JUSTUS-LIEBIG-UNIVERSITÄT GIESSEN

Computational Chemistry Day

Configuration and reactivity of diamondoids on a Cu(111) surface

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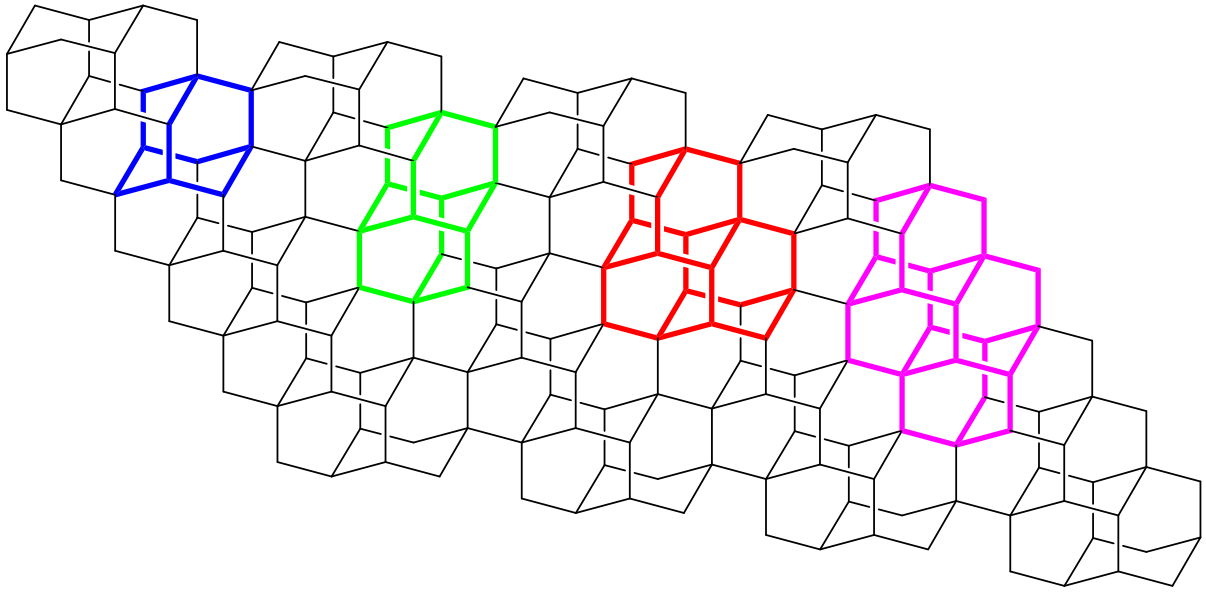
Computational Chemistry Day 2019
Faculty of Pharmacy and Biochemistry, University of Zagreb

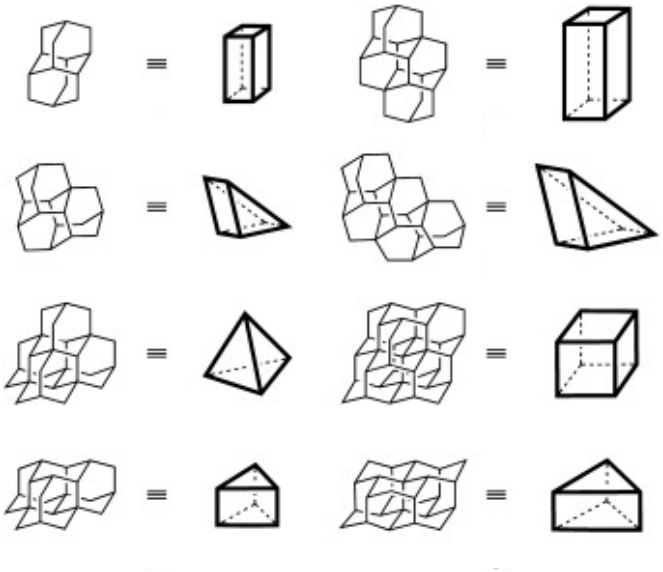
May 11, 2019



- diamondoids – saturated cage hydrocarbons, structure comparable with the crystal lattice of diamond
- structural rigidity, low strain, thermodynamic stability, lipophilicity
- higher diamondoids => more isomers

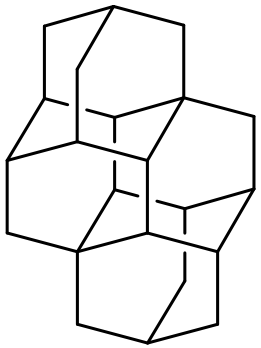
H. Schwertfeger, A. A. Fokin, P. R. Schreiner, *Angew. Chem., Int. Ed.* **2008**, *47*, 1022; M. A. Gunawan, J.-C. Hierso, D. Poinsot, A. A. Fokin, N. A. Fokina, B. A. Tkachenko, P. R. Schreiner, *New J. Chem.* **2014**, *38*, 28; L. Wanka, K. Iqbal, P. R. Schreiner, *Chem. Rev.* **2013**, *113*, 3516.

- isolation from petroleum

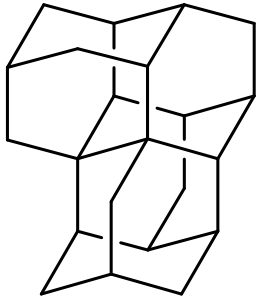


Dahl, J. E.; Liu, S. G.; Carlson, R. M. *Science* **2003**, *299*, 96; Fokin, A. A.; Gunchenko, P. A.; Novikovsky, A. A.; Shubina, T. E.; Chernyaev, B. V.; Dahl, J. E. P.; Carlson, R. M. K.; Yurchenko, A. G.; Schreiner, P. R. *Eur. J. Org. Chem.* **2009**, 5153.

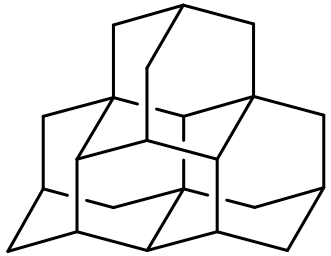
- tetramantane – first of the higher diamondoids



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



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



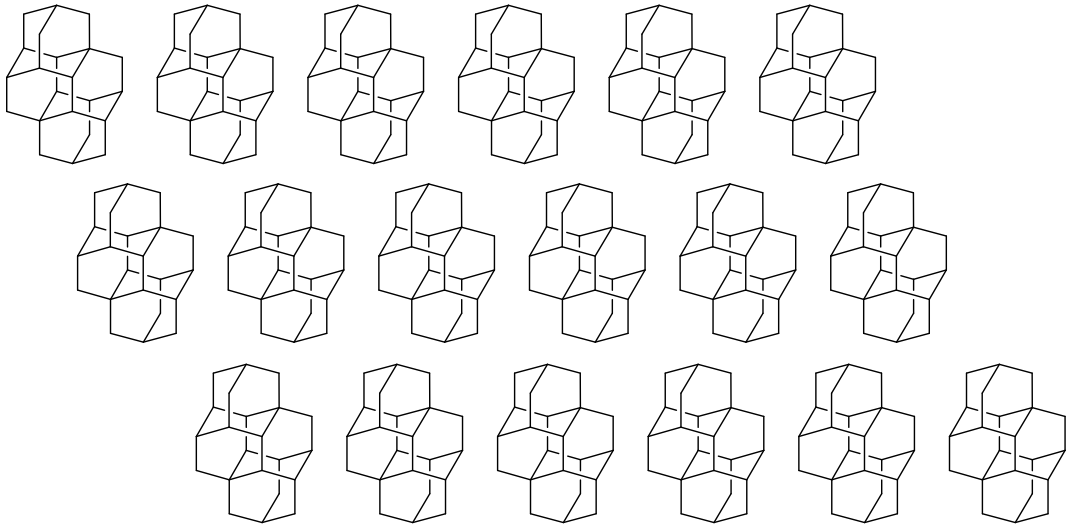
[1(2)3]tetramantane
C_{3v} symmetry
disk-like (*iso*)

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

A. T. Balaban, P. v. R. Schleyer, *Tetrahedron* **1978**, *34*, 3599; P. R. Schreiner, A. A. Fokin, H. P. Reisenauer, B. A. Tkachenko, E. Vass, M. M. Olmstead, D. Bläser, R. Boese, J. E. P. Dahl, R. M. K. Carlson, *J. Am. Chem. Soc.* **2009**, *131*, 11292; A. T. Balaban, D. C. Young, J. Plavec, K. Pečnik, M. Pompe, J. E. P. Dahl, R. M. K. Carlson, *Magn. Reson. Chem.* **2015**, *53*, 1003.

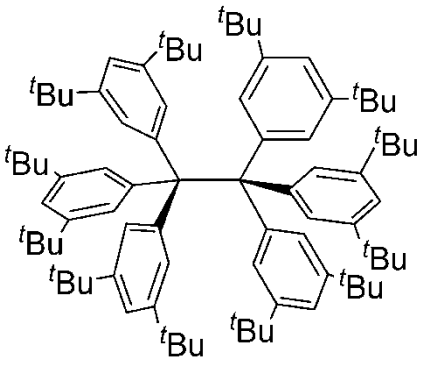
Interactions between molecules in the formed monolayers

- deposition of tetramantanes on Cu(111) and Au(111) surfaces
- STM (*scanning tunneling microscopy*) and AFM (*atomic force microscopy*) study of the self-assembly and the formed 2D lattice
- quantification of London dispersion (LD) interactions using computational methods

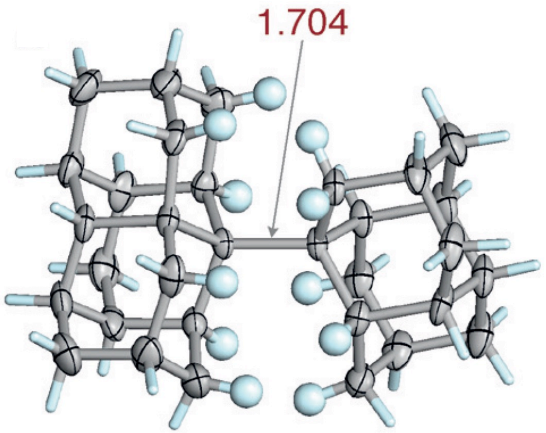


London dispersion

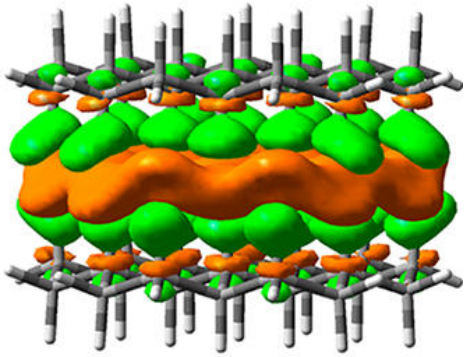
- acting in molecules due to interactions between induced dipoles
- the effect grows with the number of atom pairs that are interacting
- pronounced in bulky, polarizable molecules



- hexaphenylethane stabilized with *t*Bu groups



- the longest known alkane C–C bond

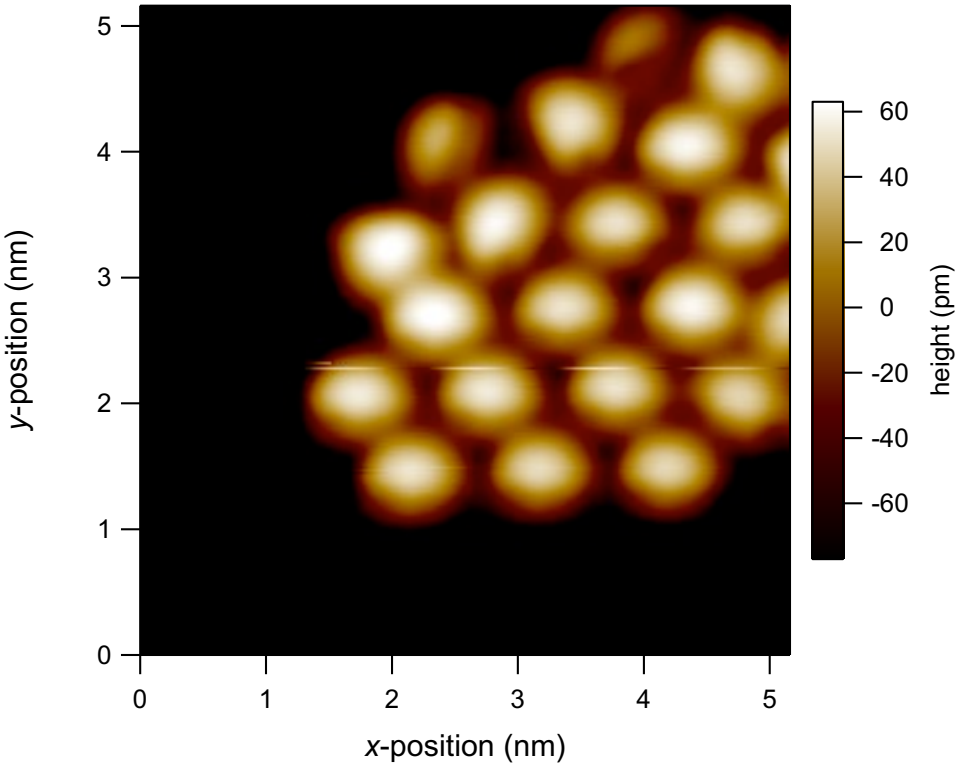


- important in σ–σ interactions of graphane

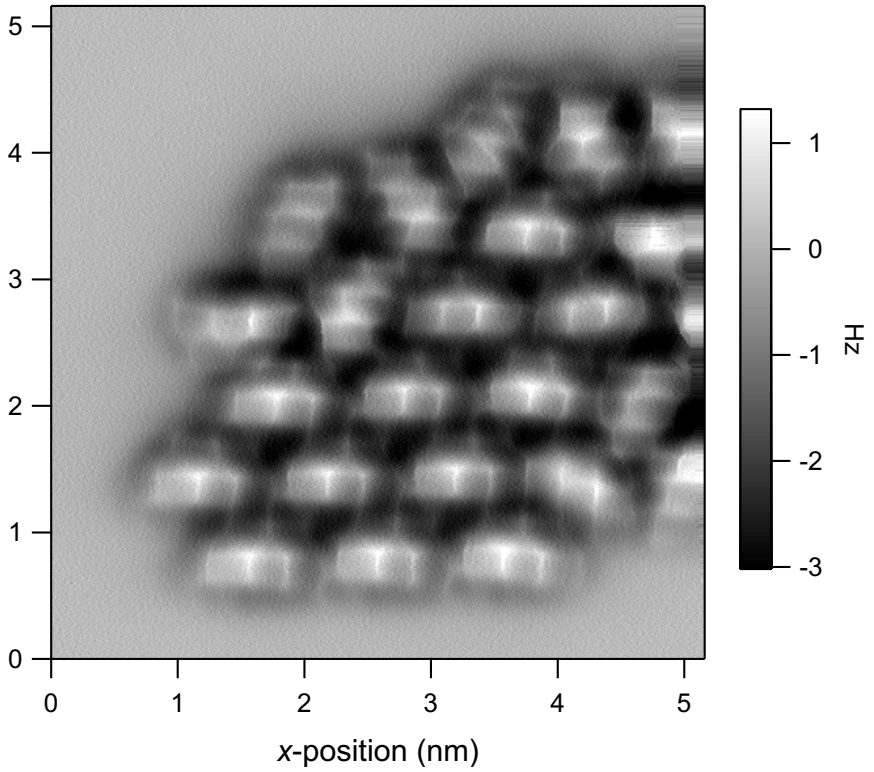
J. P. Wagner, P. R. Schreiner, *Angew. Chem., Int. Ed.* **2015**, *54*, 12274; C. Wang, Y. Mo, J. P. Wagner, P. R. Schreiner, E. D. Jemmis, D. Danovich, S. Shaik, *J. Chem. Theory Comput.* **2015**, *11*, 1621; S. Grimme, P. R. Schreiner, *Angew. Chem., Int. Ed*. **2011**, *50*, 12639.

- Cu(111) surface with a [121]tetramantane monolayer

STM image

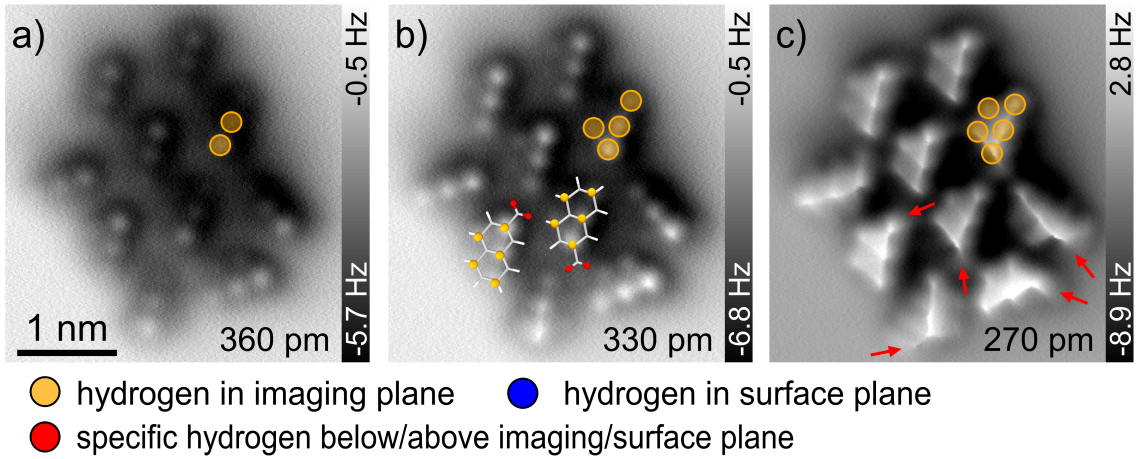


AFM image

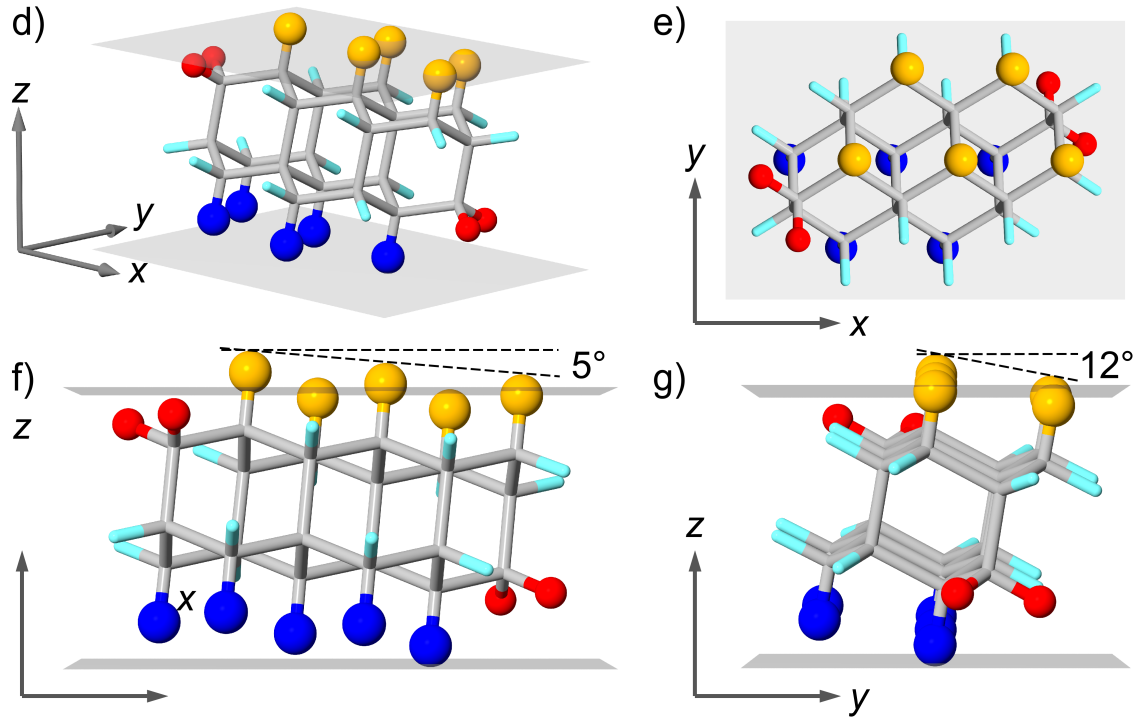


Ebeling, D.; Šekutor, M.; Stiefermann, M.; Tschakert, J.; Dahl, J. E. P.; Carlson, R. M. K.; Schirmeisen, A.; Schreiner, P. R. *ACS Nano* **2017**, *11*, 9459.

Tetramantanes on metal surfaces



AFM images at different hights of the CO tip



- [121]tetramantane is achiral but the molecules are adsorbed on the surface under an angle (5 °), making the system chiral (on-surface chirality)

Ebeling, D.; Šekutor, M.; Stiefermann, M.; Tschakert, J.; Dahl, J. E. P.; Carlson, R. M. K.; Schirmeisen, A.; Schreiner, P. R. *ACS Nano* **2017**, *11*, 9459.

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

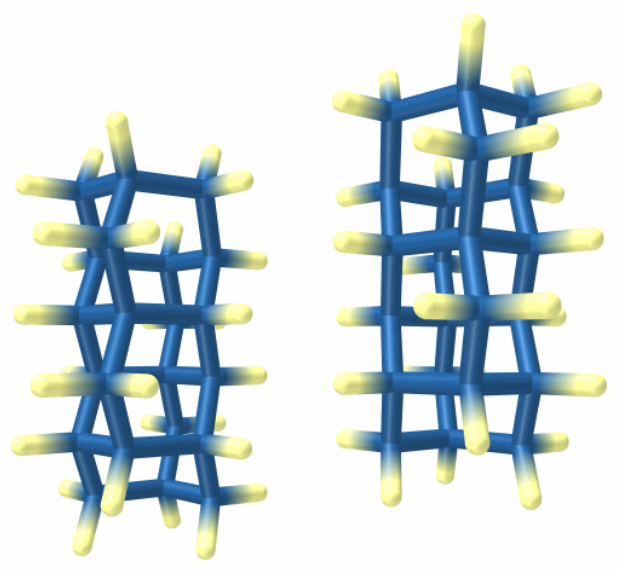
- density functional theory (DFT) — **Gaussian**
  - B3LYP functional with and without Grimme's D3 correction with Becke-Johnson (BJ) damping
  - M06-2X functional parametrized for medium-range correlation
- second order Møller–Plesset perturbation theory (MP2)
- *ab initio* coupled cluster method (CCSD(T))
- complete basis set extrapolation (CBS) — **ORCA 4**

Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104; Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, *32*, 1456; Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215; Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157; Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *Chem. Phys. Lett.* **1988**, *153*, 503; Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968; Truhlar, D. G. *Chem. Phys. Lett.* **1998**, *294*, 45; Riley, K. E.; Hobza, P. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2011**, *1*, 3.

- different orientations of [121]tetramantane dimers computed

interaction energy => quantification of London dispersion attraction

$$\Delta H_{\text{interaction}} = H_{\text{complex}} - 2\, H_{[121]\text{tetramantane}}$$



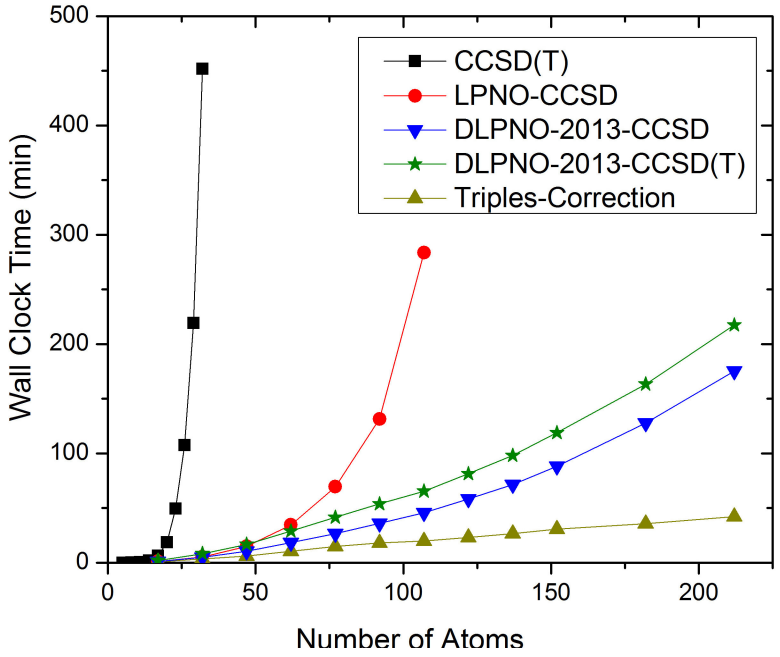
DLPNO-CCSD(T) method

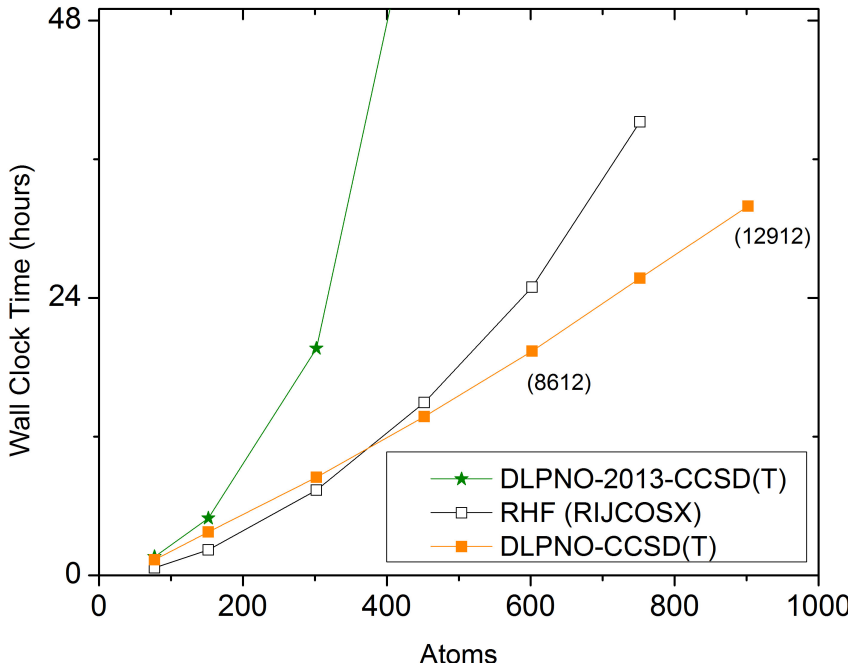
- **d**omain based **l**ocal **p**air **n**atural **o**rbital (DLPNO) methodology largely improved in ORCA 4
- near linear scaling with system size (with respect to CPU and memory) => significant speeding of the CC technique
- CC computations on large systems
- localization of internal orbitals => reduction of the number of electron pairs to be correlated (pair correlation energies fall off sharply with distance)
- truncation of pair natural orbitals (PNOs), enables faster convergence of the pair wavefunction
- PNO space for a given electron pair is local (located in the same region of space as the electron pair)

ORCA

Riplinger, C.; Neese, F. *J. Chem. Phys.* **2013**, *138*, 034106; Riplinger, C.; Sandhoefer, B.; Hansen, A.; Neese, F. *J. Chem. Phys.* **2013**, *139*, 134101; Riplinger, C.; Pinski, P.; Becker, U.; Valeev, E. F.; Neese, F. *J. Chem. Phys.* **2016**, *144*, 024109.
ORCA Manual, https://orcaforum.cec.mpg.de/OrcaManual.pdf

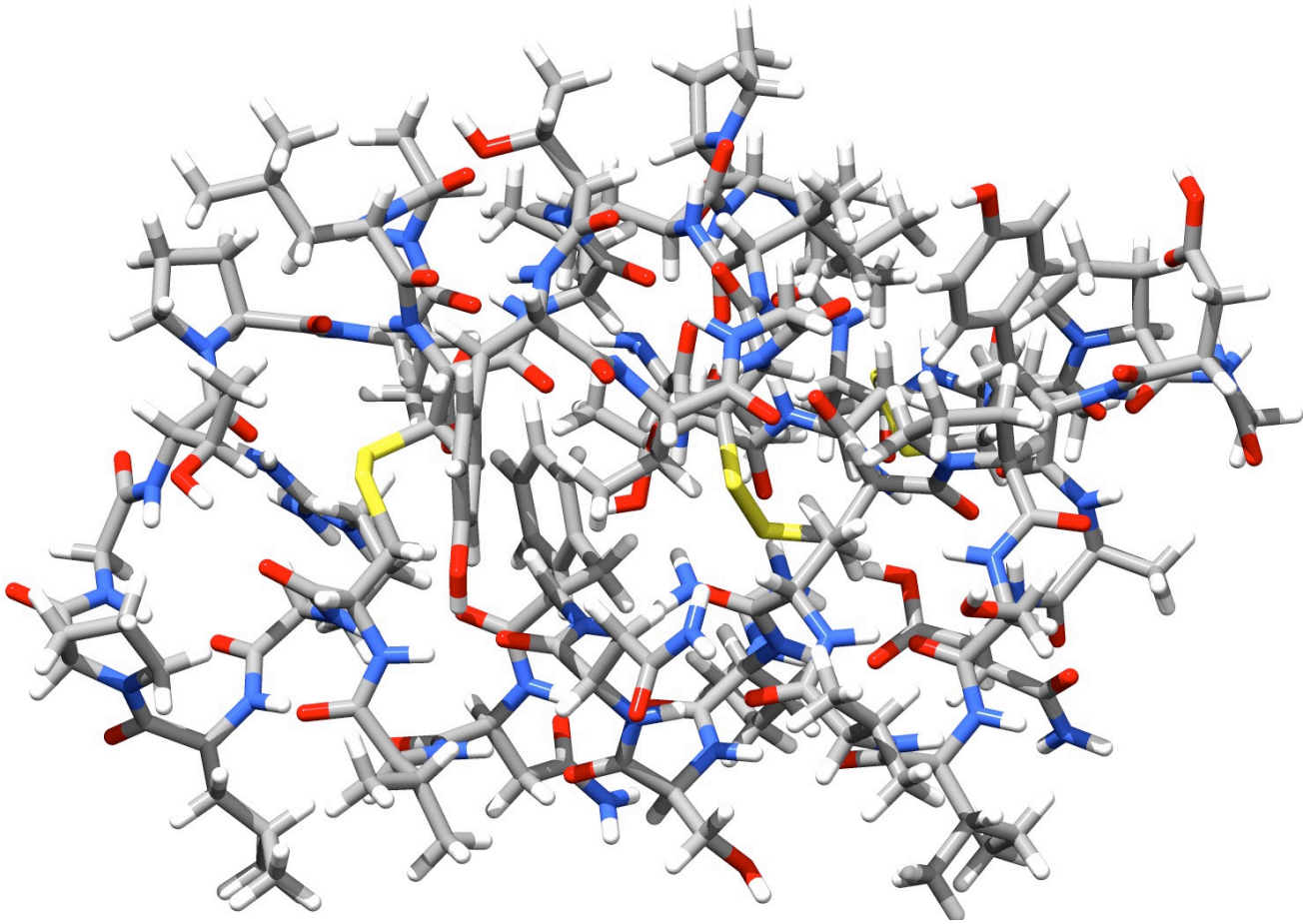
Scaling comparison





Scaling behavior of the canonical CCSD, LPNO-CCSD and DLPNO-CCSD(T) methods

ORCA Manual, https://orcaforum.cec.mpg.de/OrcaManual.pdf



Crambin protein – the first protein treated with a CCSD(T) level *ab initio* method

DLPNO-CCSD(T)/def2-SVP, 644 atoms, single core of a Linux computer, 4 days

Riplinger, C.; Sandhoefer, B.; Hansen, A.; Neese, F. *J. Chem. Phys.* **2013**, *139*, 134101.
ORCA Manual, https://orcaforum.cec.mpg.de/OrcaManual.pdf

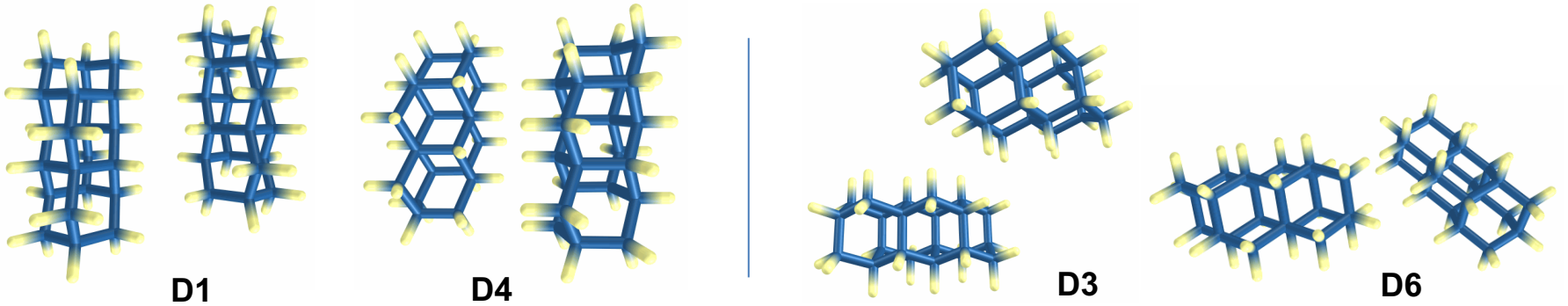
Local Energy Decomposition (LED) analysis

- decomposing of coupled cluster energy into physical meaningful contributions => a new feature in ORCA 4
- insights into the nature of intermolecular interactions
- however, only the total energy is an observable and decomposition is to some extent arbitrary
- two fragments need to be defined and the corresponding interaction energy is decomposed
- *TightPNO* settings need to be defined for weakly interacting systems (*e.g.*, London dispersion bound complexes)

ORCA Manual, https://orcaforum.cec.mpg.de/OrcaManual.pdf
Schneider, W. B.; Bistoni, G.; Sparta, M.; Saitow, M.; Riplinger, C.; Auer, A. A.; Neese, F. *J. Chem. Theory Comput.* **2016**, *12*, 4778–4792.

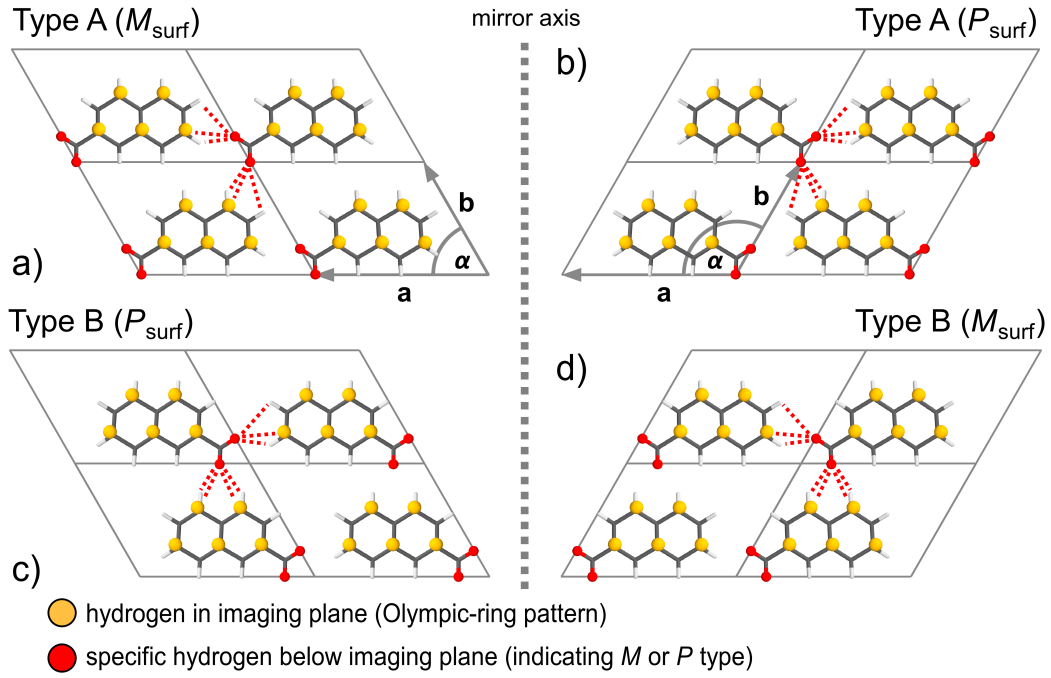
Table 1. Interaction energies, ΔH(0 K), for dispersion complexes of two [121]tetramantanes in kcal mol^{-1}.

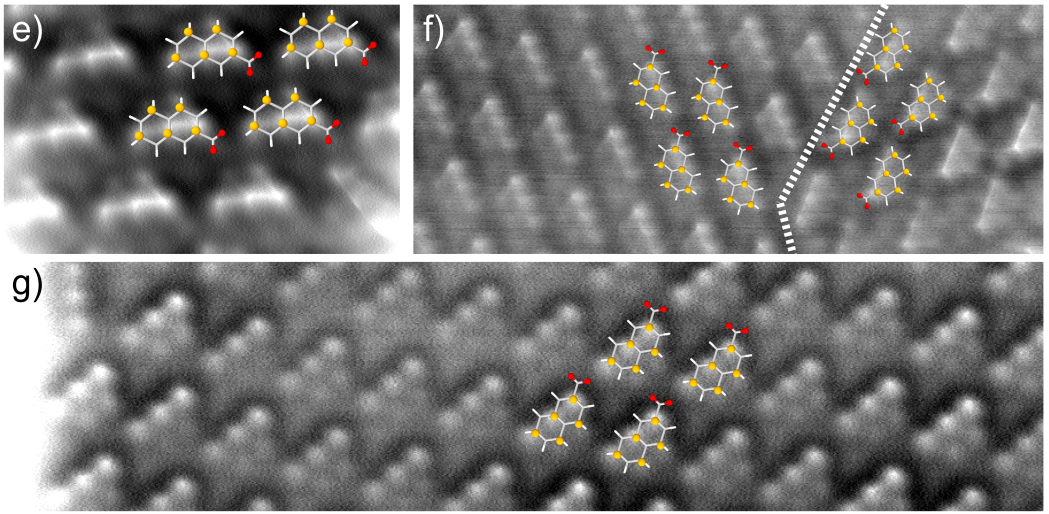
Level of theory	D1	D2	D3	D4	D5	D6	D7	D8
B3LYP/6-31G(d,p)	0.0	0.1	0.2	0.1	–0.2	0.0	–0.3	–0.2
B3LYP-D3(BJ)/6-31G(d,p)	–8.8	–4.0	–5.7	–8.5	–7.4	–4.7	–7.5	–8.2
M06-2X/6-31G(d,p)	–5.9	–2.6	–3.4	–5.4	–4.5	–2.2	–4.3	–4.7
RI-MP2/cc-pVDZ	–7.8	–3.3	–4.7	–8.0	–6.6	–3.7	–6.3	–7.4
RI-MP2/cc-pVTZ	–9.0	–3.7	–5.5	–8.9	–7.4	–4.2	–7.4	–8.4
RI-MP2/CBS	–9.9	–4.0	–6.1	–9.7	–8.1	–4.6	–8.1	–9.2
DLPNO-CCSD(T)/cc-pVDZ	–6.3	–2.8	–3.7	–6.5	–5.3	–2.9	–4.9	–6.0
DLPNO-CCSD(T)/CBS	–8.3	–3.4	–5.1	–8.2	–6.8	–3.8	–6.7	–7.8
LED analysis (CCSD)	–7.2	–2.8	–4.5	–6.8	–5.9	–3.8	–6.3	–6.8



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

Tetramantanes on metal surfaces





- type A and B of surface chirality for tetramantane islands
- composed of M_{surf}- and P_{surf}-type of [121]tetramantane molecules
- equal cell parameters but different orientation

e) type A (P_{surf}) island on Cu(111)

f) 2 type A (P_{surf}) islands on Au(111)

g) type A (M_{surf}) island on Au(111)

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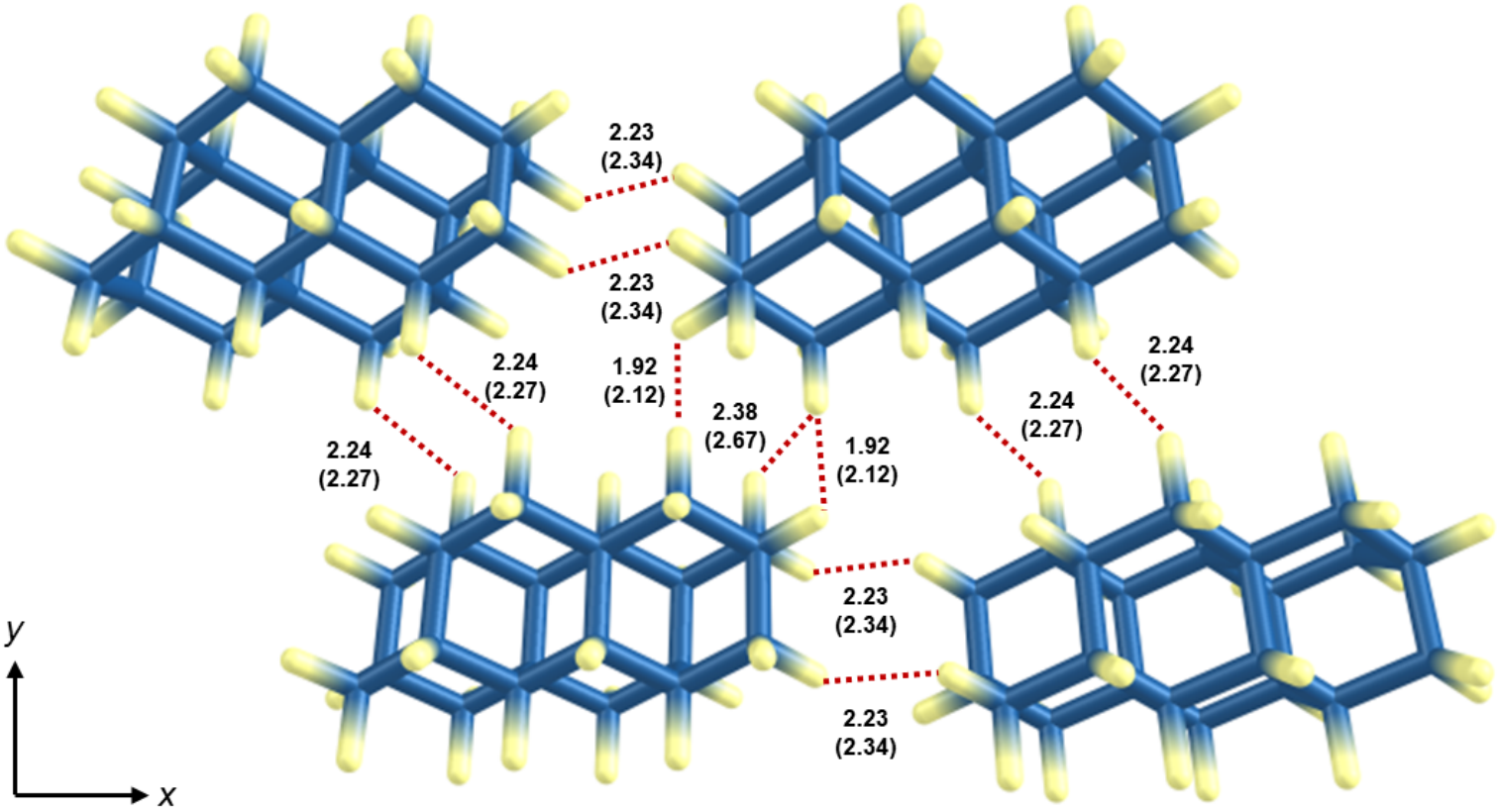
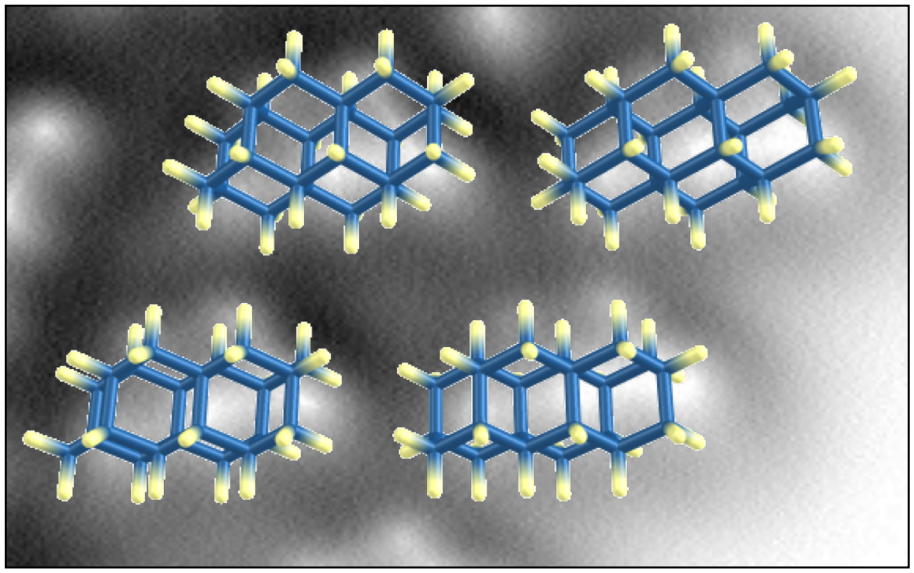


- close contacts between [121]tetramantane molecules on a Ag(111) surface; selected H–H distances are given in Å and values in parentheses correspond to the distances on a Cu(111) surface
- structures computed at the B3LYP-D3(BJ)/6-31G(d,p) level of theory

Ebeling, D.; Šekutor, M.; Stiefermann, M.; Tschakert, J.; Dahl, J. E. P.; Carlson, R. M. K.; Schirmeisen, A.; Schreiner, P. R. *ACS Nano* **2017**, *11*, 9459.



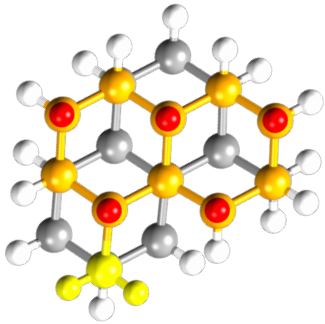
- computed structure of dispersion complexes consisting of four [121]tetramantanes superimposed on the AFM image

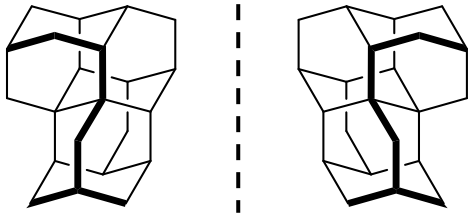
Table 2. Interaction energies, ΔE, of dispersion complexes of four [121]tetramantanes in kcal mol^{-1}.

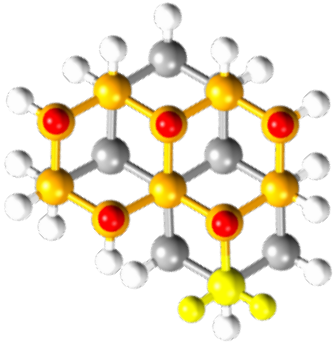
	Type	ΔE	Type	ΔE
Au(111)	A (+5°)	–19.3	A (–5°)	–19.1
Au(111)	B (+5°)	73.6	B (–5°)	–4.4
Cu(111)	A (+5°)	–20.6	A (–5°)	–19.5
Cu(111)	B (+5°)	33.7	B (–5°)	–7.0

- AFM imaging found only type A on both metal surfaces => in line with computational results

Ebeling, D.; Šekutor, M.; Stiefermann, M.; Tschakert, J.; Dahl, J. E. P.; Carlson, R. M. K.; Schirmeisen, A.; Schreiner, P. R. *ACS Nano* **2017**, *11*, 9459.

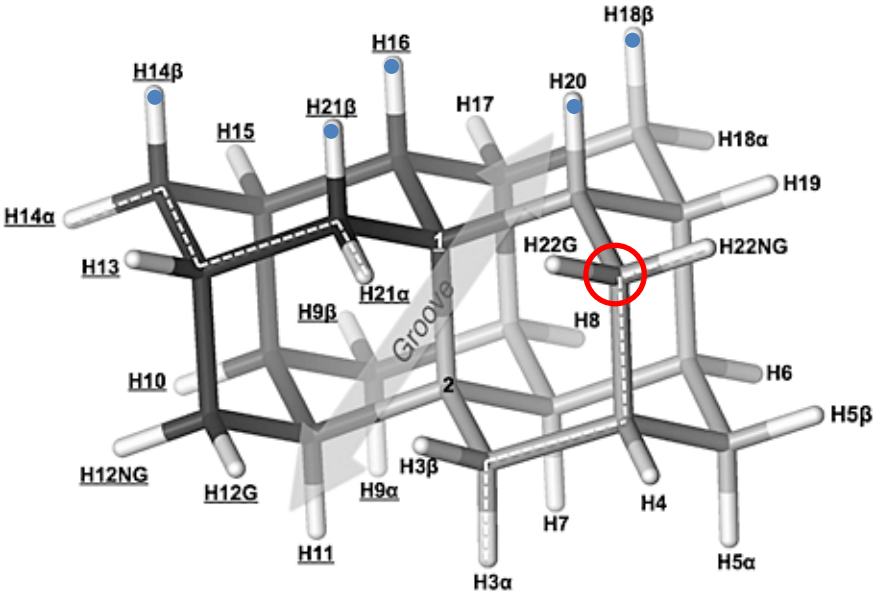




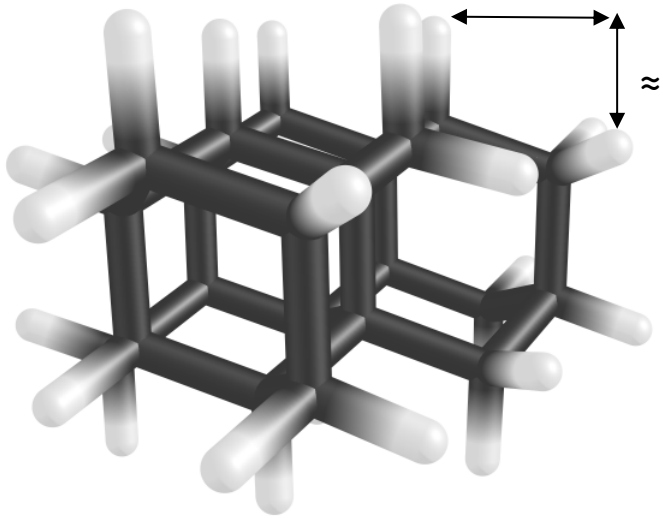


[123]tetramantane

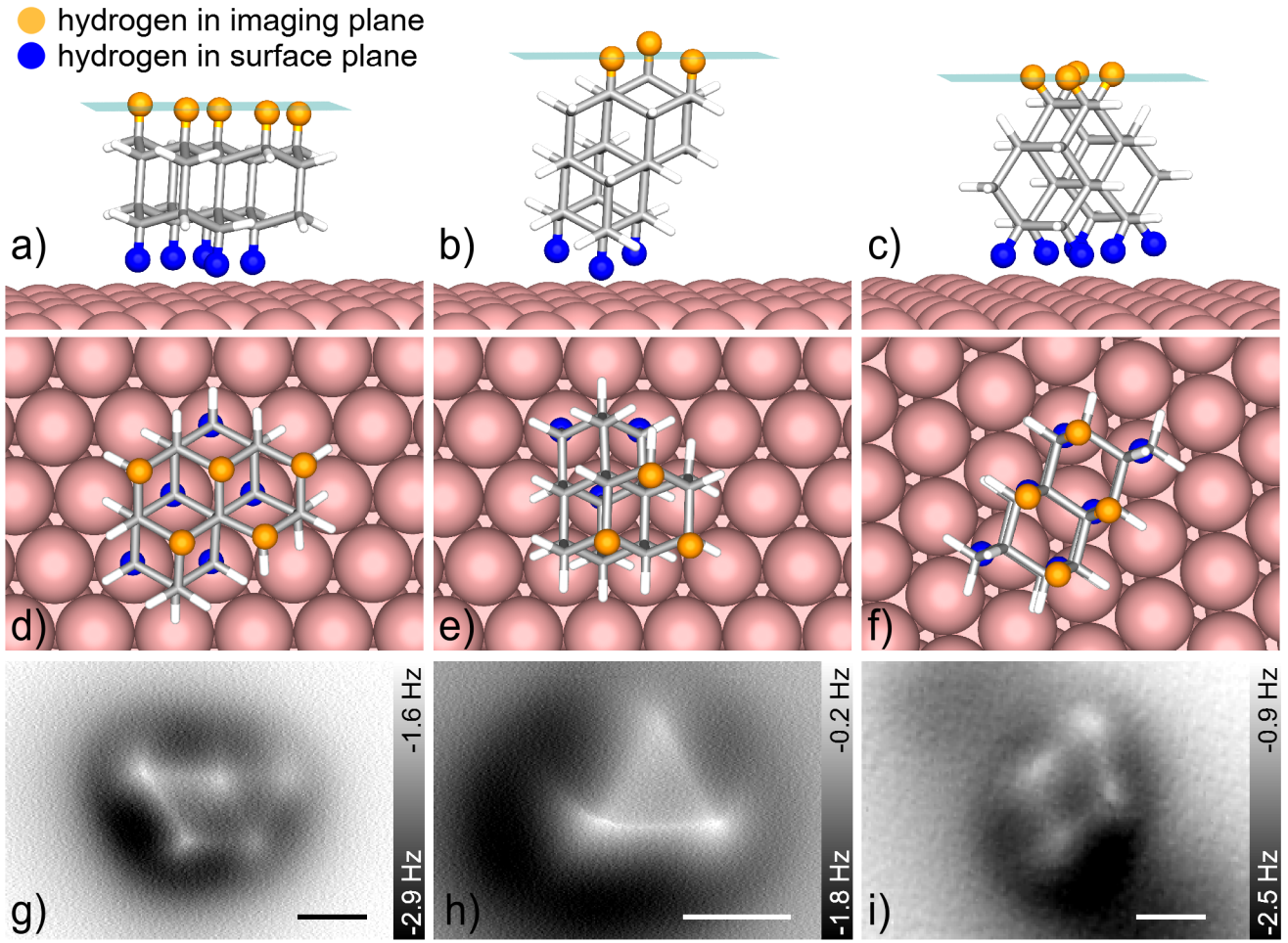
Helical chirality:
M = „left"
P = „right"



P

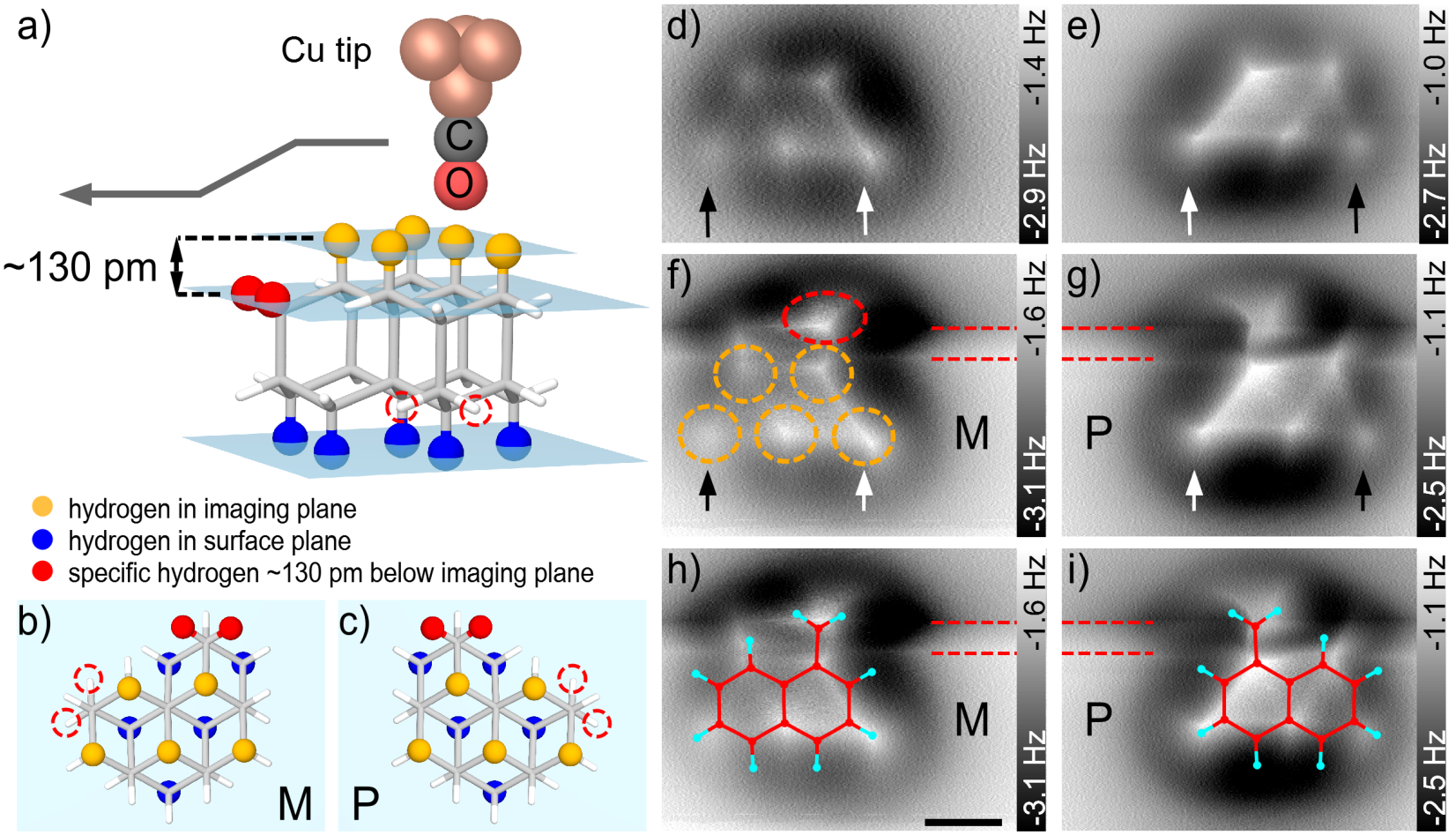


P. R. Schreiner, A. A. Fokin, H. P. Reisenauer, B. A. Tkachenko, E. Vass, M. M. Olmstead, D. Bläser, R. Boese, J. E. P. Dahl, R. M. K. Carlson, *J. Am. Chem. Soc.* **2009**, *131*, 11292; A. T. Balaban, D. C. Young, J. Plavec, K. Pečnik, M. Pompe, J. E. P. Dahl, R. M. K. Carlson, *Magn. Reson. Chem.*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



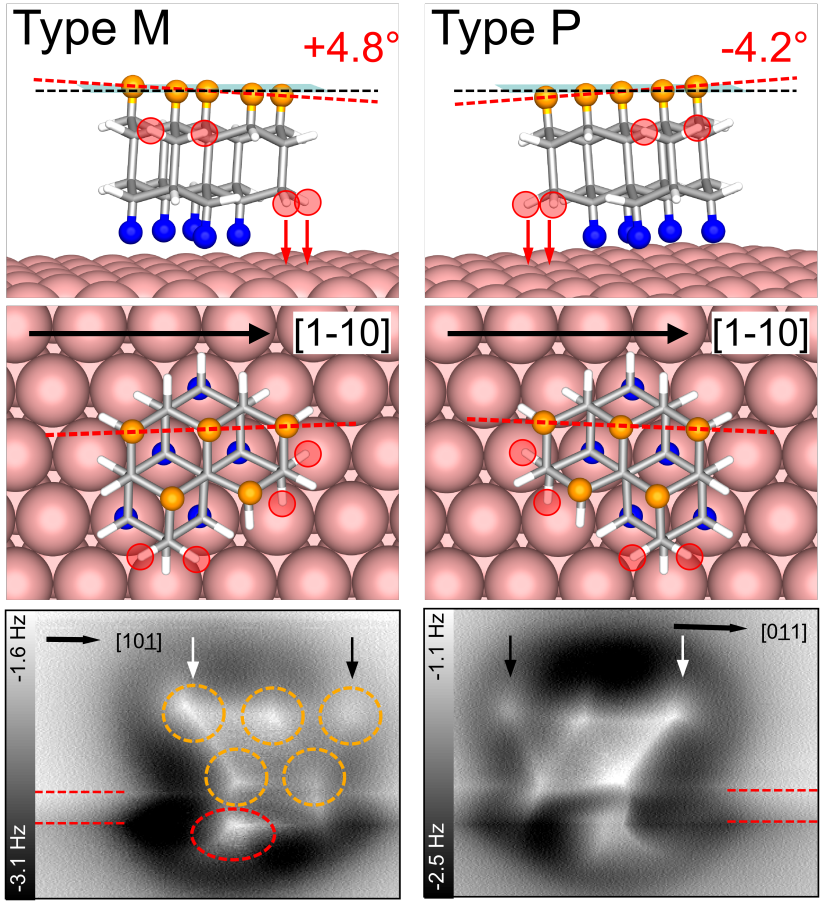
- different orientations of (*M*)-[123]tetramantane
- patterns: Olympic rings (d,g), triangle (e,h) and rhombus (f,i)

Ebeling, D.; Šekutor, M.; Stiefermann, M.; Tschakert, J.; Dahl, J. E. P.; Carlson, R. M. K.; Schirmeisen, A.; Schreiner, P. R. *Nat. Commun.* **2018**, *9*, 2420.



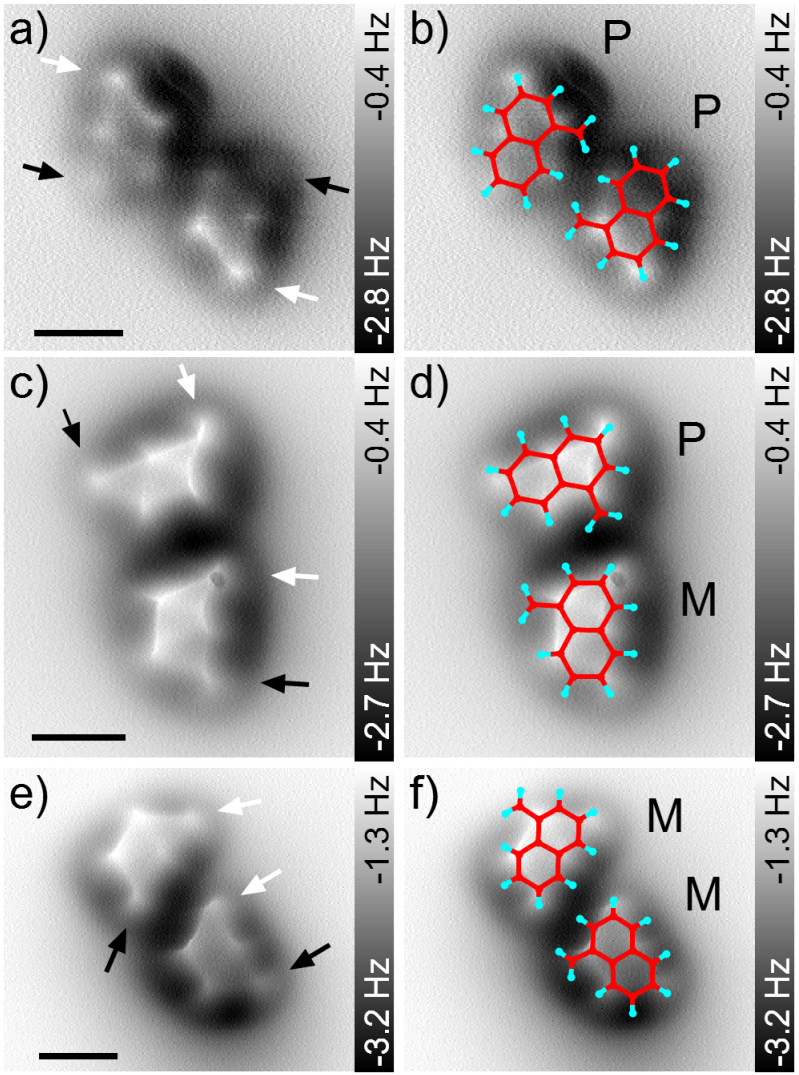
- [123]tetramantanes on Cu (111) with the Olympic ring pattern
- absolute configuration can be determined by locating two specific hydrogen atoms (red) ≈130 pm below the imaging plane

Ebeling, D.; Šekutor, M.; Stiefermann, M.; Tschakert, J.; Dahl, J. E. P.; Carlson, R. M. K.; Schirmeisen, A.; Schreiner, P. R. *Nat. Commun.* **2018**, *9*, 2420.



- (*M*)- and (*P*)-[123]tetramantane on Cu(111); tilting by +4.8° ((*M*)-type) and –4.2° ((*P*)-type) caused by attractive forces between the two specific hydrogens and the Cu surface atoms

Ebeling, D.; Šekutor, M.; Stiefermann, M.; Tschakert, J.; Dahl, J. E. P.; Carlson, R. M. K.; Schirmeisen, A.; Schreiner, P. R. *Nat. Commun.* **2018**, *9*, 2420.



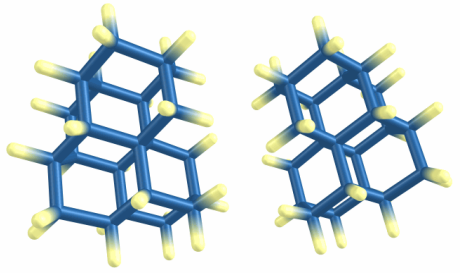
- [123]tetramantane forms two-molecule LD complexes on a Cu(111) surface
- both homochiral (*M*-*M* and *P*-*P*) and heterochiral (*M*-*P*) pairs were found when a racemate was used

a, b (*P*,*P*) dimer
c, d (*M*,*P*) dimer
e, f (*M*,*M*) dimer

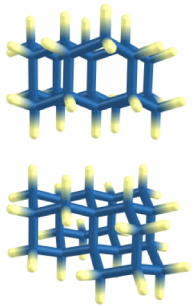
Ebeling, D.; Šekutor, M.; Stiefermann, M.; Tschakert, J.; Dahl, J. E. P.; Carlson, R. M. K.; Schirmeisen, A.; Schreiner, P. R. *Nat. Commun.* **2018**, *9*, 2420.

Table 2. Interaction energies, ΔH(0 K), for dispersion complexes of (*M*)- and (*P*)-[123]tetramantanes in kcal mol^{-1}.

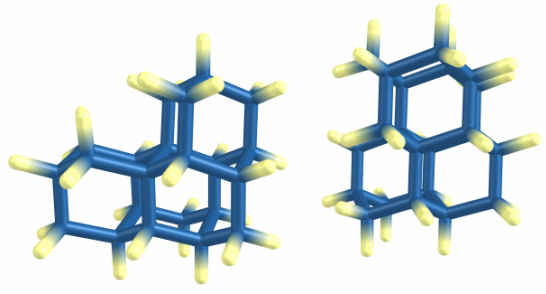
Level of theory	MP1	MP2	MP3	MP4	MP5	MP6
B3LYP-D3(BJ)/6-31G(d,p)	–5.1	–7.7	–6.4	–7.7	–6.2	–6.4
M06-2X/6-31G(d,p)	–3.4	–5.9	–3.5	–4.7	–4.0	–4.2
RI-MP2/cc-pVDZ	–4.2	–6.9	–5.4	–6.4	–5.5	–5.4
RI-MP2/cc-pVTZ	–4.8	–7.7	–6.1	–7.4	–6.0	–6.2
RI-MP2/CBS	–5.2	–8.3	–6.7	–8.1	–6.5	–6.7
DLPNO-CCSD(T)/cc-pVDZ	–3.4	–5.5	–4.2	–5.0	–4.4	–4.3
DLPNO-CCSD(T)/CBS	–4.4	–6.9	–5.5	–6.7	–5.5	–5.6
LED analysis (CCSD)	–4.0	–6.6	–5.2	–6.6	–4.9	–5.1



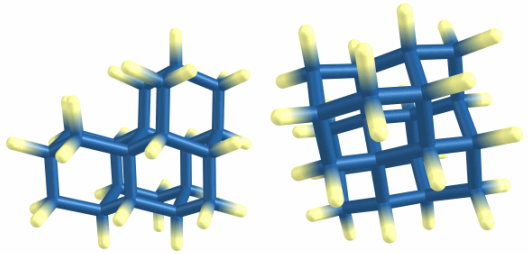
MP2



MP4



MP5

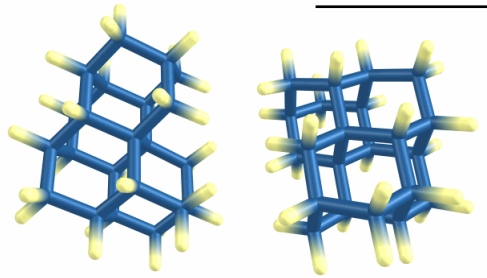


MP6

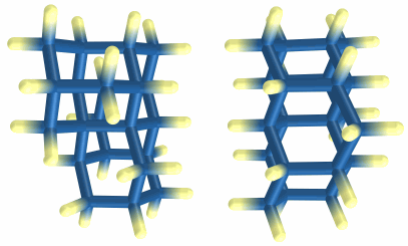
[a] Interaction energies are defined as a difference between the energy of the complex and the energy of two [123]tetramantane molecules. [b] ZPVEs used to obtain ΔH for MP2 and CCSD(T) computed at the B3LYP-D3(BJ)/6-31G(d,p) level of theory.

Table 3. Interaction energies, ΔH(0 K), for dispersion complexes of two (*M*)-[123]tetramantanes in kcal mol^{-1}.

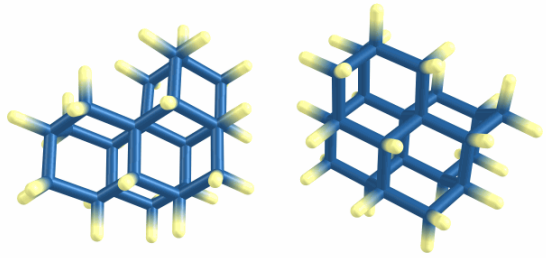
Level of theory	M1	M2	M3
B3LYP-D3(BJ)/6-31G(d,p)	–7.5	–7.7	–5.5
M06-2X/6-31G(d,p)	–5.5	–4.6	–3.7
RI-MP2/cc-pVDZ	–6.8	–6.5	–4.5
RI-MP2/cc-pVTZ	–7.4	–7.5	–5.3
RI-MP2/CBS	–7.9	–8.2	–5.8
DLPNO-CCSD(T)/cc-pVDZ	–5.5	–5.1	–3.6
DLPNO-CCSD(T)/CBS	–6.6	–6.8	–4.9
LED analysis (CCSD)	–6.3	–6.6	–4.5



M1



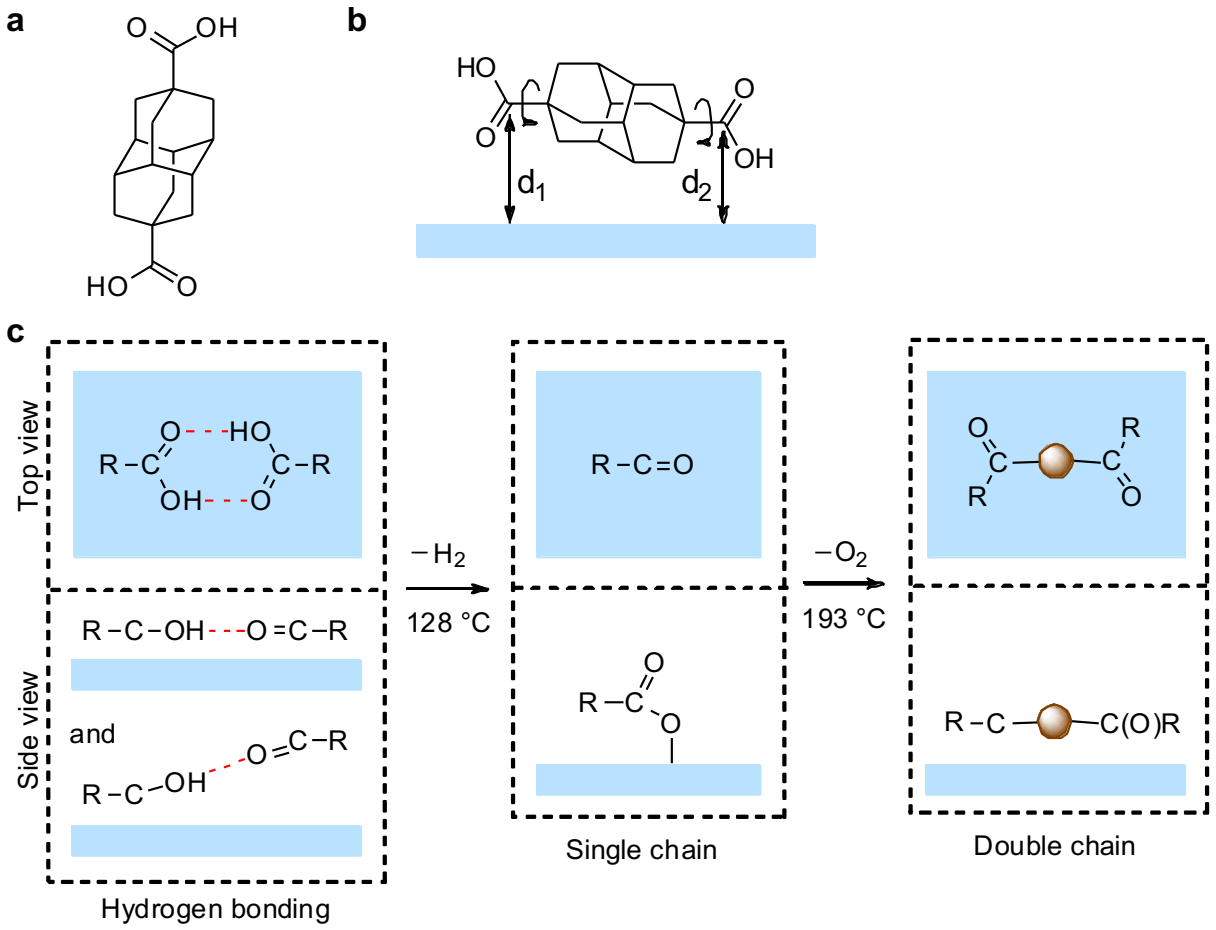
M2



M3

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

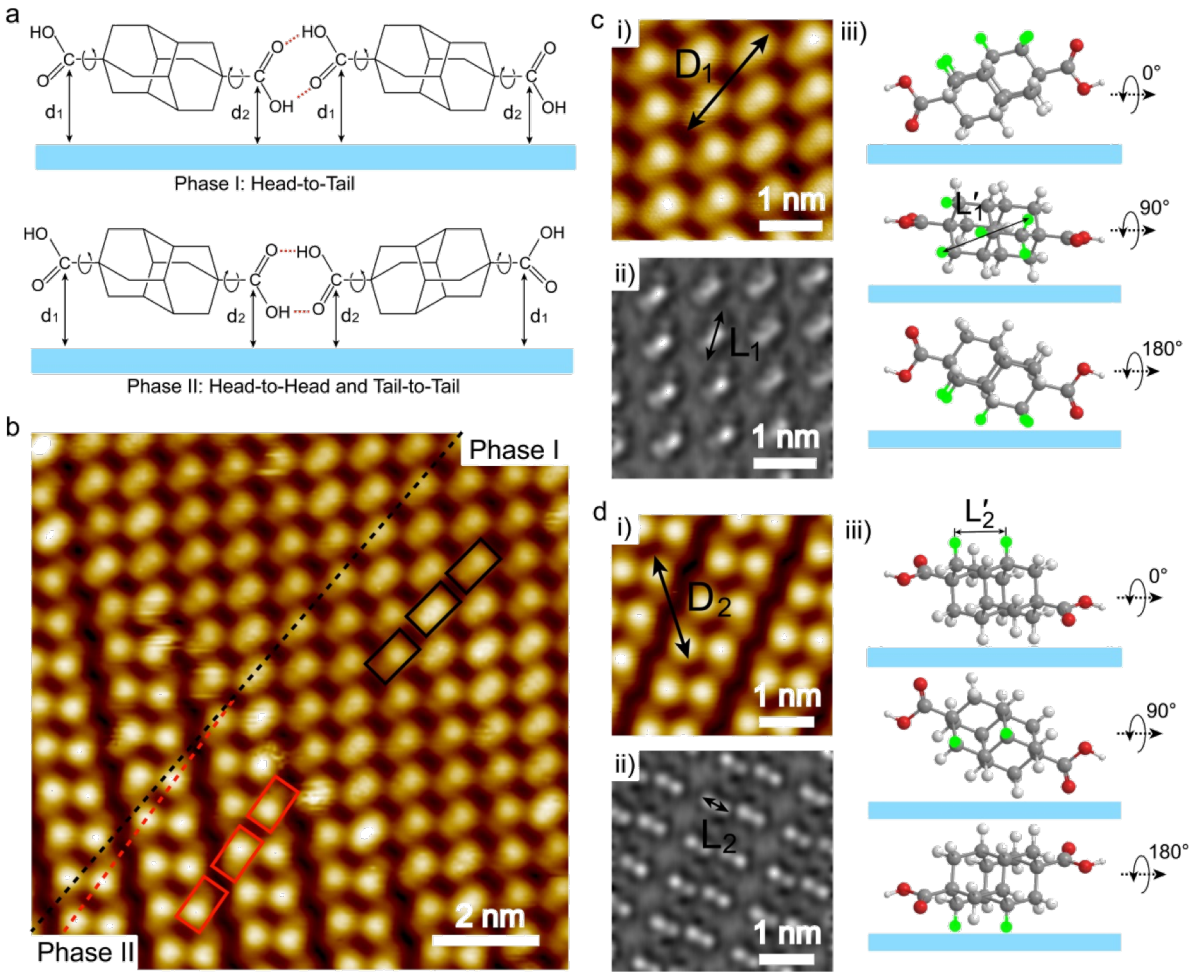
- reactivity of 4,9-diamantane dicarboxylic acid (DDA) on Cu(111)



- stepwise dehydrogenation and deoxygenation

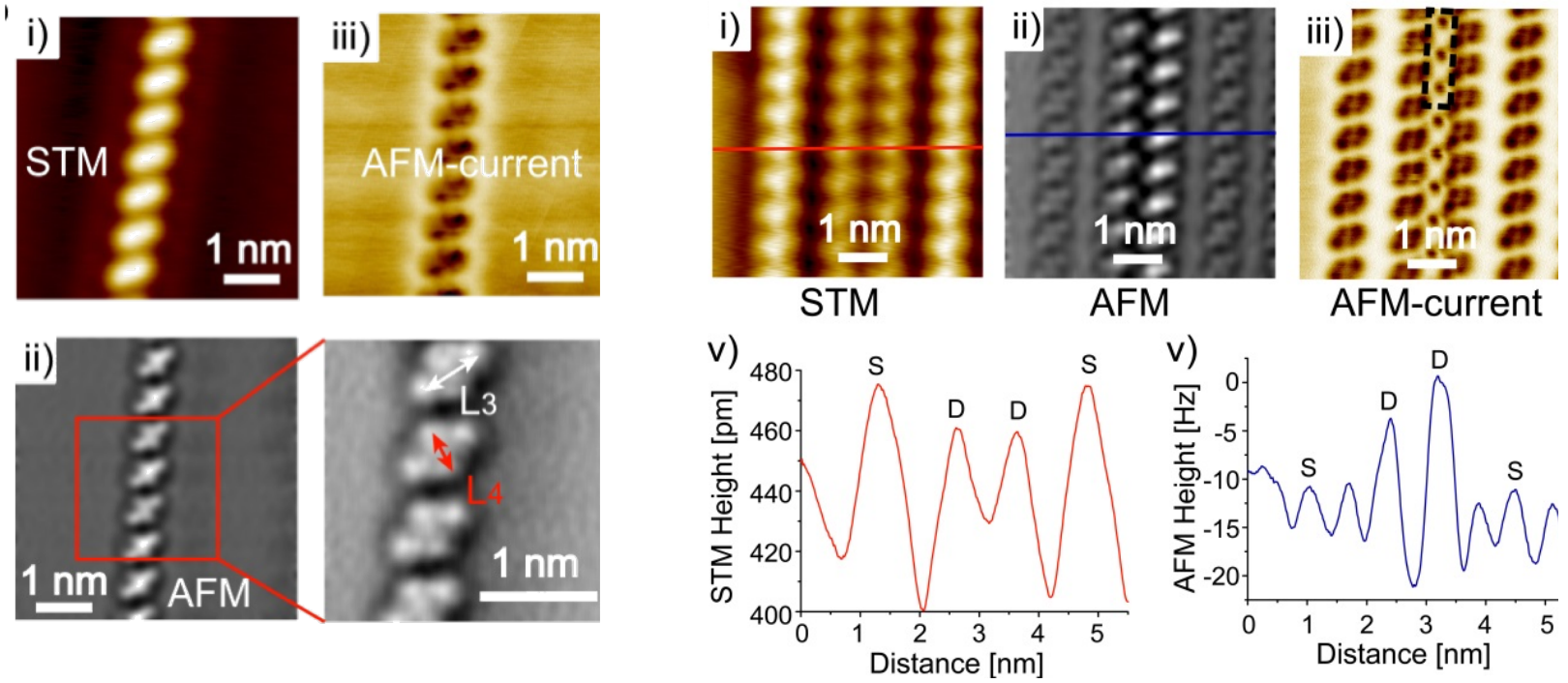
Gao, H.-Y.; Šekutor, M.; Liu, L.; Timmer, A.; Schreyer, H.; Mönig, H.; Amirjalayer, S.; Fokina, N. A.; Studer, A.; Schreiner, P. R.; Fuchs, H. *J. Am. Chem. Soc.* **2019**, *141*, 315.

Reactivity of a diamantane diacid on metal surfaces



- self-assembled DDA on a Cu(111) surface engaging in hydrogen bonding

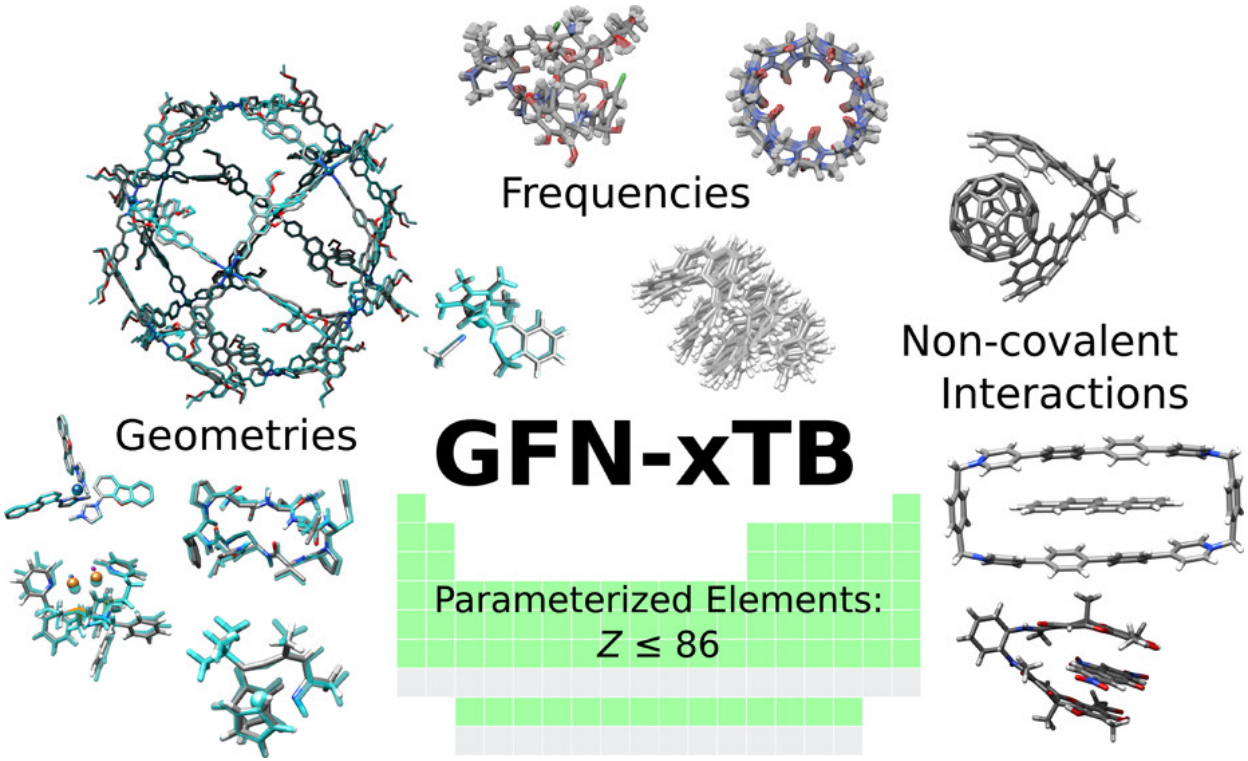
Gao, H.-Y.; Šekutor, M.; Liu, L.; Timmer, A.; Schreyer, H.; Mönig, H.; Amirjalayer, S.; Fokina, N. A.; Studer, A.; Schreiner, P. R.; Fuchs, H. *J. Am. Chem. Soc.* **2019**, *141*, 315.



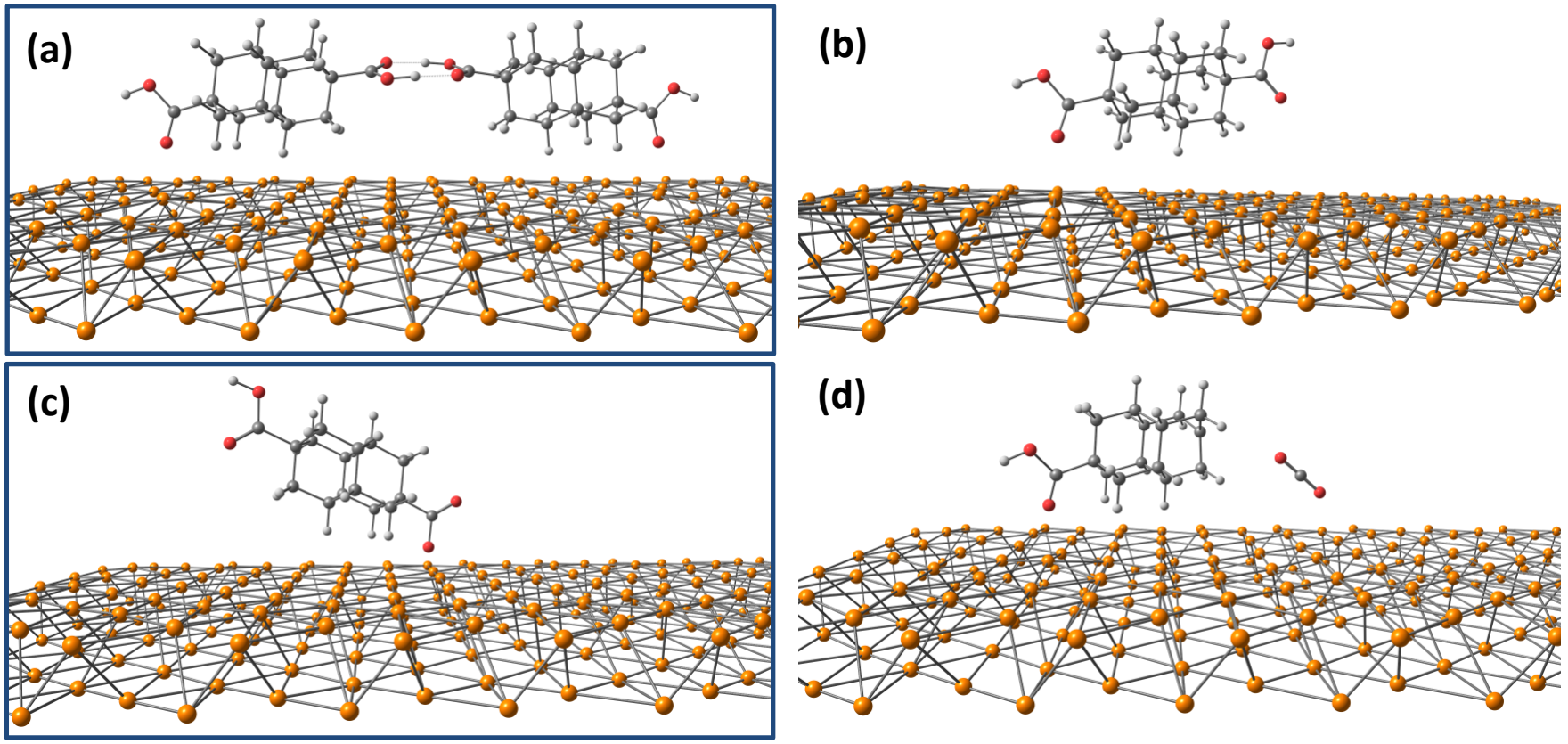
- formation of single chains on the Cu(111) surface => dehydrogenation as the first step upon thermal treatment
- formation of double chains on the Cu(111) surface => dehydroxylated DDA molecules forming double chains with a copper atom in the middle

Gao, H.-Y.; Šekutor, M.; Liu, L.; Timmer, A.; Schreyer, H.; Mönig, H.; Amirjalayer, S.; Fokina, N. A.; Studer, A.; Schreiner, P. R.; Fuchs, H. *J. Am. Chem. Soc.* **2019**, *141*, 315.

- semiempirical computations of DDA molecules on a Cu(111) surface using the GFN-xTB approach
- **GFN-xTB** = **G**eometry, **F**requency, **N**oncovalent, e**X**tended **T**ight **B**inding



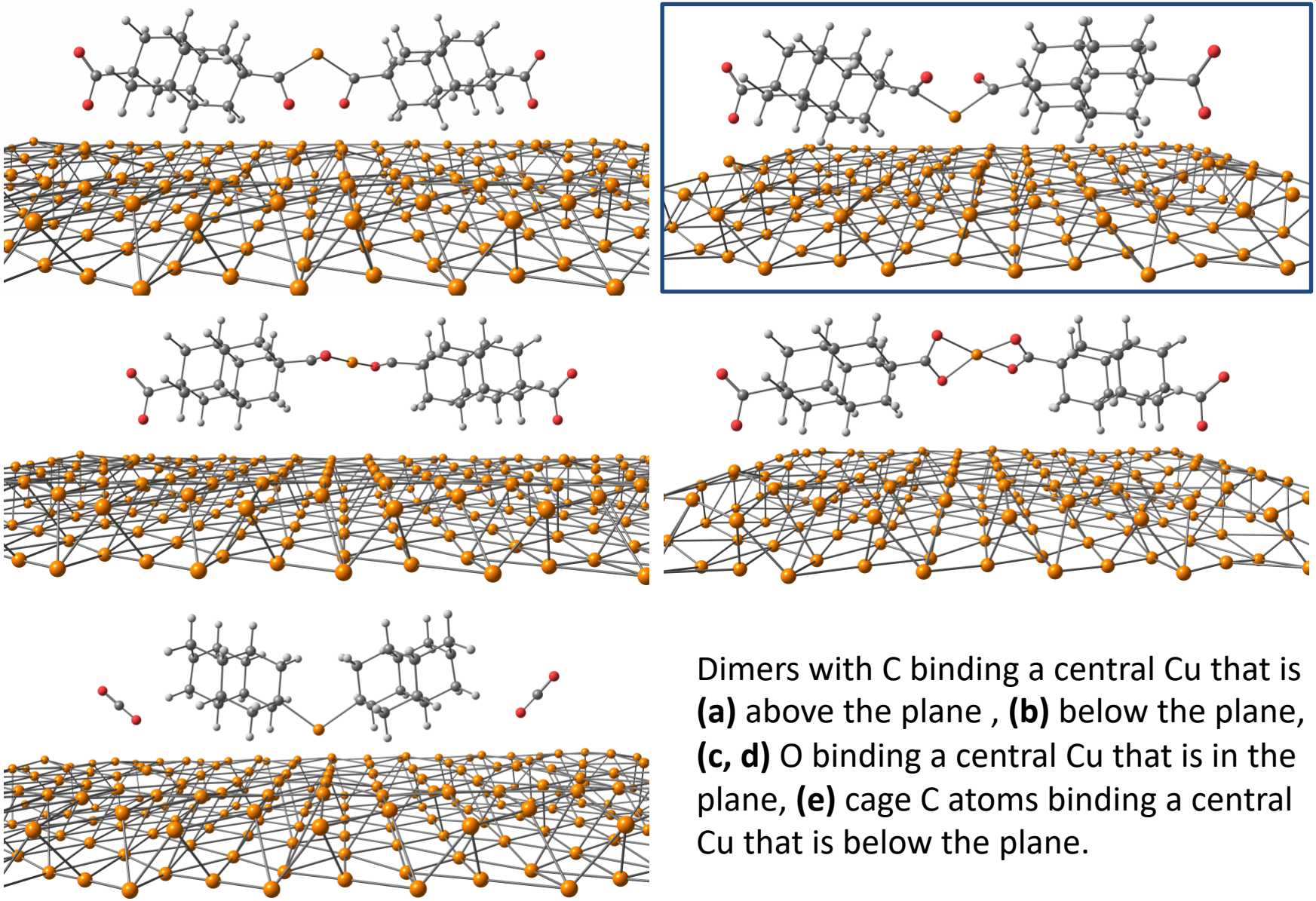
Grimme, S.; Bannwarth, C.; Shushkov, P. *J. Chem. Theory Comput.* **2017**, *13*, 1989.



(a) two DDA molecules engaging in hydrogen bonding, **(b)** individual DDA formed upon thermal treatment, **(c)** dehydrogenated DDA interacting with the copper surface *via* the carboxylate group, **(d)** dehydrogenated DDA interacting with the copper surface *via* the acid group.

Gao, H.-Y.; Šekutor, M.; Liu, L.; Timmer, A.; Schreyer, H.; Mönig, H.; Amirjalayer, S.; Fokina, N. A.; Studer, A.; Schreiner, P. R.; Fuchs, H. *J. Am. Chem. Soc.* **2019**, *141*, 315.

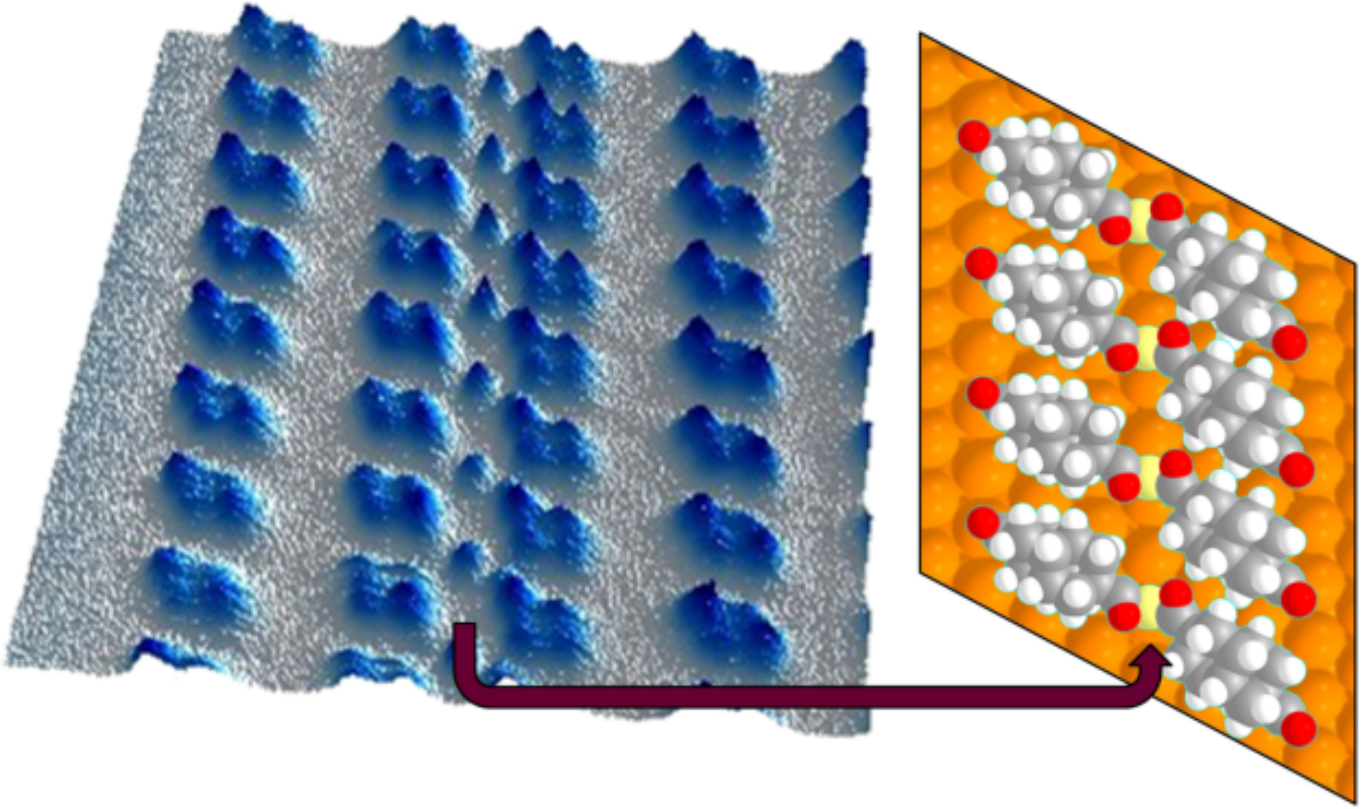
Reactivity of a diamantane diacid on metal surfaces



Dimers with C binding a central Cu that is **(a)** above the plane , **(b)** below the plane, **(c, d)** O binding a central Cu that is in the plane, **(e)** cage C atoms binding a central Cu that is below the plane.

Gao, H.-Y.; Šekutor, M.; Liu, L.; Timmer, A.; Schreyer, H.; Mönig, H.; Amirjalayer, S.; Fokina, N. A.; Studer, A.; Schreiner, P. R.; Fuchs, H. *J. Am. Chem. Soc.* **2019**, *141*, 315.

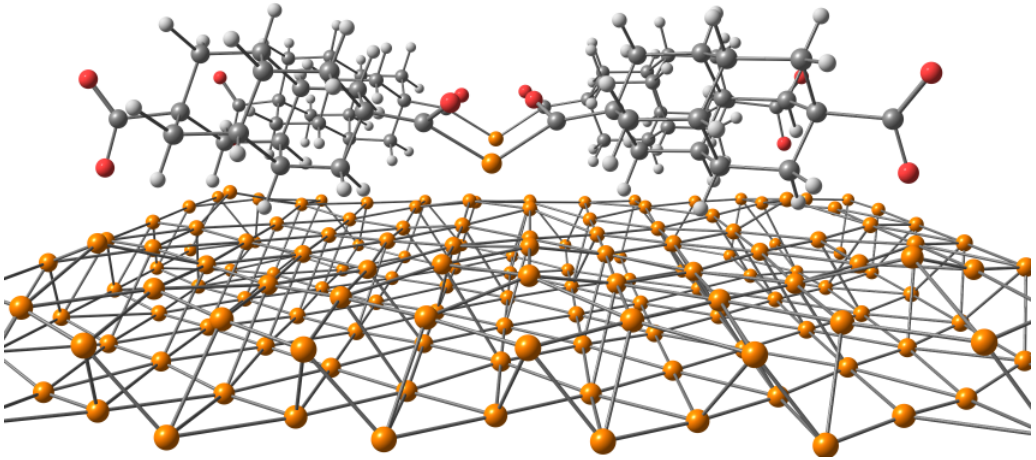
- double chain on the Cu(111) surface

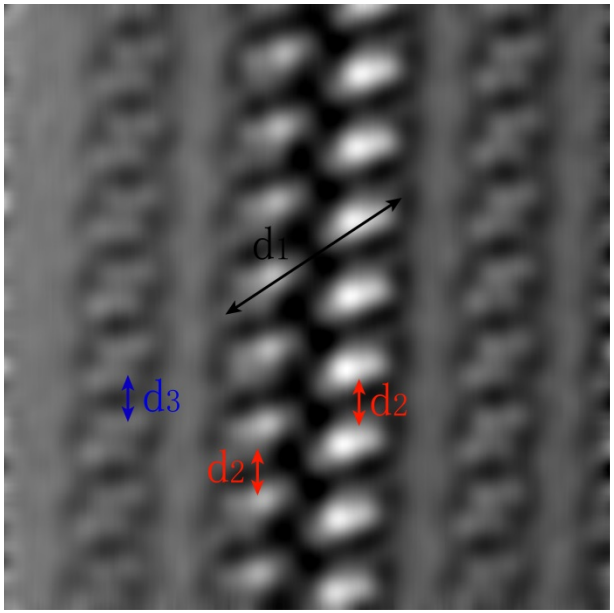


- nanowire consisting of a row of single copper atoms

Gao, H.-Y.; Šekutor, M.; Liu, L.; Timmer, A.; Schreyer, H.; Mönig, H.; Amirjalayer, S.; Fokina, N. A.; Studer, A.; Schreiner, P. R.; Fuchs, H. *J. Am. Chem. Soc.* **2019**, *141*, 315.

- metallic chain anchored by DDA scaffolds on a Cu(111) surface





Computed structure

d_1(**C**OOH-**C**OOH) = 1.85 nm

d_2(**C**H-**C**H) = 0.38 nm

AFM image of double chains

d_1 = 1.85 ± 0.02 nm

d_2 = d_3 = 0.37 ± 0.02 nm

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Summary

- self-assembly of [121]tetramantanes on metal surfaces driven by London dispersion => uniform 2D lattice
- dispersion stabilization less for [123]tetramantanes => homochiral and heterochiral pairs on the surface
- tilting of tetramantane molecules => interaction with the surface
- DDA molecules form a 2D network of hydrogen bonds
- upon thermal annealing DDA undergoes dehydrogenation and then dehydroxylation
- formation of single and double chains
- molecular copper nanowire anchored by DDA scaffolds

Acknowledgements

Prof. Dr. Kata Majerski
All members of LSOC

Prof. Dr. Peter R. Schreiner
Dr. Natalie A. Fokina
Prof. Dr. André Schirmeisen
Dr. Daniel Ebeling
Prof. Dr. Harald Fuchs
Dr. Hong-Ying Gao

HrZZ
Croatian Science Foundation

Unterstützt von / Supported by
Alexander von Humboldt
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