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

Ryan Groome

2021 CAP Virtual Congress

Department of Physics, Engineering Physics, and Astronomy
Queen’s University

Supervisor: Dr. Alastair McLean

May 27, 2021
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
  - \((\text{NHC})_2\text{Au}\) 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
  - $\text{NHC}^{\text{Me}}$
  - $\text{NHC}^{\text{Et}}$
  - $\text{EtNHC}^{\text{iPr}}$

**Flat-lying (NHC)$_2$Au complexes**

- Double herringbone
- Rhombic
- Oblique
- Chiral Kagome
- Oblique

**8.0 x 8.0 nm$^2$**
Effect of wingtip structure (cont.)

- Monte-Carlo simulation of \((\text{NHC})_2\text{Au}\) complexes
  - Discretized interaction model
  - Move probability given by the Boltzmann distribution

- Aim to investigate (and predict) self-assembled structures
Effect of wingtip structure (cont.)

- NHCs with bulkier wingtip groups (iPr, tBu) 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\textsuperscript{iPr} adsorption configurations

Approx. one atomic step  \[ \Delta z \]  Upright, surface-bound NHC

Flat-lying (NHC)\textsubscript{2}Au complex

Upright, adatom-bound NHC

Increasing surface coverage  \[ \rightarrow \]  Critical coverage

Saturated monolayer

Low coverage  Moderate coverage  Critical coverage  Saturation coverage

2D gas phase

Mixed lattice

Surface-bound lattice

Vacancy islands

Complexes

Zig-zag lattice

Single phase of upright, adatom-bound NHCs
Effect of temperature

- Heating promotes
  - Ordering
  - Healing of vacancy islands
  - Irreversible formation of (NHC)$_2$Au 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 be 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
A special thanks to many outstanding collaborators!

- **My group (STM)**
  - Queen’s Physics
    - Alex Inayeh
    - Alastair McLean

- **NHC synthesis**
  - Queen’s Chemistry
    - Ishwar Singh
    - Alex Veinot
    - Cathleen Crudden

- **Density functional theory**
  - UFU Physics
    - Felipe Crasto de Lima
    - Roberto Hiroki Miwa

- **Statistical mechanics**
  - UM, Queen’s Physics
    - Andrei Klishin
    - Greg van Anders
References


