Institut für Organische Chemie der Justus-Liebig-Universität

# Cage compounds and self-assembling

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28.10.2010

Giessen

# Structure of Self-Assembled Monolayers

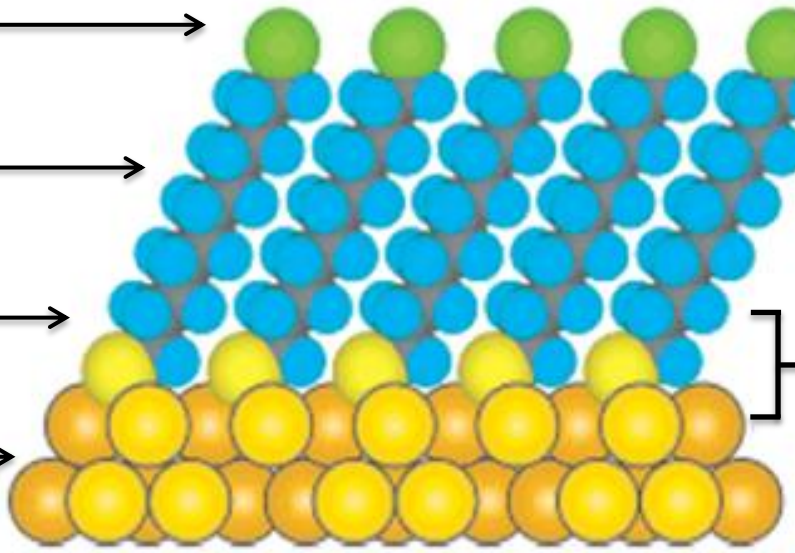
Organic Interface:
- ✧ Determines surface properties
- ✧ Presents chemical functional groups

Terminal Functional Group

Spacer (Alkane Chain)

Ligand or Head Group

Metal Substrate

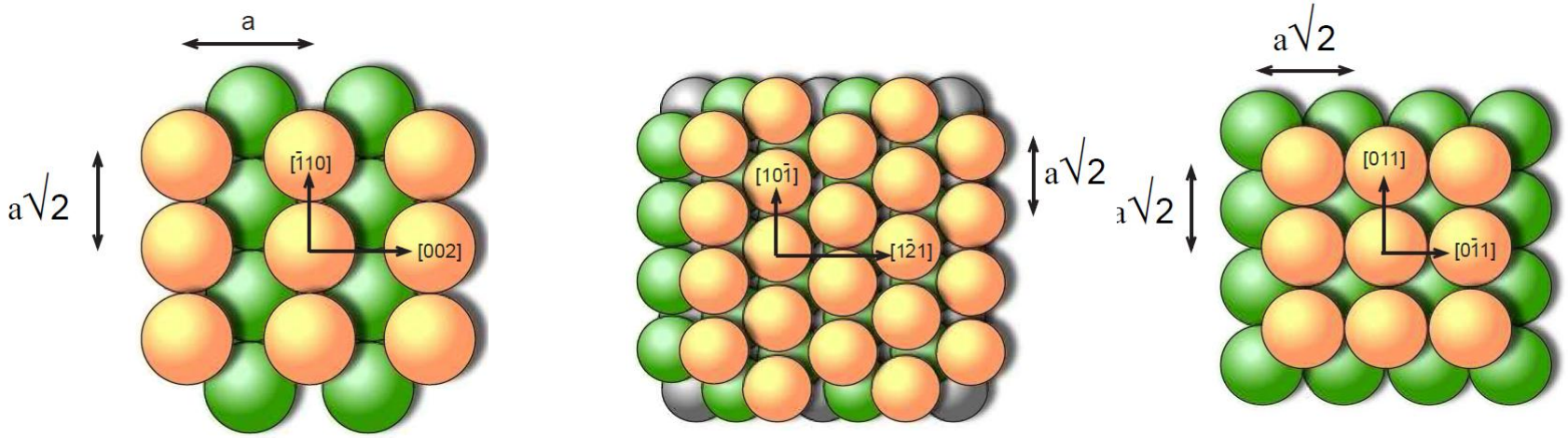


Organic Interface (1-3 nm):
- ✧ Provides well-defined thickness
- ✧ Act as a physical barrier
- ✧ Alters electronic conductivity and local optical properties

Metal-Sulfur Interface:
- ✧ Stabilizes surface atoms
- ✧ Modifies electronic states

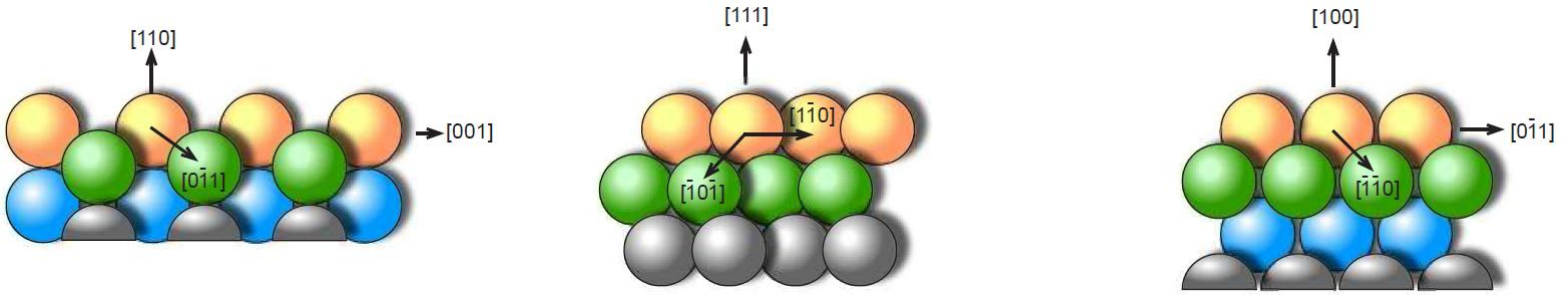
Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. *Chem. Rev*. **2005**, 105, 1103-1169.

# Metal Crystal Faces



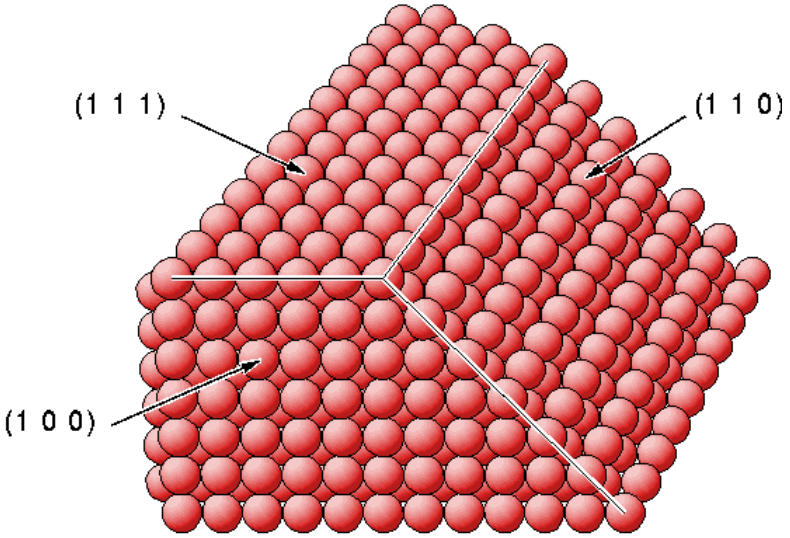

**a** = unit cell length

## Cross-Sectional View

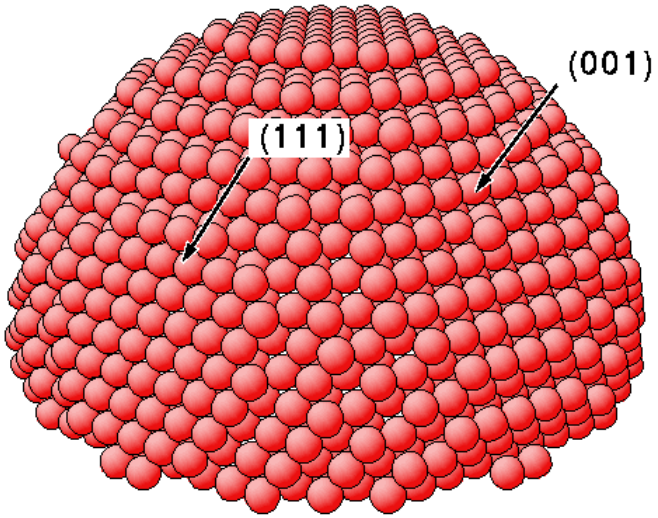



B. Liu, Y. Li, A. S. Mathews, Y. Wanga, W.Yan, S. Abraham, C.-S. Ha, D.-W. Park, I. Kim *Reactive & Functional Polymers* **2008**, 68, 1619–1624;
C. Sinkel, S. Agarwal, N. A. Fokina, P. R. Schreiner *Journal of Applied Polymer Science* **2009**, 114, 2109–2115.

# Intersection of Different Surfaces in Irregular-shaped Samples

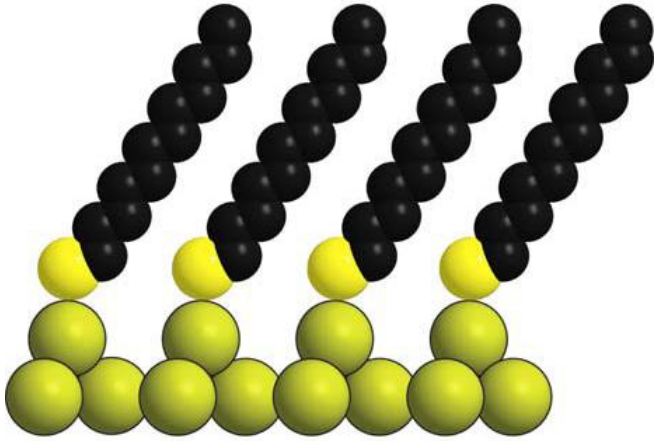



an Angled Corner

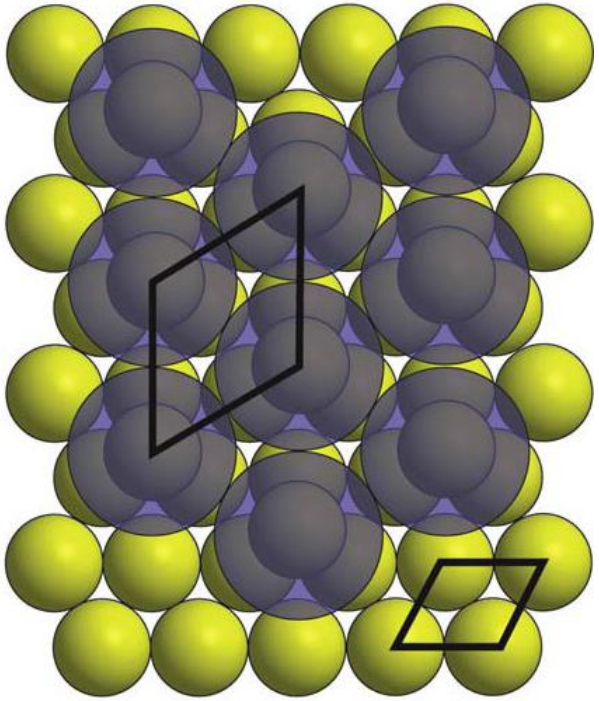



a Spherical Tip

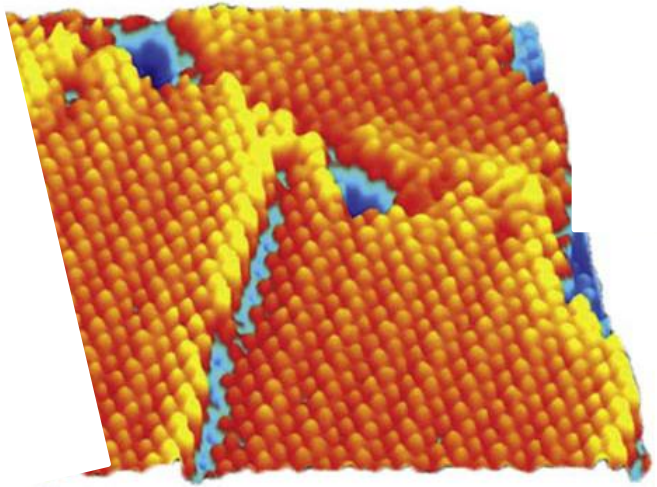
# The n-Alkanethiolate SAM on Au{111} as a Model System for Self-assembly



Idealized ordered structure with molecules on gold adatom binding sites and with ~30° tilt relative to surface normal



The hexagonal lattice:
a) of n-alkanethiolate (blue circles, (√3× √3)*R*30° unit cell)
b) of Au{111} (yellow circles, 1×1 unit cell)



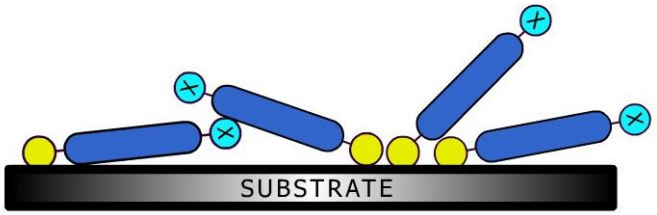
A STM image reveals ordered, hexagonal packing, with domain boundaries between the well-ordered regions

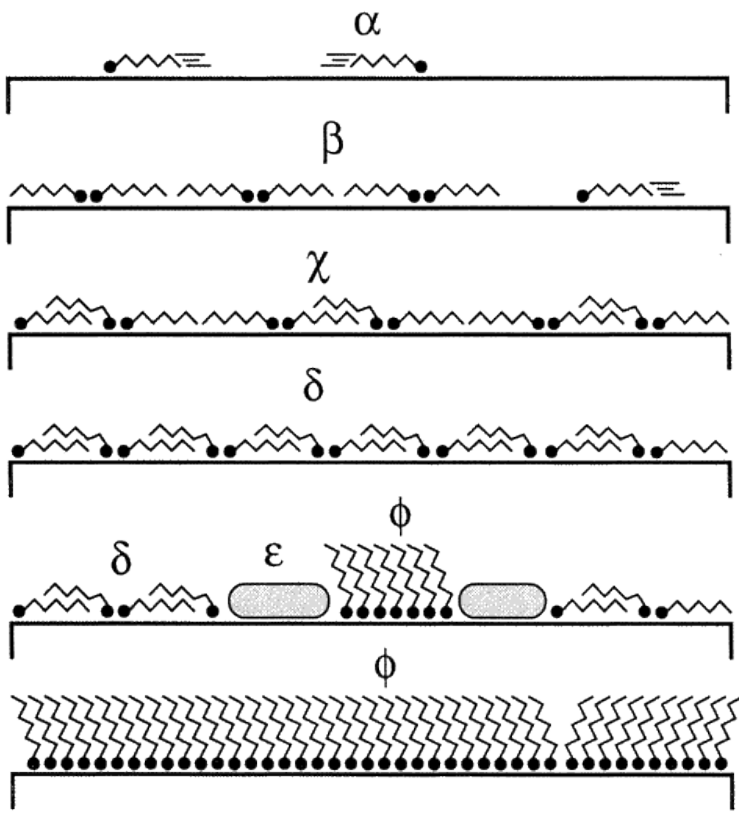
J. N. Hohman, S. A. Claridge, M. Kim, P. S. Weiss *Mater. Sci. Eng., R,* **2010**, 70,188–208.

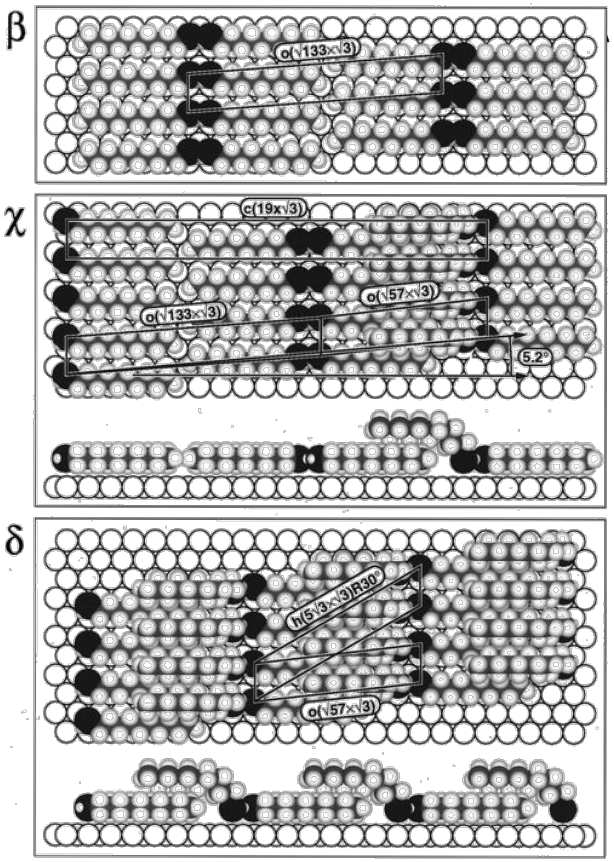
# Commonly Applied Techniques for SAMs Studying

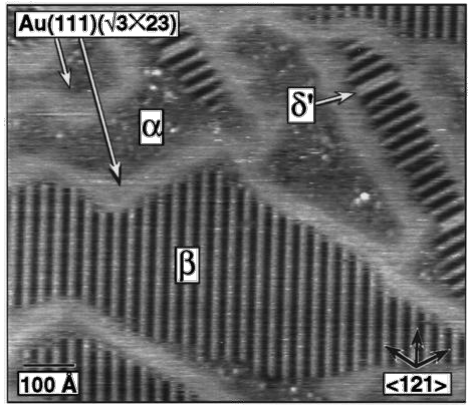
- Scanning tunneling microscopy (STM)
- Atomic force microscopy (AFM)
- X-ray photoelectron spectroscopy (XPS)
- Near-edge X-ray adsorption fine structure (NEXAFS)
- Grazing incidence X-ray adsorption fine structure (GIXAFS)
- Cyclic voltammetry (CV)
- Infrared reflectance absorption spectroscopy (IRRAS)

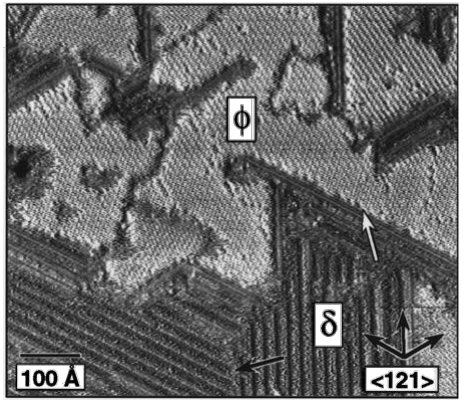
# Laying Down Phases of Decanethiol on Au{111}



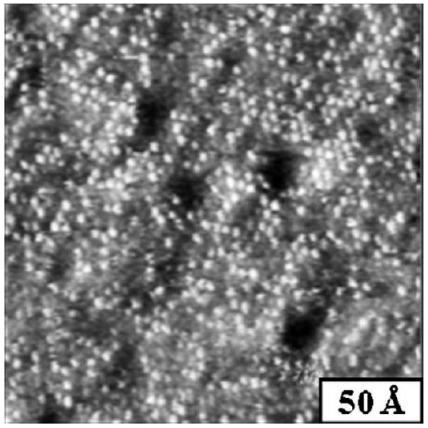



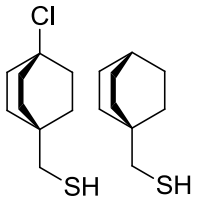



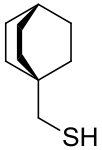



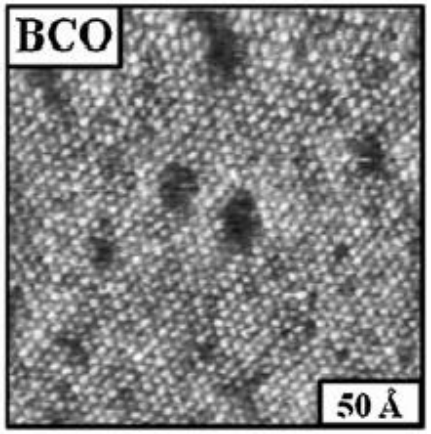

G. E. Poirier *Langmuir*, **1999**, *15*, 1167-1175.

# Self-assembly of Sub-diamondoid Cages

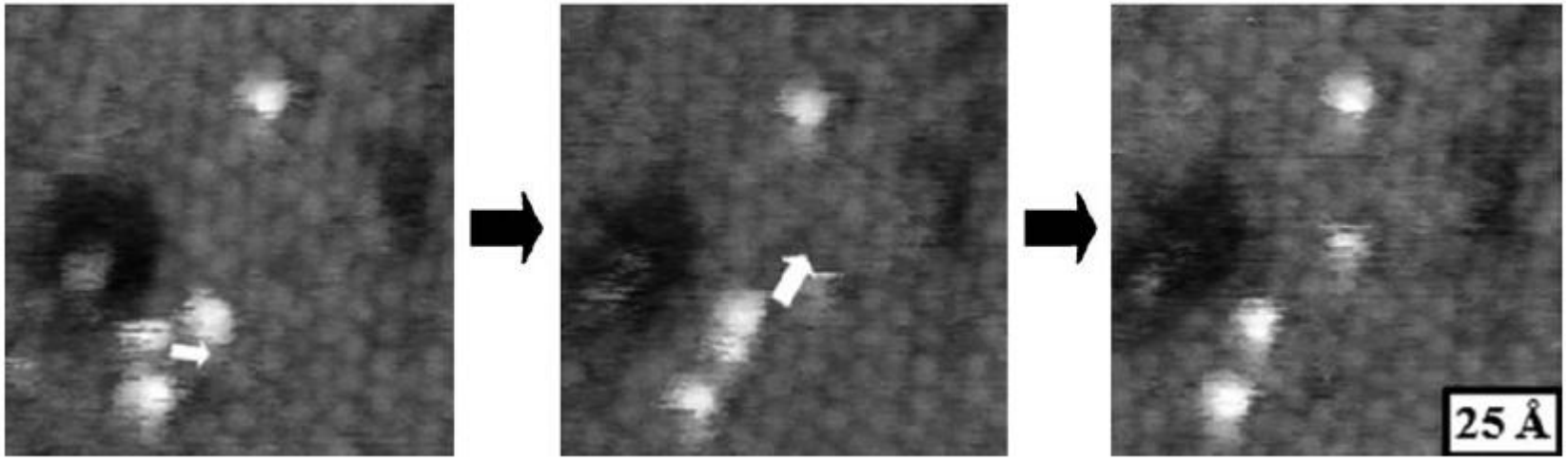


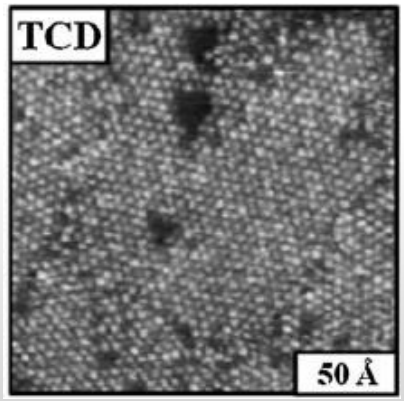



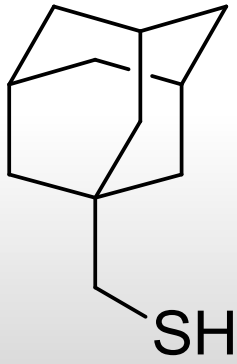


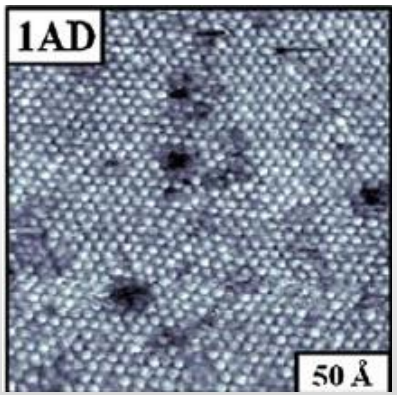


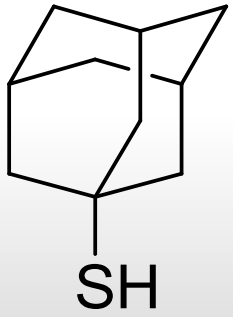

S. Fujii, M. Fujihira, *Nanotechnology* **2006**, *17*, S112;
S. Wakamatsu, S. Fujii, U. Akiba, M. Fujihira *Nanotechnology* **2003**, *14*, 258.

# Assemblies Based on Single Adamantane Unit

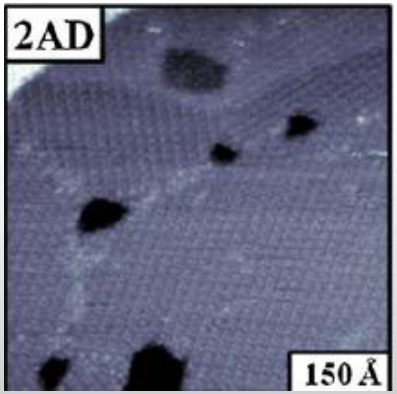


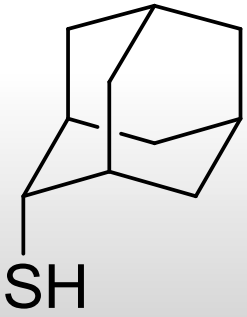




(7×7)*R*21.79° unit cell 6.72 Å nearest neighbor spacing

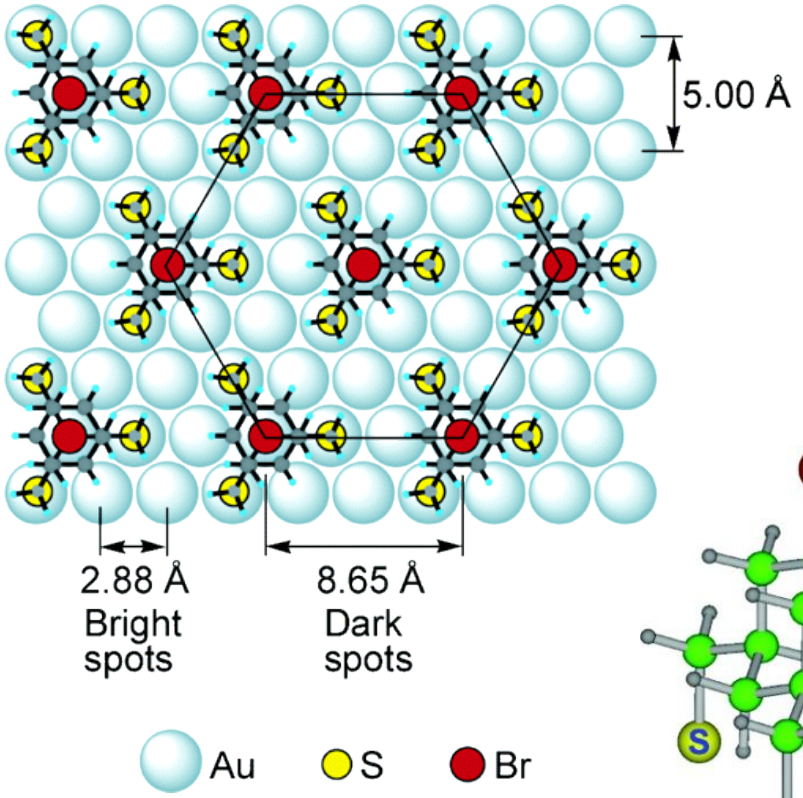


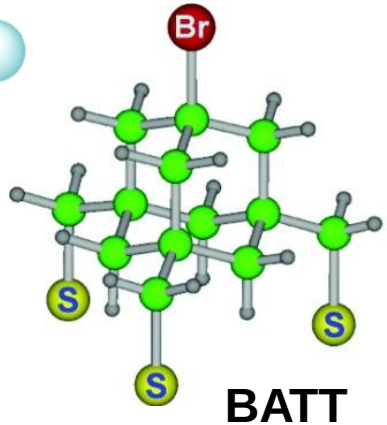




(4×4) unit cell
6.65 Å nearest neighbor spacing

M. Kim, J. N. Hohman, E. I. Morin, T. A. Daniel, P. S. Weiss *J. Phys. Chem. A* **2009**, *113*, 3895;
S. Fujii, U. Akiba, M. Fujihira *J. Am. Chem. Soc.* **2002**, *124*,13629.

# 1-Bromo-3,5,7-tris(mercaptomethyl)adamantane (BATT) and its SAM

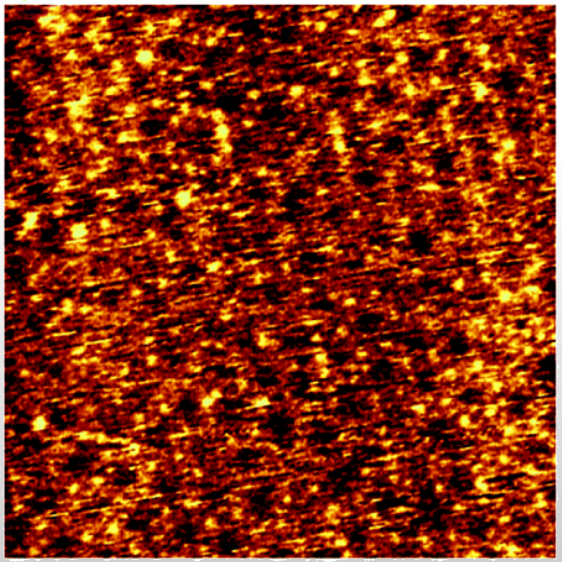


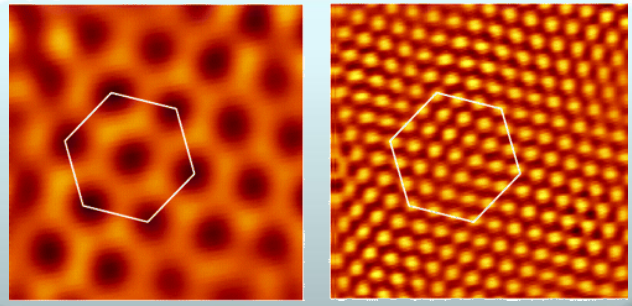

**BATT**

a) STM image of the SAM of **1** on a Au(111) surface

(a)



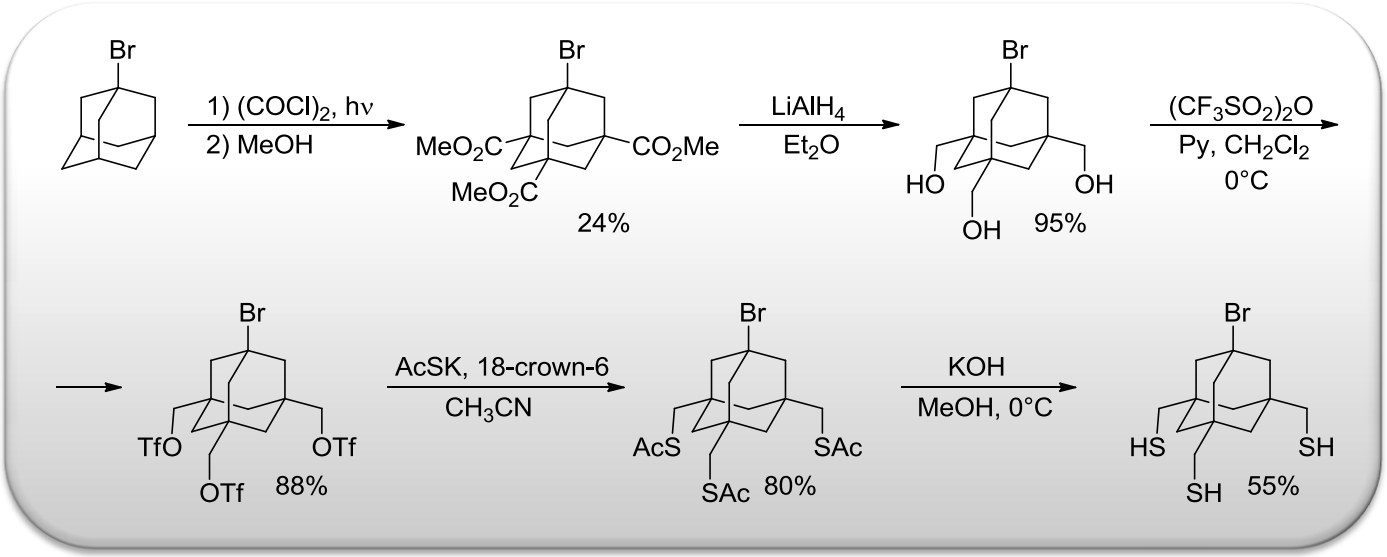
(b)

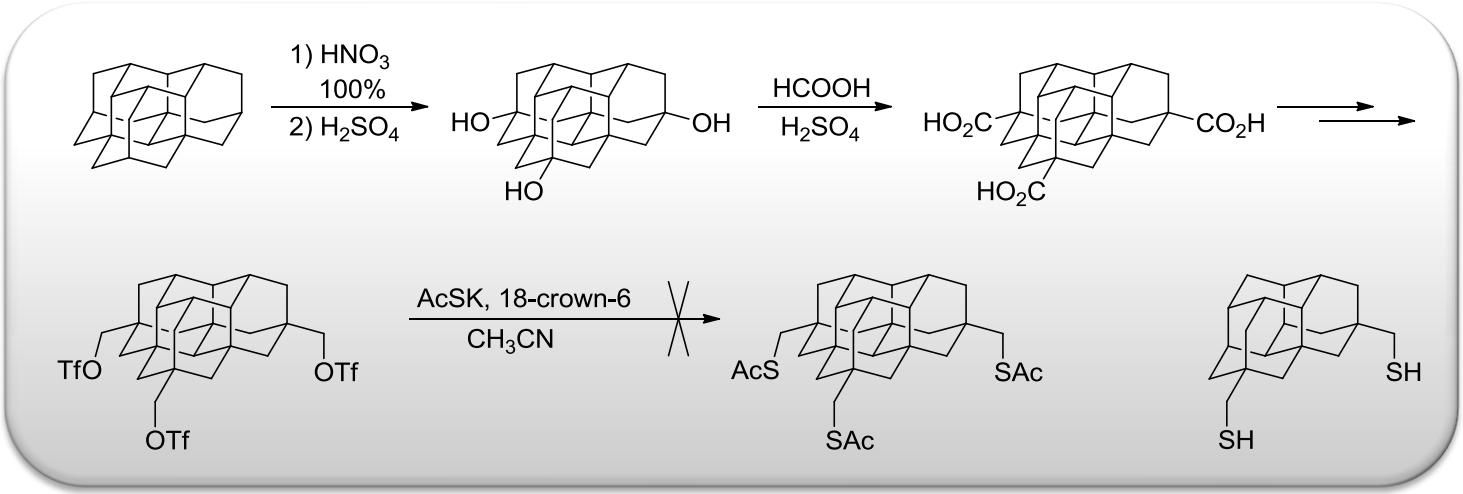


b) images were obtained by inverse Fourier transform of each of the two intense frequency components obtained by two-dimensional Fourier transform of the raw image.

T. Kitagawa, Y.Idomoto, H. Matsubara, D. Hobara, T. Kakiuchi, T. Okazaki, K. Komatsu *J. Org. Chem*, **2006**, *71*, 1362-1369.

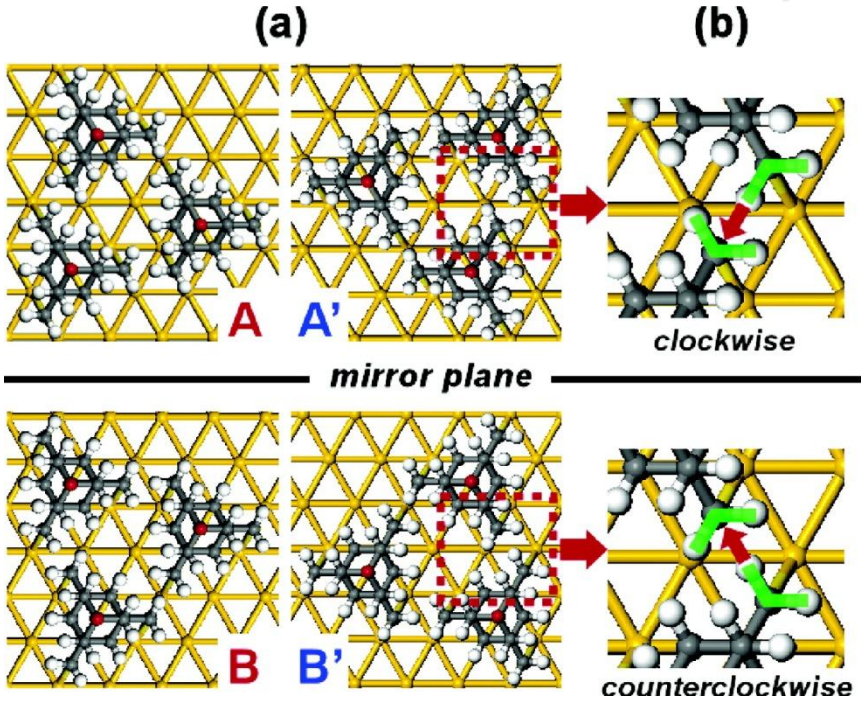
# Synthesis of 1-Bromo-3,5,7-tris(mercaptomethyl)adamantane and [1(2)3]Tetramamantane Analog

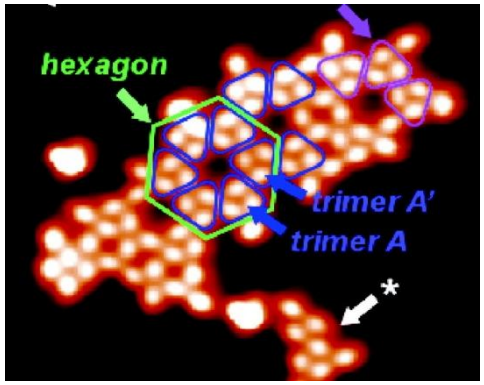


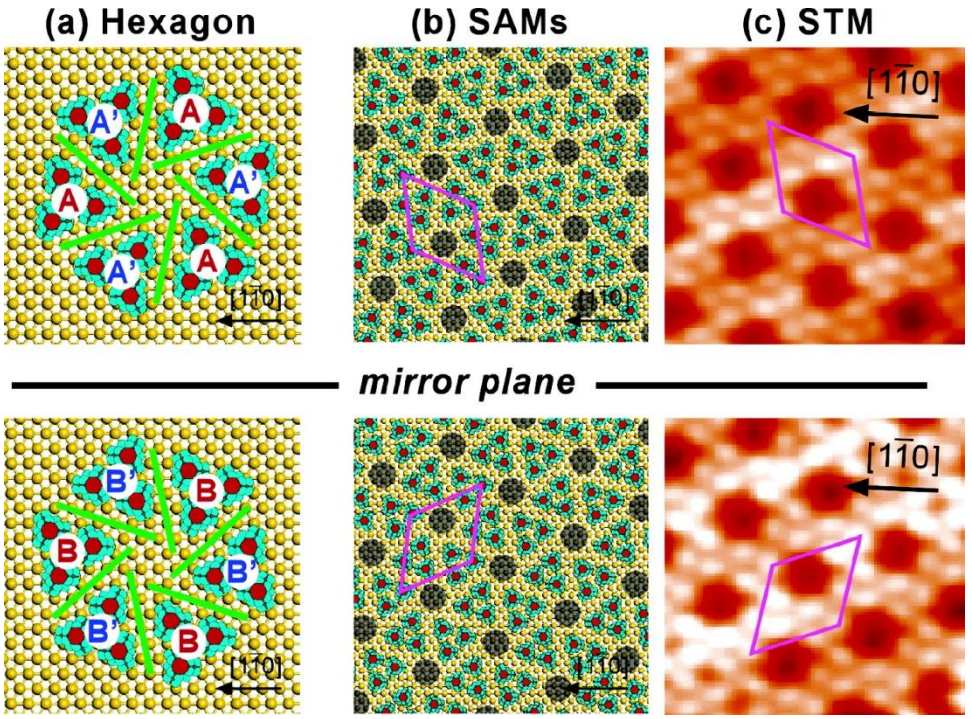

T. Kitagawa, Y.Idomoto, H. Matsubara, D. Hobara, T. Kakiuchi, T. Okazaki, K. Komatsu *J. Org. Chem*, **2006**, *71*, 1362-1369.

# Schematic self-assembly models of BATT on Au{111} surface



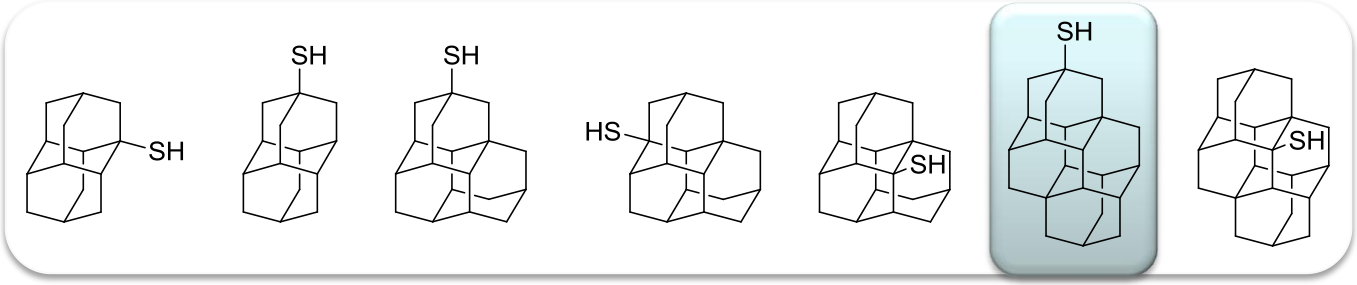




- ✧ The hierarchical assembly is passed from trimer to hexagon and then to SAMs
- ✧ Each enantiomeric hexagon is composed of the same chiral trimers
- ✧ Periodicities are represented as $\begin{pmatrix} 10 & 4 \\ 6 & 10 \end{pmatrix}$ and $\begin{pmatrix} 10 & 6 \\ 4 & 10 \end{pmatrix}$

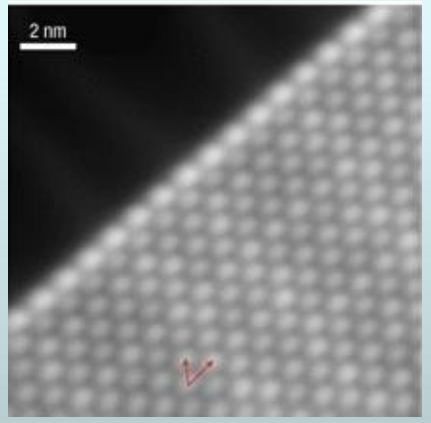



S. Katano, Y. Kim, H. Matsubara, T. Kitagawa, M. Kawai, J. Am. Chem. Soc. **2007**, *129*, 2511-2515.

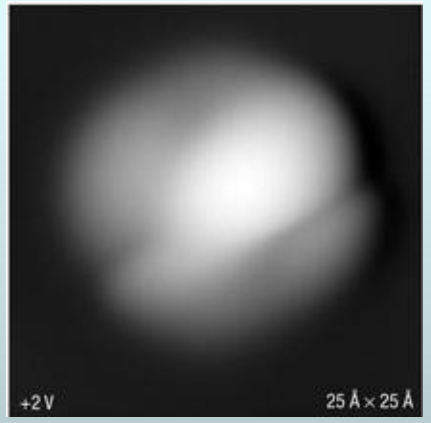
# Self-assembly of higher diamondoids



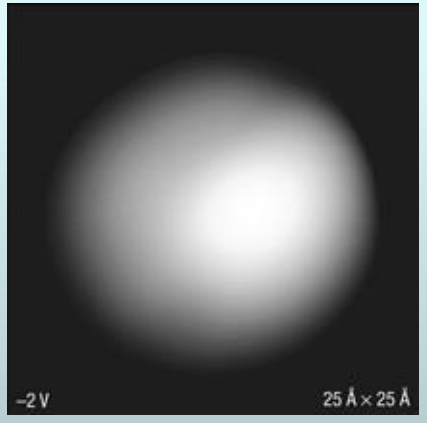

Constant-current STM topograph




Individual [121]tetramantanethiol molecule



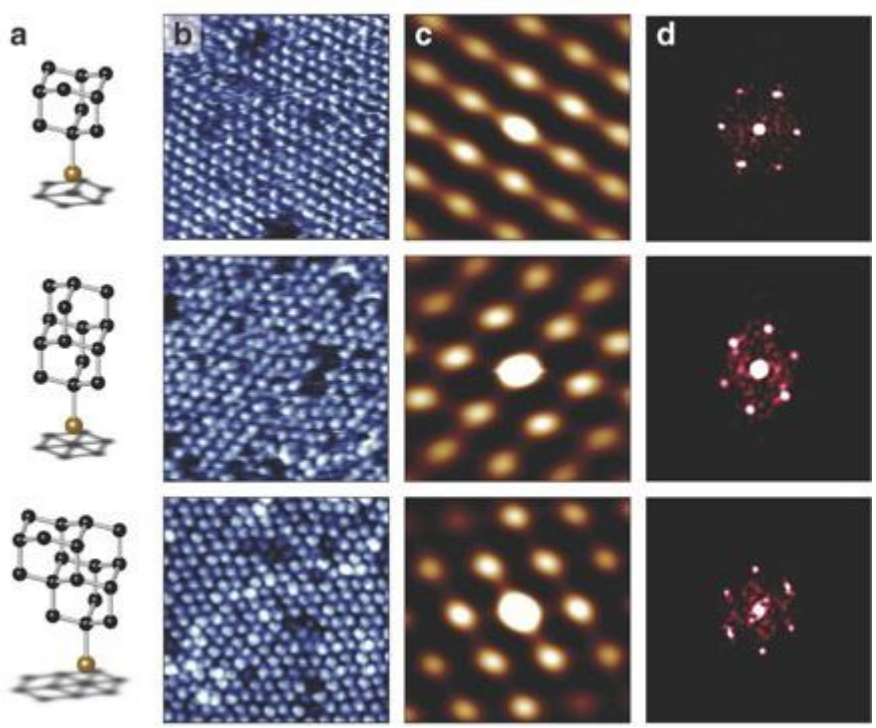

sample bias of +2.0 V
(probes the unoccupied
local electronic density of states)

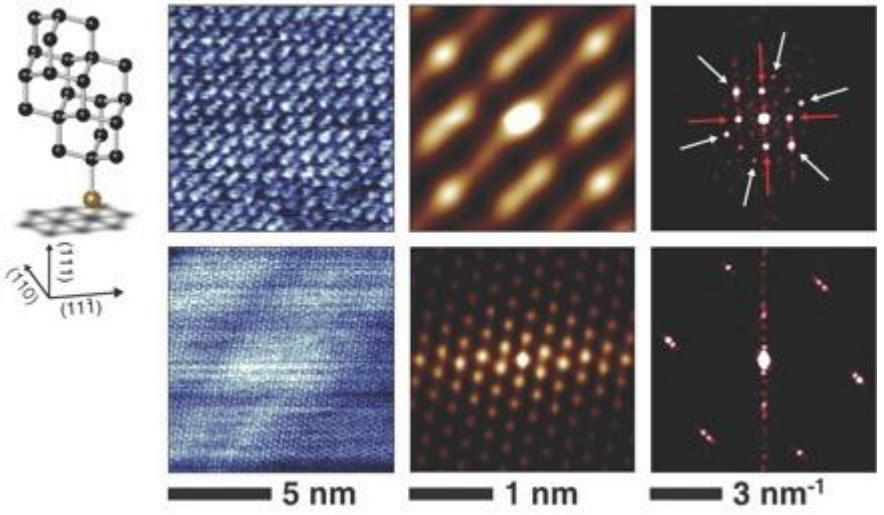


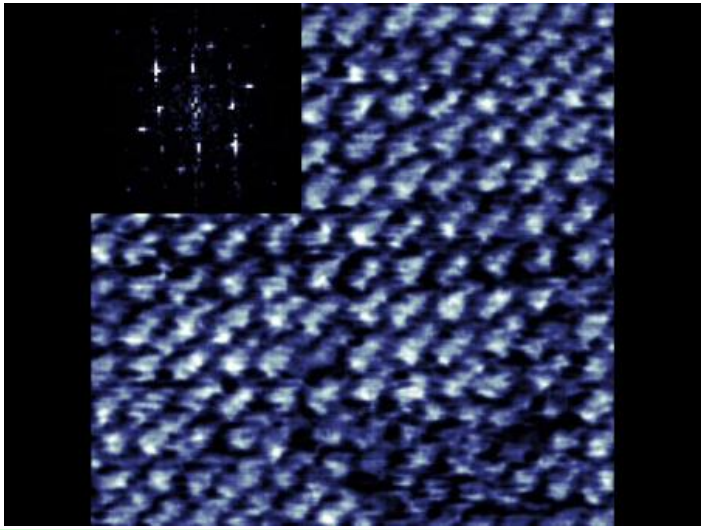

sample bias of –2.0 V
(probes occupied electronic states)

Y.Y. Wang, E. Kioupakis, X.H. Lu, D. Wegner, R. Yamachika, J.E. Dahl, R.M.K. Carlson, S.G. Louie, M.F. Crommie *Nat. Mater.* **2008**, *7*, 38-42.

# Structural Hierarchy of Diamondoid Thiols SAMs

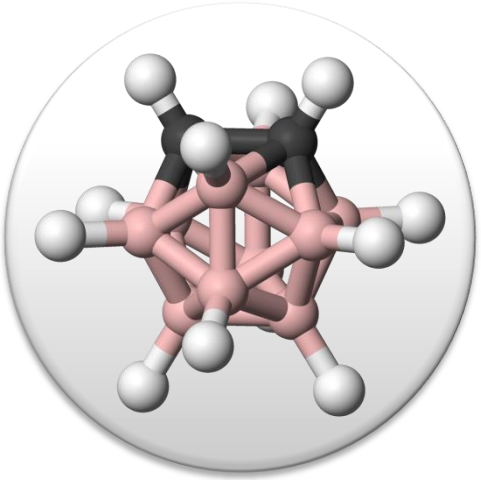


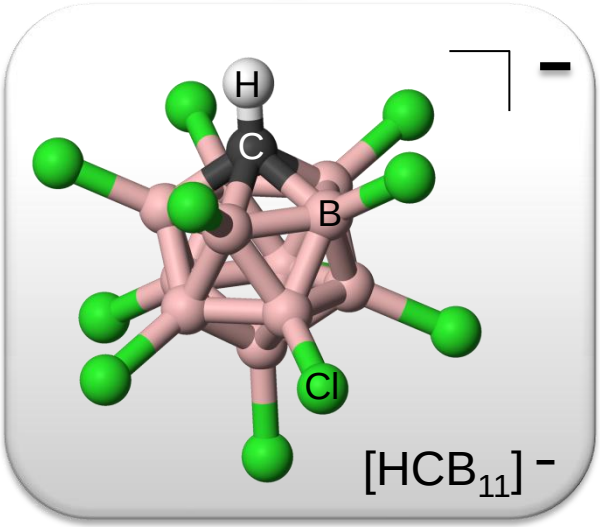



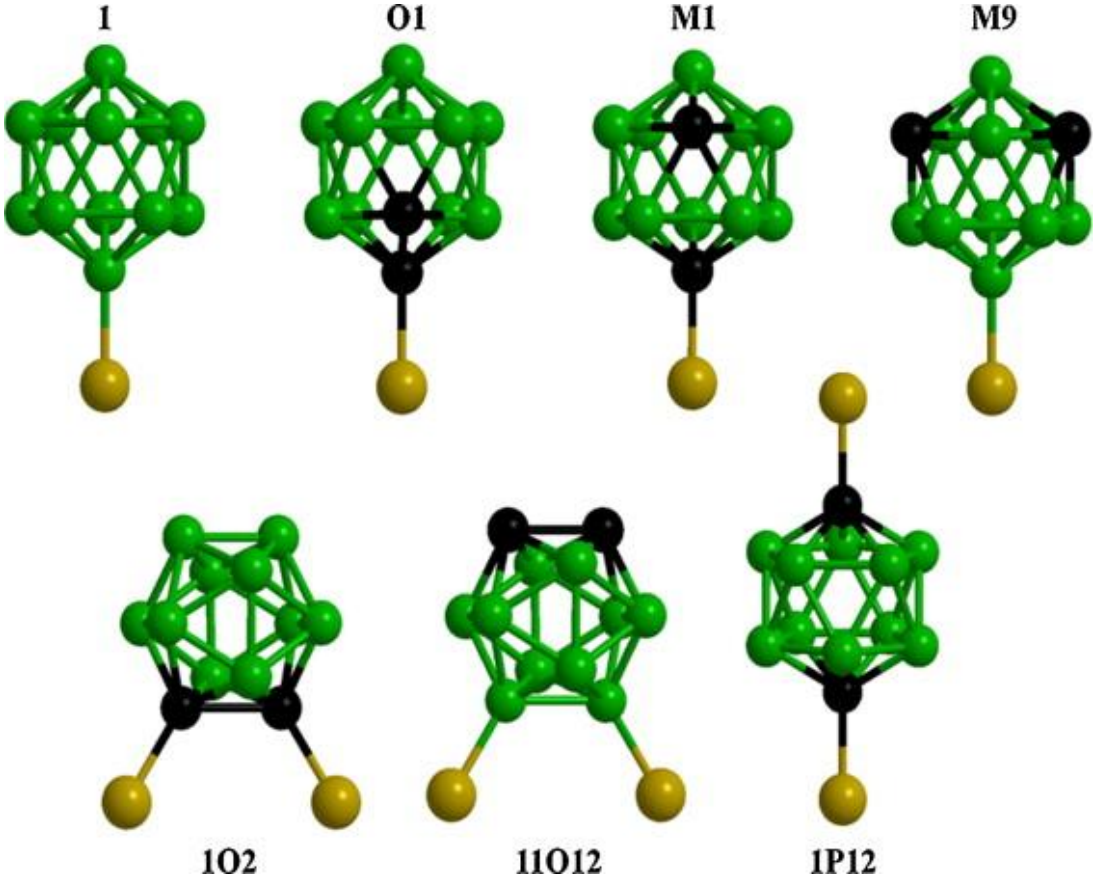
J. C. Randel, W. Mar, M. J. Preiner, R. G. Harris, J. D. Fabbri, N. A. Melosh, M. Khazaei, K. Esfarjani, J. E. P. Dahl, R.M. K. Carlson, B. A. Tkachenko, A. A. Fokin, P. R. Schreiner, H. C. Manoharan **2011**, submitted.

# Carborane Thiols



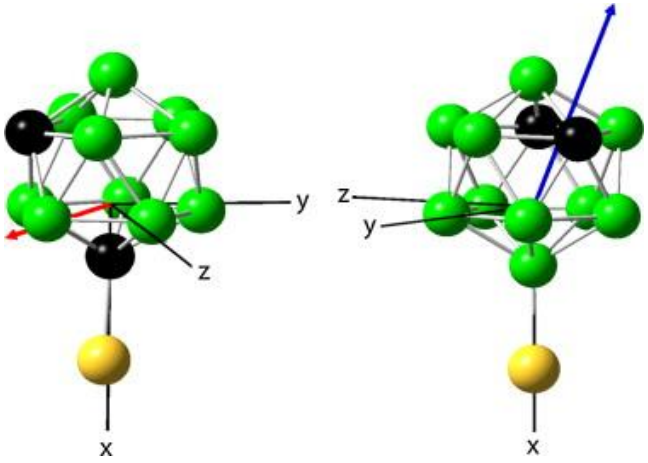



Carboranethiol Isomers for which SAMs have been reported




J. N. Hohman, S. A. Claridge, M. Kim, P. S. Weiss *Mater. Sci. Eng., R,* **2010**, 70,188–208;
M. Juhasz, S. Hoffmann, E. Stoyanov, K.-C. Kim, C. A. Reed *Angew. Chem. Int. Ed.* **2004**, *43*, 5352 –5355.

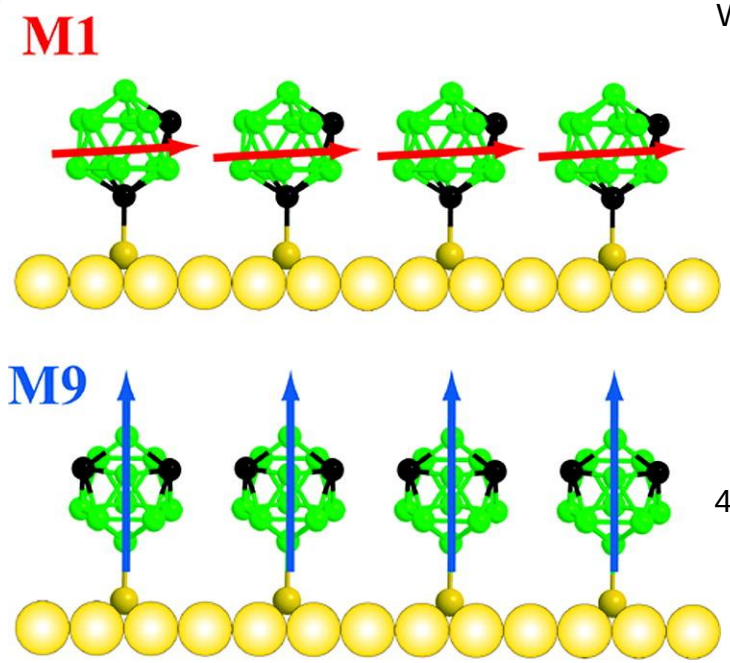
# M1 and M9 Carboranethiols and their Self-assembly




**M1** (1.06D) **M9** (4.08D)

arrow points in the direction of positive charge

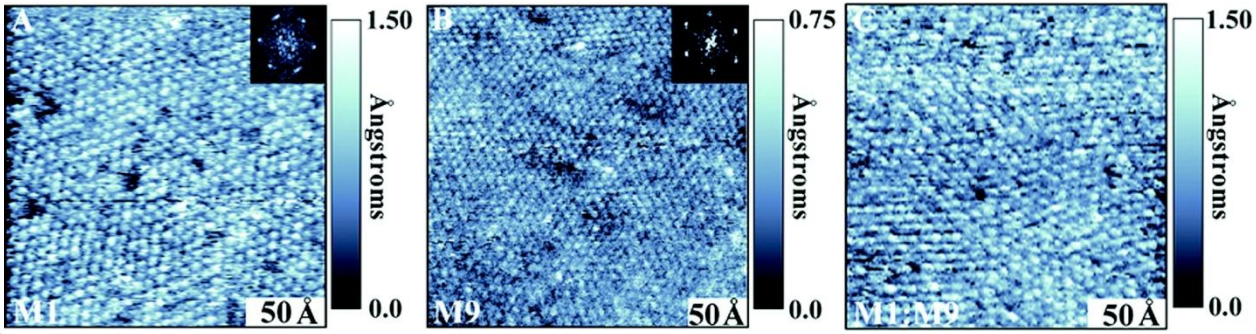
unsubstituted *m*-carborane has been calculated to be 2.84 D




Work Function Decrease

90 ± 20 meV

480 ± 20 meV

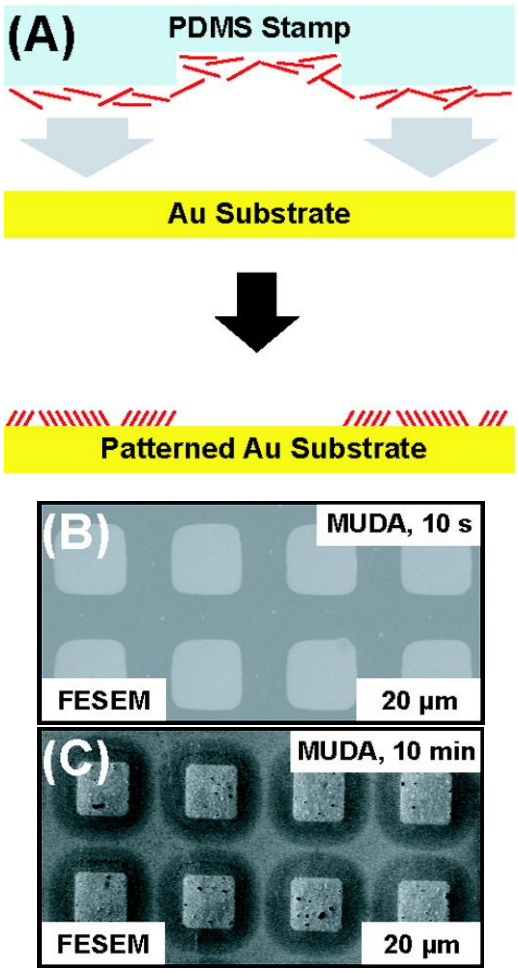


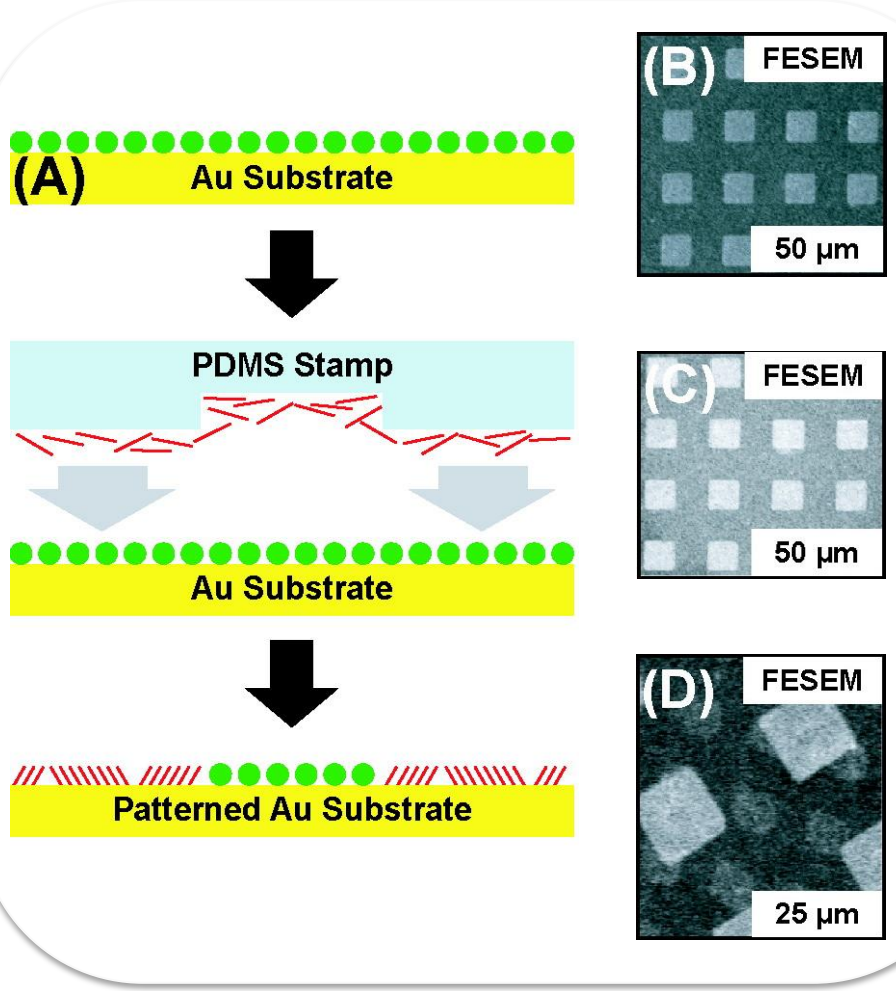

(√19×√19)*R*23.4° unit cell

7.2 ± 0.4 Å nearest neighbor spacing

J. N. Hohman, P. P. Zhang, E. I. Morin, P. Han, M. Kim, A. R. Kurland, P. D. McClanahan, V. P. Balema, P. S. Weiss *ACS Nano*, **2009**, *3*, 527.

# Microdisplacement Printing




**FESEM = Field Emission Scanning Electron Microscopy**
**MUDA = 11-mercaptoundecanoic acid**

C. Srinivasan, T. J. Mullen, J. N. Hohman, M. E. Anderson, A. A. Dameron, A. M. Andrews, E. C. Dickey, M. W. Horn, P. S. Weiss *ACS Nano* **2007**, *1*, 191-201.

Thank you for your attention!

# Diamantylderivatives Exploration