Self-assembly of molecules on surfaces

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6th RES Users' Meeting

UAM
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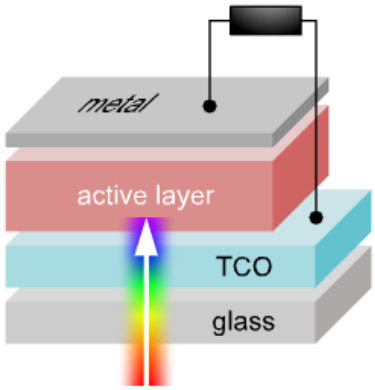
Outline

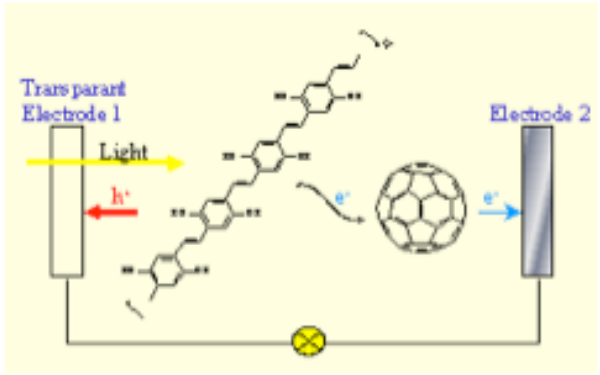
- Motivation
- Examples of molecules deposited on surfaces
- Graphene/Ru(0001)
- TCNQ / Graphene/Ru(0001)
- Conclusions

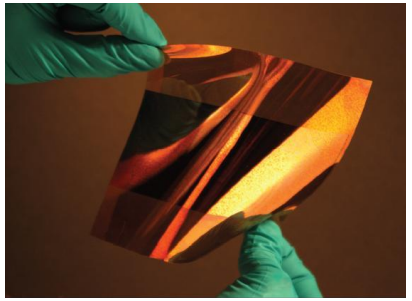
1. Motivation

- Self-assembly of functionalized molecules on solid surfaces is an important tool to fabricate devices with applications on molecular electronics.

- Increase of efficiency of organic solar cells.







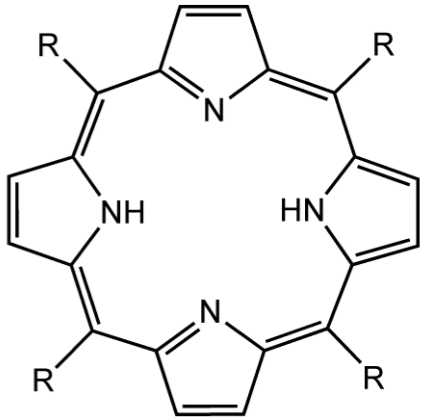
- Understand the factors governing self-assembly: intermolecular forces, molecule-substrate interactions.

- Model the changes in the adsorbed molecule and the substrate.

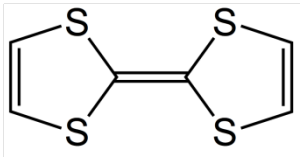
Molecules for organic photovoltaic (OPV) devices

Electron donors:

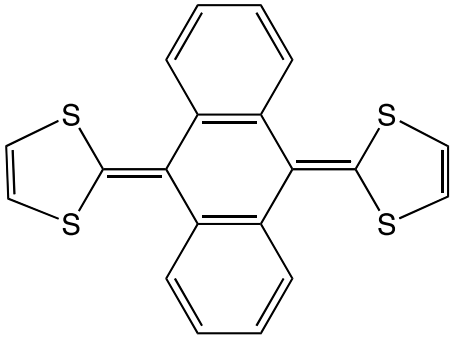
Porphyrins



TTF

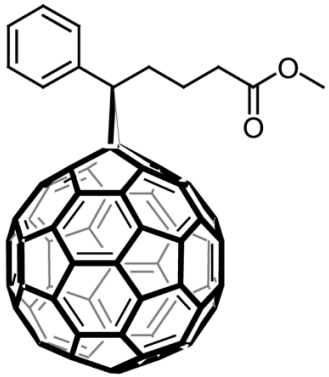


exTTF

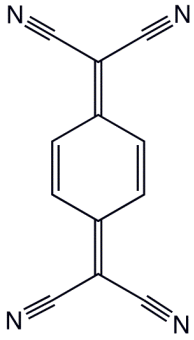


Electron acceptors:

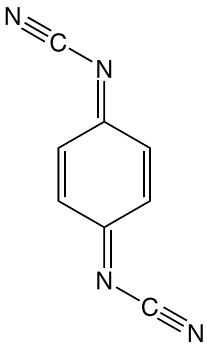
PCBM



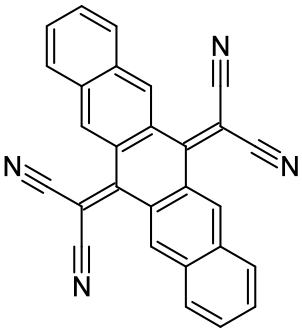
TCNQ



DCNQI



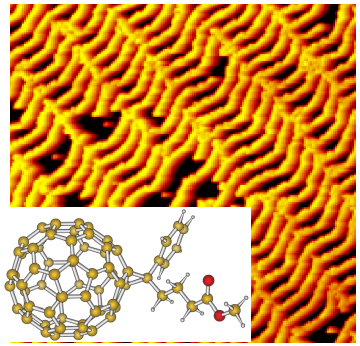
TCPQ

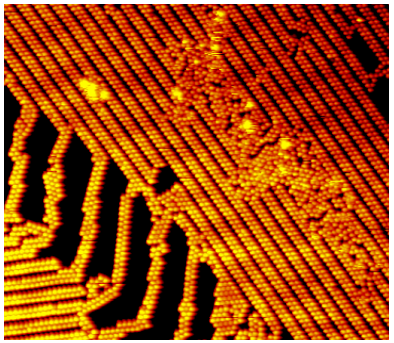


Electron acceptors

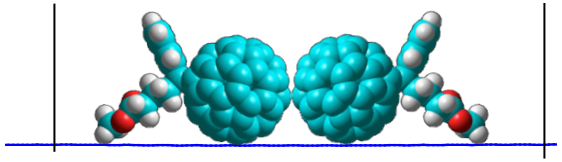
PCBM/Au(111)

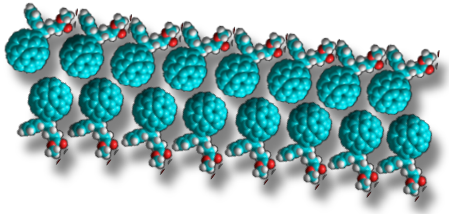
Angew. Chem 46, 7484 (2007)
ChemPhysChem. 9, 1030 (2008)

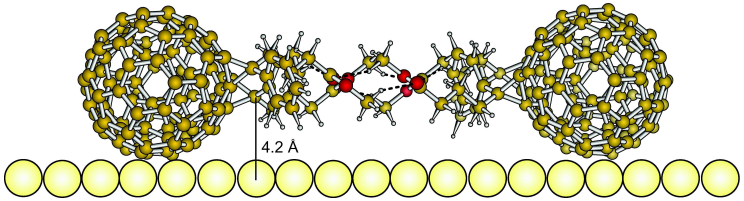




Two different phases depending on the coverage

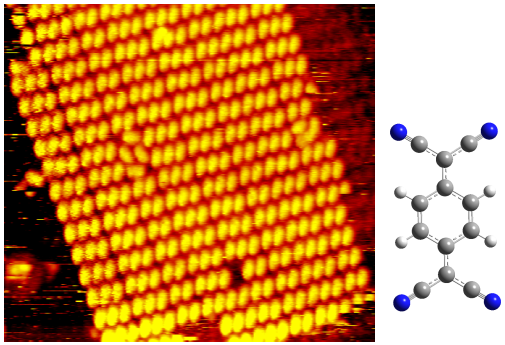




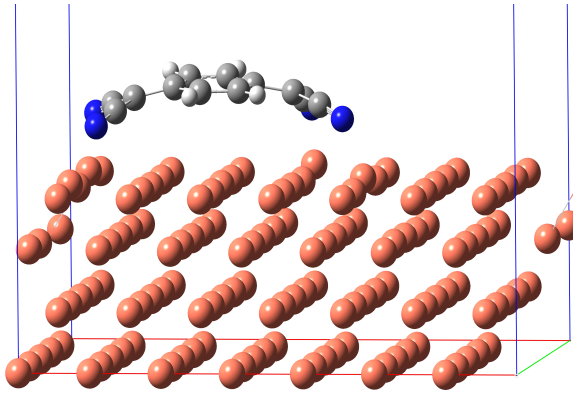


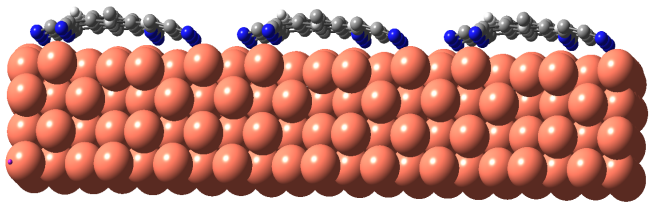
TCNQ/Cu(100)

Nature Chem 2, 374 (2010)

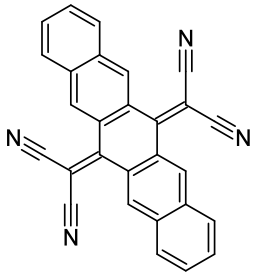


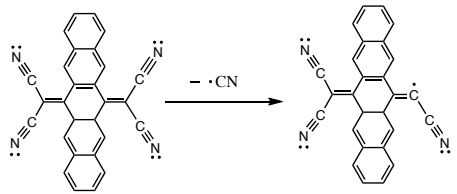
Large distortion of the molecule and the surface

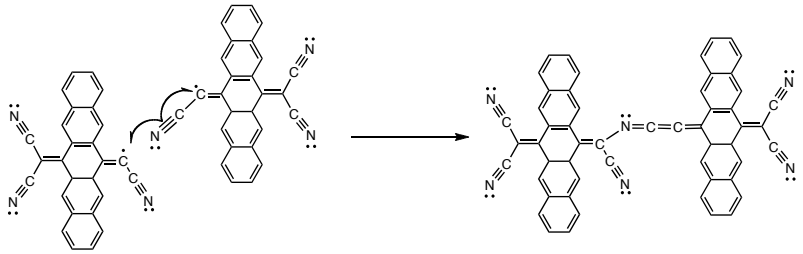


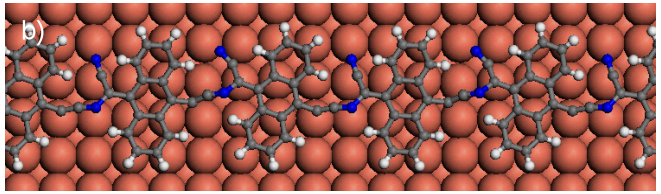


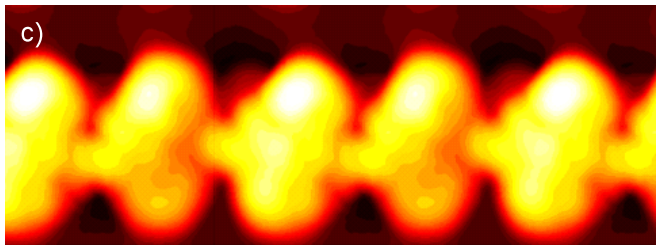
New polymerization reactions TCPQ/Cu(100)



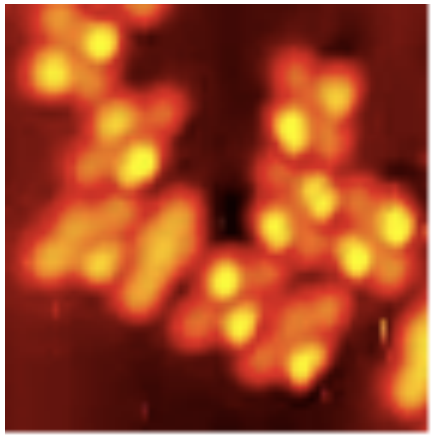




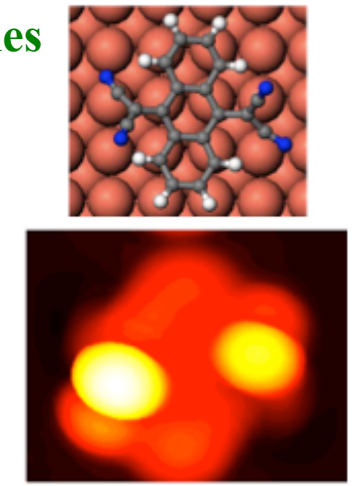




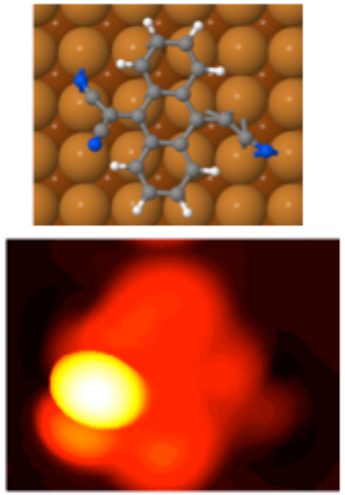
Evidence for intermediate species



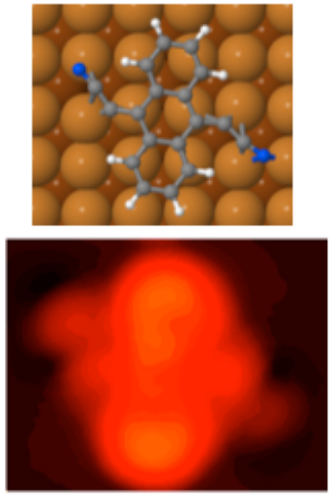
Nature Chem Submitted



TCAQ (intact)



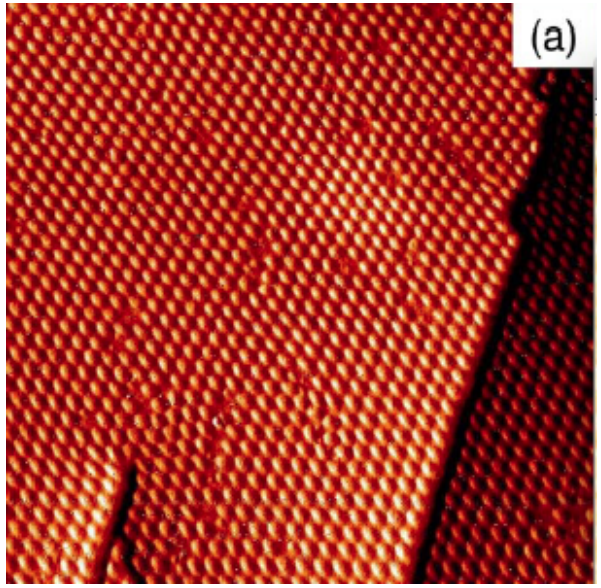
TCAQ –1CN

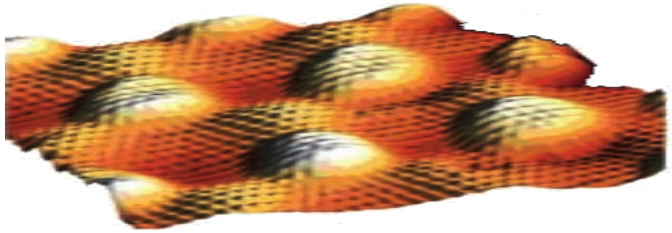


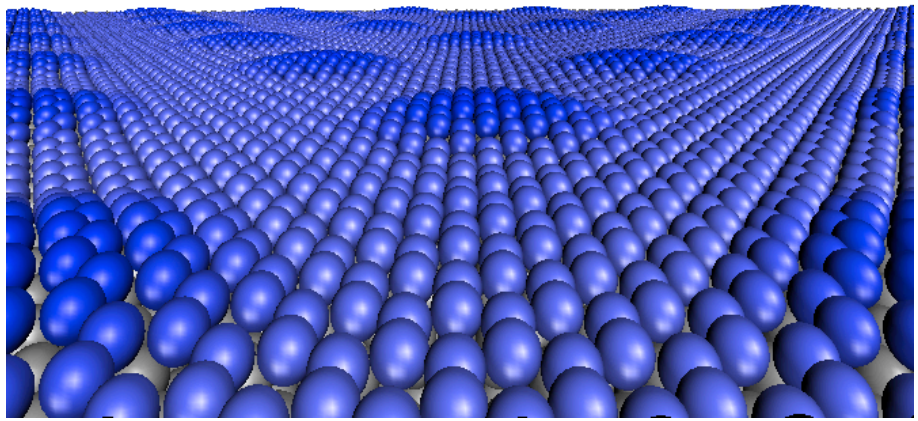
TCAQ – 2CN

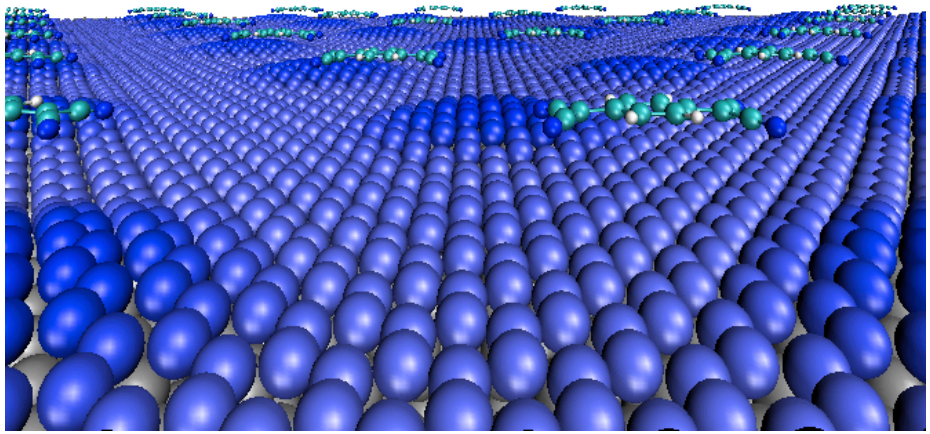
TCNQ Graphene/Ru(0001)

Graphene/Ru(0001) Special Surfaces with periodic modulations



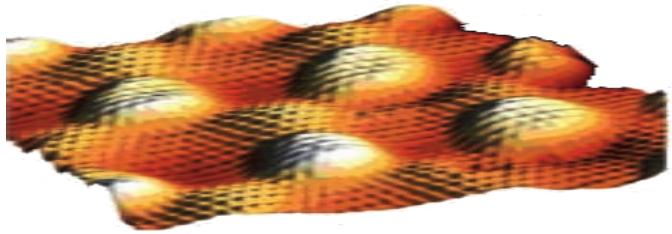






Epitaxial graphene on Ru(0001)

- Mismatch between the lattice constant of graphene (2.46 Å) and the one of Ru(0001) (2.7 Å)
- Spatially modulated chemical interaction between C and Ru atoms
- The surface has two different areas (low/high) with different electronic density that can induce self-assembly



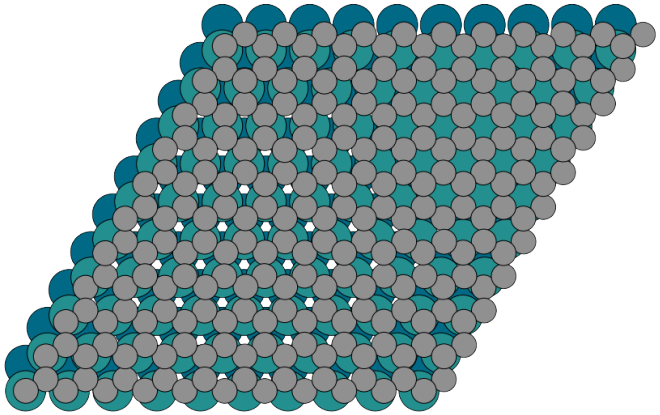
PCCP 101, 099703 (2008)
PRL 101, 126102 (2008)
New J. Phys. 12, 093018 (2010)

Technique	Graphene corrugation (Å)
Low Energy Electron Diffraction	1.5
Surfrace X-Ray Diffraction	0.82 - 1.5
Helium Atom Scattering	0.15 – 0.4
STM (V_s = -1 V)	1.0
Density Functional Theory corrugation: 1.5 Å -1.7 Å	

Theoretical Model

DFT: PBE functional + van der Waals interactions – Grimme correction

Periodic bounday conditions
(11×11) graphene unit cells forced over
(10x10) Ru(0001) unit cells – 3 (5) Ru layers
Calculation involves 421 atoms (621)



Account for the Moirè pattern.
Do not account for Moiré/Ru(0001) rotation

Graphene and topmost Ru(0001) allowed to relax
(D-correction included in relaxation)

Charge analysis using Bader's theory

Tersoff-Hamann to simulate STM images

VASP program
Γ-point only BZ sampling
Ru semi-core included
E_{cut} = 400 eV
Residual forces criterion = 0.01 eV/Å^3

Theoretical Results

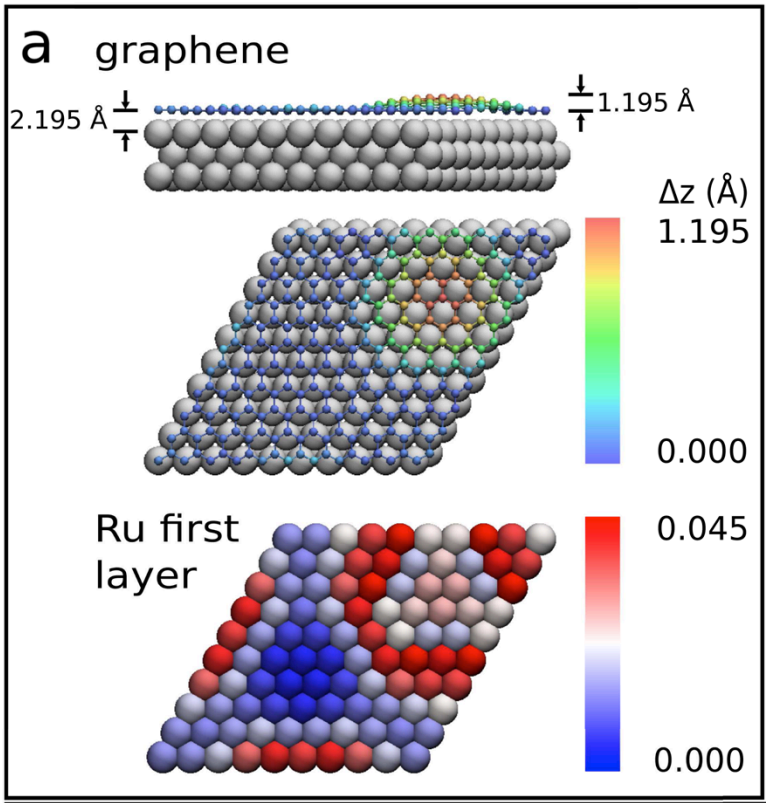
Graphene/Ru(0001)

Phys. Rev. Lett. 106, 186102 (2011)
Phys. Rev. B 85, 121404 (2012)

d_{min} (C/Ru) = 2.19 Å
Binding Energy = 0.2 eV/C atom

Graphene corrugation = 1.19 Å

Ripple height is about 0.4 Å lower compared to standard DFT



Residual forces on C atoms :

With Dispersion Correction

C atoms
Forces

Theoretical Results

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Phys. Rev. Lett. 106, 186102 (2011)
Phys. Rev. B 85, 121404 (2012)

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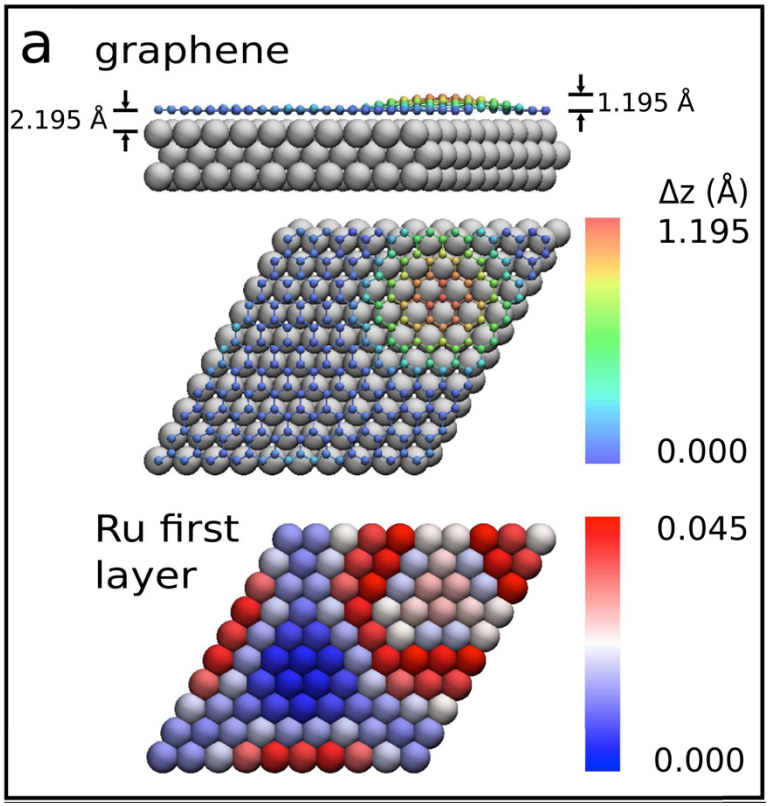
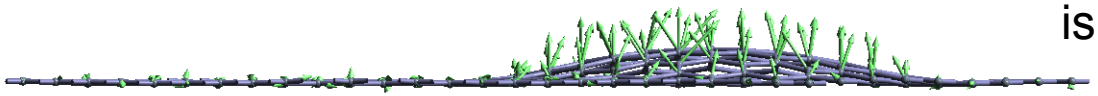


Residual forces on C atoms :

Without Dispersion Correction



C atoms
Forces

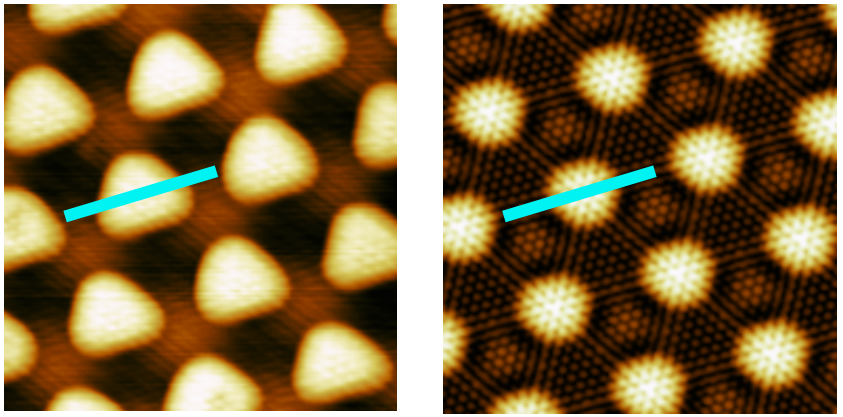
Contribution from dispersion forces is localized on the ripple region

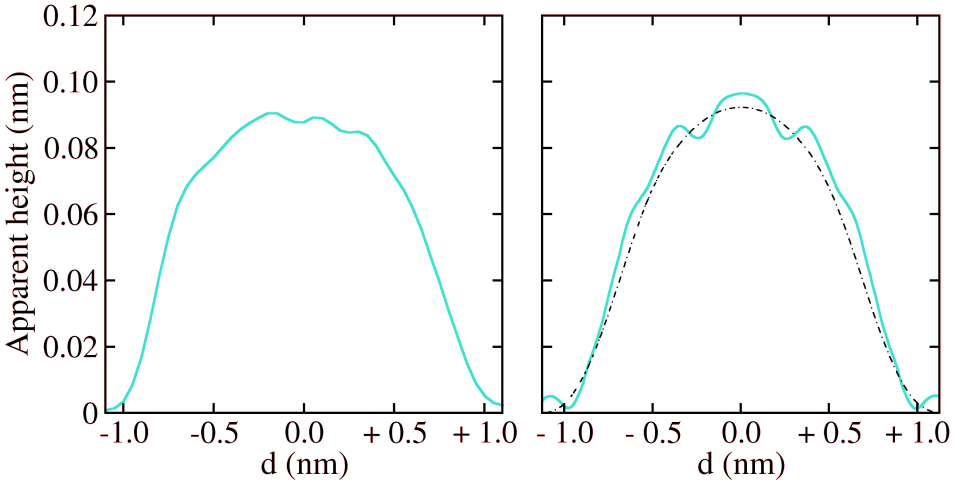
Neglecting the dispersion contribution leads to an increase of the ripple height 1.59 Å (+ 25%)

Comparison STM Topography - Apparent Height

Experimental
V_s = -1.0 V

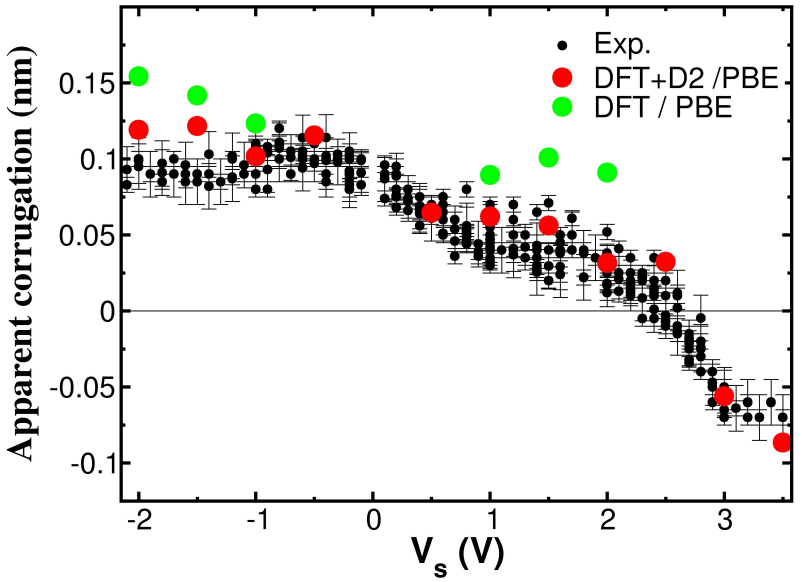
Simulated (Tersoff-Hamann)
Electron density isocontour
1.69×10^{-4} Å^{-3}

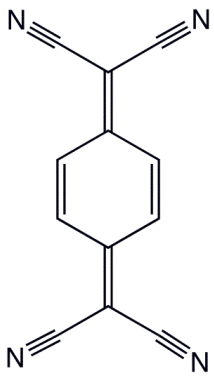




Apparent corrugation vs. Voltage

Corrugation: 1.19 Å 1.59 Å



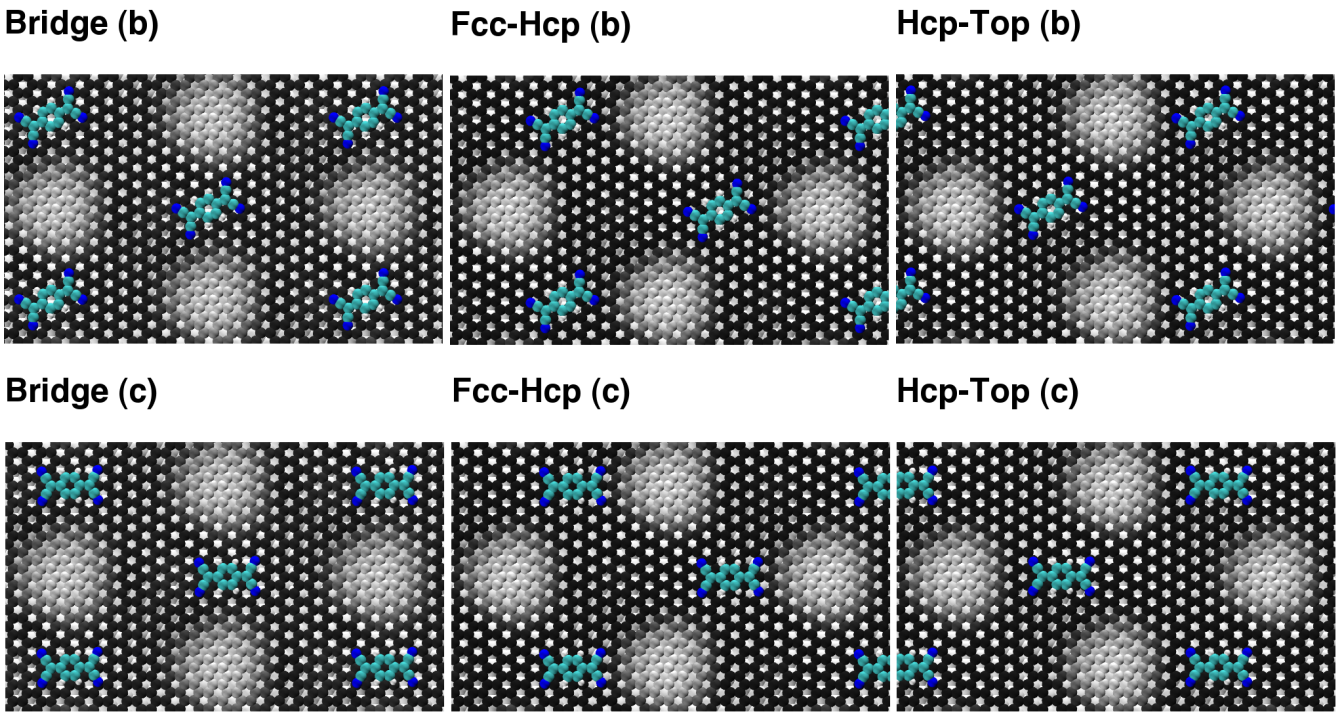


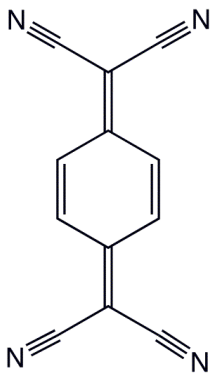
TCNQ Graphene/Ru(0001)

position	bridge	fcc-hcp	hcp-top
Adsorption Energy (eV)			
b	-2.62	-2.48	-2.38
c	-2.58	-2.53	-2.37

Adsorption on the low areas of the moiré (0.25 eV lower E)

No preferential adsorption configuration





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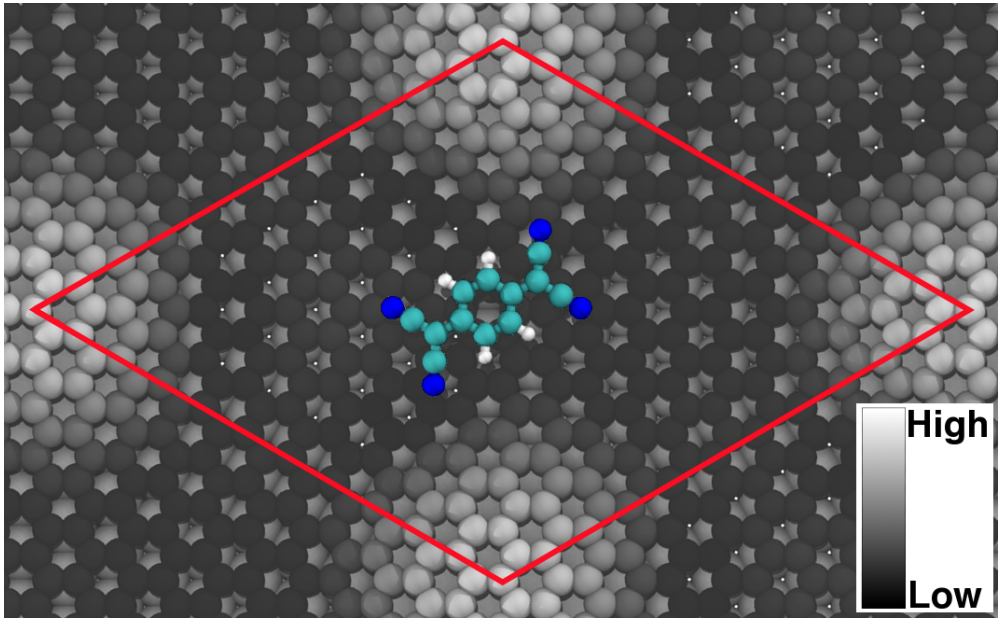
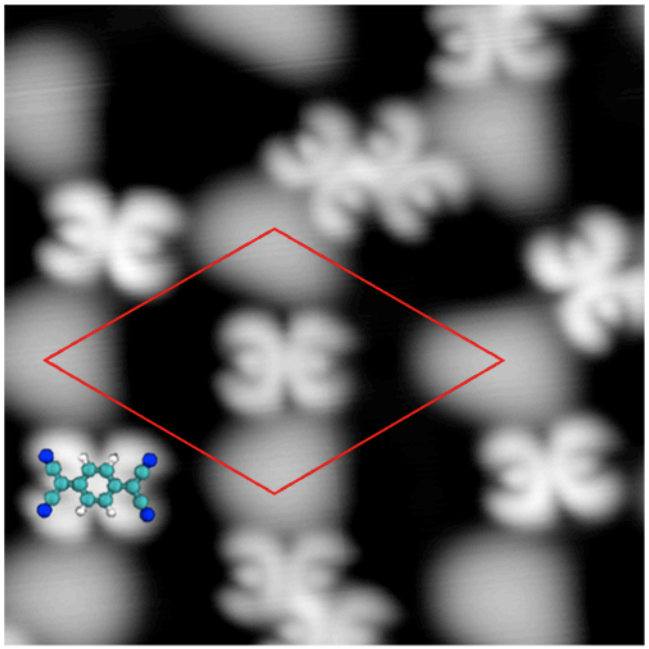
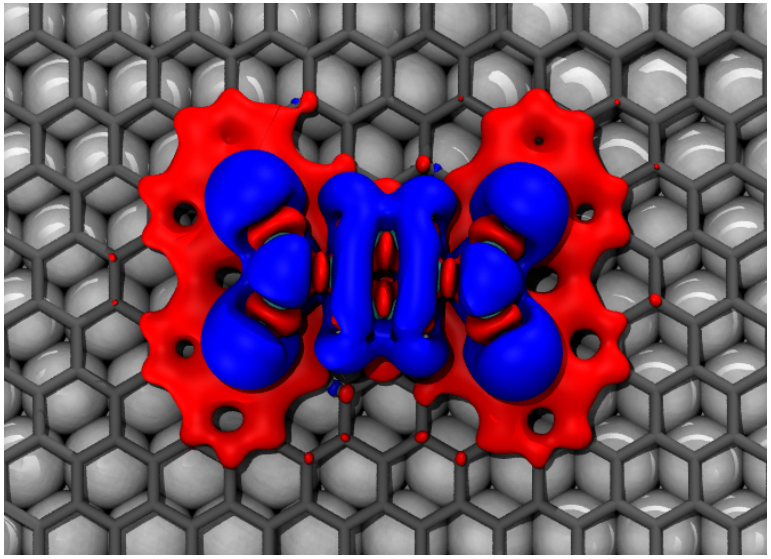
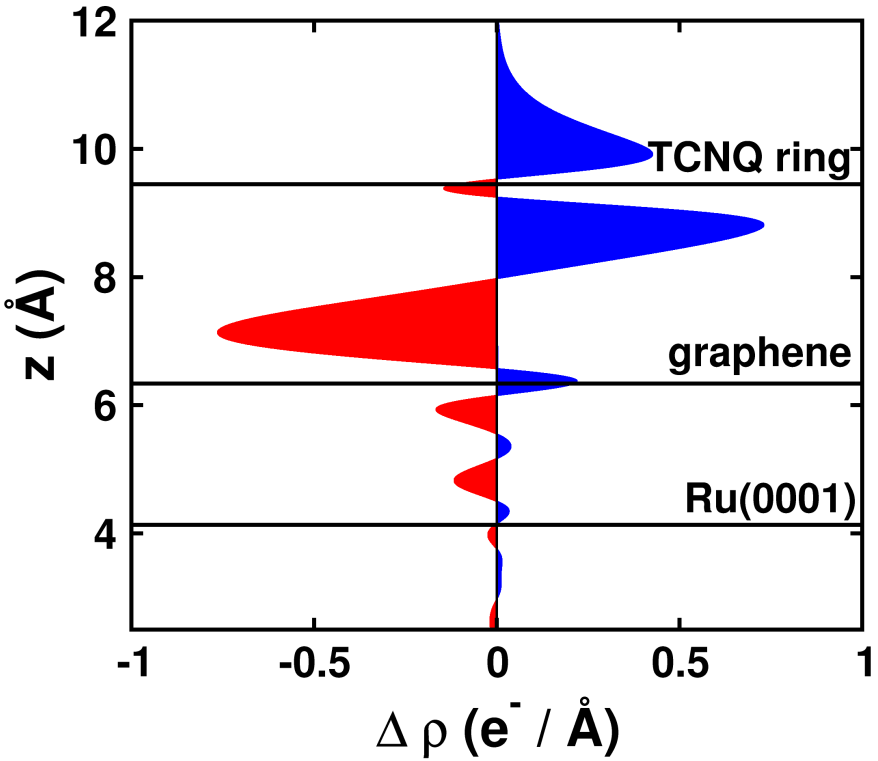




Electronic density redistribution

Blue: el. accumulation
Red: el. depletion



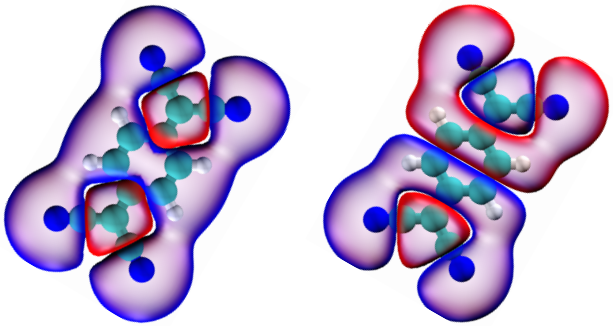


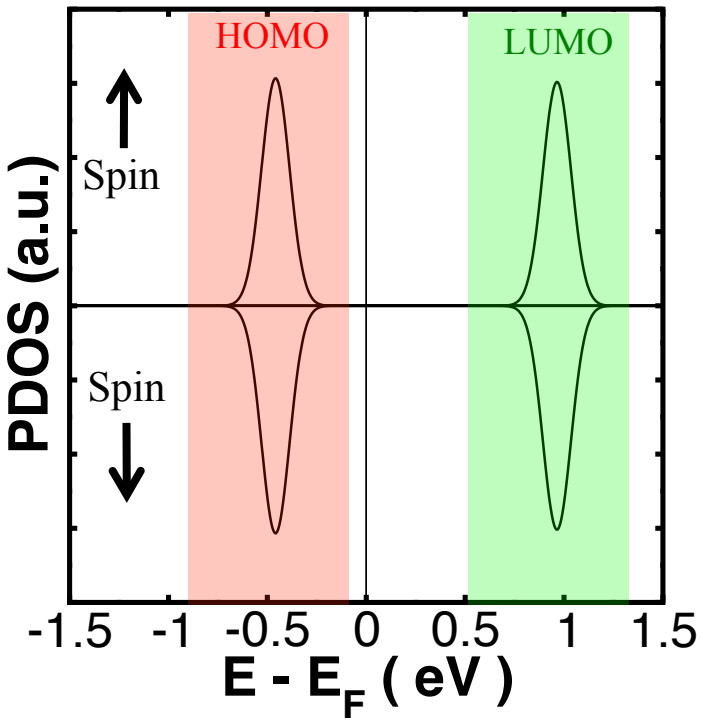
Charge redistribution

(Bader) : 1.05 electrons

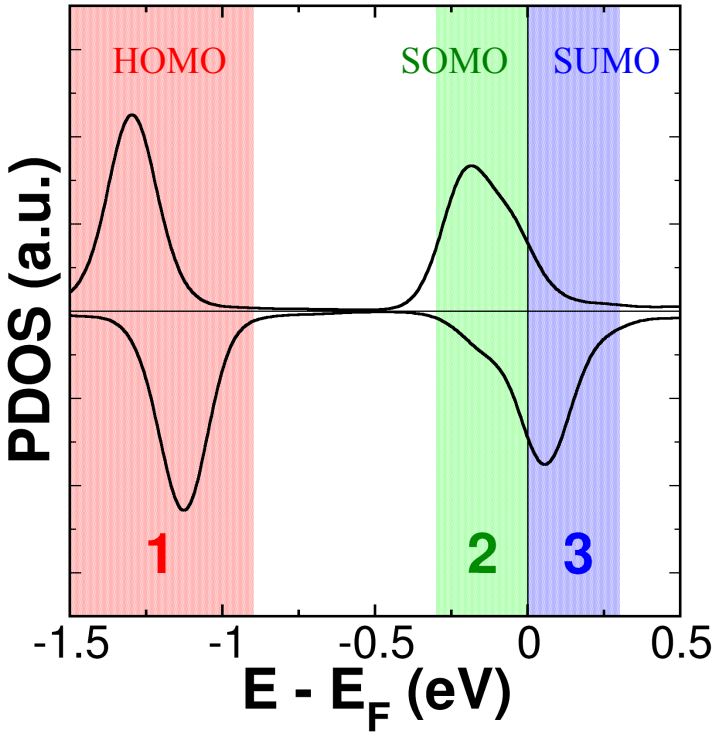
(xy-integrated) : 1.0 electrons

PDOS on (s,p) atomic orbitals



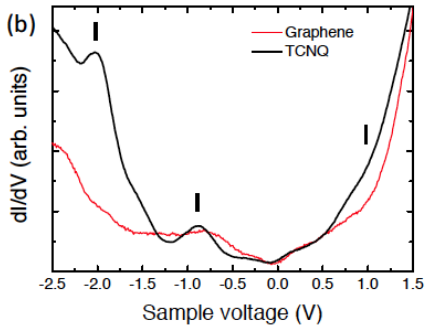


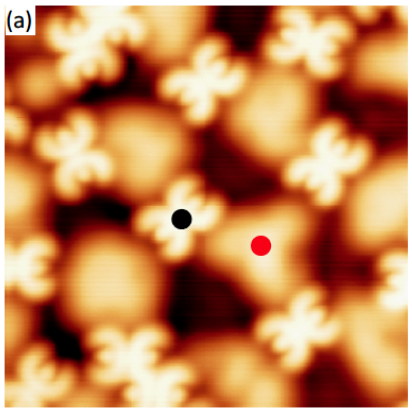
TCNQ in gas phase



TCNQ on gr/Ru(0001)

Comparison with STM experiments

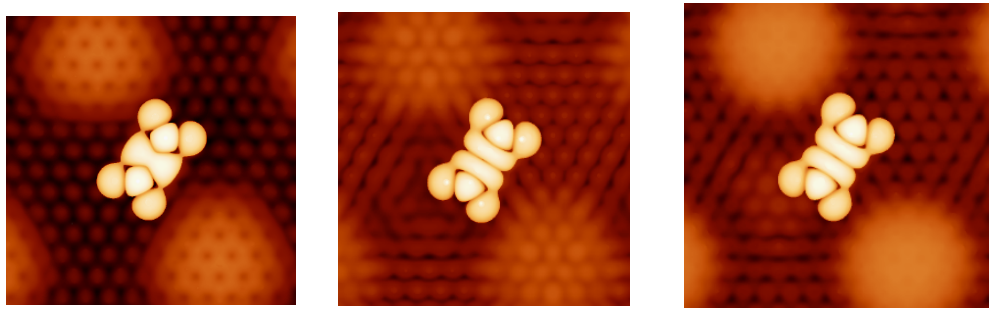


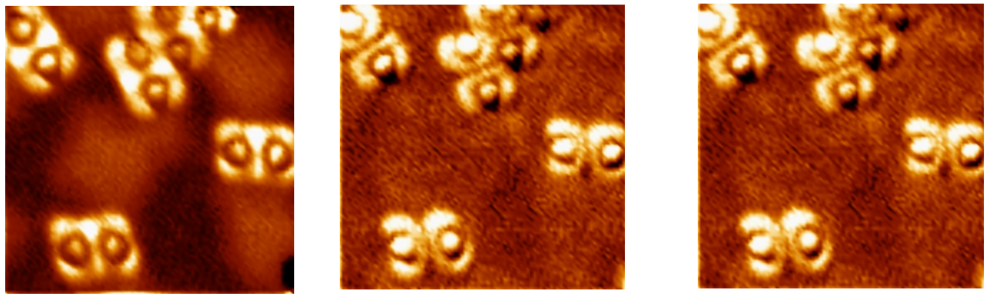


LDOS [-1.5eV:0.9eV]

LDOS [-0.3eV:0eV]

LDOS [0eV:0.3eV]

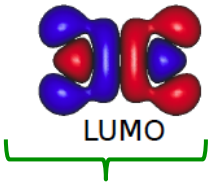


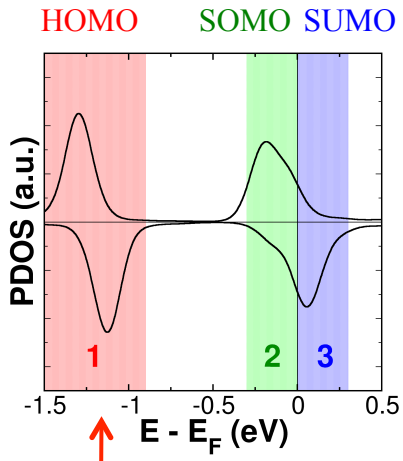


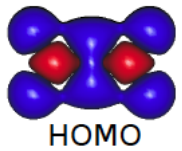
HOMO (V = -2.04V)

SOMO (V = -0.86V)

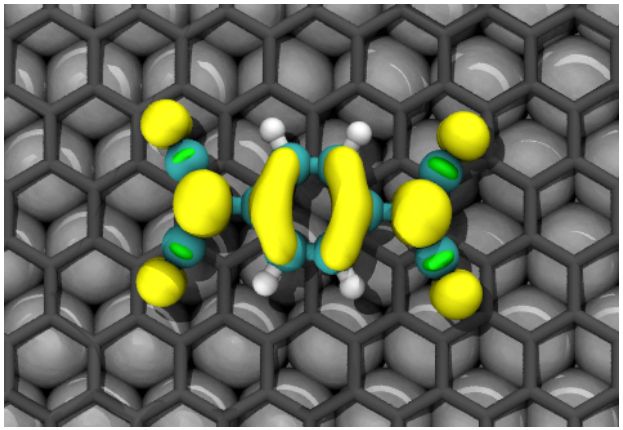
SUMO (V = +1.01V)



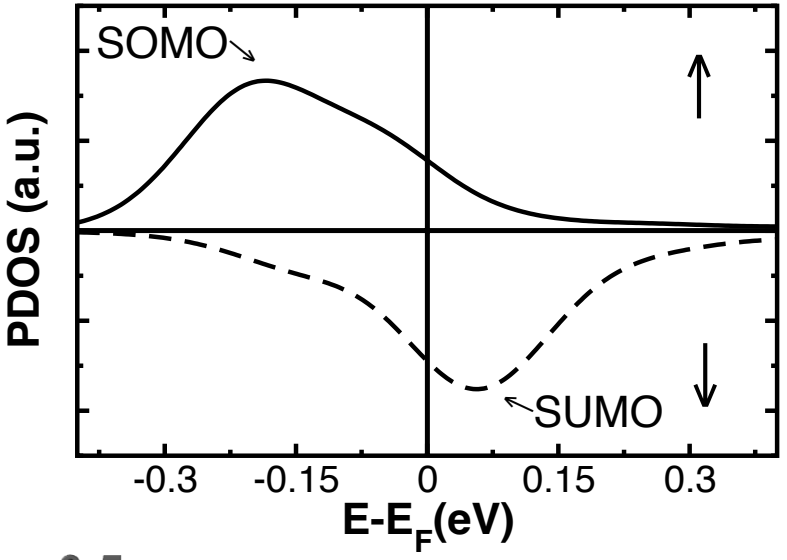




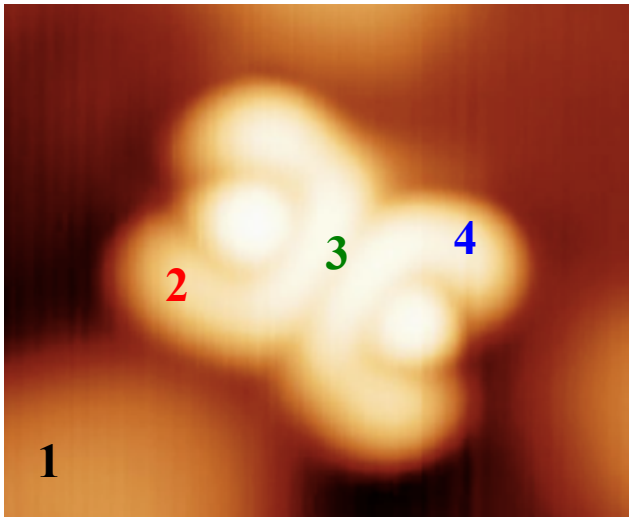
Spin density redistribution



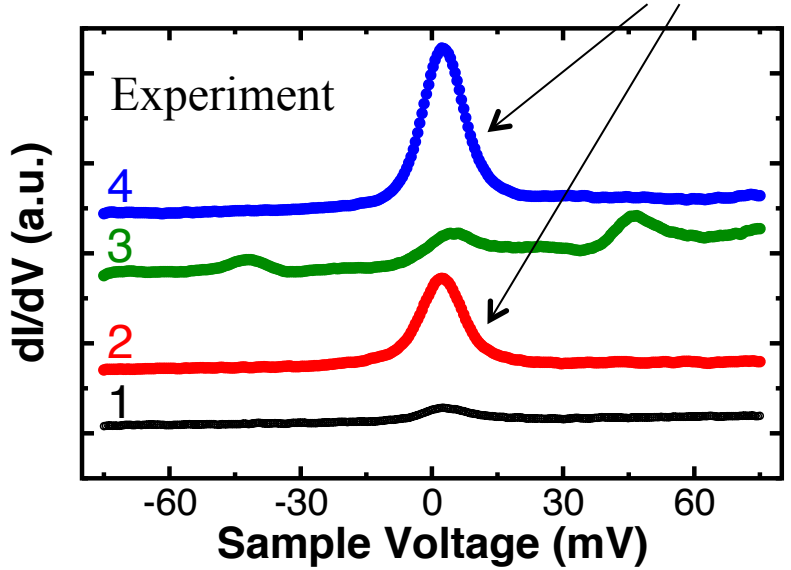
Yellow: positive Green: negative



Magnetic moment = 0.5 μ_B

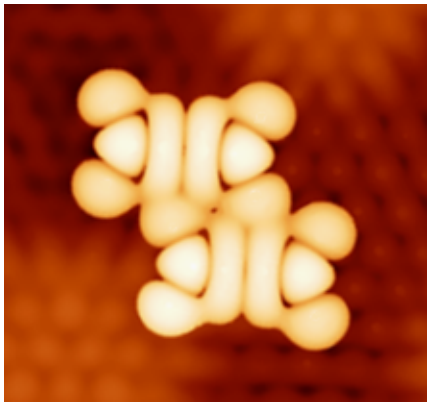


Kondo peak

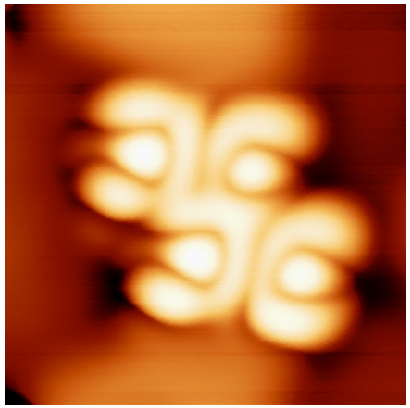


TCNQ Dimer on graphene/Ru(0001)

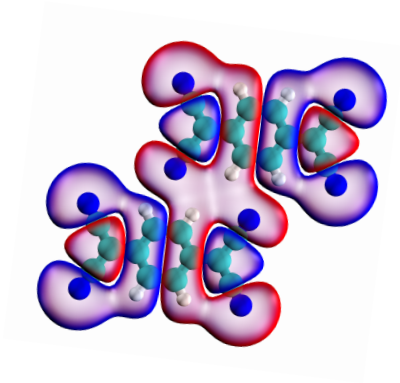
LDOS [-0.4eV:0eV]

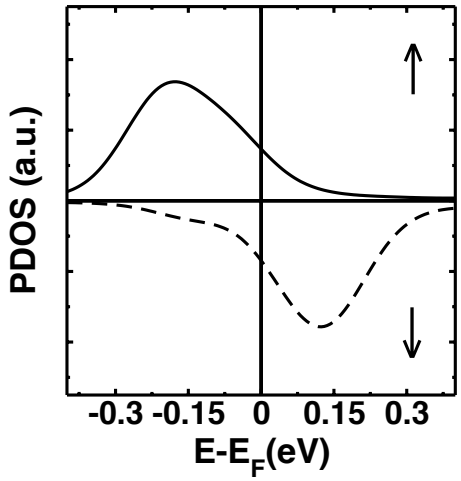


Exp: V=-0.4V

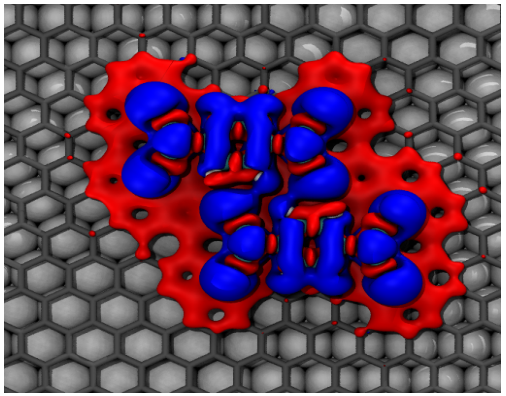


Gas phase





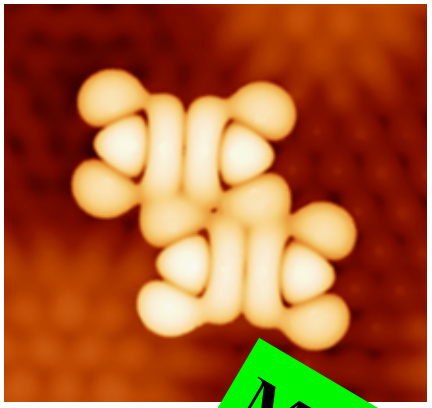
PDOS on TCNQ (s,p) orbitals



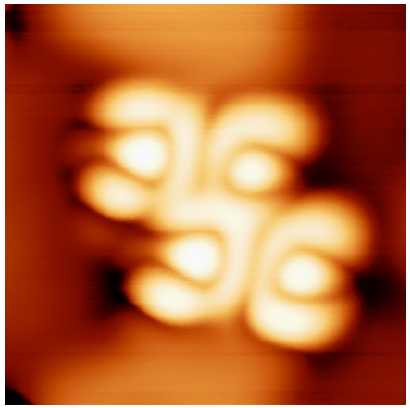
Electronic density redistribution

TCNQ Dimer on graphene/Ru(0001)

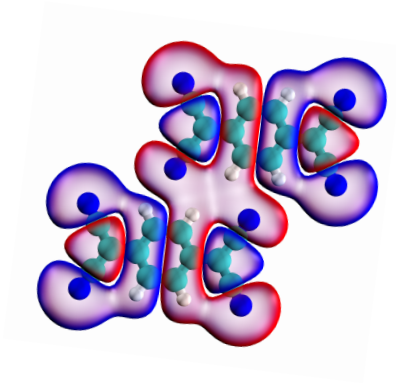
LDOS [-0.4eV:0eV]



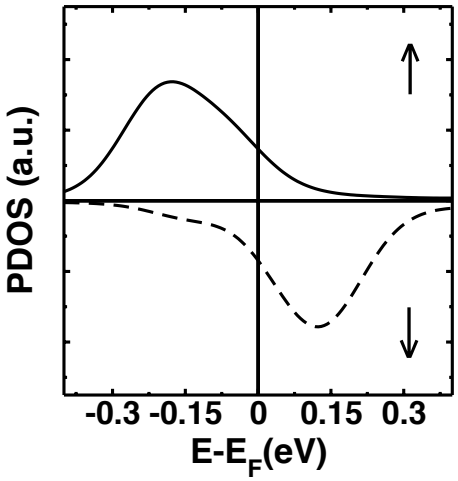
Exp: V=-0.4V



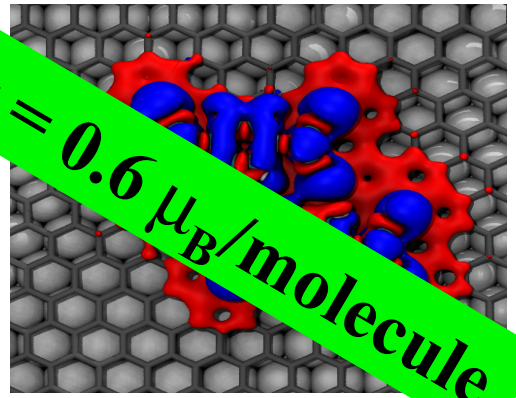
Gas phase



Magnetic moment = 0.6 μ_B/molecule

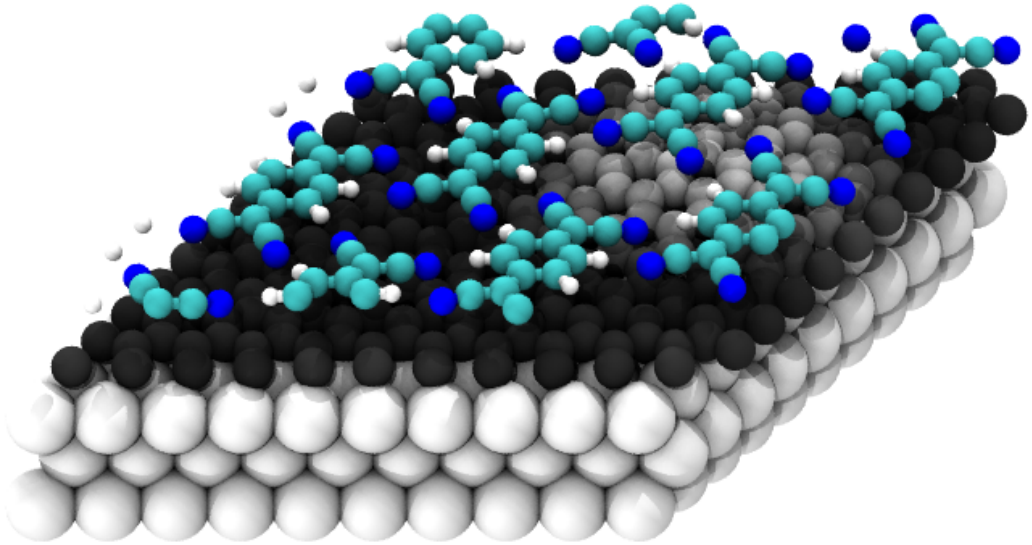


PDOS on TCNQ (s,p) orbitals



Electronic density redistribution

TCNQ-monolayer on graphene/Ru(0001)



Model

1 TCNQ molecule on top of the ripple

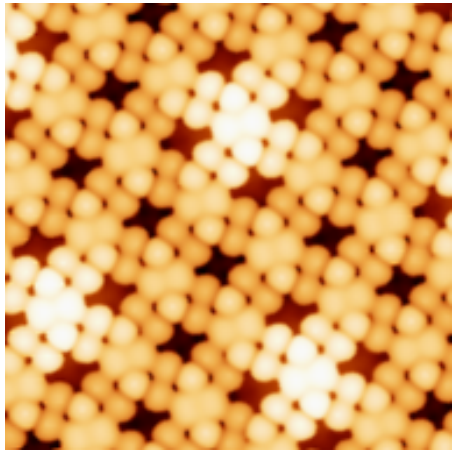
Used to simulate STM images

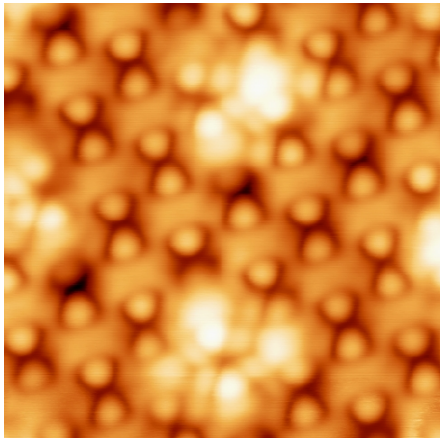
Charge transfer = 0.6-0.7 electrons/molecule

Science (submitted)

STM images for TCNQ-ml/graphene/Ru(0001)

LDOS
[-1.5eV:0.9eV]

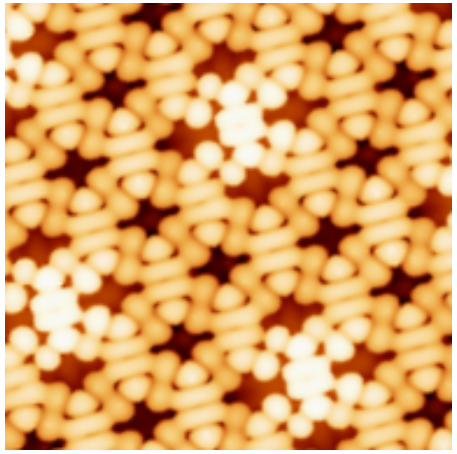


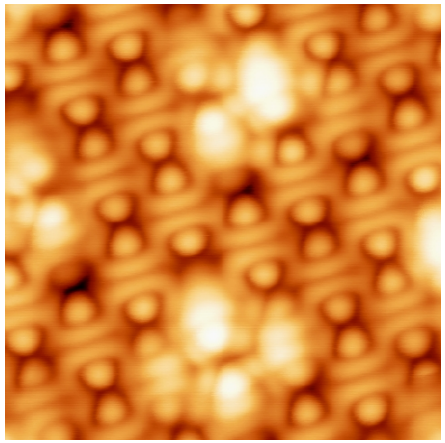


(V = -2.0V)

HOMO

LDOS
[-0.3eV:0eV]

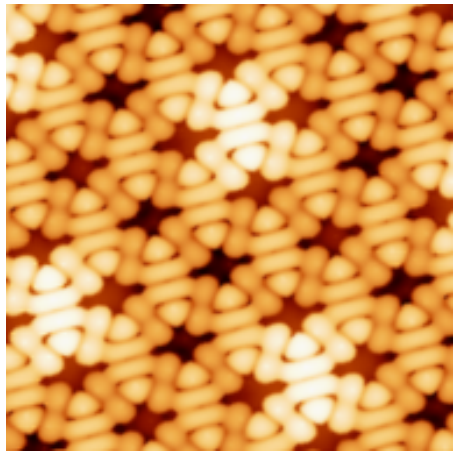


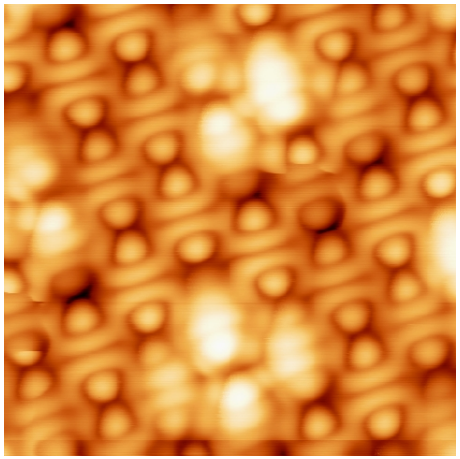


(V = -0.8V)

SOMO

LDOS
[0eV:0.3eV]

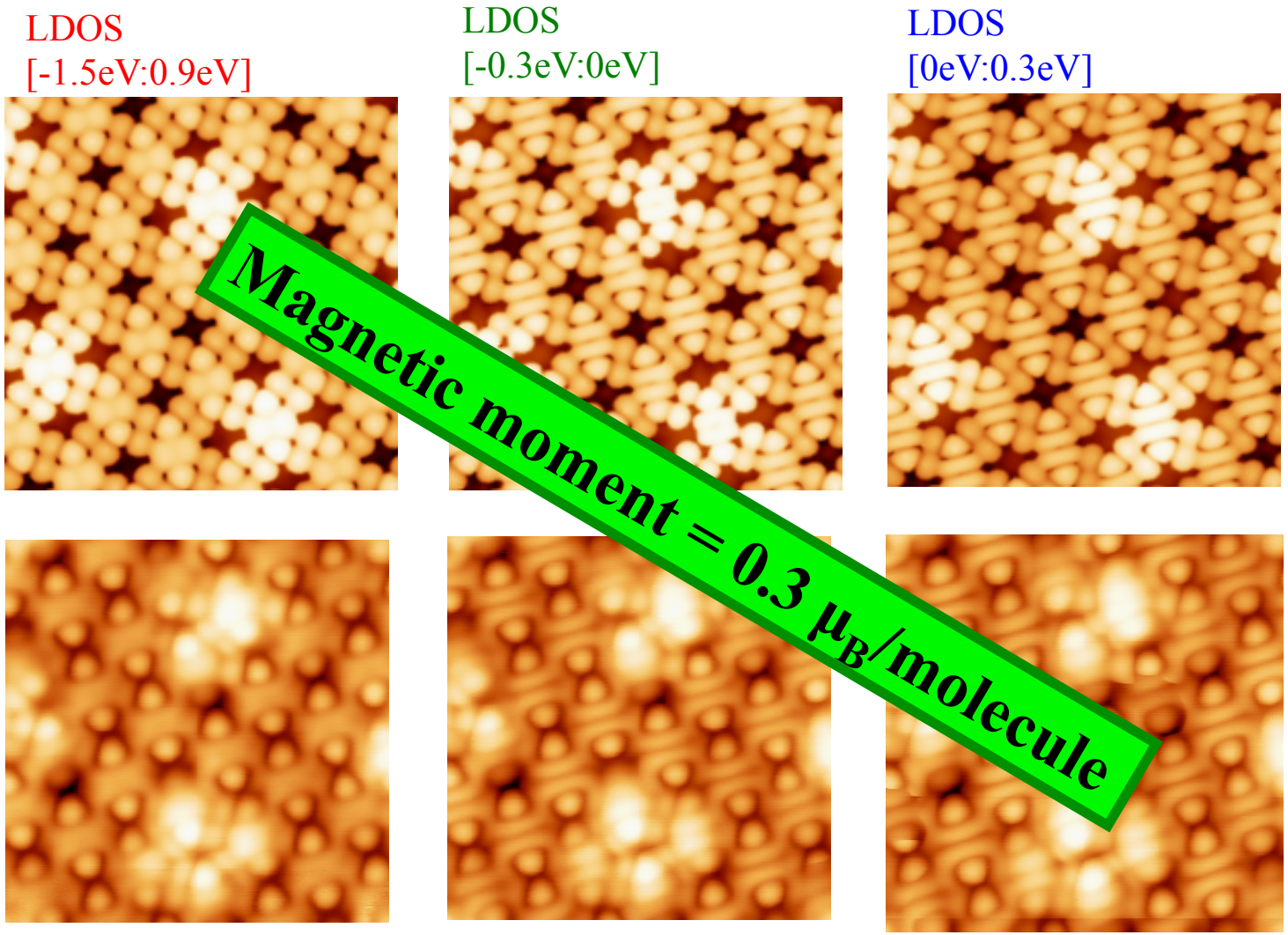




(V = +1V)

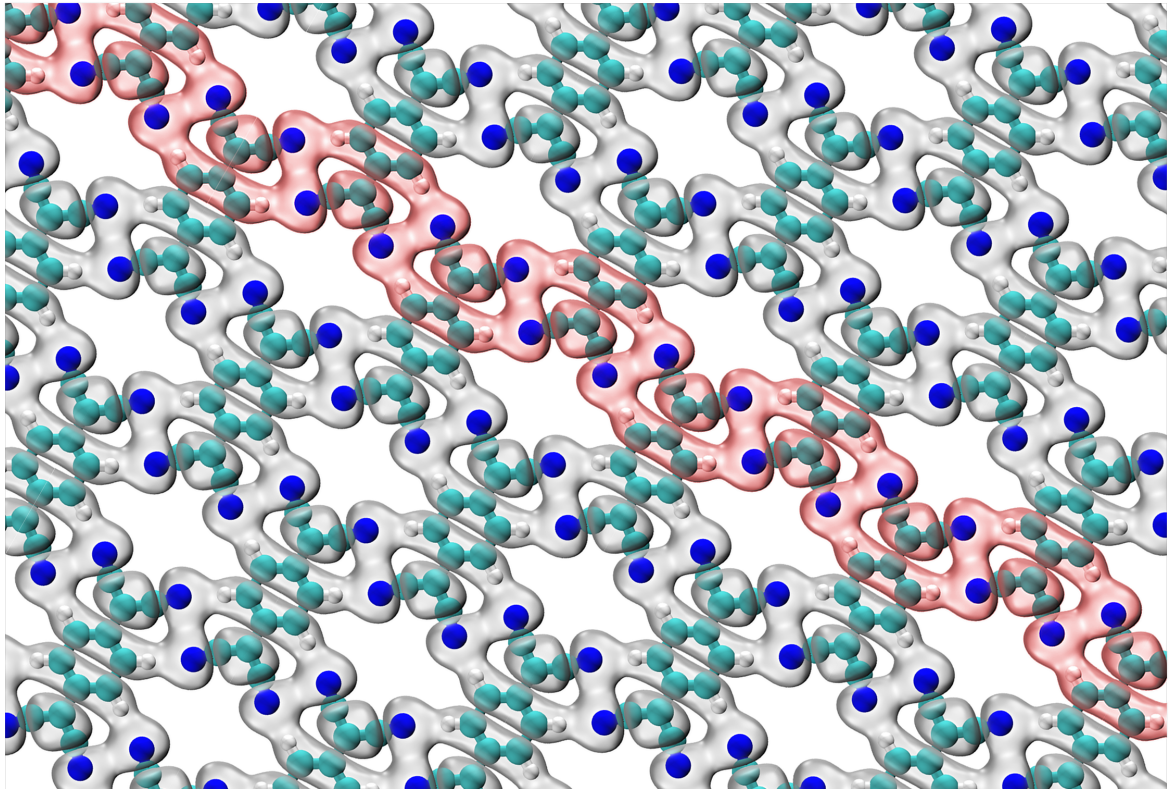
SUMO

STM images for TCNQ-ml/graphene/Ru(0001)

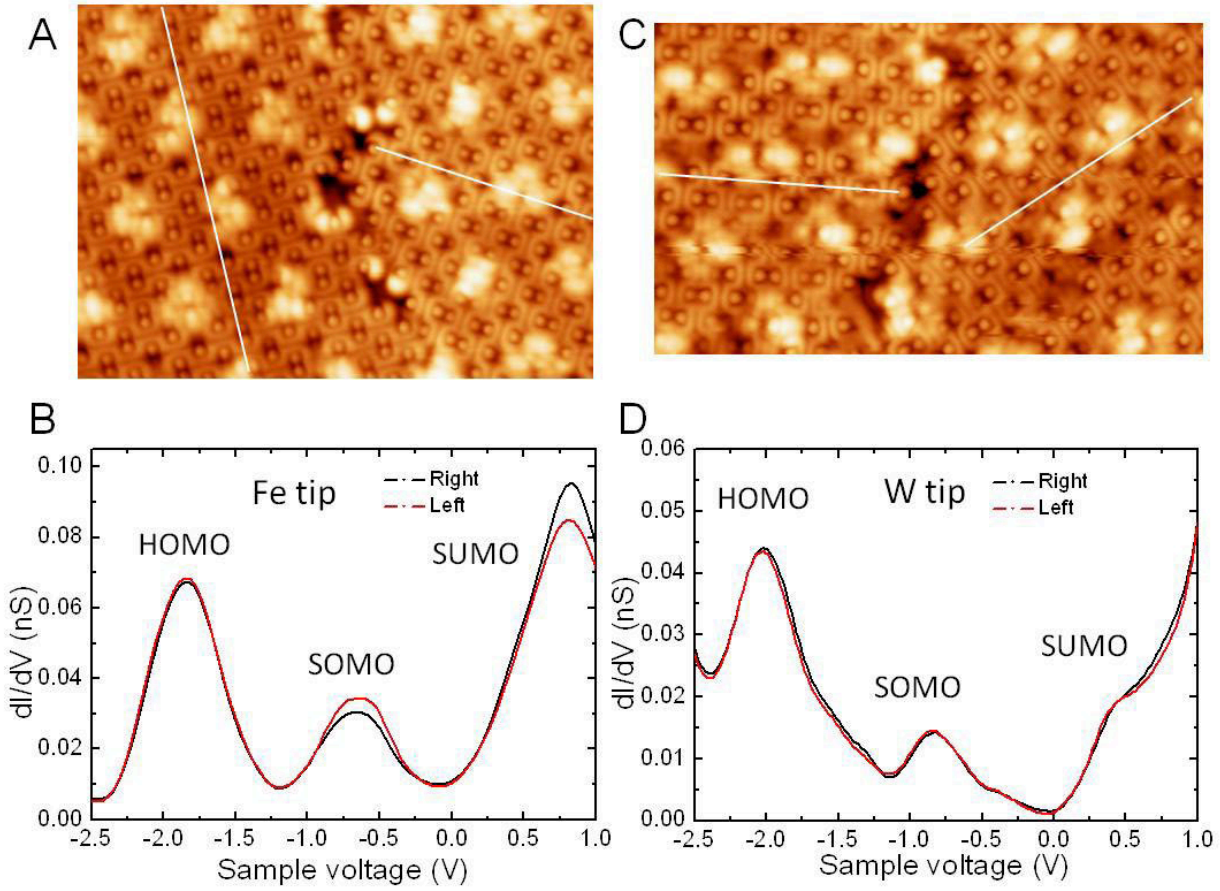


TCNQ-monolayer

Singly occupied band and 1st unoccupied band



Experimental confirmation
Spin-polarized STM measurement



Science (submitted)

Conclusions

- **Computational modelling as a necessary tool to understand self-assembly patterns and electron transfers.**

- **Graphene/Ru(0001)**
  Van der Waals interactions are crucial to describe the corrugation of the system and the electron density distribution

- **TCNQ on graphene/Ru(0001)**

  Graphene decouples the orbitals of TCNQ from the electronic states of the metal allowing a direct imaging of the electronic structure

  Single TCNQ molecules acquire charge and develop sizeable magnetic moment

  Monolayer behaves as a 2D organic ferromagnetic metal

Acknowledgments

Theory

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Experiments

Department of Condensed Matter Physics – LASUAM- IMDEA – Nanoscience

D. Ecija, C. Urban, M. Trelka, R. Otero, J.M. Gallego, M. Garnica, S. Barja, B. Borca
A.L. Vazquez de Parga, R. Miranda

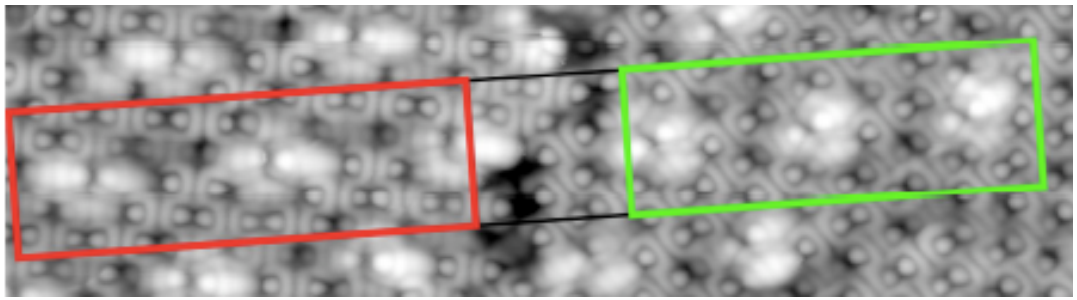
Department of Organic Chemistry (U. Complutense Madrid)

L. Sánchez, M. A. Herranz, N. Martín,

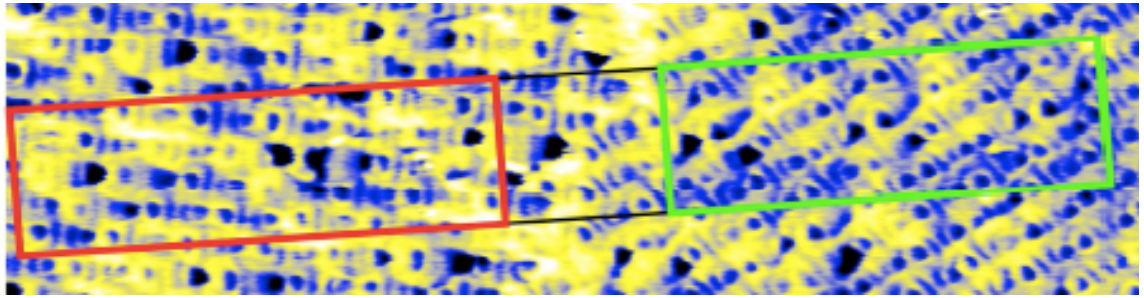
Thank you for your attention

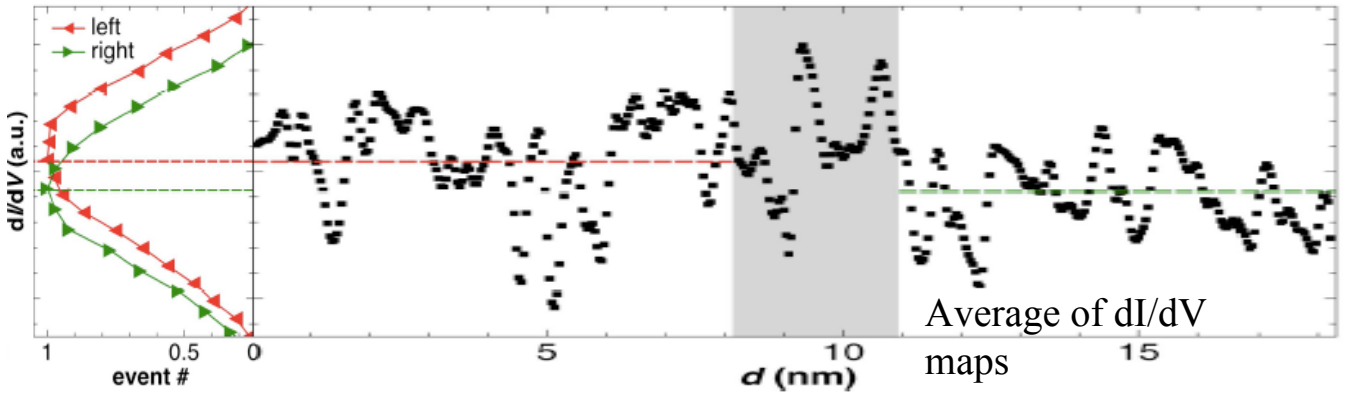
Experimental confirmation
Spin-polarized STM measurement

STM topography (-0.7 V)



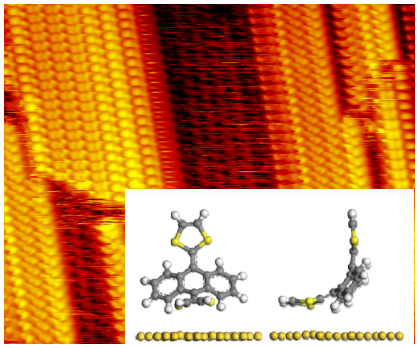
Spin-polarized dI/dV (-0.7 V)





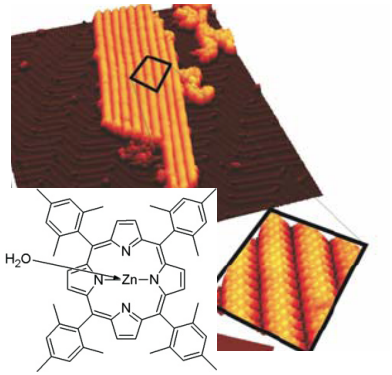
Science (submitted)

Electron donors



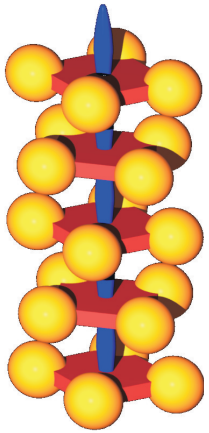
Ex-TTF/Au(111)

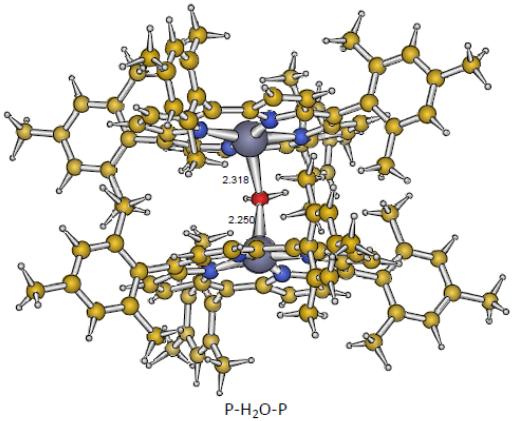
JPC C 114, 6503 (2010)



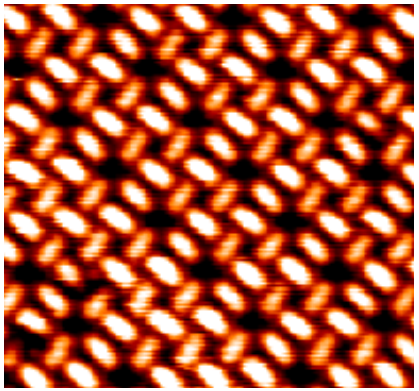
Zn-Porphyrine/Au(111)

CrysEngComm 13, 5591 (2011)





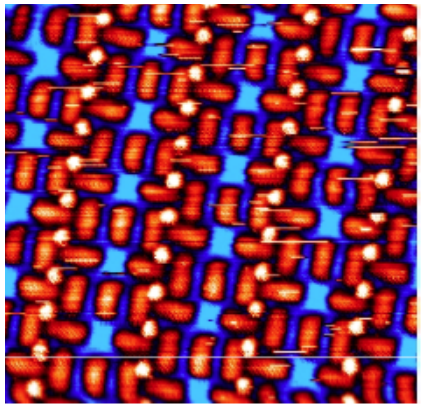
Co-deposition



TCNQ/Cu(111)

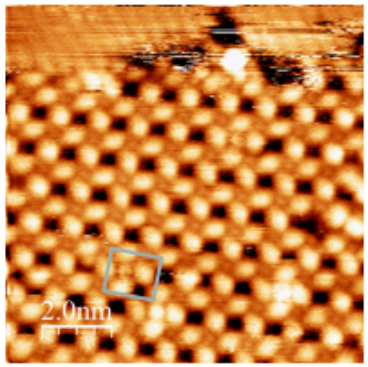
PCCP (Submitted)

Fe



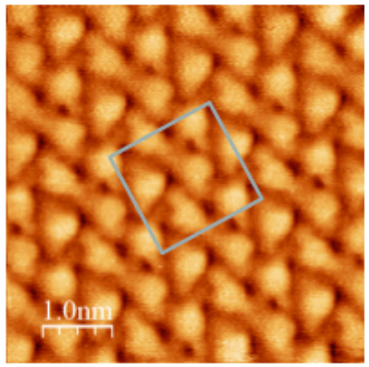
Fe/TCNQ/Cu(111)

Changes in the activation barriers for isomerisation (DCNQI)

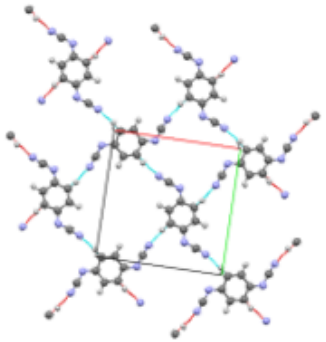


T(STM) = –60 ºC

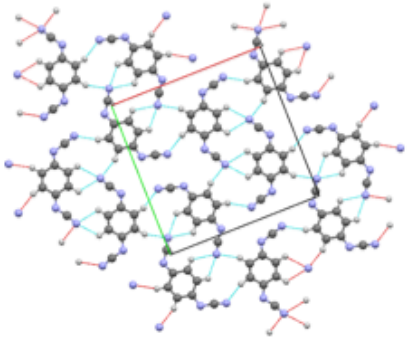
annealing



T(STM) = 15 ºC



anti



syn