

Diamondoid assemblies on metal surfaces

Seminar talk presented by
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January 13th, 2017

*Institute of Organic Chemistry
Justus-Liebig-University Giessen*



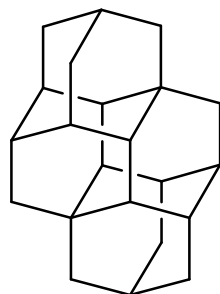
1. Self-assembly of [121]tetramantane on Cu(111)
2. Chiral [123]tetramantanes on Cu(111)



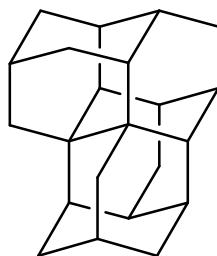
1. Self-assembly of [121]tetramantane on Cu(111)



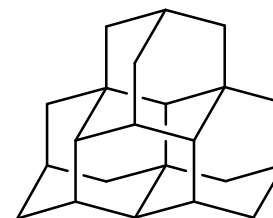
➤ tetramantane – first of the higher diamondoids



[121]tetramantane
 C_{2h} symmetry
rod-shaped (*anti*)



± [123]tetramantane
 C_2 symmetry
helical (*skew*)



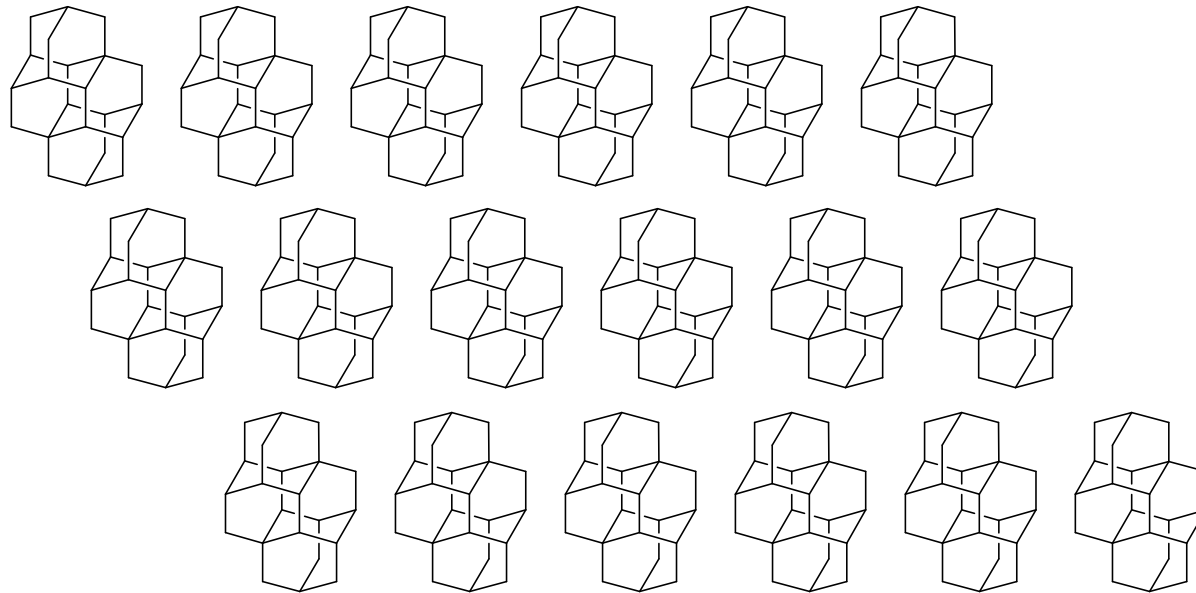
[1(2)3]tetramantane
 C_{3v} symmetry
disk-like (*iso*)

➤ the fourth cage can be "added" in 4 possible ways => 4 isomers



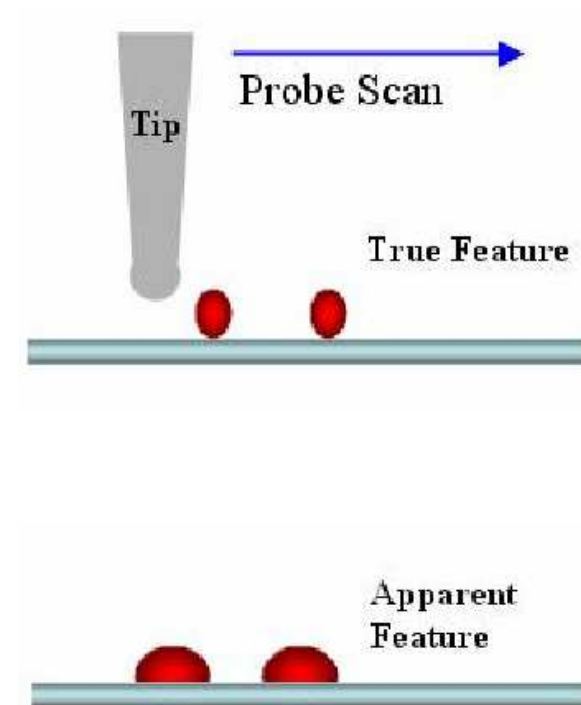
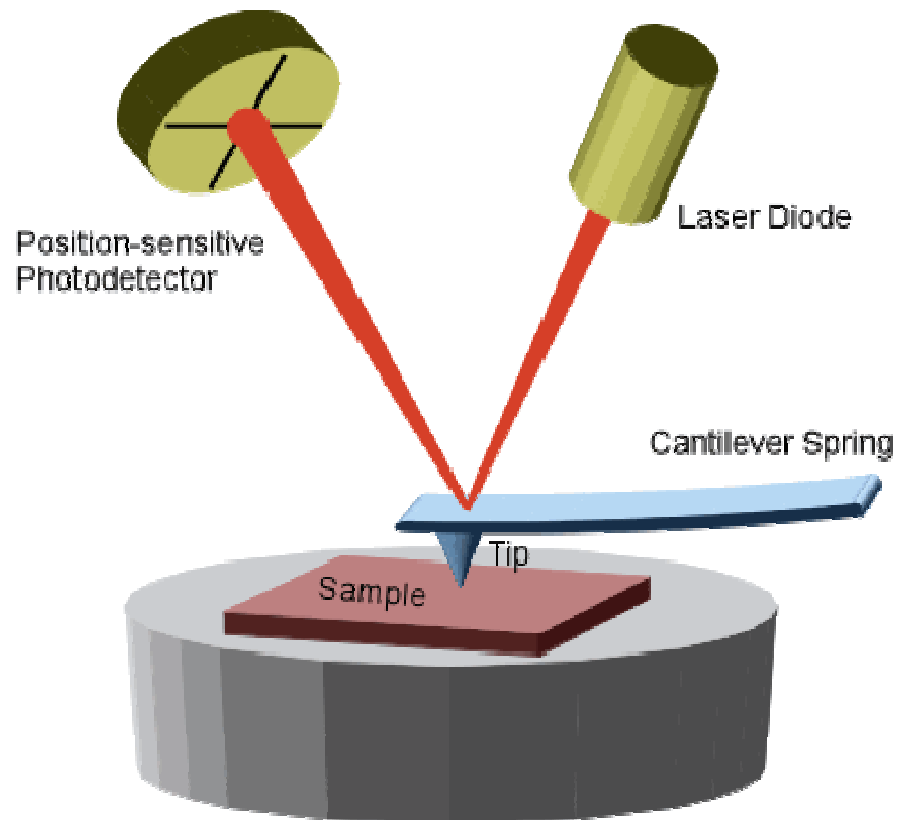
Objectives:

- deposition of [121]tetramantane on a Cu(111) surface in UHV conditions
- AFM study of on-surface self-assembly and the formed 2D lattice
- quantification of London dispersion (LD) interactions using computational methods



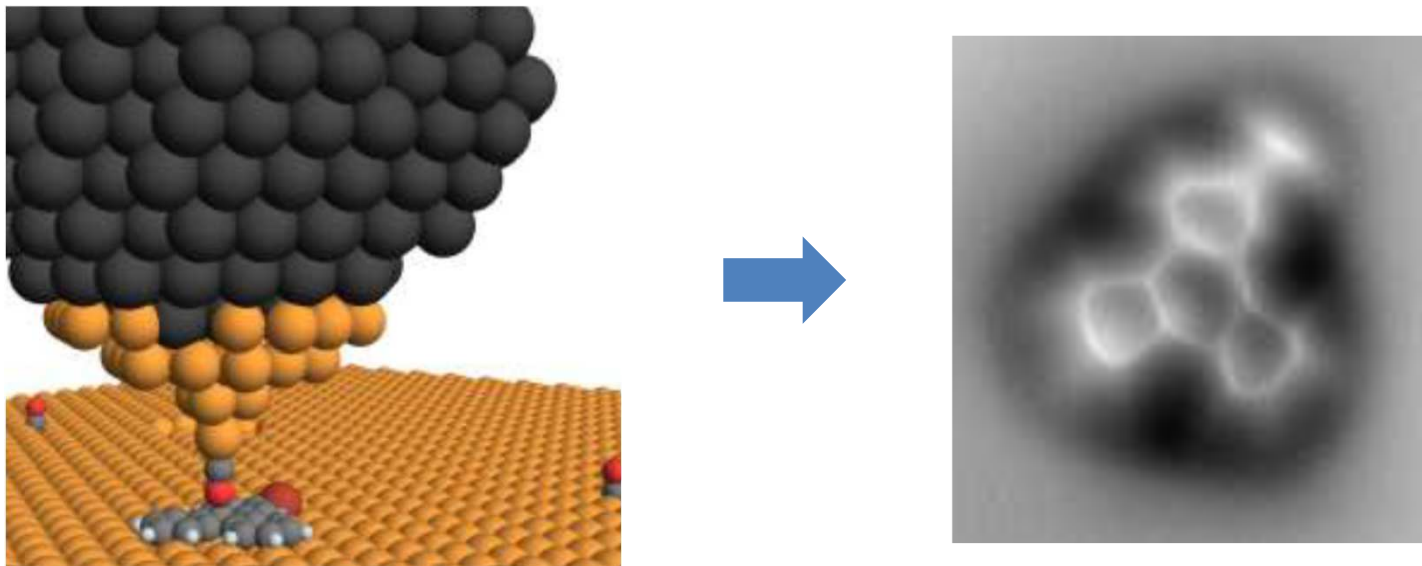


- working principle of atomic force microscopy (AFM)





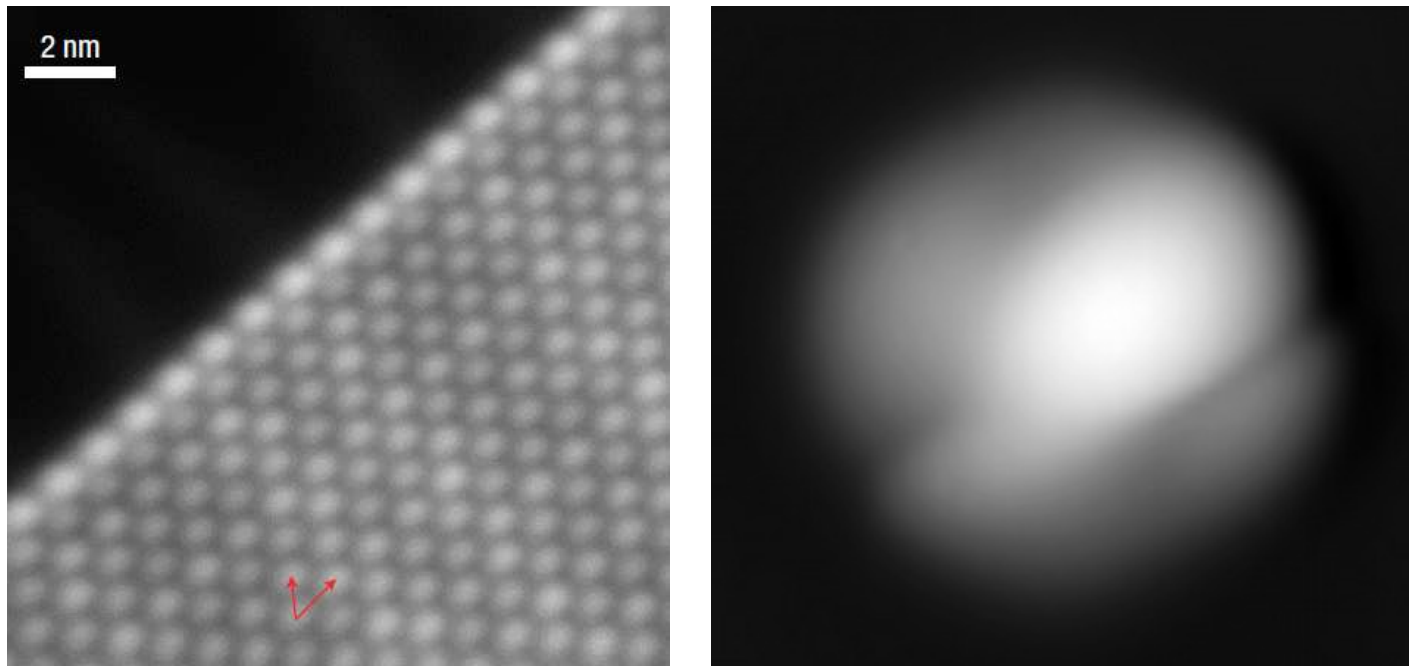
- bond imaging by atomic force microscope (AFM) with a CO tip
- direct identification of chemical structure and orientation of the absorbed molecule



- known method problems: image distortion, bond sharpening, artificial bonds



- Wang, Crommie *et al.* studied [121]tetramantane deposited on Au(111) using STM

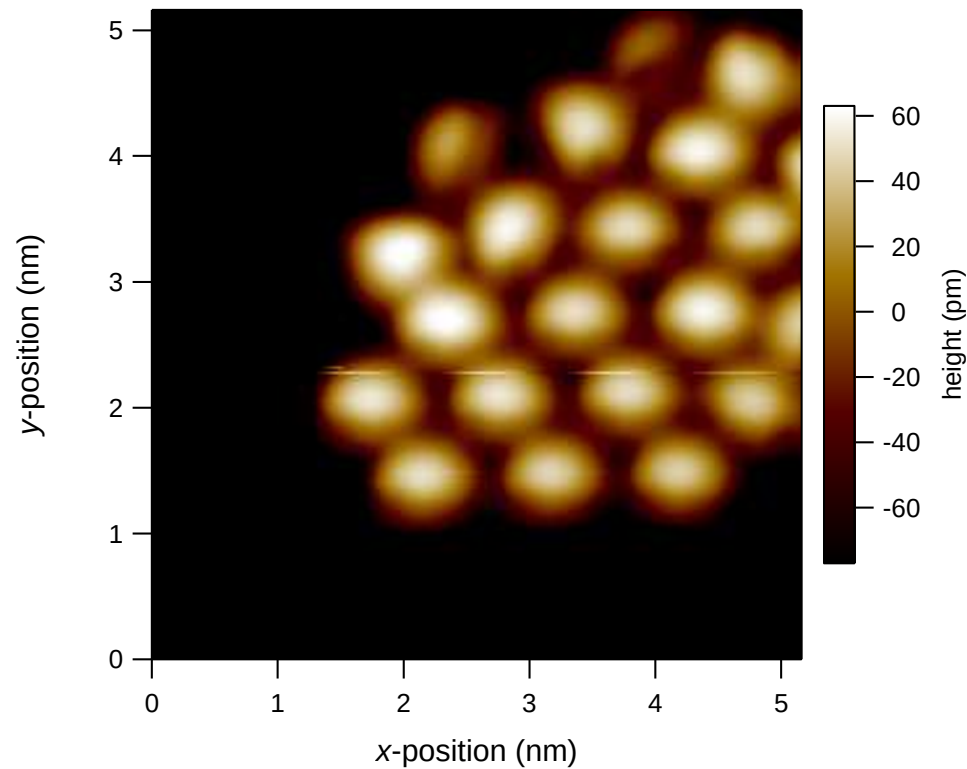


- difficulties with distinguishing between structural features and orientation of the molecule

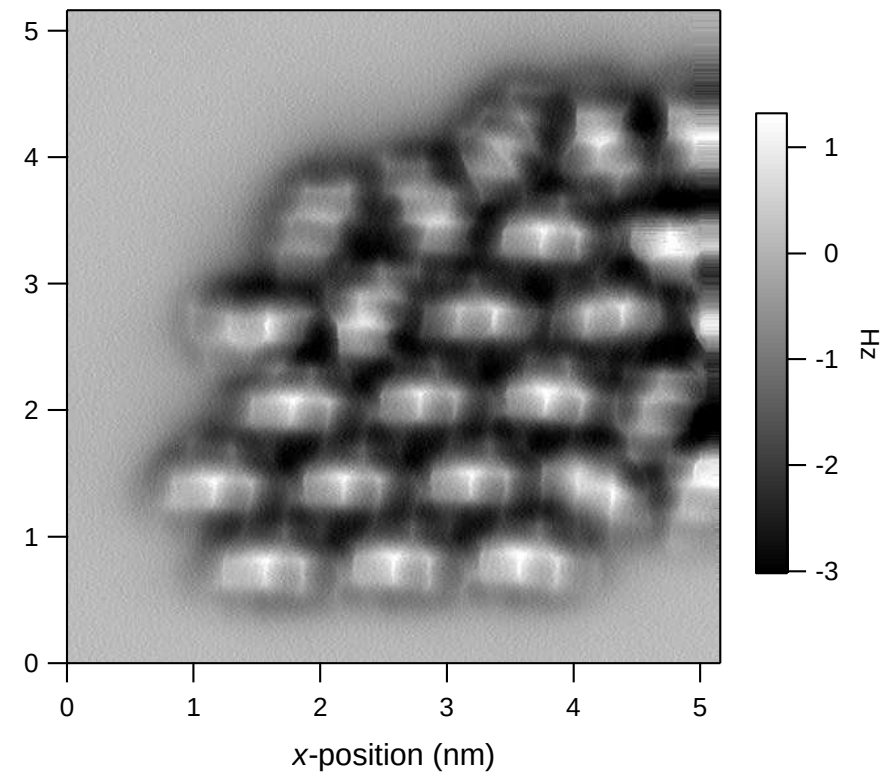


- [121]tetramantane deposited on Cu(111) in UHV conditions

STM data from Cu(111) surface



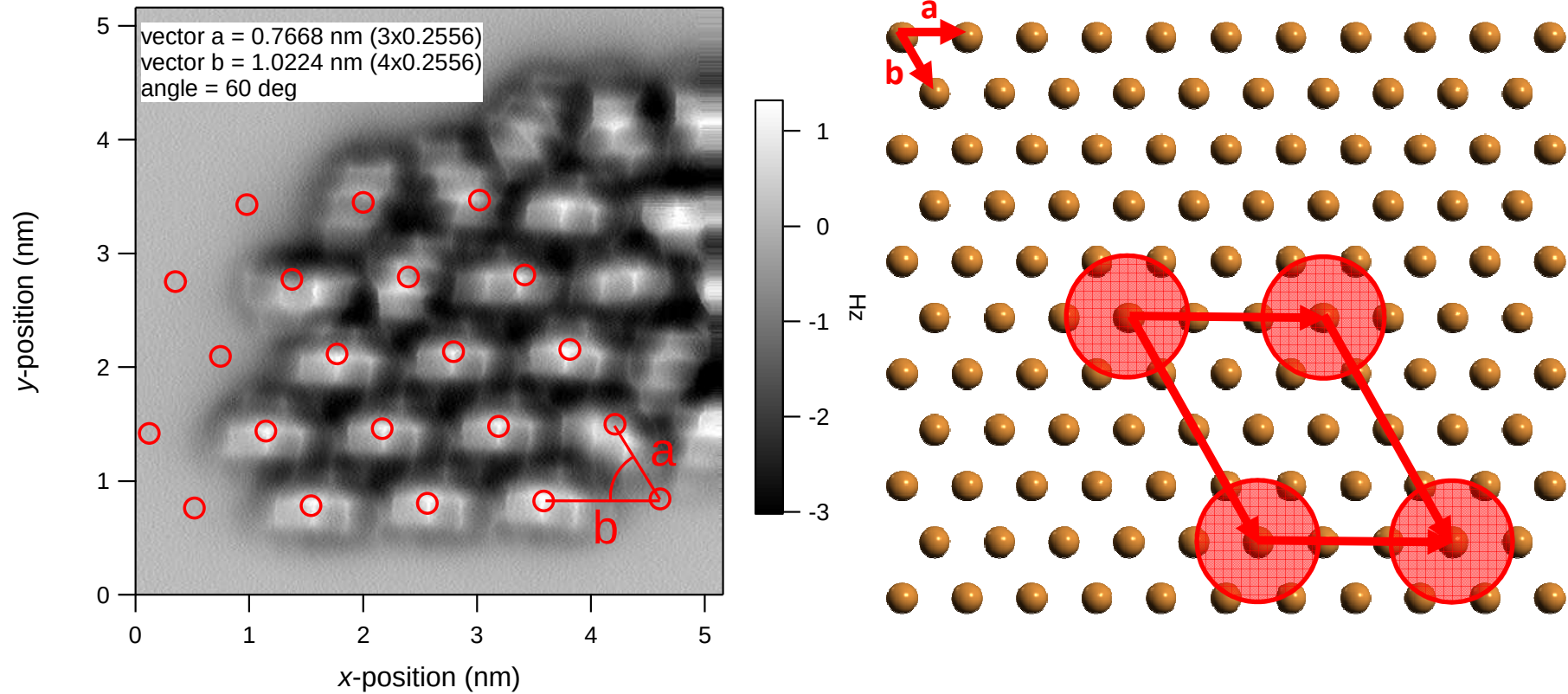
AFM data from Cu(111) surface



- calibrated and with drift correction



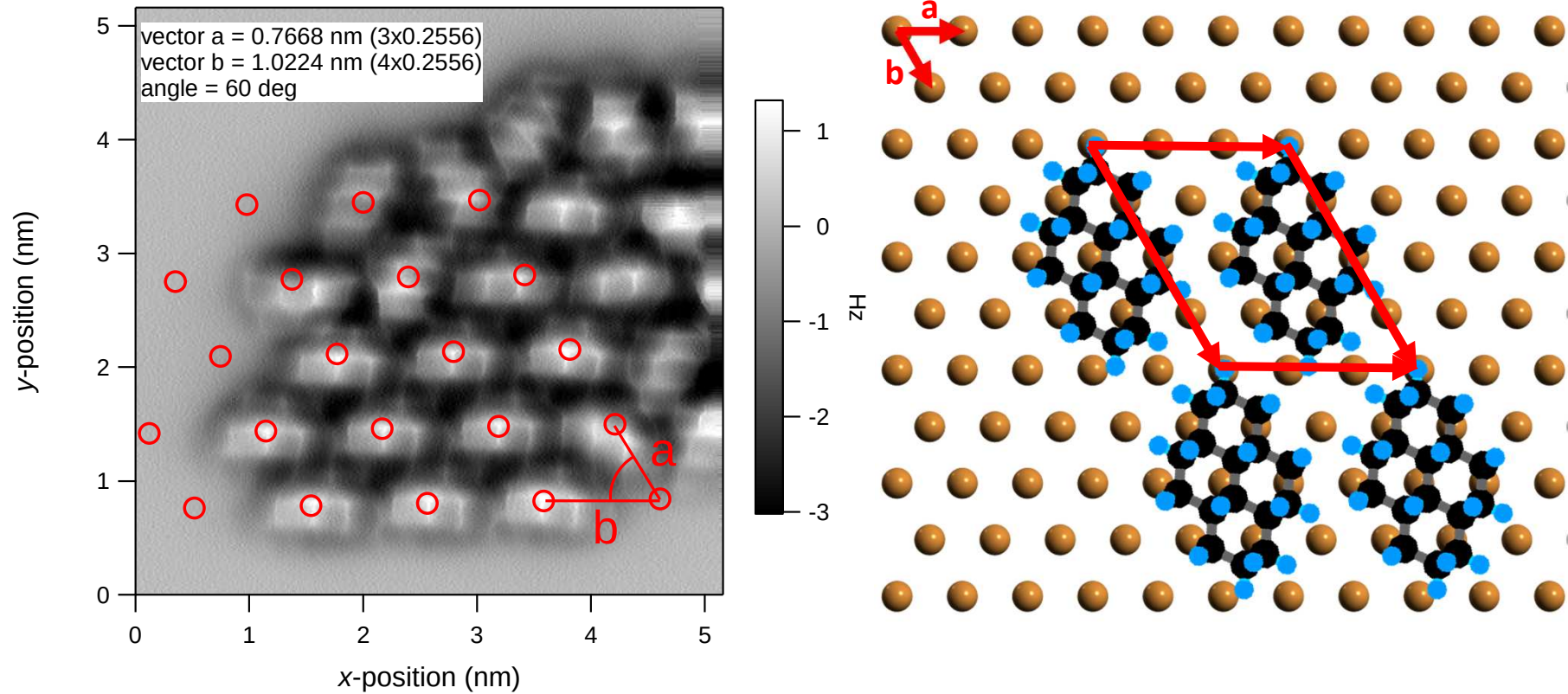
➤ surface reconstruction of [121]tetramantane on Cu(111)



➤ the unit cell is 3 times as long in direction **a** and 4 times as long in direction **b**



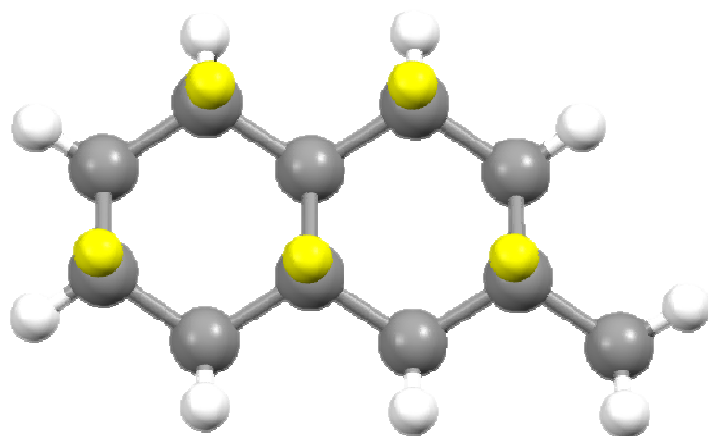
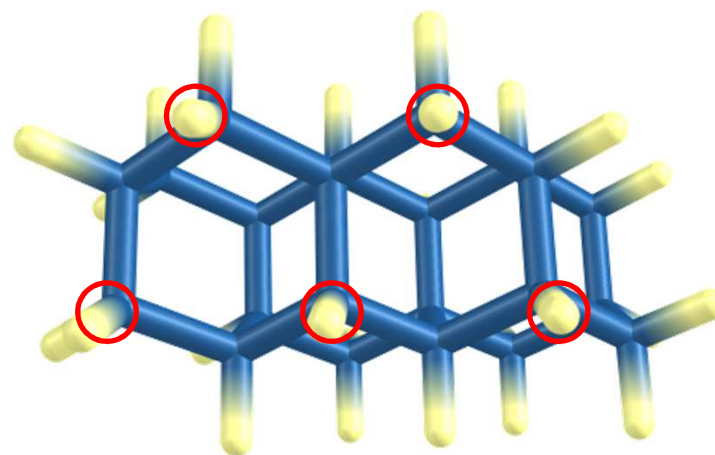
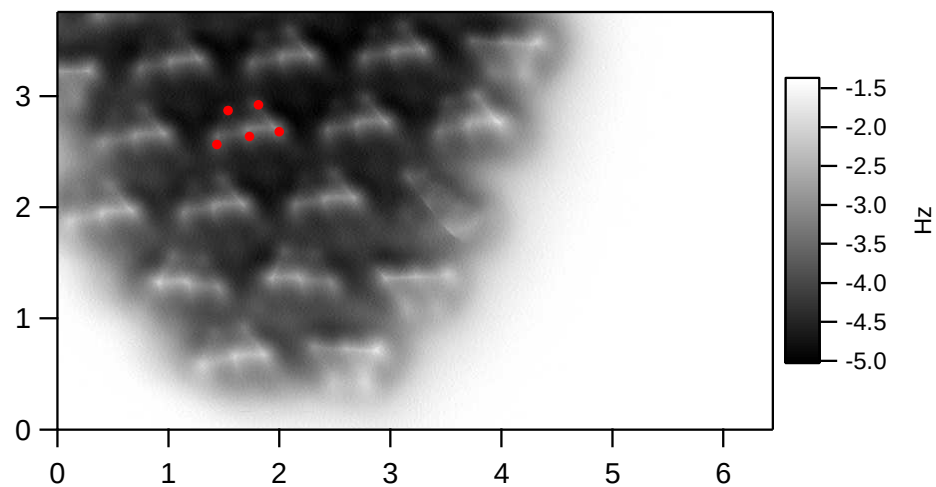
➤ surface reconstruction of [121]tetramantane on Cu(111)



Cu(111): $a = 2.556 \text{ \AA}$, $b = 2.556 \text{ \AA}$, $\alpha = 60^\circ$
[121]tetramantane: $a = 7.668 \text{ \AA}$, $b = 10.224 \text{ \AA}$, $\alpha = 60^\circ$

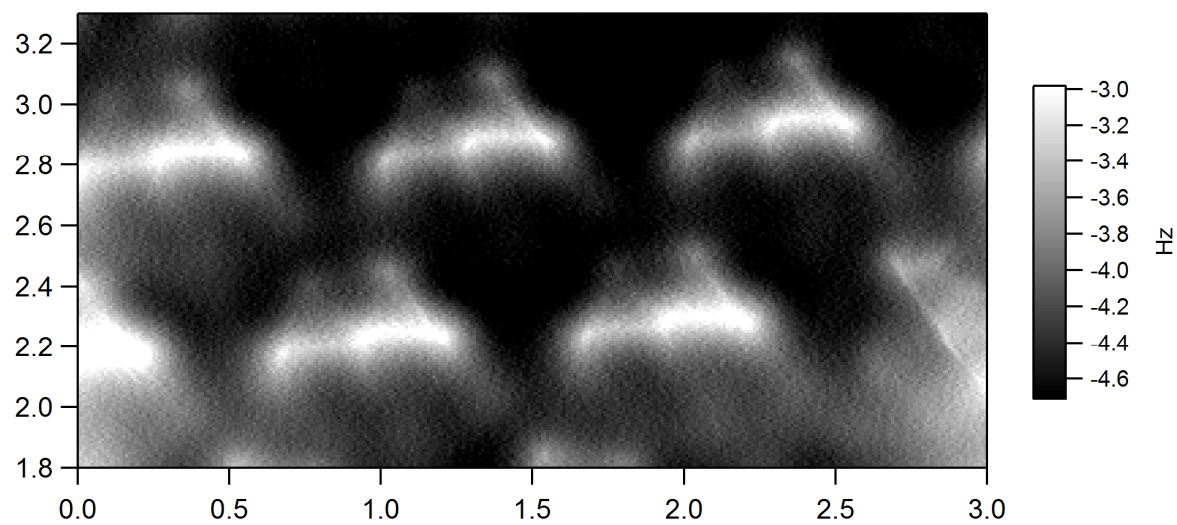
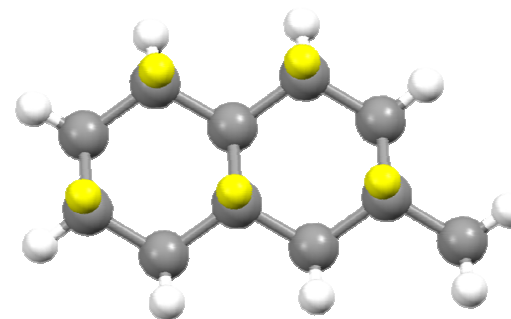
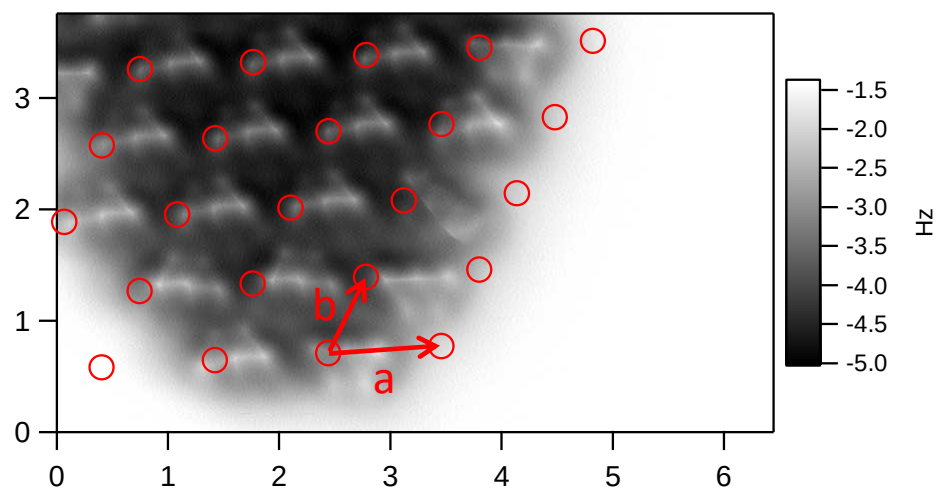
➤ 3x4 reconstruction on Cu(111)

Self-assembly of [121]tetramantane on Cu(111)

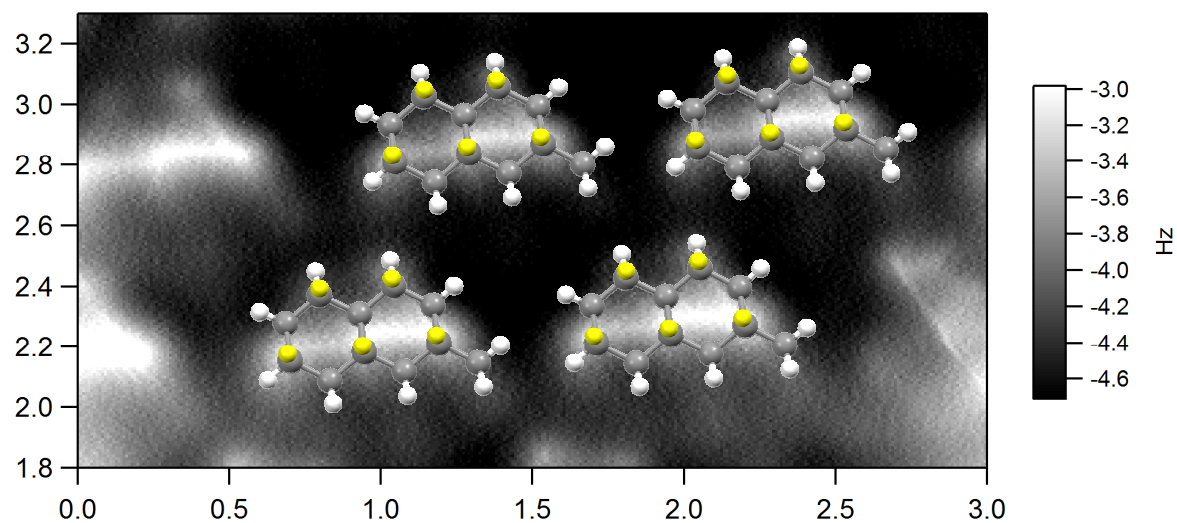
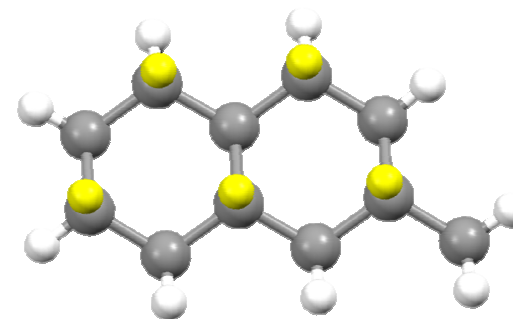
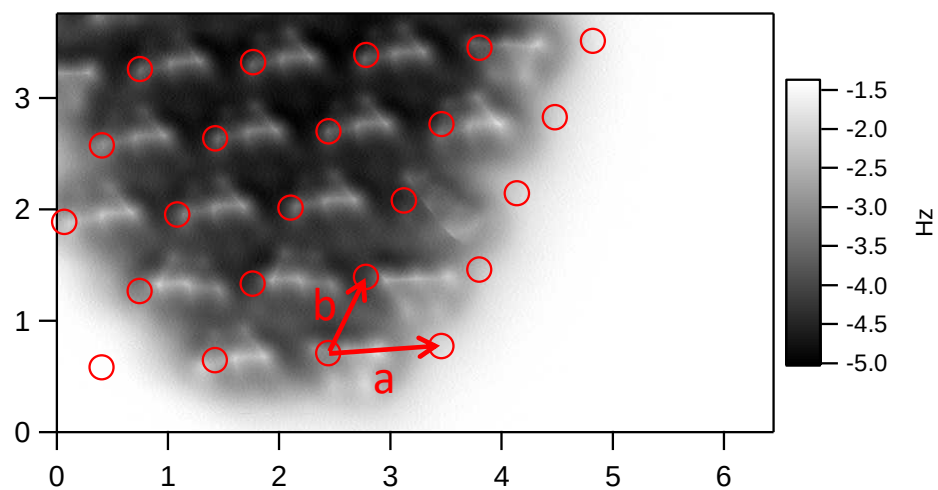


part of the tetramantane
cage that would be
"visible" to the CO tip

Self-assembly of [121]tetramantane on Cu(111)



Self-assembly of [121]tetramantane on Cu(111)





Quantification of attractive forces between two [121]tetramantanes using computational methods:

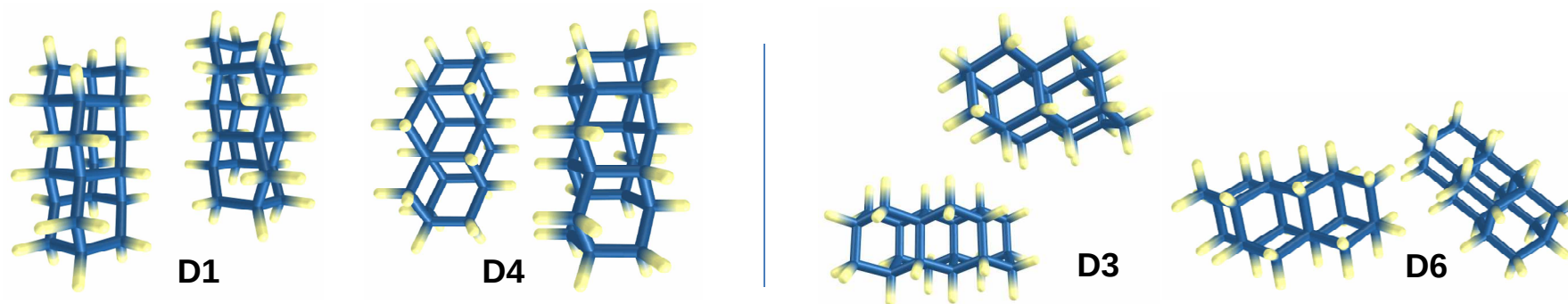
- density functional theory (DFT)
 - B3LYP functional with and without Grimme's D3 correction with Becke-Johnson (BJ) damping
 - M06-2X functional parametrized for medium-range correlation
- second order Møller–Plesset perturbation theory (MP2)
- *ab initio* coupled cluster method (CCSD(T))
- complete basis set extrapolation (CBS)

Self-assembly of [121]tetramantane on Cu(111)



Table 1. Interaction energies, $\Delta H(298)$, of [121]tetramantane LD-bound complexes (**D1–D8**) in kcal mol⁻¹. Geometries for MP2 and CCSD(T) single-point computations were optimized at the B3LYP-D3(BJ)/6-31G(d,p) level of theory.^{a, b}

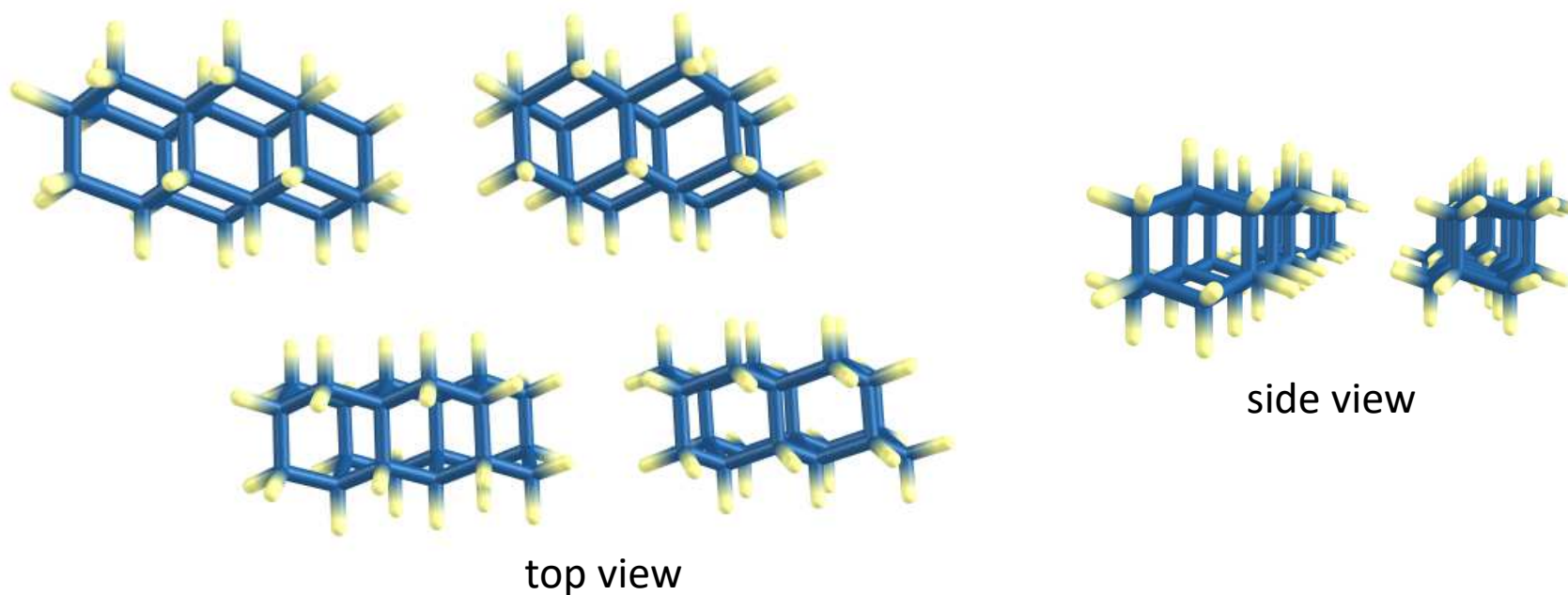
Level of theory	D1	D2	D3	D4	D5	D6	D7	D8
B3LYP/6-31G(d,p)	0.0	0.1	0.2	0.1	-0.2	0.0	-0.3	-0.2
B3LYP-D3(BJ)/6-31G(d,p)	-8.8	-4.0	-5.7	-8.5	-7.4	-4.7	-7.5	-8.2
M06-2X/6-31G(d,p)	-5.9	-2.6	-3.4	-5.4	-4.5	-2.2	-4.3	-4.7
MP2/cc-pVDZ	-7.8	-3.3	-4.7	-8.0	-6.6	-3.7	-6.3	-7.4
MP2/cc-pVTZ	-9.0	-3.7	-5.5	-8.9	-7.4	-4.2	-7.4	-8.4
MP2/CBS	-10.0	-4.0	-6.2	-9.8	-8.1	-4.7	-8.2	-9.3
CCSD(T)/cc-pVDZ	-11.6	-7.6	-7.3	-9.5	-7.7	-8.7	-6.1	-9.3
CCSD(T)/CBS	-13.7	-8.3	-8.8	-11.2	-9.2	-9.7	-7.9	-11.1



^a Interaction energies are defined as a difference between the energy of the complex and the energy of two (*M*)-[121]tetramantane molecules. ^b ZPVEs used to obtain $\Delta H(298)$ for MP2 and CCSD(T) computed at the B3LYP-D3(BJ)/6-31G(d,p) level of theory.



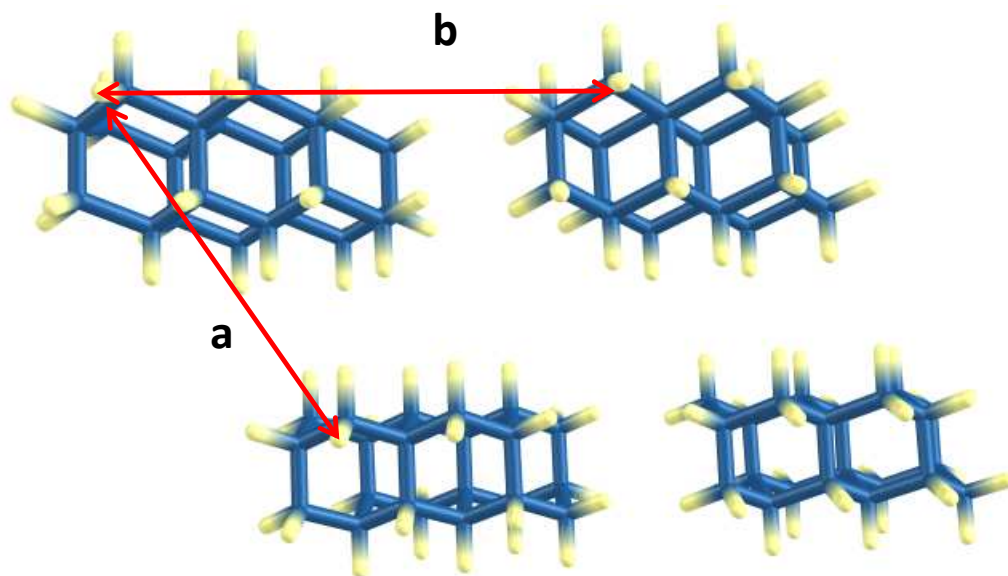
- four interacting [121]tetramantanes computed at B3LYP-D3(BJ)/6-31G(d,p) level of theory



- close contacts between the hydrocarbons ($\approx 2.4 \text{ \AA}$)



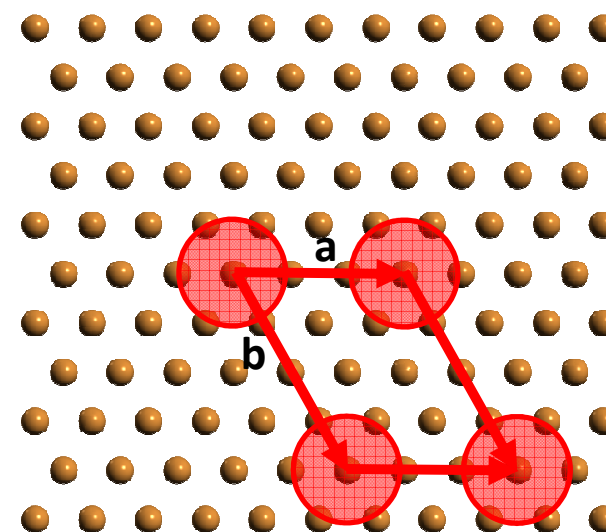
- four interacting [121]tetramantanes computed at B3LYP-D3(BJ)/6-31G(d,p) level of theory



computation:

$$a = 8.41 \text{ \AA}$$

$$b = 10.21 \text{ \AA}$$



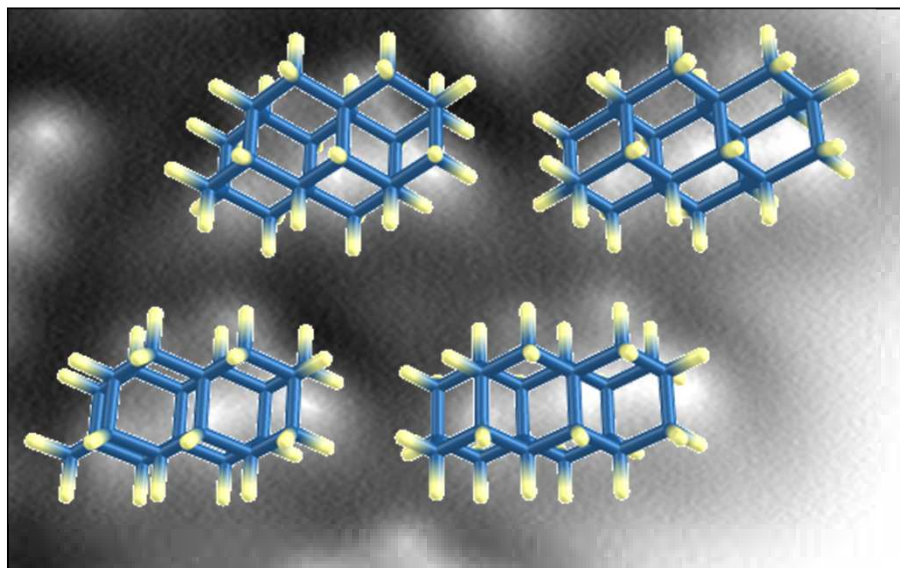
3x4 reconstruction on Cu(111):

$$a = 7.67 \text{ \AA}$$

$$b = 10.22 \text{ \AA}$$



- four interacting [121]tetramantanes computed at B3LYP-D3(BJ)/6-31G(d,p) level of theory



- match between the AFM image and the computed structure



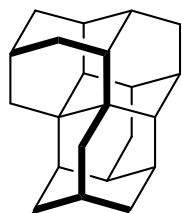
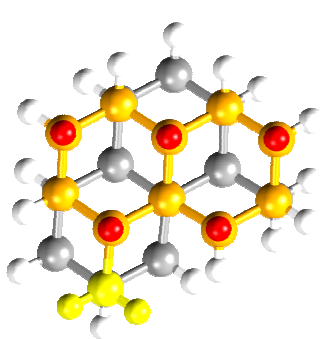
Summary and outlook

- on-surface self-assembly of [121]tetramantanes
- formation of a hydrocarbon 2D lattice on Cu(111)
- London dispersion forces significant between two interacting [121]tetramantanes
- AFM measurements on Au(111) surface necessary to confirm that LD is the driving force for assembly (rule out the role of copper)
- modelling of [121]tetramantanes including the Cu lattice; hybrid ab-initio/force-field computations (hybrid QM/MM)

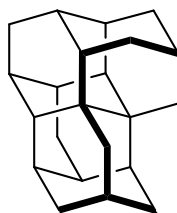


2. Chiral [123]tetramantanes on Cu(111)

Chiral [123]tetramantanes on Cu(111)

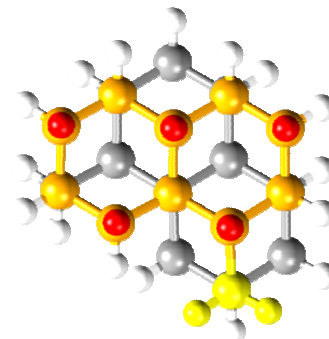


M

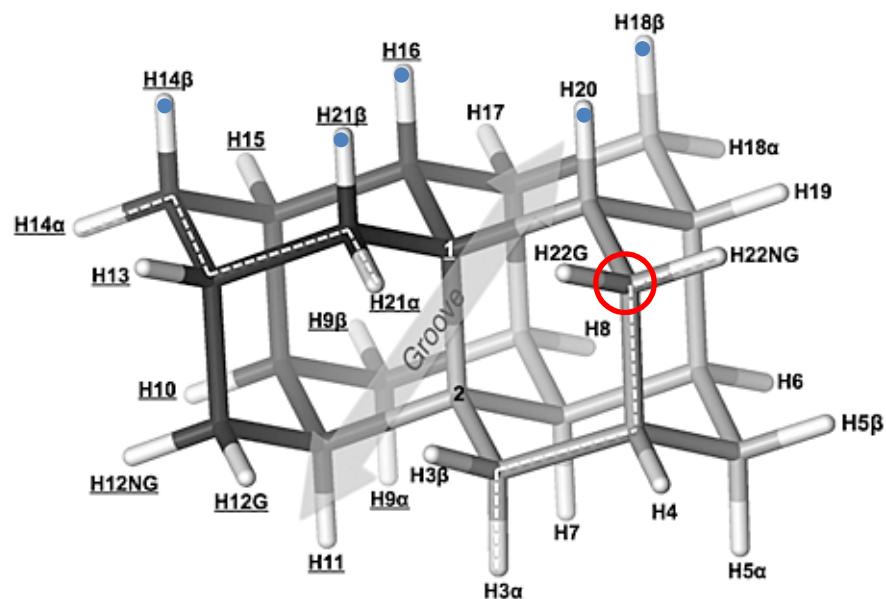


P

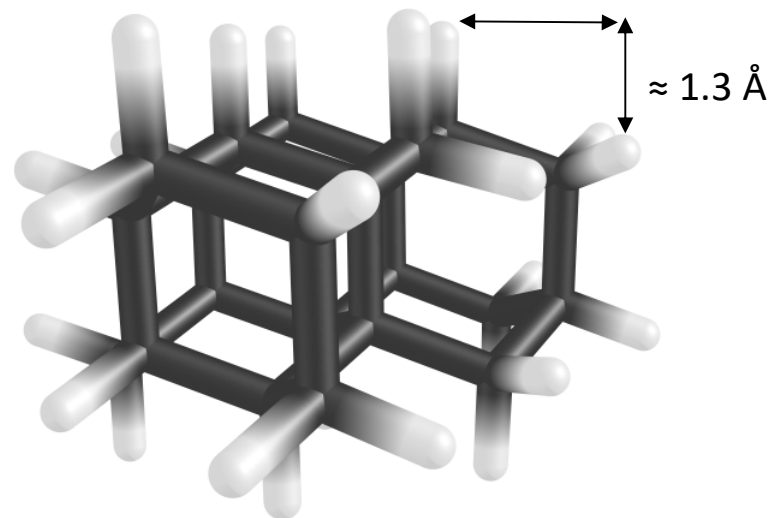
[123]tetramantane



Helical chirality:
M = "left handed"
P = "right handed"



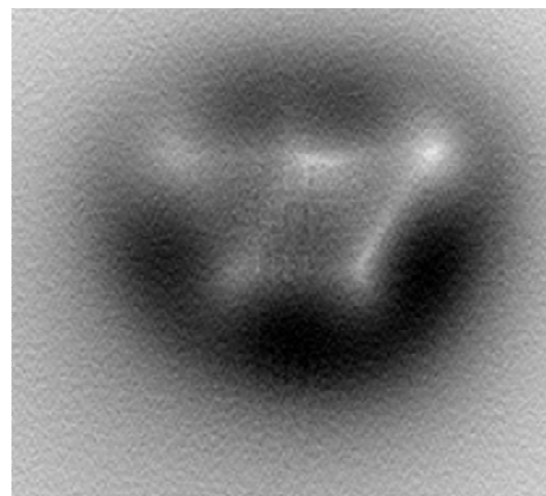
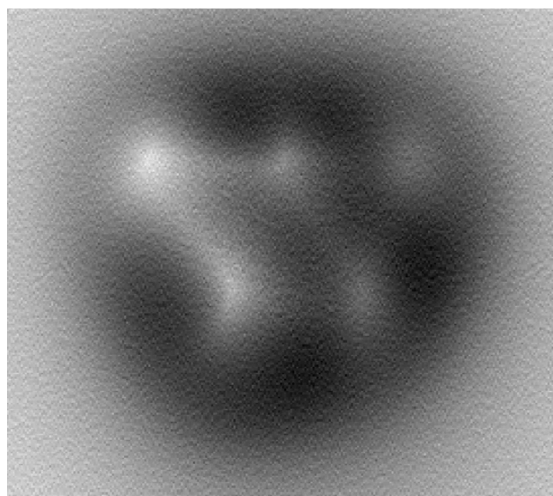
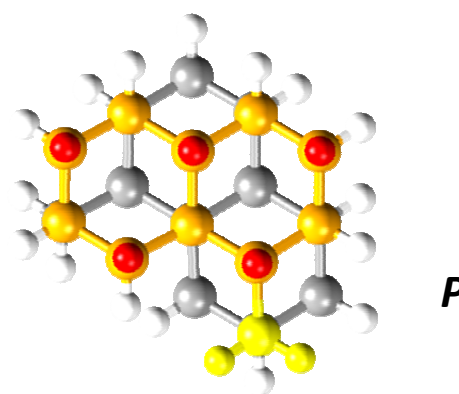
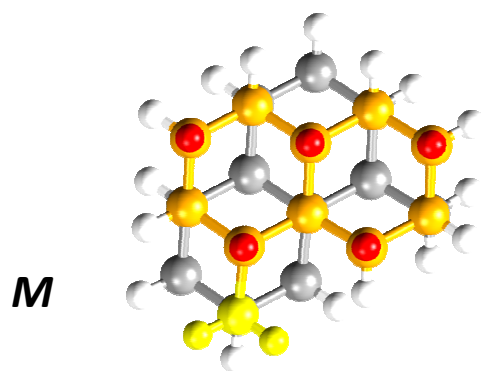
P



Schreiner, P. R.; Fokin, A. A.; Reisenauer, H. P.; Tkachenko, B. A.; Vass, E.; Olmstead, M. M.; Bläser, D.; Boese, R.; Dahl, J. E. P.; Carlson, R. M. K. *J. Am. Chem. Soc.* **2009**, *131*, 11292; Balaban, A. T.; Young, D. C.; Plavec, J.; Pečnik, K.; Pompe, M.; Dahl, J. E.; Carlson, R. M. K. *Magn. Reson. Chem.* **2015**, *53*, 1003.

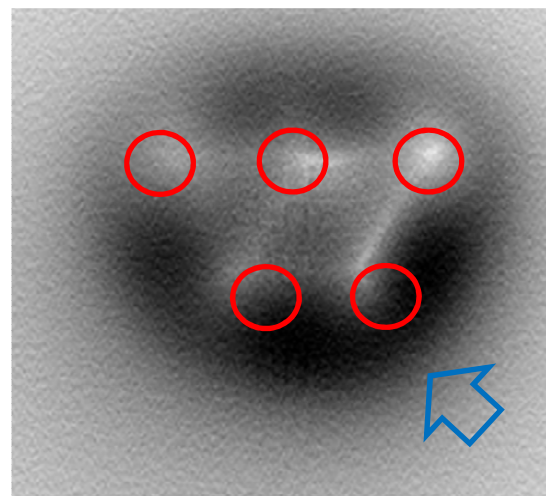
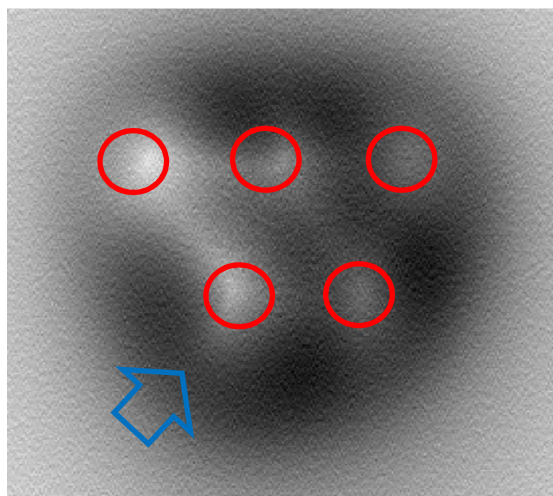
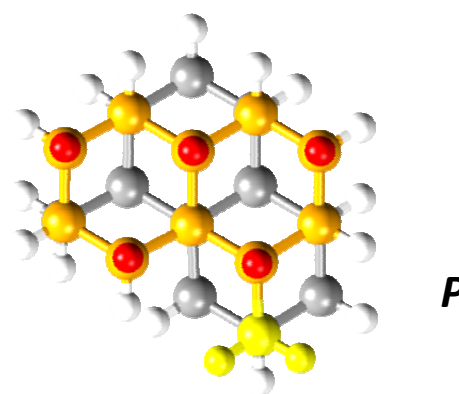
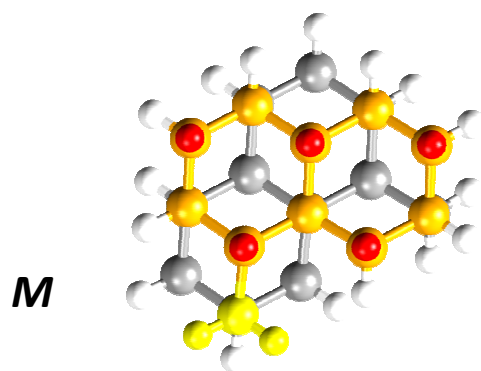


➤ (*M*) and (*P*)-[123]tetramantane deposited on Cu(111)



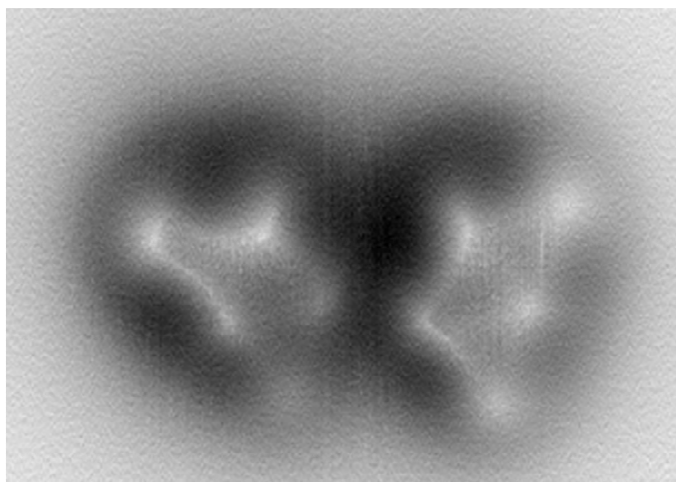


➤ (*M*) and (*P*)-[123]tetramantane deposited on Cu(111)





- [123]tetramantanes form two-molecule complexes on a Cu(111) surface



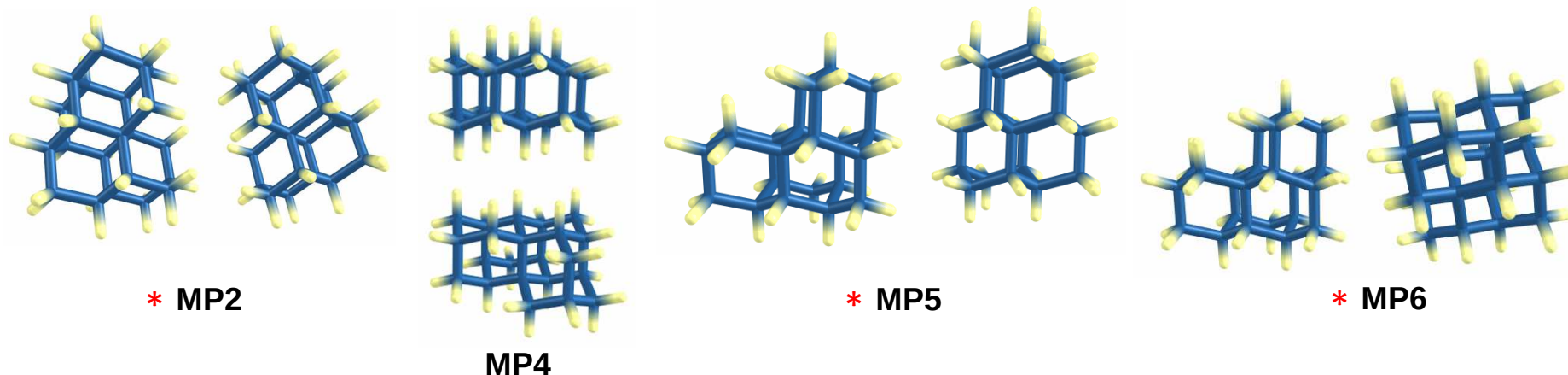
- both homochiral (*M-M* and *P-P*) and heterochiral (*M-P*) pairs found when a racemic mixture was used



Table 3. Interaction energies, $\Delta H(298)$, of LD-bound complexes of (*M*)- and (*P*)-[123]tetramantane (**MP1–MP6**) in kcal mol^{−1}. Geometries for MP2 and CCSD(T) single-point computations were optimized at the B3LYP-D3(BJ)/6-31G(d,p) level of theory.^{a, b}

Level of theory	MP1	MP2	MP3	MP4	MP5	MP6
B3LYP-D3(BJ)/6-31G(d,p)	−5.1	−7.7	−6.4	−7.7	−6.2	−6.4
MP2/cc-pVDZ	−4.2	−6.9	−5.4	−6.4	−5.5	−5.4
MP2/cc-pVTZ	−4.8	−7.7	−6.1	−7.4	−6.0	−6.2
MP2/CBS	−5.3	−8.3	−6.7	−8.2	−6.6	−6.8
CCSD(T)/cc-pVDZ	1.7	−1.7	−0.9	2.1	−1.3	1.1
CCSD(T)/CBS	0.7	−3.2	−2.2	0.4	−2.5	−0.3

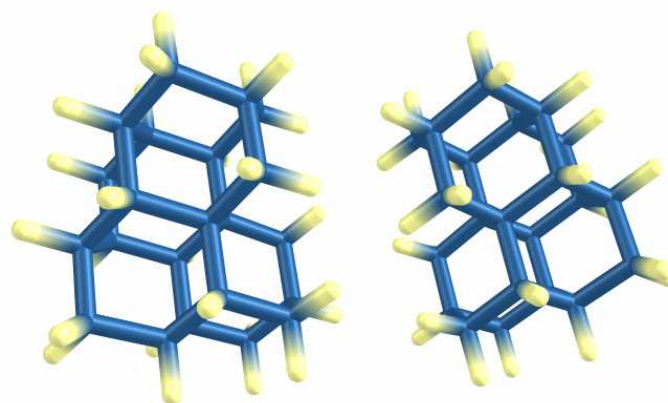
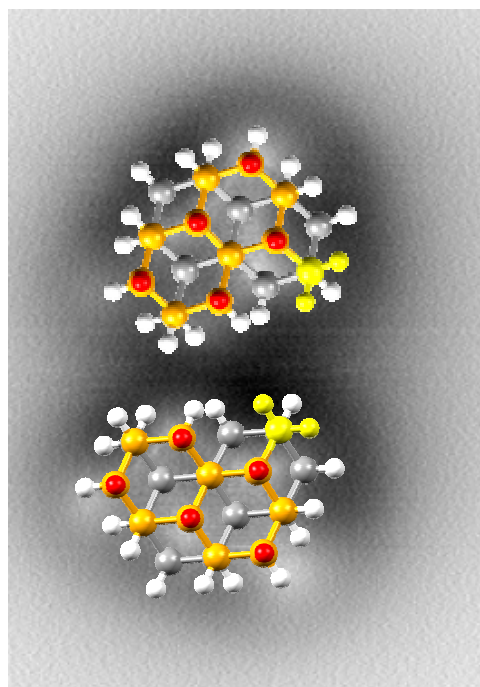
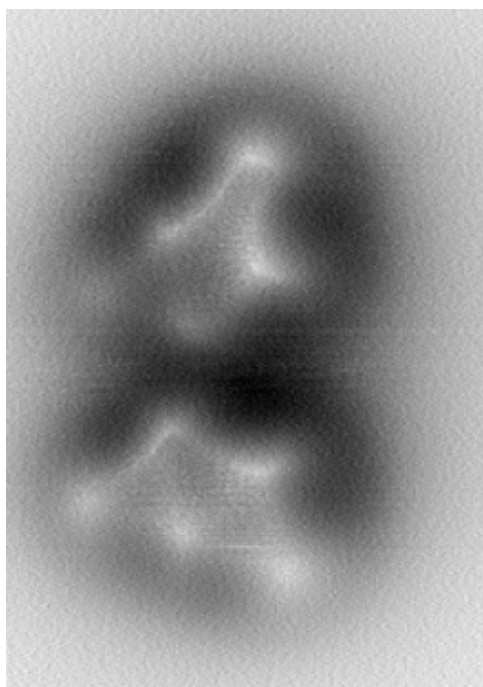
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^a Interaction energies are defined as a difference between the energy of the complex and the energy of two (*M*)-[123]tetramantane molecules. ^b ZPVEs used to obtain $\Delta H(298)$ for MP2 and CCSD(T) computed at the B3LYP-D3(BJ)/6-31G(d,p) level of theory.



- match between the AFM image and the computed **MP2** structure

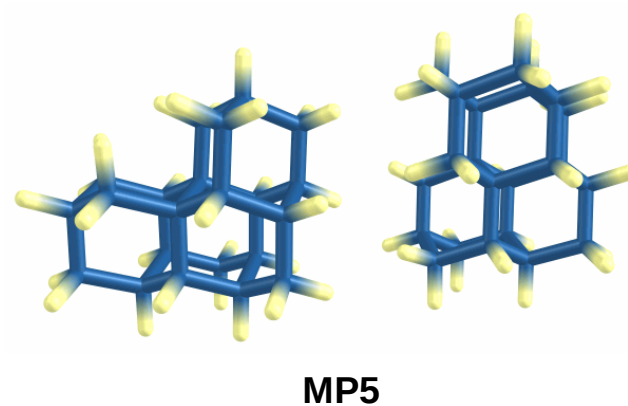
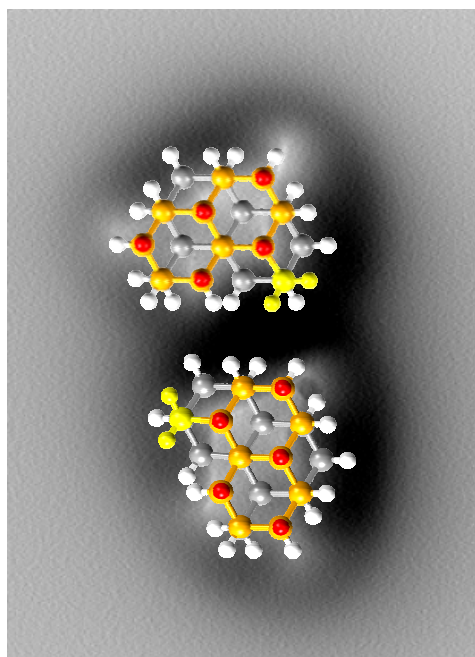
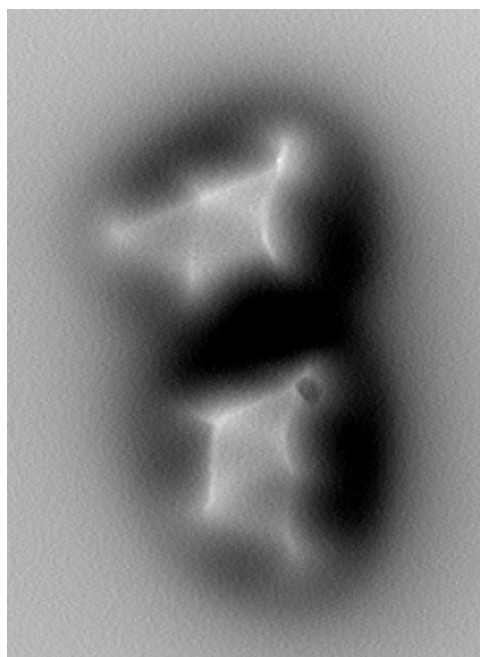


MP2

- the most stable LD-complex in the computed series



- match between the AFM image and the computed **MP5** structure



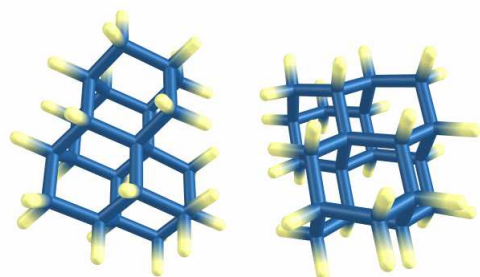
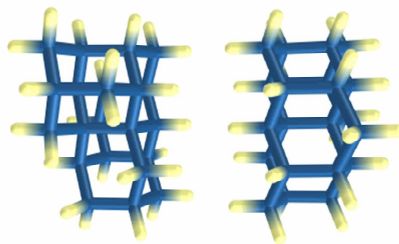
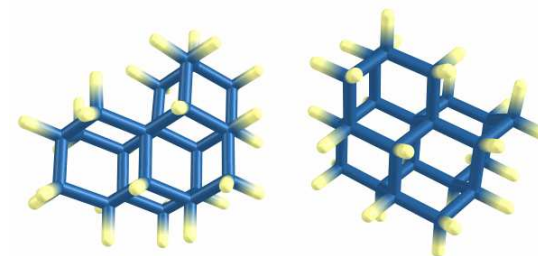
- energetically favorable LD-complex



Table 2. Interaction energies, $\Delta H(298)$, of LD-bound complexes of (*M*)-[123]tetramantane (**M1–M3**) in kcal mol^{−1}. Geometries for MP2 and CCSD(T) single-point computations were optimized at the B3LYP-D3(BJ)/6-31G(d,p) level of theory.^{a, b}

Level of theory	M1	M2	M3
B3LYP-D3(BJ)/6-31G(d,p)	−7.5	−7.7	−5.5
MP2/cc-pVDZ	−6.8	−6.5	−4.5
MP2/cc-pVTZ	−7.4	−7.5	−5.3
MP2/CBS	−7.9	−8.3	−5.9
CCSD(T)/cc-pVDZ	−3.4	1.3	1.6
CCSD(T)/CBS	−4.5	−0.5	0.3

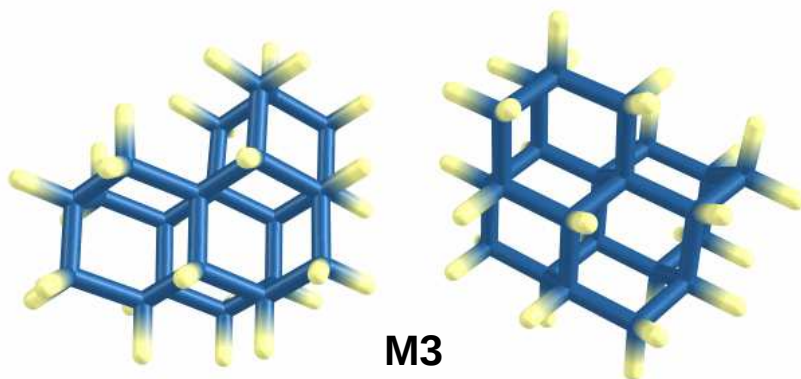
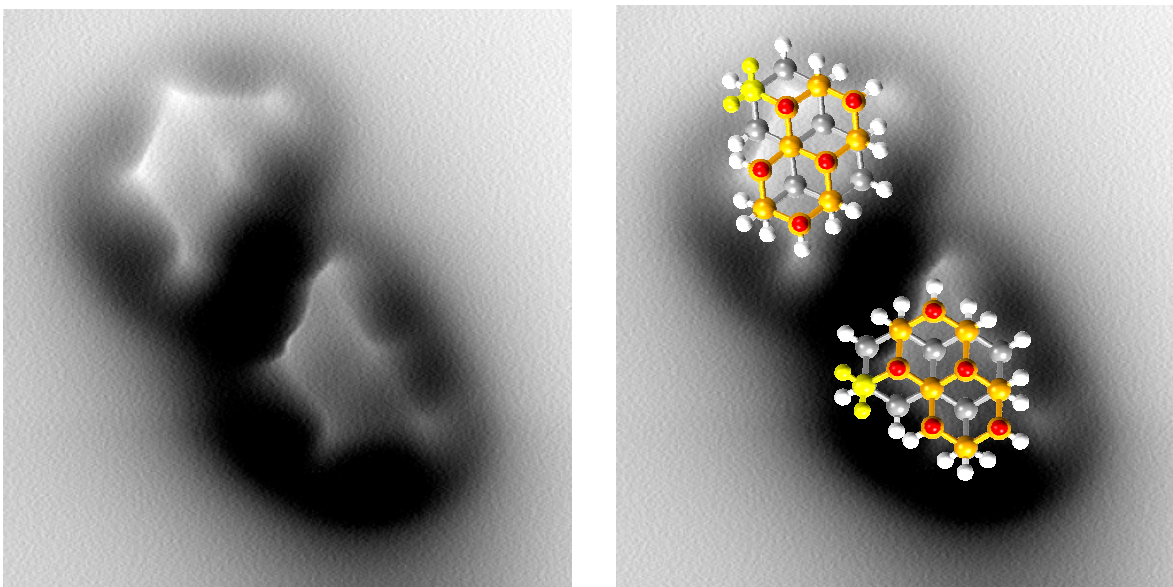
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**M1****M2***** M3**

^a Interaction energies are defined as a difference between the energy of the complex and the energy of two (*M*)-[123]tetramantane molecules. ^b ZPVEs used to obtain $\Delta H(298)$ for MP2 and CCSD(T) computed at the B3LYP-D3(BJ)/6-31G(d,p) level of theory.



- match between the AFM image and the computed **M3** structure



Energetically less stable
LD-complex!



Summary and outlook

- on-surface interactions between two [123]tetramantanes
- London dispersion forces stabilize the complexes but less than for [121]tetramantanes
- AFM measurements on Au(111) surface necessary to confirm the findings
- hybrid QM/MM computations of [123]tetramantanes on the Cu lattice



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The PRS group

*Thank you for
your attention...*

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