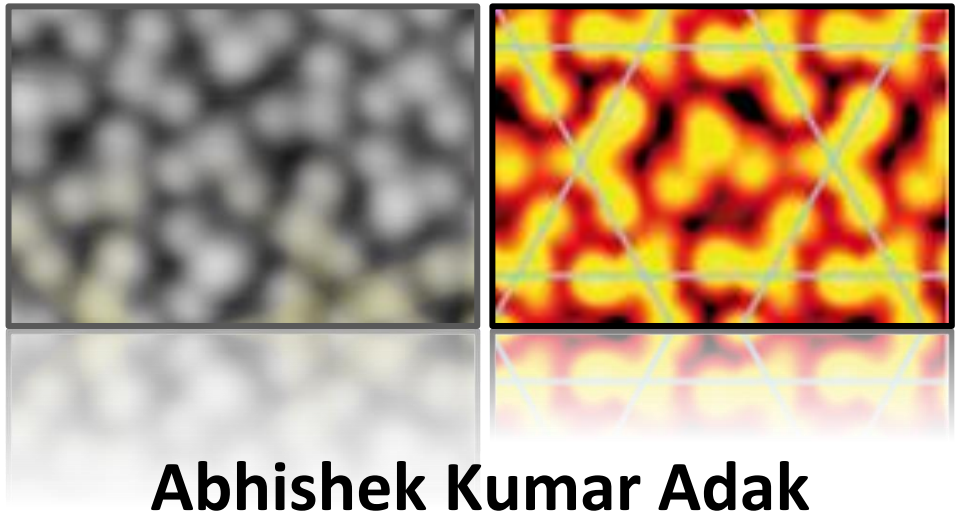
Insights from density functional theory into the formation and rotation of an enantiospecific assembly of molecular raffle wheels

15th March, 2022



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Rotation in an Enantiospecific Self-Assembled Array of Molecular Raffle Wheels

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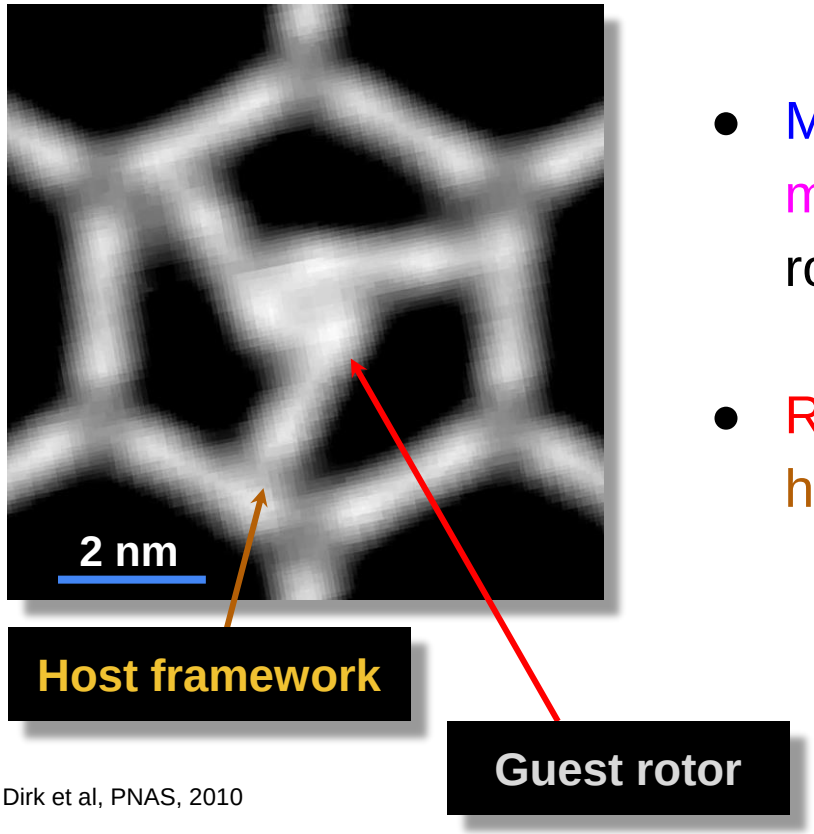
Computational resources: TUE-CMS, NSM-ParamYukti.

Molecular rotors

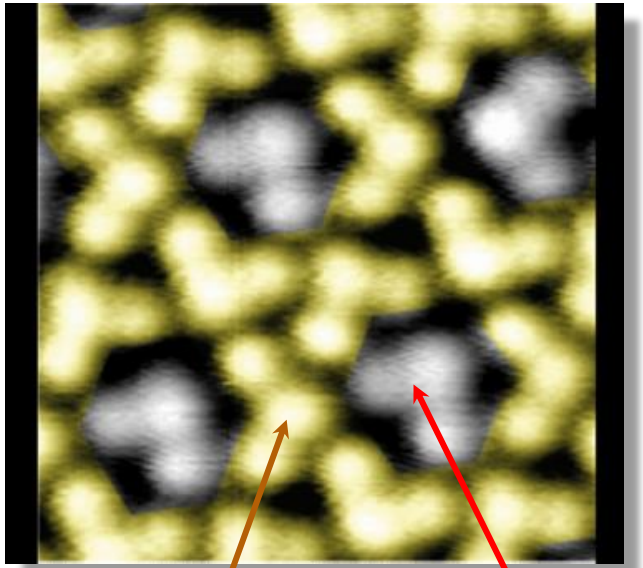
Artificially synthesized molecular rotor



Dirk et al, PNAS, 2010

- Molecular rotor is a class of molecular motors which is capable of continuous rotation under an energy input.
- Rotors are guest molecules rotating inside a host framework.

Our system; BPP-COOH on Ag(111)



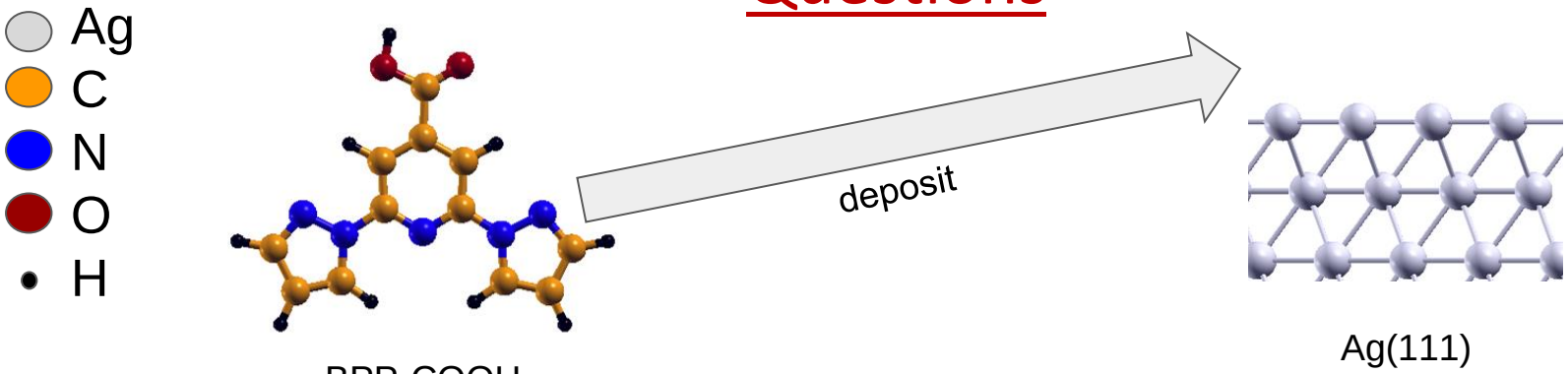
Host framework

Guest rotor

(Colors added to aid visualisation)

- Both host and guest molecules are the same species (BPP-COOH).
- Host molecules get deprotonated, form a kagome network and are stationary.
- Guest molecules remain protonated, occupy the cavities of the host framework and rotate.

Questions



- Which isomer of BPP-COOH is found on the surface?
- What is the energy landscape for rotation, and what determines it?
- What if the guest molecules are also deprotonated?
- What is the origin of observed enantiospecificity?

Computational details

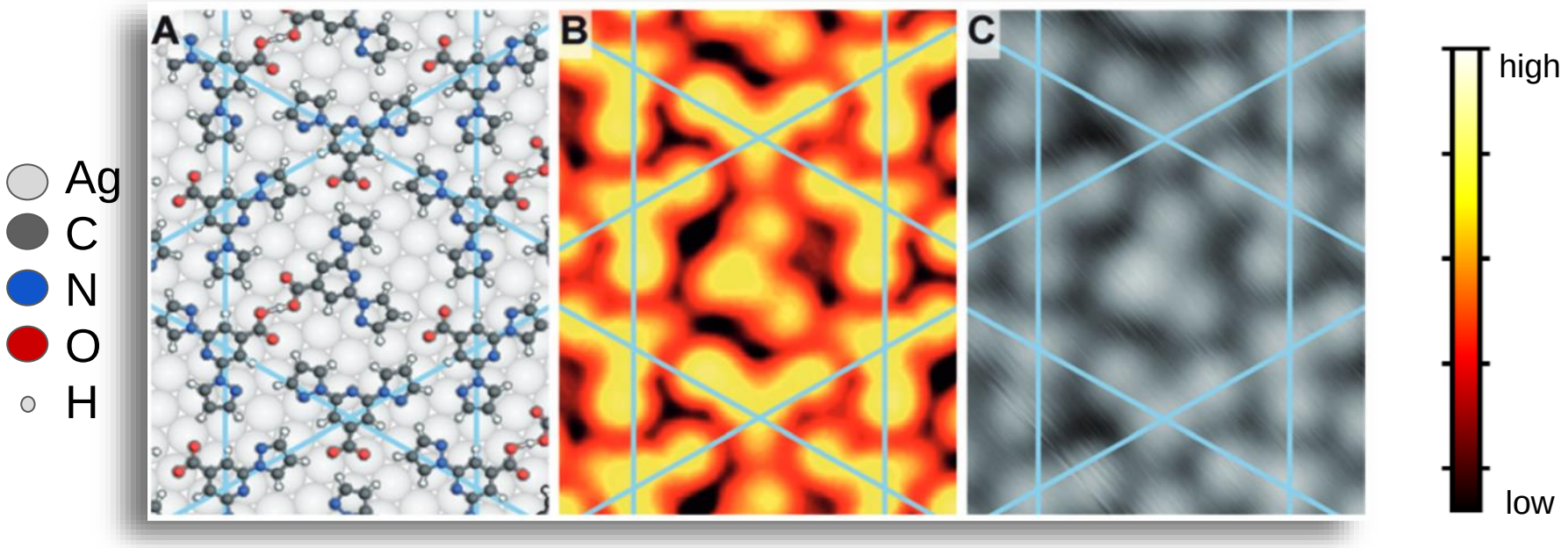
- Density functional theory method.
- Quantum ESPRESSO package, PWscf.
- Plane wave basis set,

  wavefunction cutoff = 35 Ry

  charge density cutoff = 350 Ry

- Ultrasoft pseudopotentials.
- Exchange-Correlation interactions: PBE-GGA
- k-point sampling: zone centre only.
- Marzari-Vanderbilt smearing, width = 0.005 Ry.
- Grimme-D2 method to incorporate dispersion interactions.

Structure: agreement between expt and calculation



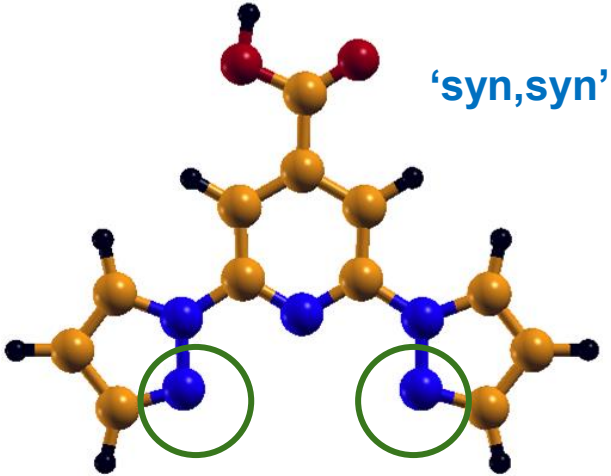
‘Global Minimum’ from DFT

Simulated STM

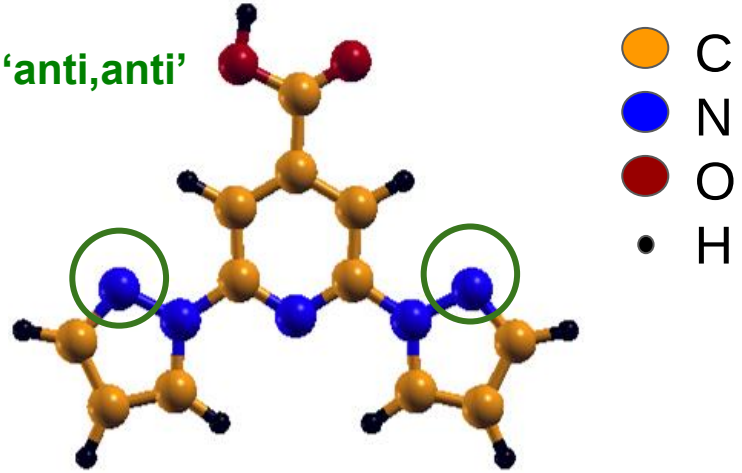
Experiment STM

Q1: Which isomer of BPP-COOH is found on the surface?

Two possibilities for structural isomer found on Ag(111):



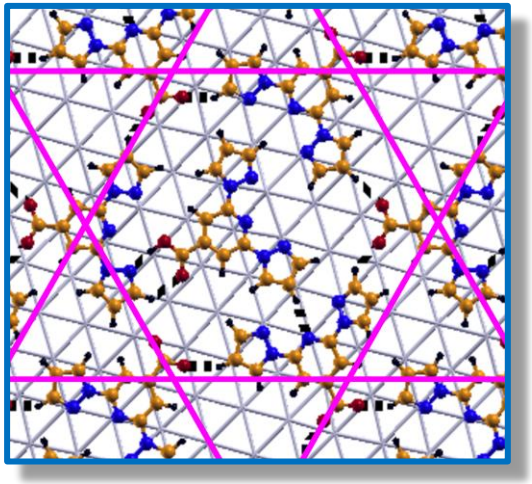
Found in some Fe coordinated complexes



Favored in gas phase

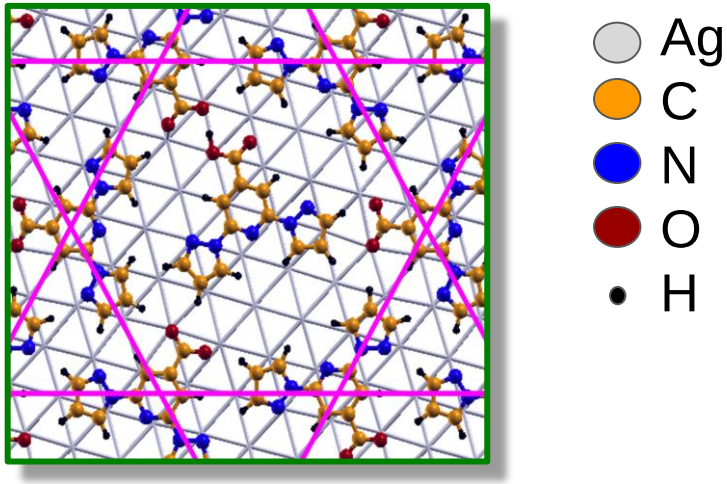
Q1: DFT energetics & geometry support ‘anti,anti’ isomer on Ag(111)

‘syn,syn’



Higher in energy

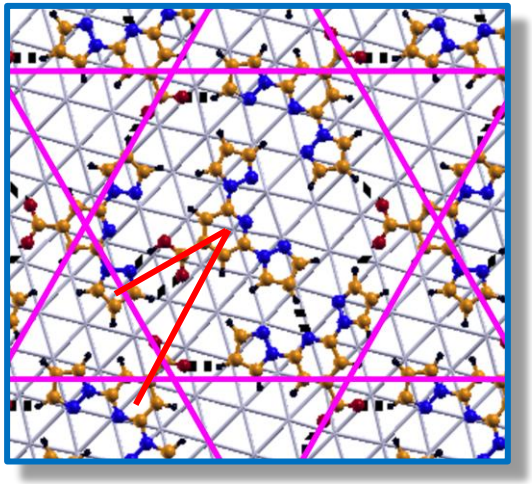
‘anti,anti’



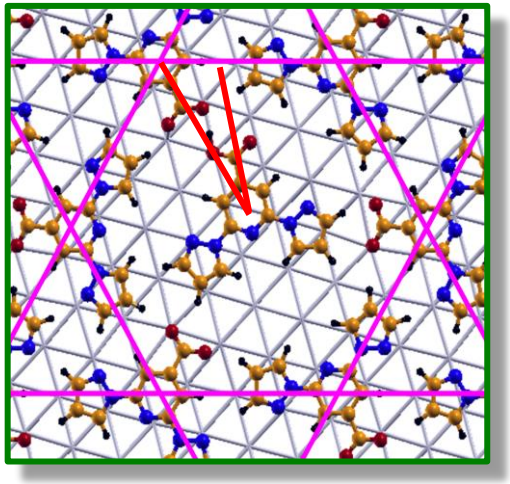
Lower in energy by 1.84 eV/cell

Q1: DFT energetics & geometry support ‘anti,anti’ isomer on Ag(111)

‘syn,syn’



‘anti,anti’



Higher in energy

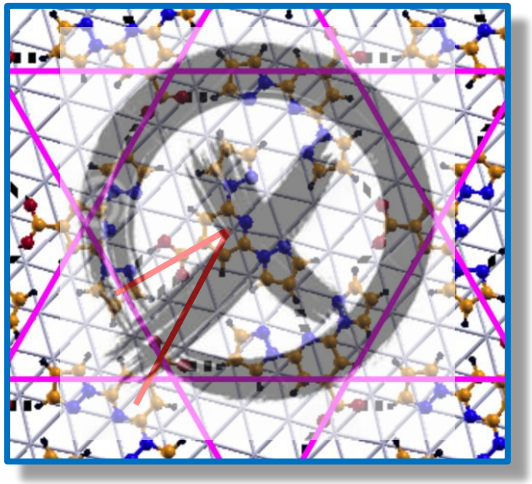
$\theta_{min} = 32^{o}$: doesn’t match expt.

Lower in energy by 1.84 eV/cell

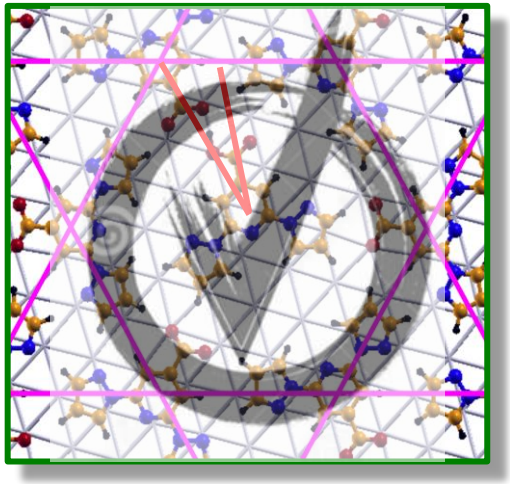
$\theta_{min} = 15^{o}$: matches expt.

Q1: DFT energetics & geometry support ‘anti,anti’ isomer on Ag(111)

‘syn,syn’



‘anti,anti’



Ag
C
N
O
H

Higher in energy

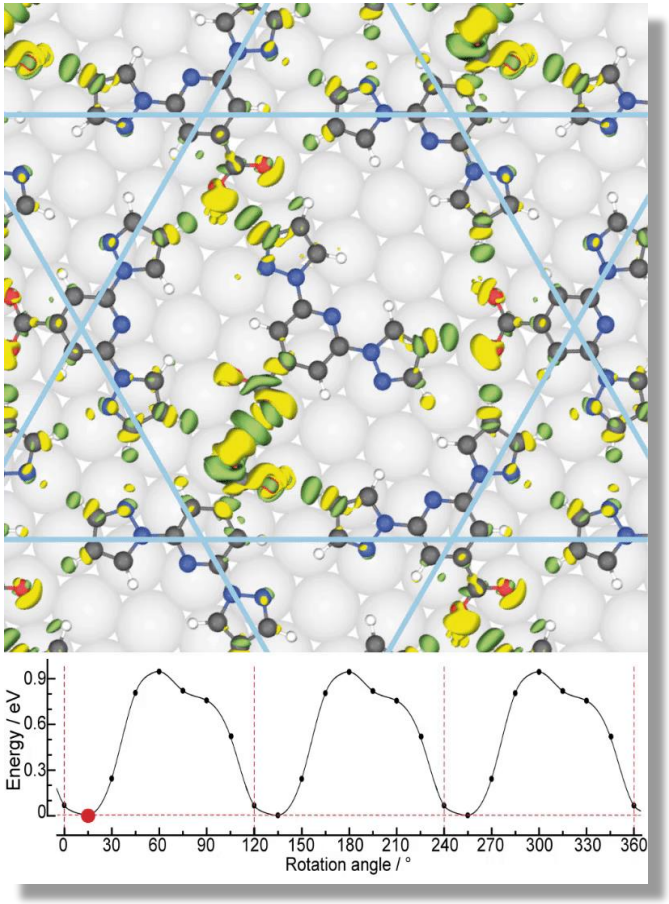
$\theta_{min} = 32^{o}$: doesn’t match expt.

Lower in energy by 1.84 eV/cell

$\theta_{min} = 15^{o}$: matches expt.

Q2: Rotational energy landscape determined by H-bonds

Ag
C
N
O
H

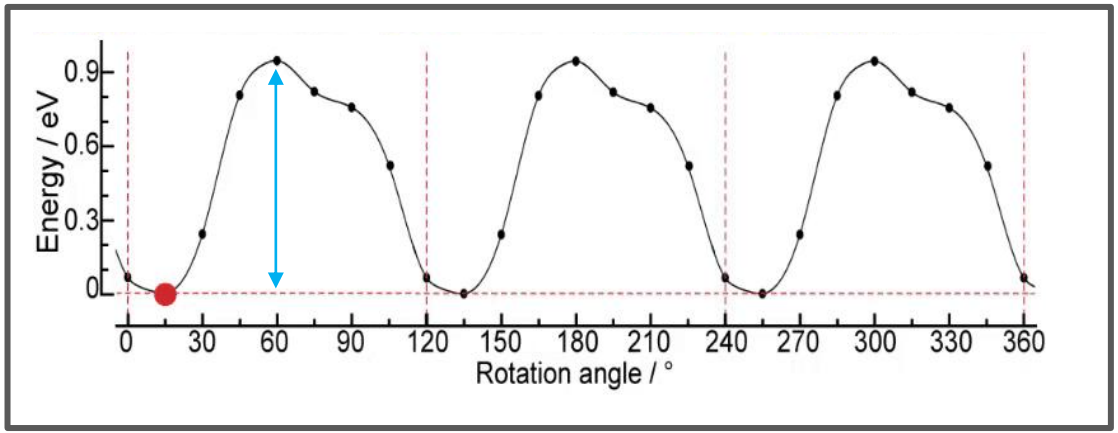


As guest molecule rotates, it makes & breaks hydrogen bonds (alternating green & yellow lobes) with host network.

H-bonds made: energy low
H-bonds absent: energy high

Q2: Theory & expt agree for rotational energy barrier

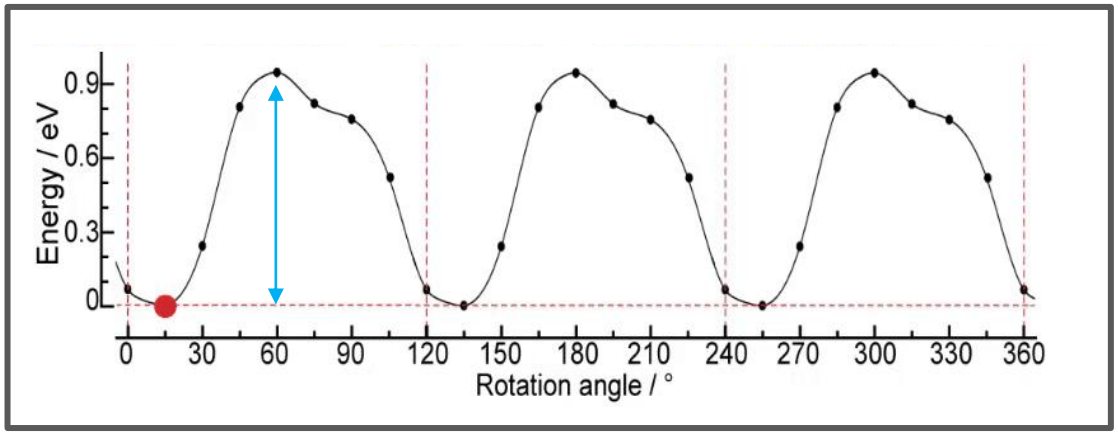
Rotation energy barrier from DFT = 0.944 eV

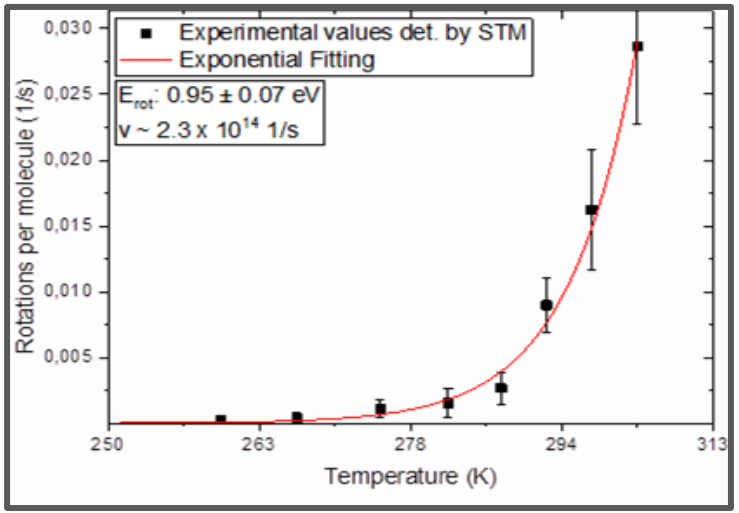


Q2: Theory & expt agree for rotational energy barrier

Rotation energy barrier from DFT = 0.944 eV

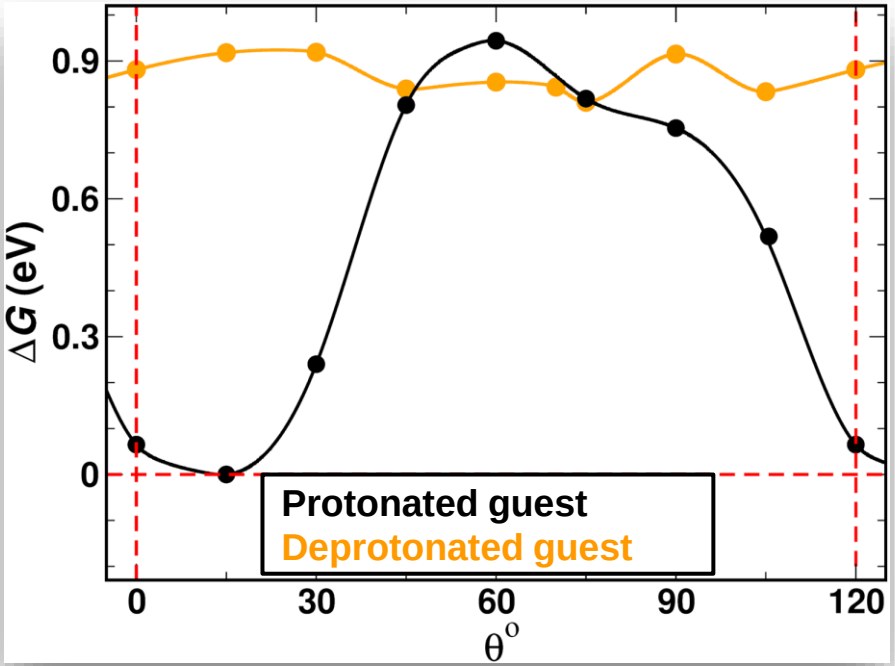
Rotation energy barrier from expt = 0.95 ± 0.07 eV





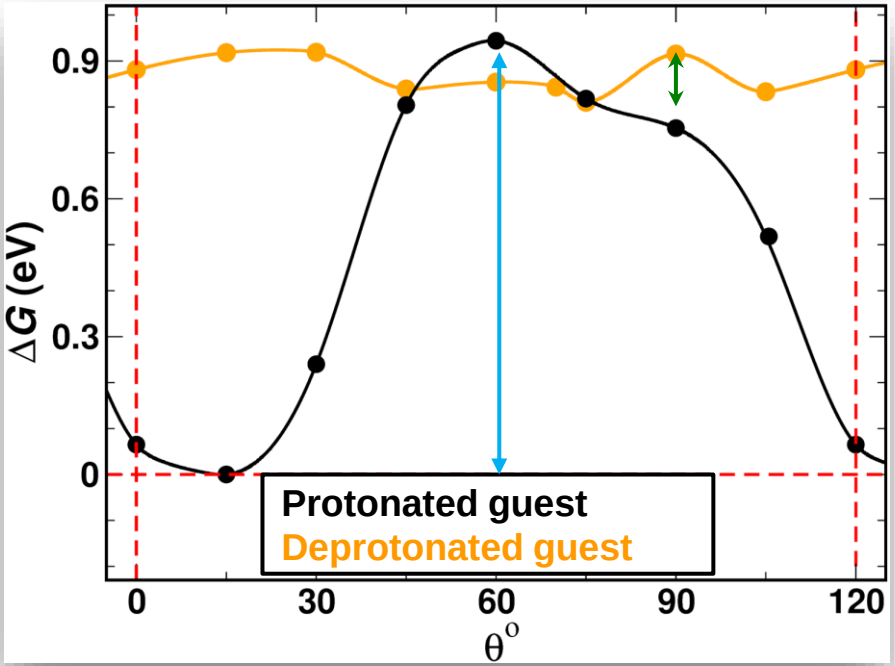
Excellent agreement between calculation and expt.

Q3: What if guest is also deprotonated?



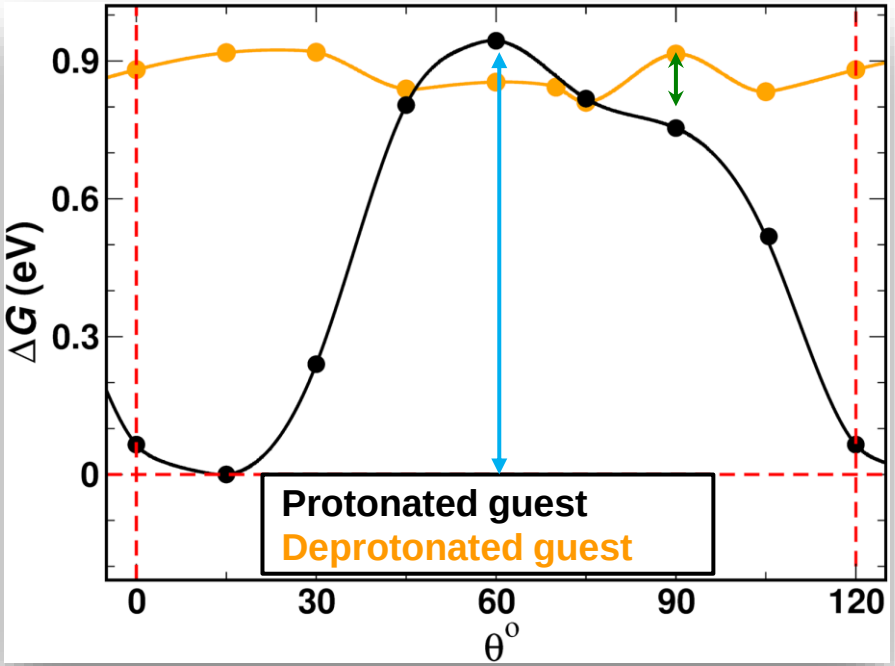
- Deprotonated guest higher in energy than protonated guest.

Q3: What if guest is also deprotonated?



- Deprotonated guest higher in energy than protonated guest.
- However deprotonated rotational energy barrier is much lower than protonated rotational barrier.

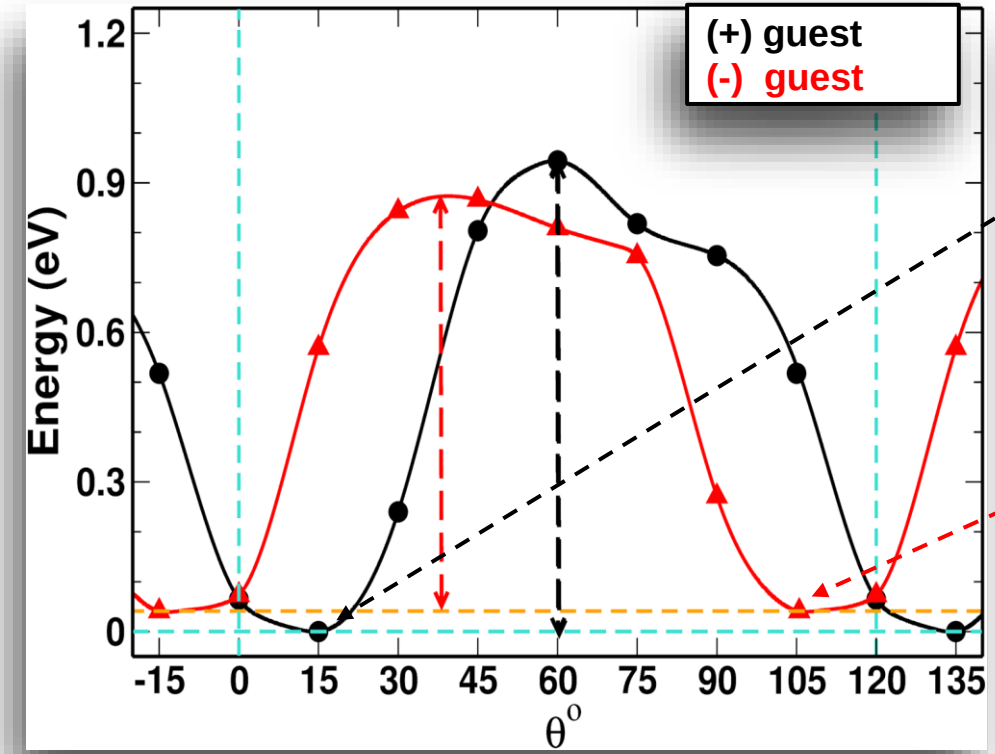
Q3: What if guest is also deprotonated?

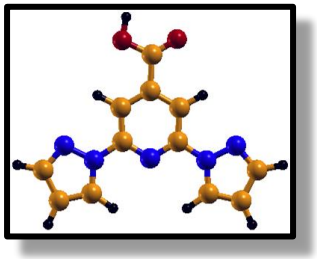


- Deprotonated guest higher in energy than protonated guest.
- However deprotonated rotational energy barrier is much lower than protonated rotational barrier.
- Deprotonated guests may explain a few rapidly rotating rotors seen in experiment.

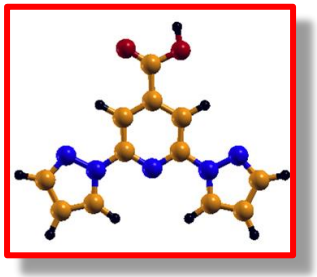
Q4: Enantiospecificity arises from twist angle between Ag(111) & host kagome network

Energy landscape for rotation of guest





(+) enantiomer is lower in energy by 41 meV/molecule



(-) enantiomer is higher in energy.

Conclusions

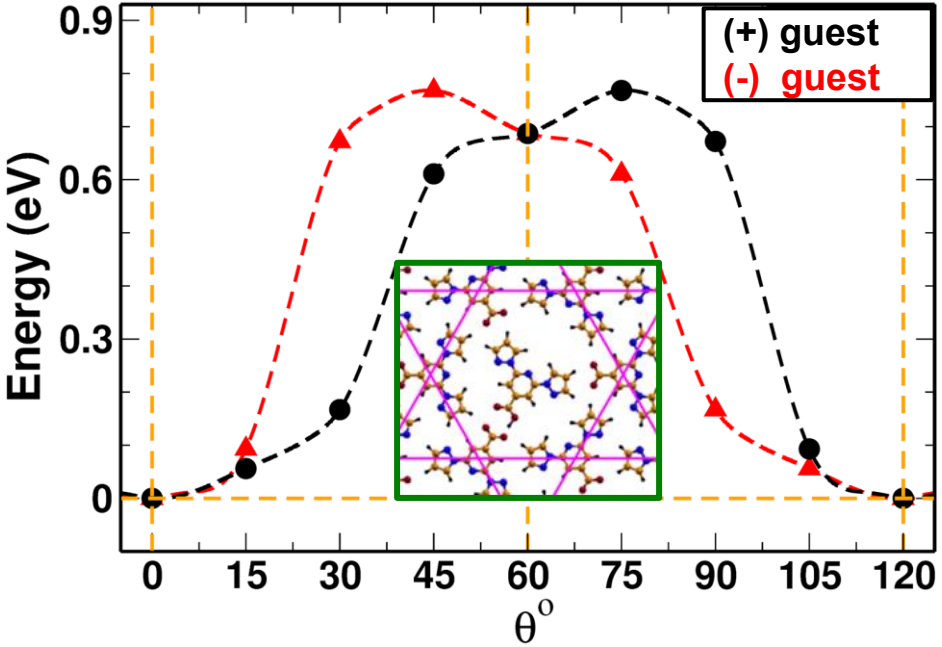
- We have made and studied a molecular rotor.
- DFT estimated energy barrier (0.94 eV) for punctuated pirouette of rotor agrees excellently with experiment (0.95 ± 0.07 eV).
- Global minima positions of guest agree in experiment and DFT.
- Features in rotational energy landscape correlated to making and breaking of host-guest H-bonds.
- Constant current STM simulated at global minimum structure matches with experimental STM image.
- Symmetry analysis explains chiral induction due to twist angle between substrate and host network.
- Our studies provide an insight into the areas of enantioselective organometallic adsorption and molecular rotors.

Thank You !

Backup slides

Result 3: Explanation of the preference for (+) guest: Slide 1

Graph a: Rotation of guest wrt host network (no substrate present)

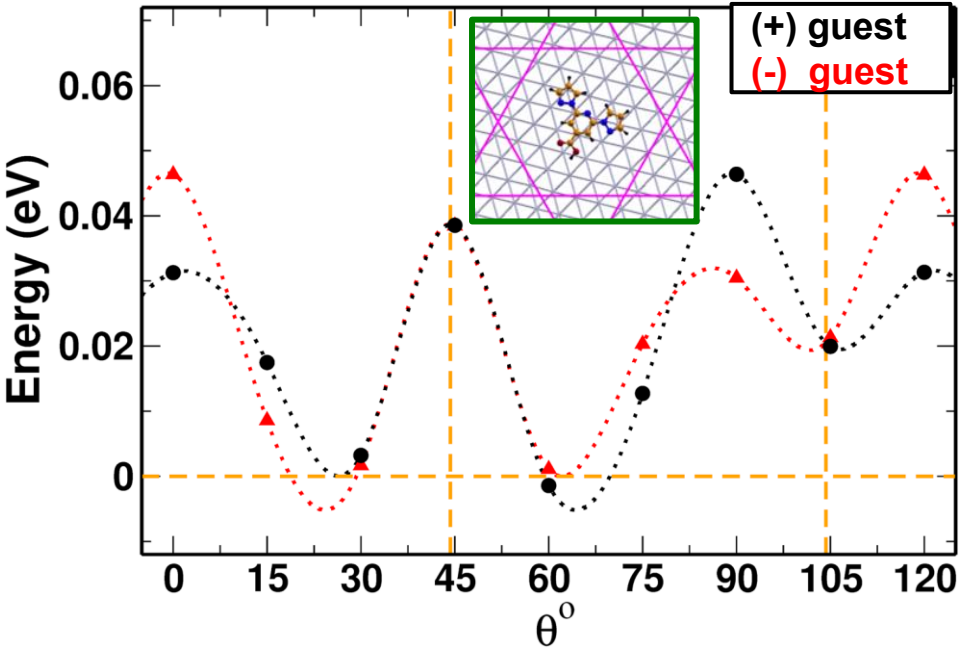


Reflection planes (-)↔(+) at 0° & 60°.

(-) & (+) degenerate.

Both have minimum at 0°.

Graph b: Rotation of guest wrt substrate (no host present)



Reflection planes (-)↔(+) at 44.273° &104.273°.

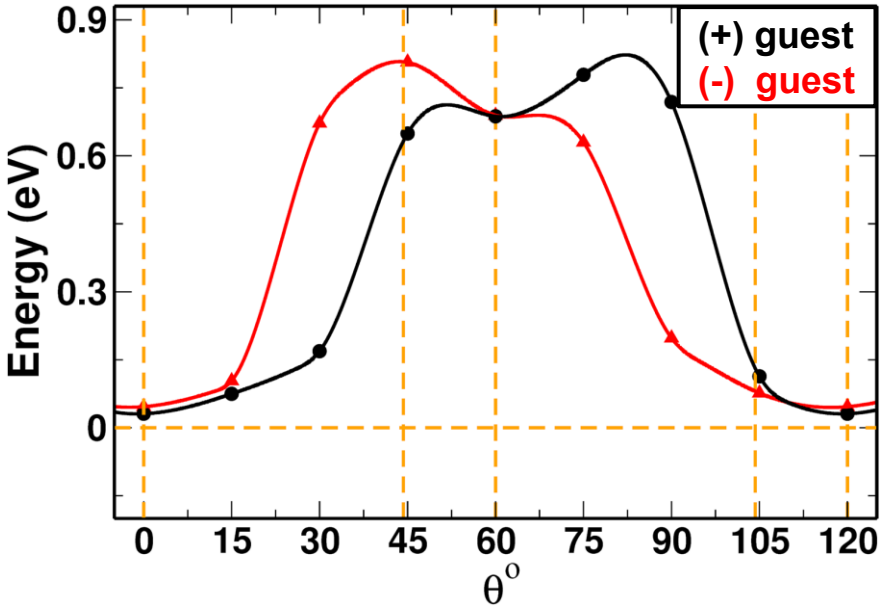
(-) & (+) degenerate.

(-) minimum at 24.25° and (+) minimum at 64.29°.

Result 3: Explanation of the preference for (+) guest: Slide 2

Graph c:

Sum of graphs a & b from previous slide.

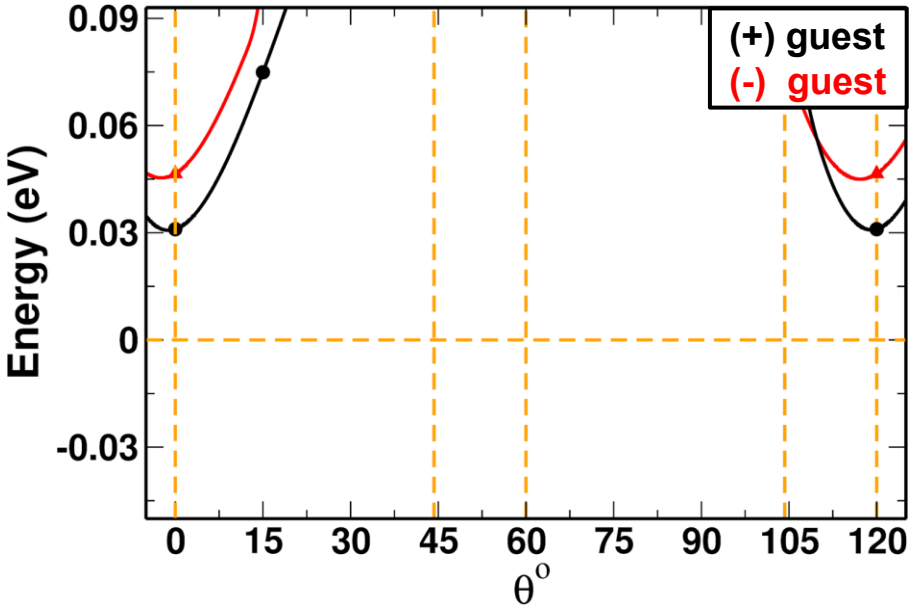


Degeneracy between (+) & (-) broken.

(+) lower in energy than (-) at minima.

Graph d:

Zoomed in portion of graph c



ΔE = 15 meV, minimum at 0°

These differ from values on slide 17 due to synergistic effects when both host and substrate are present.