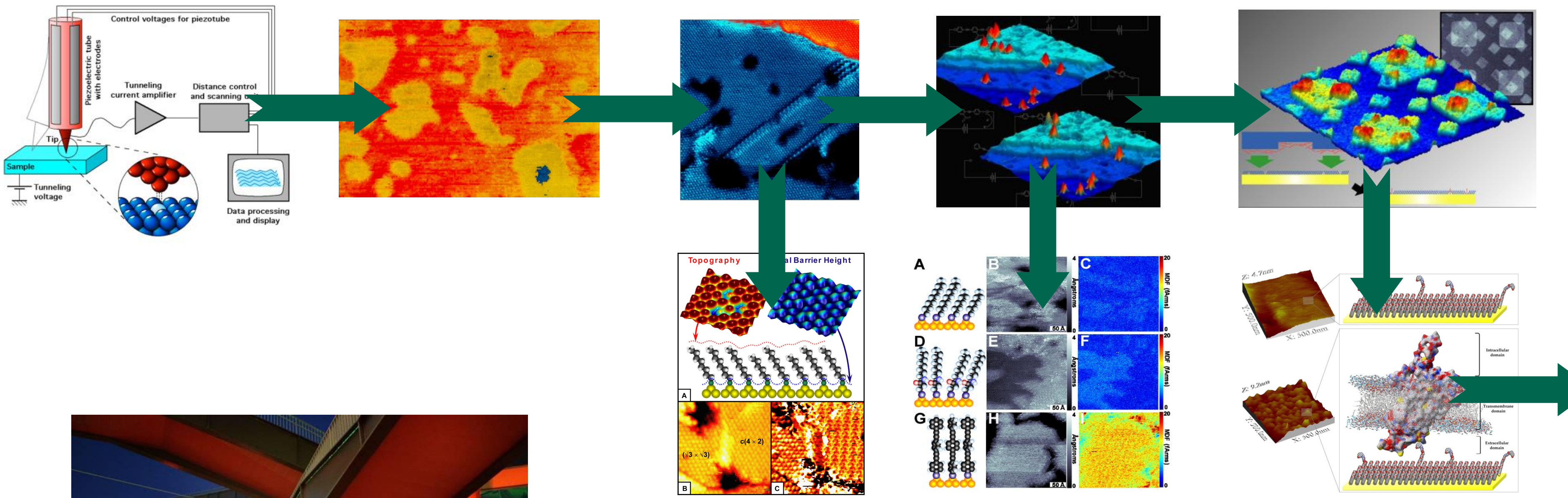
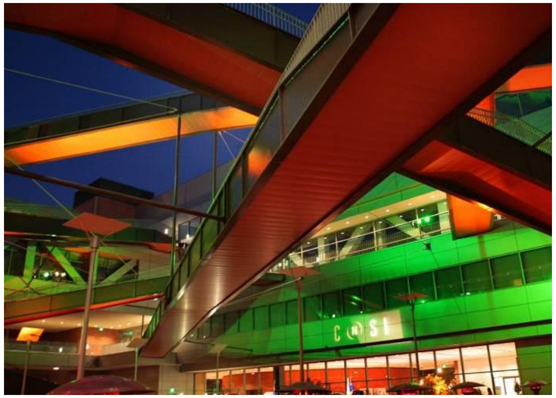
文部科学省 Ministry of Education, Culture, Sports, Science and Technology

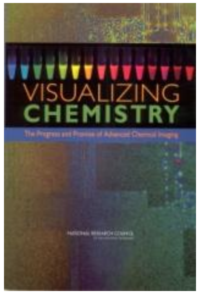
New Tools Enable New Science and New Capabilities

Develop and apply new tools to solve scientific problems

New and enhanced "eyes" will enable increasingly complex, precise, and (multi)functional assemblies







Mieko Yuki
Ippodo