N-heterocyclic carbene adsorption and self-assembly on Au(111): Fine-tuning the binding mode

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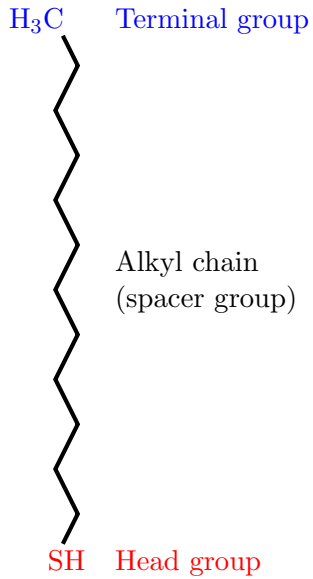
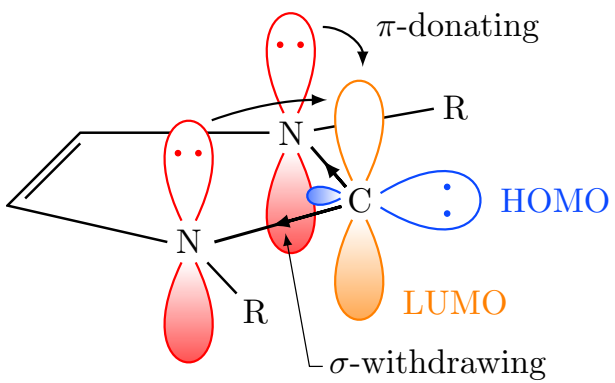
Background

- Surface functionalization is frequently achieved using self-assembled monolayers (SAMs) of alkanethiols [1, 2]
  - Controlled adjustment of the terminal functional group
  - Applications include lab-on-chip sensors [3, 4]
  - Thermal and oxidative instability can limit commercial use [5, 6]



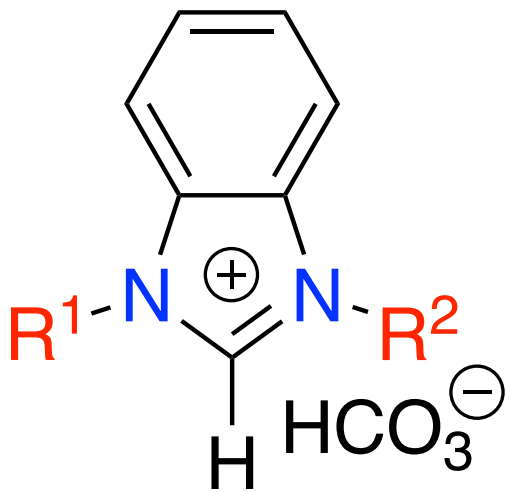
- *N*-heterocyclic carbenes (NHCs) are alternative, possibly superior, surface anchors [6, 7, 8]



Methods

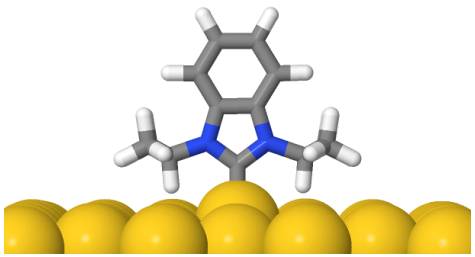
- Low-temperature scanning tunnelling microscopy (STM) study of NHC adsorption and self-assembly on Au(111)
- Structurally different NHCs to determine factors that control orientation, ordering, mobility, and adatom involvement

- NHCs SAMs prepared in vacuum by flash deposition of the hydrogen carbonate salt
- Constant-current STM imaging performed at 77 K

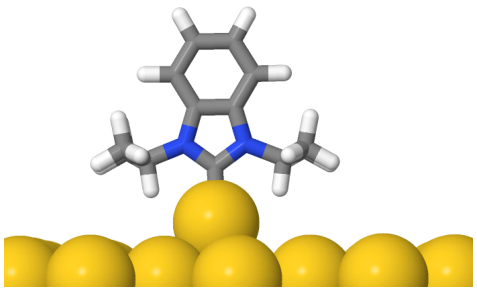


NHC adsorption modes on Au(111)

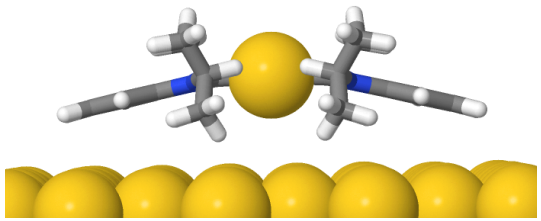
- NHCs adopt multiple distinct binding modes on Au(111)



Surface-bound NHC



Adatom-bound NHC

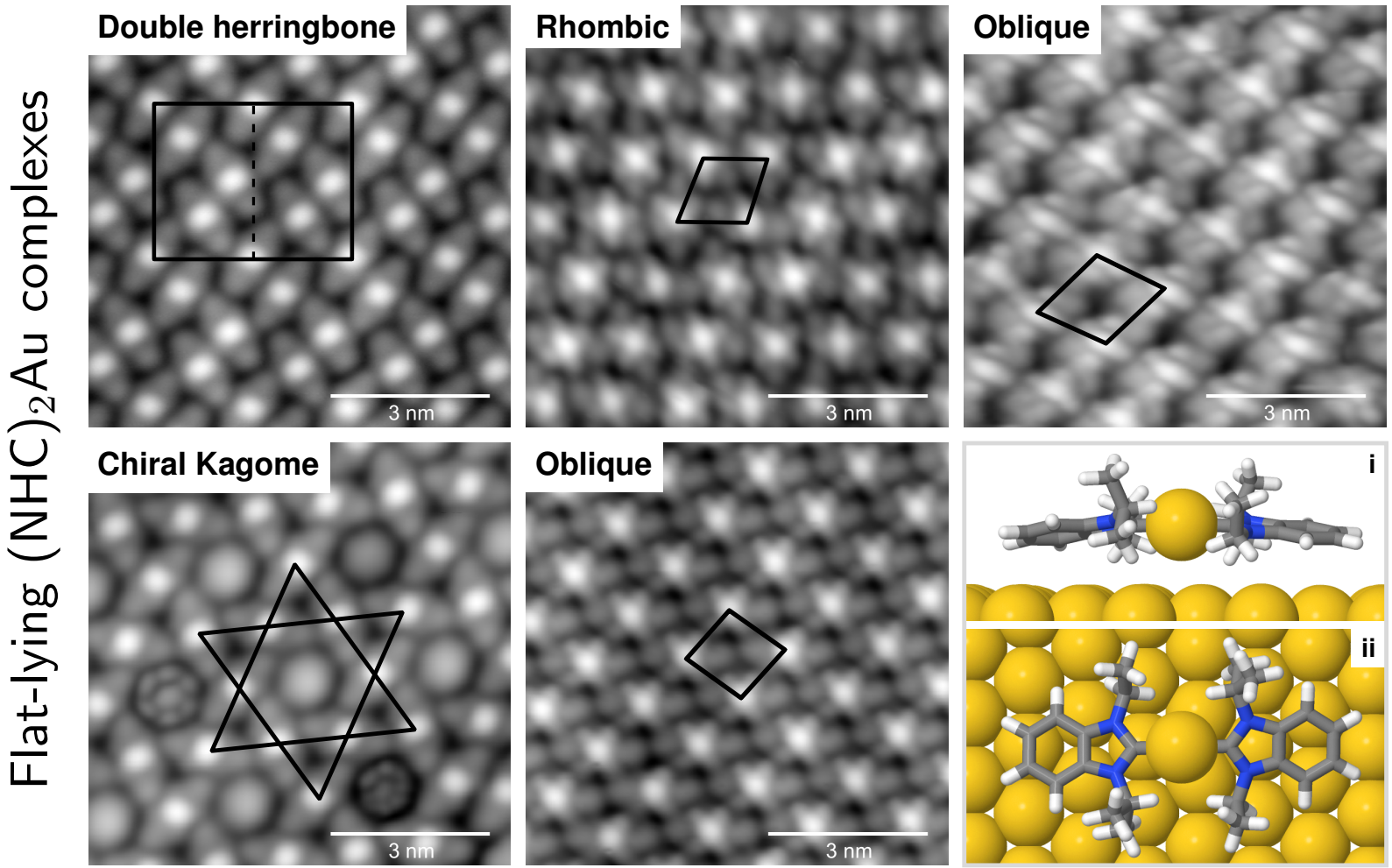


$(NHC)_2Au$ complex

- Binding and self-assembly dependent on
  - Wingtip structure
    - Substituents on the nitrogen atoms
  - Surface coverage
    - Monitored from sub-monolayer up to saturation
  - Temperature
    - Substrate temperature during deposition and upon post-deposition annealing

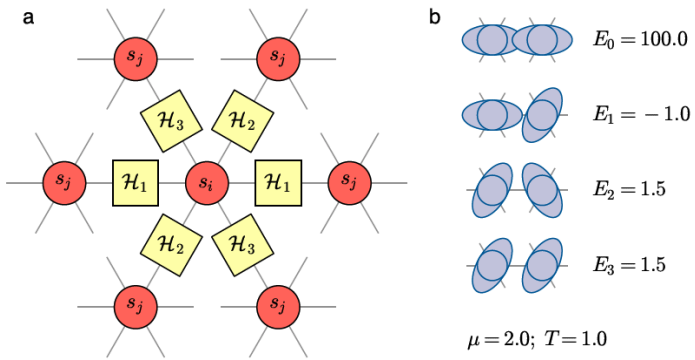
Effect of wingtip structure

- SAMs prepared on room-temperature Au(111) surfaces



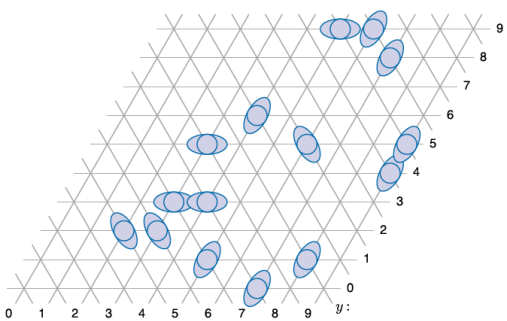
Effect of wingtip structure (cont.)

- Monte-Carlo simulation of $(NHC)_2Au$ complexes
  - Discretized interaction model
  - Move probability given by the Boltzmann distribution

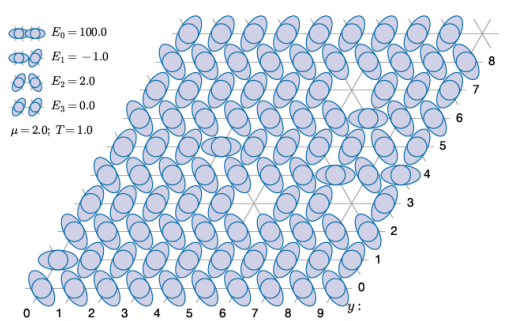


- Aim to investigate (and predict) self-assembled structures

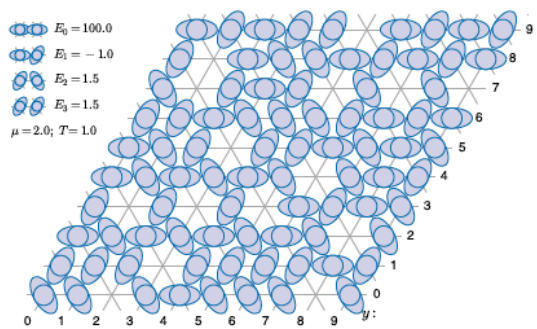
System state



Herringbone pattern

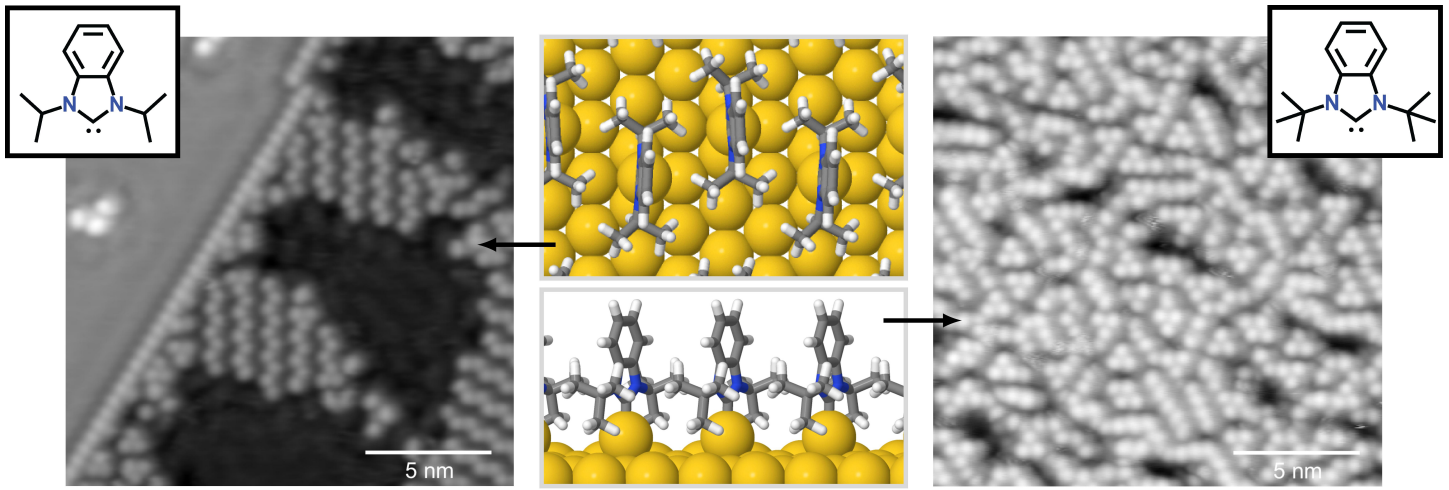


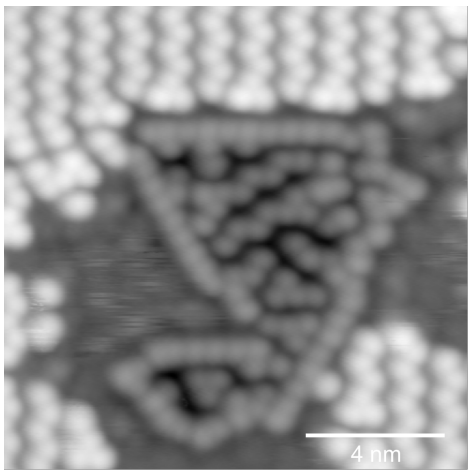
Kagome pattern



Effect of wingtip structure (cont.)

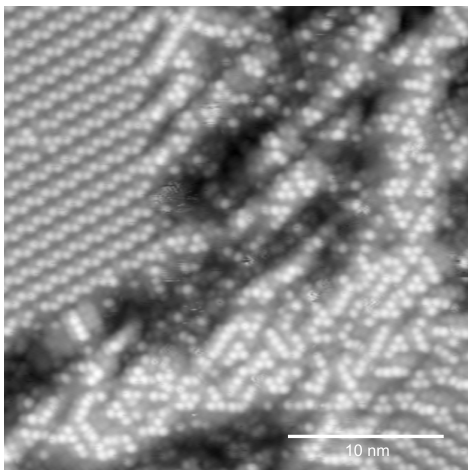
- NHCs with bulkier wingtip groups (*i*Pr, *t*Bu) stand upright on adatoms





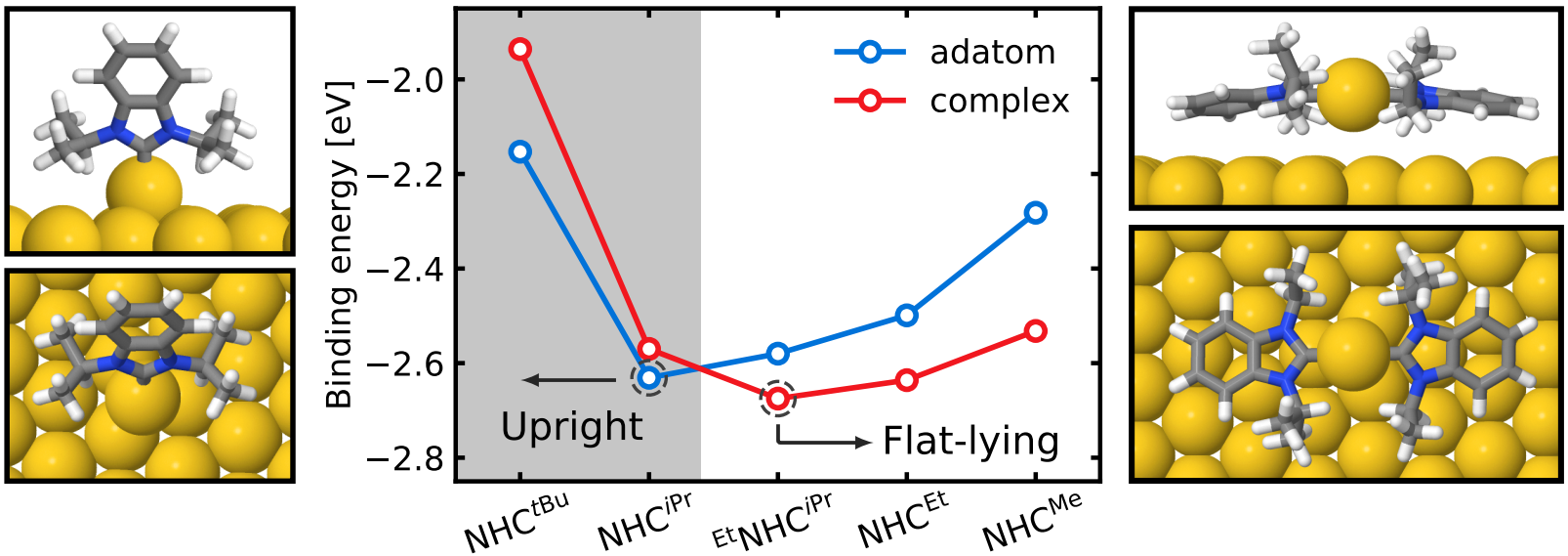
Experimental evidence includes

- Vacancy islands
- Lattice structure
- Co-deposition experiment
- Apparent height comparison at steps



Effect of wingtip structure (cont.)

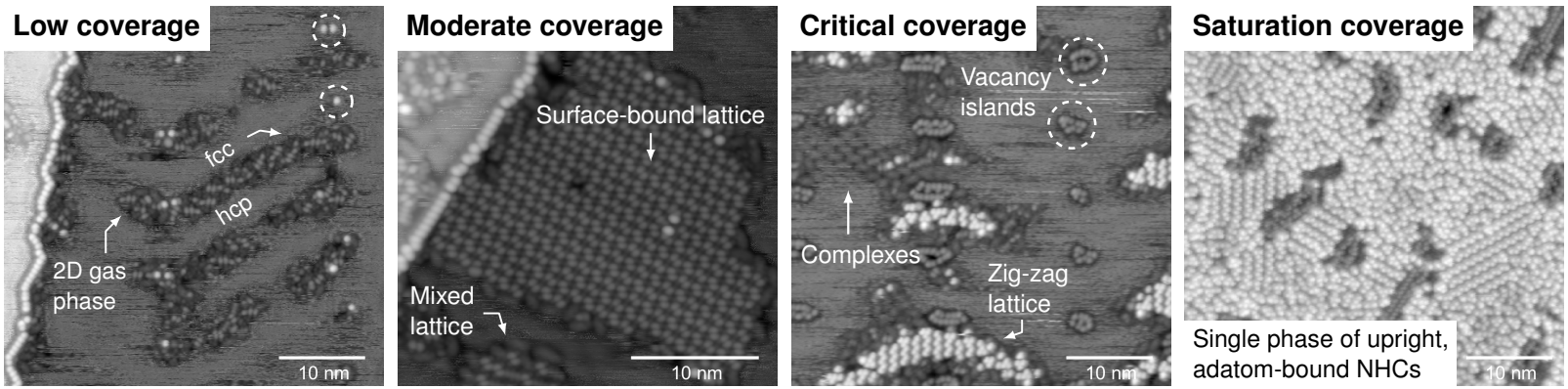
- Experimental observations consistent with *ab initio* DFT calculations



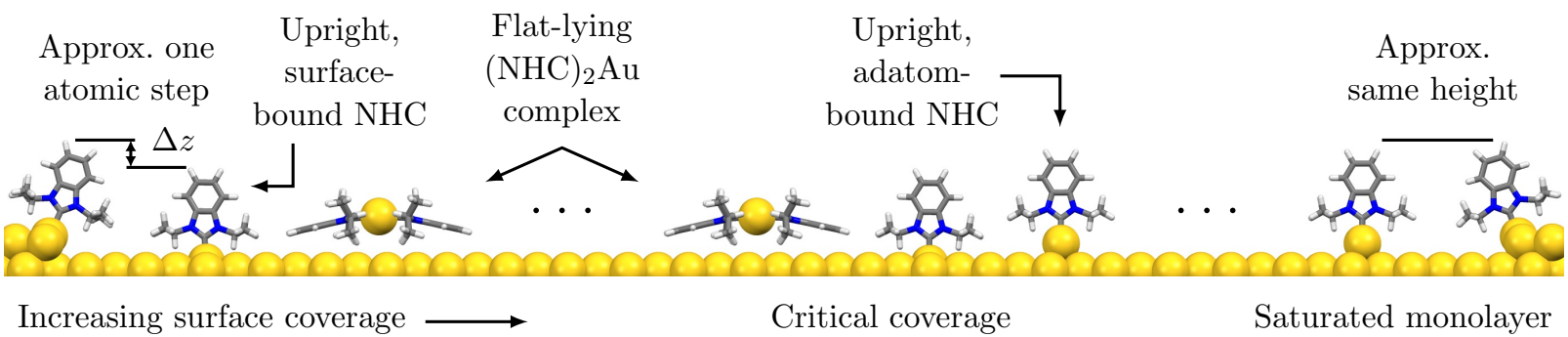
- Fine-tuning of the wingtip substituents provides flexibility in controlling the binding mode
  - Surface coverage and substrate temperature are also critical factors

Effect of surface coverage

- NHC binding also depends on the surface coverage
  - Associated with the production of Au adatoms

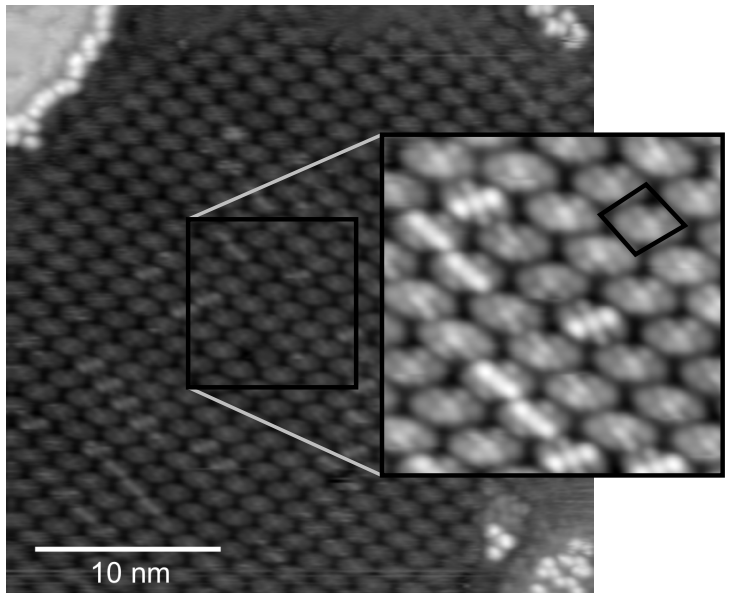


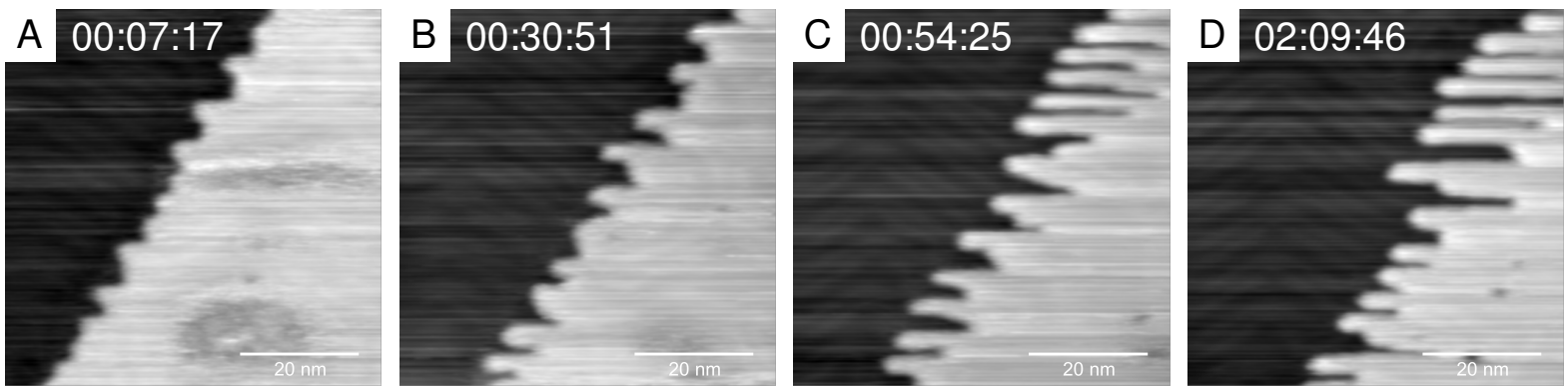
- Coverage-dependent NHC$^{i\mathrm{Pr}}$ adsorption configurations



Effect of temperature

- Heating promotes
  - Ordering
  - Healing of vacancy islands
  - Irreversible formation of $(NHC)_2Au$ complexes
- Deposition onto LN_2-cooled surfaces
  - Precursor phase resulting in magic finger growth





Conclusions and future outlook

- Conclusions
  - NHC adsorption critically depends on wingtip structure, surface coverage and substrate temperature
  - These factors determine NHC orientation, ordering, mobility, and adatom involvement
  - Understanding, and the ability to tune, the binding mode may important for future NHC-SAM applications
- Recommendations
  - Low-temperature STM imaging
  - Complementary imaging modalities
  - Chemical/entropic control of the upright adsorption mode
    - Crystal surface
    - NHC structure
    - Deposition method

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  - Roberto Hiroki Miwa
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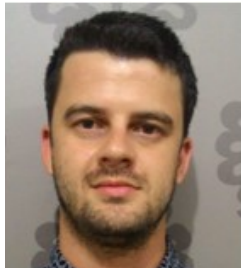
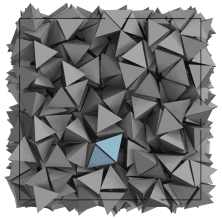
  - Greg van Anders









References

[1] C. D. Bain, E. B. Troughton, Y. T. Tao, J. Evall, G. M. Whitesides, and R. G. Nuzzo. Formation of monolayer films by the spontaneous assembly of organic thiols from solution onto gold. *Journal of the American Chemical Society*, 111(1):321–335, 1989.

[2] J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, and G. M. Whitesides. Self-assembled monolayers of thiolates on metals as a form of nanotechnology. *Chemical Reviews*, 105(4):1103–1169, 2005.

[3] X. Fan, I. M. White, S. I. Shopova, H. Zhu, J. D. Suter, and Y. Sun. Sensitive optical biosensors for unlabeled targets: A review. *Analytica Chimica Acta*, 620(1-2):8–26, 2008.

[4] X. D. Hoa, A. G. Kirk, and M. Tabrizian. Towards integrated and sensitive surface plasmon resonance biosensors: A review of recent progress. *Biosensors and Bioelectronics*, 23(2):151–160, 2007.

[5] C. Vericat, M. E. Vela, G. Benitez, P. Carro, and R. C. Salvarezza. Self-assembled monolayers of thiols and dithiols on gold: New challenges for a well-known system. *Chemical Society Reviews*, 39(5):1805–1834, 2010.

[6] C. M. Crudden, J. H. Horton, I. I. Ebralidze, O. V. Zenkina, A. B. McLean, B. Drevniok, Z. She, H.-B. Kraatz, N. J. Mosey, T. Seki, E. C. Keske, J. D. Leake, A. Rousina-Webb, and G. Wu. Ultra stable self-assembled monolayers of N-heterocyclic carbenes on gold. *Nature Chemistry*, 6(5):409–414, 2014.

[7] C. M. Crudden, J. H. Horton, M. R. Narouz, Z. Li, C. A. Smith, K. Munro, C. J. Baddeley, C. R. Larrea, B. Drevniok, B. Thanabalasingam, A. B. McLean, O. V. Zenkina, I. I. Ebralidze, Z. She, H.-B. Kraatz, N. J. Mosey, L. N. Saunders, and A. Yagi. Simple direct formation of self-assembled N-heterocyclic carbene monolayers on gold and their application in biosensing. *Nature Communications*, 7, 2016.

[8] G. Wang, A. Rühling, S. Amirjalayer, M. Knor, J. B. Ernst, C. Richter, H.-J. Gao, A. Timmer, H.-Y. Gao, N. L. Doltsinis, F. Glorius, and H. Fuchs. Ballbot-type motion of N-heterocyclic carbenes on gold surfaces. *Nature Chemistry*, 9(2):152–156, 2017.